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▶ REACTION RATES, upon which output from chemical processes primarily depends, attain special significance in a war of production when prodigious demand cannot be met simply by enlarging plants. Hence, a discussion of this subject now possesses urgent interest for production men as well as scientists. Ten papers in this issue are devoted to it.

▶ PREDICTION of reaction rates is examined in considerable detail by Daniels (page 504) who points out the importance of including all hidden factors in the calculation. Examples are given of the application of several rules employed and these are compared.

▶ RATES OF ORGANIC REACTIONS can be calculated from the fundamental physical properties of the molecules, and the calculations provide a useful framework for correlating empirical observations, according to Eyring, Hulburt, and Harman (page 511). Applications of the theory to a number of different types of reactions are given.

▶ **PERFORMANCE** of small-scale units for carrying out gas-solid reactions is correlated by Hurt (page 522) with that of plant production units. The method, especially useful when the intermediate steps of development must be shortened or omitted, is illustrated by the platinum-catalyzed oxidation of sulfur dioxide.

► CATALYSTS function properly only in the optimum temperature range for the reaction involved. Because changes in heat always occur during reaction, the heat transfer characteristics of the catalyst bed necessarily control the design of converters. Wilhelm, Johnson, and Acton (page 562) discuss this phase of design of equipment for catalytic processes.

► ESTERIFICATION of acetic acid by alcohol in the vapor phase over silica gel catalyst has been investigated by Hoerig, Hanson, and Kowalke (page 575), who find mass transfer through a condensed phase on the catalyst to be the controlling factor in rate.

▶ RATES OF REACTIONS involving solid catalysts conform to general equations based on the theory of activated adsorption by Hougen and Watson (page 529). They propose quantitative expressions for the effects of the several factors involved.

• OXIDATION of sulfur dioxide over platinized asbestos is used by Uyehara and Watson (page 541) to exemplify the application of the generalized theory presented in the preceding paper. Experimental data conform to an equation based on the assumption that rate is controlled by the surface reaction between adsorbed sulfur dioxide and atomic oxygen.

► CATALYTIC HYDROGENATION possesses special interest through its wide industrial applications. Anderson and Rowe (page 554) describe unique equipment, devised to study reactions of this type as well as other high-pressure processes, and having important advantages over other apparatus.

▶ HYDROGENATION of isooctene over nickel catalyst has been studied by Beckmann, Pufahl, and Hougen (page 558) using the equipment of Anderson and Rowe. Rate equations have been developed to correlate experimental results. ▶ SOFTENING OF WATER by cation exchangers was investigated by du Domaine, Swain, and Hougen (page 546), and the results of the experiments were reduced to a differential rate equation. From this, both performance and design of commercial softeners are charted.

▶ LUBRICATING OILS in service undergo oxidation catalyzed by the metals in contact with them. Larsen and Armfield (page 581) have investigated this catalytic reaction as it occurs in internal combustion engines. While massive metals are active, the fine particles worn from engine parts are much more so. Three representative oils were used in the experiments.

• EXTENDERS added to pigments in lusterless olive drab enamels appear not to affect durability so long as pigment makes up less than 60 per cent of the total volume of solids, according to Beck (page 594). Life of the enamel is shortened if the pigment bulks larger than that.

▶ PLANT HORMONES, defined as physiologically active compounds, have fired many imaginations, and Zimmerman (page 596) reviews recent progress in the use of such materials on the basis of work done at the Boyce Thompson Institute for Plant Research.

▶ PROPANE's widening uses as a refrigerant lend special interest to its thermodynamic properties provided in detail by Stearns and George (page 602). Both tables and graphs are given.

▶ BARIUM AND STRONTIUM CHLORIDES can be recovered from fusions of their respective sulfates with calcium chloride and extraction with aqueous methanol, according to Shreve and Wiegandt (page 608). Conversion of a soluble modification of anhydrite, produced in the aqueous reaction, to an insoluble form is apparently accomplished by the fusion, since water can also be used as the solvent for recovering the chloride.

▶ LACTOSE adsorbs riboflavin during crystallization from whey, and the product thus formed is believed by Leviton (page 589) to have a useful function in supplying riboflavin for human consumption. The concentration of riboflavin in the crystals is a linear function of its concentration in the original solution.

▶ VAPOR-LIQUID equilibrium data on twenty-three binary liquid systems are presented by Othmer (page 614). Included are: acetaldehyde with toluene, benzene, and furfural; acetone with benzene and monochlorobenzene; water with propionic and butyric acids; acetic acid with seventeen other liquids; butanol with butyl butyrate; and methyl ethyl ketone with propionic acid. Apparatus used is described in detail.

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Vol. 35, No. 5



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May, 1943

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1. What grade will you 3. How will you design for economy and for conservation of steel?

2. What finish will 4. How can you be sure serve you best? of sound welds?

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CRACKING petroleum, despite the age of the basic process, continues so fruitful in industry as to encourage search for further modifications to yield even greater values for the future. The introduction of catalysts into the cracking reaction has immensely increased the range of its usefulness and at the same time the area to be explored for a proper understanding of the mechanism involved. On that we shall learn details of what happens to cyclohexane.

Brine from oil wells presents a special disposal problem in the field. In its stay above ground, conditions are reached which favor precipitation of calcium carbonate to clog porous structures when it is pumped into the earth again. We shall learn how the remarkable stabilizer, sodium hexametaphosphate, improves that condition.

Selective solvents have performed near miracles in separating constituents of petroleum. Now, we learn, a somewhat similar technique may yield equally valuable results in separating constituents of what we have traditionally called the "fixed oils". Amazing and most useful is the parting of such oils as soybean into fractions possessing different degrees of unsaturation by the simple expedient of solvent extraction.

Another solvent problem now vexing has to do with the highly useful zein, a protein from corn. A group of helpful binary solvents for this material enlarge its applications; it is already important as a coating through its resistance to greases.

Design problems are always important. This time we shall learn of a new still to determine vapor-liquid equilibrium data essential in the design of fractional distillations.

Heat capacity of gases, also essential in many design problems, are calculated by a new and better method to be described for us.

Similarly, viscosities of fluids are needed in designing vital parts of equipment for every type of process. Often experimental values are missing in required ranges and hence calculation is used to extrapolate them. An improved method for this purpose will prove valuable.

Behaviors of starch and glue in swelling in water will be discussed for the light they throw on these important materials and their applications.

Alkylation and dealkylation are suggested as methods of separating individuals from the usual complex mixtures of cresols and xylenols. Despite its apparent complexity, the method, we are assured, works.

Then we shall learn more about the behavior of Buna S with petroleum products, information we shall find most useful as the synthetic rubber program gets into production.

From the Detroit meeting of the SOCIETY come two well received articles, one dealing with the newer art and contributions of the petroleum industry, the other a passing show of the rubber field (the censor willing).

And there will, as always, be much more.

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A NOTE to cheer the engineer worrying about delivery of new equipment is sounded by the Graver Tank & Mfg. Co. What with the publization of shortages, everyone knows

that it's a major task to get machines, but, warns Graver, "Don't take it for granted that you can't get delivery. It doesn't pay to assume that everyone is too busy to build a vital piece of equipment." Often production schedules are capable at odd moments of taking care of extra work, and it may be that Graver's engineers will find just the right schedule for that needed piece of equipment.

Goodyear brings forth a new synthetic material, Resoweld, and asks us to remember this name when confronted with jobs requiring corrosion protection. The newcomer's parent is a resinous base and it resists all the alkali, acid, and salt solutions successfully handled by rubber. Going even further than rubber, it can be used with nitric and chromic acids, alcohol, petroleum oils, gasoline, linseed and vegetable oils, soaps, and such. Continuing with its properties, we read that it can be applied, in the field, to all types of metal, wood, and concrete equipment, and functions satisfactorily up to 150°F. It does not deteriorate with age and can take jolts without cracking. Resoweld, concludes Goodyear, is not a wartime expedient. With such an array of favorable properties we can only agree with that conclusion.

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N this war we need more fats for food and for explosives than we can get, even though patriotic housewives are contributing their pounds of drippings to be made into glycerine and soap. Not only the original fats, but also the derived soaps have gone to war, for example, in the synthetic-rubber industry.

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VOI. 30, NO. 5

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INDUSTRIAL AND ENGINEERING CHEMISTRY

Vol. 35, No. 5

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Like Persian masterpieces of pottery, General Ceramics Chemical Stoneware, when tapped with a hammer, will resound with a bell-like tone, showing its high quality. This test is not nearly as convincing, however, as the acid test to which General Ceramics products may be submitted with complete confidence. They are not merely acid resistant but acid *proof* throughout. This, in use, means first, the elimination of product contamination; second, greater protection of plant personnel and property because

CERAMICS COMPANY

CHEMICAL STONEWARE

there can be *no* hazardous leaking; third, longer lasting stoneware equipment, for, once installed, General Ceramics Stoneware lasts indefinitely; and fourth, its hard glazed surface makes General Ceramics Stoneware easy to keep clean.

Included in General Ceramics Chemical Stoneware for industrial use are acid proof pipe, valves, fittings, kettles, jars, pots, pumps, exhausters, coolers, condensers, acid elevators, towers, filtering equipment and tourills.

FIG. 55 CONDENSATION TOURILL

Other products include Steatite Insulators made by General Ceramics & Steatite Corp., Keasbey, N. J.

ramics Co Jenera GENERAL

CHEMICAL STONEWARE DIV. KEASBEY • NEW JERSEY

Prepared Monthly by U. S. Industrial Chemicals, Inc.

May

A Monthly Series for Chemists and Executives of the Solvents and Chemical Consuming Industries

U.S.I. CHEMICAL N

1943

Revised Data on Solox Properties Issued by U.S.I.

New Folder Lists Applications Of General-Purpose Solvent

Revised information on the specifications for Solox, the popular general-purpose solvent, has been prepared by U.S.I.

The authorized composition of Solox now calls for the addition of the following to every 100 gallons of S.D. Alcohol No. 1:

190-proof S.D. Alcohol No. 1 is used in the preparation of the Regular grade of Solox, and 200-proof for the Anhydrous grade.

Properties are as follows:

	Regu- lar	Anhy- drous
(at 60°/60° F.)	0.8158	0.7962
Color	Water White	Wate White
Flash Point (approx)	71° F.	71° F.
Coefficient of Ex- pansion (per 1° F.)	0.0006	0.0006
Weight, Lbs. per	6.790	6.630

Because of its unusual solvent powers and its mild, non-residual odor, Solox has found extensive use in a variety of industrial applications. A revised folder, now in preparation, lists many of the most important applications in fields ranging from lacquer formulation to fuel oil conditioning. Copies of this folder may be obtained by writing to U.S.I.

New Method Determines Salts in Crude Oils

NEW YORK, N. Y. — Extensive tests conducted in five laboratories of a large company with headquarters here to determine the most accurate and reproducible method of determining the salt contents of crude oils concomitant with reasonable speed and ease of manipulation have led to a new method, employing hydrochloric acid reflux apparatus.

When the separation of layers after heat application is slow, or an emulsion forms at the interface, the addition of about 5 ml. of butanol and the judicious application of heat is claimed to effect sharp separation. Butanol has broken all emulsions encountered to date.

Carbon Dioxide Useful Against Electrical Fires

The snow and gas discharged from carbon dioxide extinguishers of the first aid type are non-conductive even in the presence of voltages up to 100,000 volts alternating current so long as the extinguisher horns retain their original high dielectric qualities. These facts are the result of an investigation made by engineers of Underwriters' Laboratories, Inc. to determine the electrical conductivity of when estimations when fighting fires in or

ment.

Calcium Separated From Strontium by Use of Acetone

Calcium can be separated from strontium with fairly good results through the use of acetone as a solvent, according to a recent claim. After the two materials have been evaporated to dryness in a nitric acid solution and further dried at 170°, the calcium nitrate is extracted with acetone, in which it is very soluble, then evaporated to dryness and weighed. Strontium nitrate, only slightly soluble in acetone, remains as a residue and can be weighed separately.

Research Workers Uncover New Fields for Starch Esters

PRINCETON, N. J. — A study conducted here reveals that starch esters have potentialities for use in the coating, sizing, and adhesive industries; in the preparation of aqueous emulsions or suspensions of high polymers; and in soft rubberlike plastics.

When using such esters to form either plastics or coatings, dibutyl phthalate is recommended as a plasticizer. For example, it is claimed that a soft plastic with relatively high tack can be made with starch butyrate containing 25% dibutyl phthalate. In coatings, dibutyl phthalate minimizes checking.

Iodine Compounds of Steroids Produced by New Method

BLOOMFIELD, N. J. — A new method has been patented and assigned to a company here for the production of iodine compounds of steroids. The iodo compounds obtained are expected to find application for pharmaceutical use as therapeutic agents and also as intermediate products.

According to the invention, the hydroxy steroids are first converted into esters of true organic sulfonic acids. These are then treated with iodides, preferably in organic solvents such as acetone, at an elevated temperature whereby the corresponding steroid iodides and alkyl or aryl sulfonic acid salts are produced.

Quicker Drying Time Is Claimed for Oils Made by New Method

Better Properties Obtained by Rearrangement of Molecules

What are described as entirely new types of drying oils have been produced from soybean and linseed oils by a molecular rearrangement which introduces conjugated double bonds in place of isolated double bonds in the molecule. Superior drying and bodying properties are among the advantages claimed for these oils.

The soybean oil product is described as drying in half the time required by high quality bodied linseed oil and as gelling under heat tests in a fraction of the time required by the latter. Baking times are said to be equally short and the hardness of the dried films as good as that of dehydrated castor oil. It is reported that there is none of the tackiness of ordinary soybean oil films.

Excellent Color Retention

The color retention of these films, both in the light and in the dark, is described as outstanding, while cooking of varnishes requires less time than corresponding linseed oil varnishes. When dried without adding driers, frosting annears after one or two days.

frosting appears after one or two days. The average constants of conjugated soybean oil are as follows:

Viscosity	Z-3 or Z
Acid Value	5.9
Wijs lodine Value (400% excess)	97.1
Total Iodine Value (Woburn Method)	128.3
Difference	31.2
Diene Value (Ellis-Jones Method)	17.4
Browne Heat (600° C.)	20 minutes
Specific Gravity (25° C.)	0.9427

Tung Oil Substitute

As the cooking of conjugated linseed oil with resins proceeds very fast, it is expected to offer new possibilities in the problem of replacing tung oil. In producing this oil, the greater part of linoleic and linolenic acid occurring in linseed oil is changed into the isomeric acids containing conjugated double (Continued on uest page)



Vacuum chambers at the Woburn Degreasing Company of N. J., into which drying oils are pumped after pre-heating to change the molecular structure from isolated to conjugated double bonds.

May

U.S.I. CHEMICAL NEWS

Simple Method Devised to **Extract Resin from Shellac**

A new method for preparing pure resin from shellac was described recently, which was said to yield about 98% of the total hard resin present in the sample of shellac used.

Two litres of ethyl acetate are added to one pound of finely powdered lac and two litres of benzene added after about five min-utes. The whole mass is occasionally stirred for an hour, then the admixed liquid is filtered out by pressing through a cloth or canvas bag. The swelled residue is again treated with a mixture of one litre of ethyl acetate and one litre of benzene to free the mechanically held solvent and the soft resin along with it. The whole is again filtered and pressed in a canvas bag after ten to fifteen minutes and the residue dried in a vacuum oven at 60 to 65°. Finally, the dried mass is melted under water and drawn into fibers.

Soap Deterioration Reduced Through the Use of Acetone

PACKANACK LAKE, N. J.-The addition to a soap composition of a small quantity of a product obtainable by the reaction of an aliphatic ketone compound, such as acetone, with ammonium thiocyanate prevents or greatly reduces deterioration and oxidation of the soap, it is claimed in a patent granted to an inventor here.

In tests the reaction product was mixed in the proportion of .1% with a pure white toilet soap stock containing .07% free sodium hy-droxide and 12% moisture. It is said that the antioxidant is neutral in reaction and does not interfere with the estimation of the proper end point of the reaction in the manufacture of the soap.

New Procedure for Making Smoke Without Combustion

LOS ANGELES. Calif. - A new method for making smoke without combustion for use in screening, overcoming riotous crowds, and photography is described in a patent recently awarded to an inventor of this city. The smoke is said to be harmless and can be regulated in density.

In forming the smoke, cyclohexylamine and a volatile, normally liquid organic acid, such as acetic acid, are brought into contact with each other in the presence of atmosphere with | liquid of low boiling point such as acetone.

Obtains Higher Resistance In Hectograph Blankets

CHICAGO, Ill. - By incorporating a minor proportion of a glycol solvent in the composition, an inventor here claims that a hectograph blanket can be produced without "burnthat has exceptional heat and humidity ing resistance and high copy strength.

The following composition is one of several suggested:

Per cent

Gelatin, bloom st	trength	220	Э.,		•			•		. 7
Water		• •					• •	•	• •	.10
Phthalic glycerin	resin .	• •				• •	• •		• •	
Glycerin						• •	• •	•	• •	.12
Ethylene glycol .							• •	٠	• •	. 93/4
Formaldehyde (40)%}	• •		• •	•	• •	• •	•	• •	. /4

New Drying Oils (Continued from preceding page)

bonds. It is available in viscosities ranging from Z up. Tests show striking differences in gelation and drying times between the natural, bodied oil and its conjugated isomer which suggest its advantages for air-drying or baking finishes.

The greater activity of the conjugated double bonds permits cooking this oil with slow resins and gums which are usually not used with linseed oil alone. Frosting is produced when the oil is dried without metals. On baking this oil without driers, it sets and dries faster than either linseed oil or de-hydrated castor oil but somewhat slower than oiticica or tung oil. The hardness of the baked film is somewhat greater than linseed oil.

Conjugated Fatty Acids

Another important development from the same laboratories is conjugated fatty acids, isomerized products distinguished from their natural counterparts by the presence of a substantial proportion of conjugated double bonds which are formed by a "shifting" process from the isolated double bonds of linoleic and linoleneic acids. Viscosity can be controlled according to the amount of polymerization taking place during isomerization.

Foremost among the property changes wrought by this molecular rearrangement is said to be a greatly increased speed of polymerization. Others include light color and good color retention at elevated temperatures.

either one, or both, in vaporous form. In order to dilute and facilitate evaporation of the amine, ethyl alcohol is added. The weight of the smoke may be varied by adding a volatile

TECHNICAL DEVELOPMENTS

1043

Further information on these items may be obtained by writing to U.S.I.

An alkali cleaner and de-oxidizer for aluminum, copper, nickel and galvanized metal is described as a free-flowing powder form which is readily soluble in water. (No. 690) USI

A vitreous enamel frit is offered which is de-scribed as being luminous, phosphorescent and fluorescent. Suggested uses include war purposes, lamp shades, and license plates. (No. 691) USI

A siphon for transferring carboy acids or other dangerous liquids is announced, which is said to eliminate the possibility of carboys bursting, since the pumping action is contained within the siphon, thus creating no pressure in the carboy. (No. 692) S

USI arrived as the second sec

US I A special kettle has been designed for mixing or processing viscous materials, creams or pastes which must be heated and which have a tendency to settle to the sides of a processing vessel. A full steam or hot water jacket surrounds the kettle for heating the contents, it is said. (No. 64) US I Special cholesterol and sterol products have been developed which are said to be effective sta-bilizers, emulsifiers, and dispersing agents for such products as drugs, cosmetics, textiles, dyes, and inks. They are described as pale, odorless, semi-solid, non-volatile oils which will not thicken or dry out. Complete solubility in animal, vege-table and mineral oils and ready dispersement in soapy water is claimed. (No. 695) US I

A finish coat in color for masonry has been pro-duced which is claimed not to require priming or on undercoat. The maker says that one coat penetrates, waterproofs, preserves and beautifies masonry whether inside or out. (No. 696) US | A floor cleaning compound

A floar cleaning compound is offered which is said to be so fire-resistant that it will not burn when the flame of a blow torch is played upon it nor as the result of spontaneous combustion. It is further described as highly absorbent of oils and arcares and greases. (No. 697)

and greases. (No. 697) USI A plastic containing silicon has been developed which is said to combine the advantages of organic and inorganic compounds and which can be used as a solid or a liquid. The solid form has a melting point close to 500° F., it is claimed, while the liquid remains stable in consistency under temperature extremes. Properties can be altered by changing the organic molecules. (No. 698) (No. 698)

An adhesive is announced for sealing protective paper to plastic plane parts which is said to offer the following advantages over crude rubber adhesive: better resistance to sunlight with no "cracking-off" from the plastic, slower aging and greater uniformity of quality. (No. 699)

USI



Thereni Valve Failure

CORROSION CONQUERS ANOTHER VALVE when proper maintenance is neglected .

I starts

This wedge of an Iron Body O. S. and Y. Gate Valve should be still in use, good for many more years of service. Instead, it is worthless, discarded. Unchecked corrosion completely destroyed the threads (1) and the wedge pin (2), allowing the wedge to drop off the spindle and shut off the water

Proper Installation Would Have Minimized Trouble

The valve was installed in the main supply line, in the usual horizontal position, with spindle vertical, and was left open most of the time. As shown in above sketches, the raised spindle indicated that the valve was "open" after the wedge had dropped, and locating the cause of the stoppage was made extremely difficult.

In certain services, where a valve is infrequently operated, it is often desirable to install it with the spindle horizontal. Then, if the wedge should become detached from the spindle, it cannot fall into the closed position.

Army-Navy "E" Pen-nant, awarded to Jenkins Bros. for high achieve-ment in the production



supply. Production was stalled several hours, until the trouble was located and corrected.

Analysis of the water conditions when the valve was installed would have indicated the need for a valve made of a metal more resistant to corrosion. But, even with this wedge, proper maintenance would have checked the destruction, and prevented the serious interruption in plant operation.

Inspection at frequent intervals would have revealed the excessive corrosion, and measures could have been taken to minimize the ruinous effects, such as water treatment and periodic cleaning. The accumulation of deposit (3) which threatens the eventual destruction of the seat ring (4) would then have been prevented.

This valve failure clearly demonstrates the importance of frequent, systematic inspection, and the repair or replacement of worn parts before a valve destroys itself. It also shows the need for careful selection and proper installation of valves suited to the particular service conditions. If these simple precautions are followed, and maintenance workers are thoroughly instructed, most valve troubles can be prevented before they start.

Interruption in production may have far-reaching effects in the present emergency. It can seriously retard the delivery of material needed by our armed forces. Preventable valve failure is also an inexcusable waste of critical metals. Every management should take all steps necessary to keep valves operating at top efficiency

Consult Jenkins engineers for any advice you need in improving your system of valve conservation.

Jankins Bros., 80 White Street, New York, N. Y.; Bridgeport, Conn.; Atlanta, Ga.; Boston, Mana, Philadelphia, Pa.; Chicago, Ill. Jenkins Bros., Limited, Montreal; London. England



For every industrial, engineering, marine and power plant service . . . in Bronze, Iron, Cast Steel and Carrosian-Resisting Alloys . . . 125 to 600 lbs. pressure.

THE BRICK THAT SAVED A THOUSAND SHIPS

Dehydrated food saves shipping space. Compressed dehydrated food briquettes Save still more space. Thus, one supply ship can now carry The food equivalent of ten supply ships ... And each ship can provision ten times As many soldiers as ever before. Air conditioning and refrigeration equipment Makes possible these dehydrated food bricks . . . Dependable and efficient cooling equipment Provided by General Electric. After the war, When air conditioning and refrigeration Will again become available to the public, Take advantage of G-E experience In the fields of air conditioning and Commercial and industrial refrigeration Turn to General Electric. Air Conditioning and Commercial Refrigeration Department, Division 435, General Electric Co., Bloomfield, N. J.

Air Conditioning by GENERAL & ELECTRIC

EVERY ENGINEER SHOULD KNOW ABOUT BROWN FINTUBE HEAT EXCHANGERS

15" x 22'0" OVERALL, TYPE BFT-2 TANK SUCTION HEATER PROVIDES 1560 SQ. FT. OF EFFECTIVE SURFACE... TRANSFERS 3,060,000 BTU PER HOUR

TYPE BFT-2 OIL TANK SUCTION HEATER

PERFORMANCE DA	TA
COLD MED	IUM HOT MEDIUM
In (Shell or Tubes)	Fintubes
Medium ("Ç" 15≠ Ga.
Mealon §	il Saturated Steam
Gravity ^o API	-
Quantity GPH 60° F 9,500	
Inlet Temp. ^o F 60	250° F.
Outlet Temp. ^o F	250° F.
Heat Duty BTU/Hour	- 00
Pressure Drop #/ sq. in	-

If you want greatest known efficiency—and capacity—in transferring heat between two commodities having uneven heat transfer co-efficients, —it will pay you to thoroughly investigate Brown resistance-welded integrally-bonded Fintubes and Brown Fintube Heat Exchangers.

Through the use of Brown Fintubes having the desired number and depth of fins, the primary and secondary tube surfaces of Brown Fintube Heat

THE BROWN

Exchangers can be proportioned to the transfer co-efficients of the materials being heated or cooled. This avoids the necessity of using hundreds, sometimes thousands of feet of bare tubing to satisfy the requirement of the commodity having lower heat transfer co-efficient. It permits a fewer number, or shorter, Brown



Fintubes to be used for a given heat transfer service than if plain bare tubes were used... and results in small shells, less weight, less pressure drop, and many other important savings in manufacturing, shipping, installation and maintenance costs.

Six standard and many special types of Brown Fintube Heat Exchangers meet every requirement for effecting transfers between liquids and gases,

> and other commodities having unequal transfer co-efficients, -and provide the high thermal efficiency and trouble-free operation that only Brown resistancewelded integrally-bonded Fintubes can give you. More complete details and descriptive literature furnished gladly. Let us quote on your heat exchanger requirements.

NTUBE

120 FILBERT STREET • ELYRIA, OHIO MANUFACTURERS OF INTEGRALLY BONDED FINTUBES AND FINTUBE HEAT EXCHANGERS Blood plasma

DRYING AND DISTILLATION under extremely low absolute pressures Metallic magnesium fine pharmaceuticals

amin concentrates

Fine chemicals

Elliott four-stage steam jet ejector for drying blood plasma. This arrangement produces an absolute pressure of less than one millimeter, removing all but one per cent or less of moisture from the substance while in the frazen state.

(E) W

The Army-Navy "E" has been awarded to both the Jeannette and the Ridgway plants of Elliott Company.

ye intermediates Steam Jet EJECTORS

Extremely low absolute pressures produced by Elliott multi-stage steam jet ejectors are employed in the manufacture or processing of such substances as listed above. Such low pressures (or high vacuums) are used for these reasons:

- To avoid "cracking."
- To obtain close fractional distillation.
- To avoid any change in the substance, by subliming, as in drying blood plasma at below freezing temperatures.

Elliott engineers are leaders in the field of applying high vacuum to process work, and their pioneer efforts have proven invaluable in developing successful procedure. Their cooperation is offered in meeting your problem.

ELLIOTT COMPANY

Heat Transfer Dept., JEANNETTE, PA. DISTRICT OFFICES IN PRINCIPAL CITIES

G- 382

REMEMBER THIS NAME-RESOWELD

for all jobs requiring corrosion-protection

To serve those industries now prohibited from installing rubber linings for handling corrosives, Goodyear announces a new synthetic material equal to rubber for many uses, and superior in some.

This new material is called RESO-WELD. As its name implies, it has a resinous base. It is less critical than natural or reclaimed rubber and can be supplied under war regulations to plants having reasonable need.

RESOWELD not only resists practically all the acid, alkali and salt

solutions successfully handled by rubber, but in addition it can be used with nitric and chromic acids, alcohol, petroleum oils, gasoline, linseed and vegetable oils, soaps and similar materials destructive to rubber.

Another advantage is that RESOWELD can be applied, in the field, where absolutely necessary, to all types of metal, wood or concrete equipment other than pipe and fittings. It functions satisfactorily at temperatures up to 150°F. It does not deteriorate with age and withstands severe mechanical shock without cracking.

RESOWELD is not a wartime expedient. For complete data on any corrosion-proofing job, consult the G.T.M.-Goodvear Technical Man. Or write Goodvear, Akron, Ohio or Los Angeles, California.

Resourcid-T.M. The Goodyear Tire & Rubber Company

The recommends RESOWELD for handling

INORGANIC ACIDS (except Faming Natric) ORGANIC ACIDS (except Glacial Aratic) INORGANIC SALTS PICKLING SOLUTIONS PLATING SOLUTIONS ALKALI SOLUTIONS ALCOHOL GOODFYEAR (pure and demonstred)

FLOOR WAX AND POLISH PETROLEUM OILS DISINFECTANTS FERRIC CHLORIDE FOOD PRODUCTS

THE GREATEST NAME IN RUBBER



Bausch & Lomb Contour Measuring Projector

Today Precision Must Be Commonplace



American fighting men on our fighting fronts depend upon production line accuracy . . . for ten-

thousandths of an inch variation on the production line can mean the difference between a hit or a miss on the battleline.

The Bausch & Lomb Contour Measuring Projector makes such accuracy possible on the fastest moving production lines, because it takes many vital inspection jobs "off the surface plate" and eliminates the tedious, time-consuming computations of the "sine bar." Inspections for accuracy become routine jobs.

Throwing an accurate, sharply defined shadow image of the object under examination on a translucent screen, the B&L Contour Projector permits exact measurements or comparison with an enlarged template drawing at magnifications great enough for easy and accurate dimensioning. Here again is a Bausch & Lomb peacetime development that serves America at War. The B&L Contour Measuring Projector is helping speed production of fighting tools for our fighting men.

For Bausch & Lomb Instruments essential to Victory—priorities govern delivery schedules.

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AN AMERICAN SCIENTIFIC INSTITUTION PRODUCING OPTICAL GLASS AND INSTRUMENTS FOR MILITARY USE, EDUCATION, RESEARCH, INDUSTRY AND EVESIGHT CORRECTION



THERE'S A G-E EXPLOSION-PROOF MOTOR TO MEET IT

No one type of motor is "best" for all kinds of hazardous locations. The *right* selection may eliminate the need for fire-walls to isolate the motor, and for awkward remotedrive arrangements.

Our engineers offer to work with you to select the motor, control, and other auxiliary equipment that best combines simplicity with security on the job.

General Electric builds the most complete line of explosion-proof and dust-tight motors available, tested and listed by Underwriters' Laboratories, Inc., for specific industrial hazards.

Most of these motors are as compact as standard open types, and require even less maintenance because of their totally enclosed construction.

Information on motorizing equipment in hazardous places is given in our publication No. GEA-3647. For this or any other motor assistance that can help speed war production, just call your General Electric Representative. Or write General Electric, Schenectady, N. Y.

Three More G-E "FIRSTS" in Motors for Hazardous Places

EXPLOSION-PROOF TO 600 HP

Totally enclosed squirrel-cage motors up to 600 hp are now listed by Underwriters' Laboratories, Inc., for Class I, Group D, locations, where atmospheres may contain gasoline, petroleum vapors, acetone, alcohols, natural gas.



TESTED AND LISTED FOR COMBUSTIBLE DUSTS

Built in a wide range of types and sizes, this motor is U.L.-listed for Class II, Group F, locations—where coal dust, coke dust, or carbon black may be present.



FOR METAL DUSTS LIKE MAGNESIUM, ALUMINUM

Ordnance plants find wide application for this totally enclosed motor, tested and listed by Underwriters' Laboratories for Class II, Group E, locations.



27



This Refractory Has High Fusion Point—PLUS!

High fusion point, alone, may be the only quality you need in your refractories. But especially if you need a *combination of high fusion point with low porosity*, we would like to tell you about Corhart* Electrocast Refractories.

Corhart Electrocast Refractories are high-duty products made by melting refractory oxides in electric furnaces, then pouring into molds. They have been used almost exclusively in the glass industry for many years — are now being rapidly adopted by several other industries in which high fusion point, low porosity, extreme hardness or high specific gravity are important. Corhart Electrocast is particularly useful in fortifying severe spots which normally control the life or productivity of entire furnaces. Your inquiry will be held in confidence. *Address:* Corhart Refractories Co., *Incorporated*, 16th & Lee Streets, Louisville, Kentucky.



*Not a product, but a registered trademark.

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Is this the beginning of a miracle?

Mr. Ernest G. Enck, our technical director, thinks we should put greater emphasis in our advertising on our sizing and beneficiation of ores and minerals. We do, he emphatically reminds us, prepare a significant list of chemicals from these ores and minerals.

There are, for instance, the carbonates and chlorides of lithium and strontium; the nitrates of lithium, yttrium, caesium, thallium and zirconium; and the benzoate, chloride, hydroxide, fluoride, and stearate of lithium . . . to mention only a few. A better understanding of these underemployed chemicals is already producing startling discoveries.

Lithium stearate is a case in point. Lithium stearate or "metal soap", was just what petroleum researchers needed to compound for our fighting planes one grease which tames the biting cold of Reykjavik as easily as it does the scorching heat of Tunisia. Will the automobile industry look into the post-war possibilities of this Foote patented product? Probably! Another example is strontium. Strontium salts, now vital to the war effort, are intriguing the interest of ceramic engineers and, after the war, may well influence the making of whiteware, glazes, lustres and optical glasses.

Yet, this is only a beginning. Much of our most interesting exploratory work is still quietly bubbling within the retorts of our laboratory. Today or tomorrow it is just possible we may help you achieve another miracle of chemistry, or to start one. If you suspect we can help you now, please write us.

THIS COMES OF PLAYING WITH FIRE ...

Remember the brilliant reds of Fourth-of-July fireworks you played with as a youngster? Strontium salts! Not much practical use for strontium then. But times have changed. Strontium now rakes enemy planes with tracer bullets, strontium helps purify caustic soda —reducing the iron and manganese contents of sodium hydroxide. A salt bath containing strontium is used in heat-treating steel. Strontium, for at least a dozen reasons, is gripping the interest of ceramists. Ample amounts of strontium salts are available for research, although quantity production is limited to war uses. Post-war strontium will be plentiful and inexpensive. If you'd like to find out what you can do with strontium salts, we'd like very much to help you—now. FOOTE MINERAL COMPANY A Step Ahead in Industrial Ores and Chemicals

PHILADELPHIA • ASBESTOS • EXTON, PENNSYLVANIA Home Office: 1616 SUMMER STREET, PHILADELPHIA, PA. West Coast Representative: GRIFFIN CHEMICAL CO., San Francisco, California





Wet versus Dry Grinding

A Few Facts Most Mill Users Do Not Know!

1. Do you know that power to grind wet is less than to grind dry but this advantage may be more than offset by the very low ball and liner consumption of the same mill grinding dry?

2.—that you can secure a better graded product when grinding dry?

3. — that you can dry and grind simultaneously?

4. — that if the product is to be acid treated, leached, or if water is scarce, dry grinding may be preferred? 5.—that some physical or chemical action grinding dry has, in many cases, increased extraction?

6. — Do you know that when grinding wet, in closed circuit with the Hardinge Counter-Current Classifier, you have a positive control of your fineness and that the Classifier maintenance is next to nothing?

7.—that a short cylinder Conical Mill grinding either wet or dry eliminates dead zones, thus increasing grinding rate and insuring a close control of sizing?



Write for Bulletins 13-D, 39-A and 41

THERE'S A PUMP.... BEHIND EVERY SHELL!

In the great job of providing explosives for our armed forces, WILFLEY acid pumps play a major part. WILFLEY is the pump without a stuffing box ... therefore the pump that operates without stuffingbox troubles. It's a star performer on either continuous or intermittent service ... Effective sealing blades. No rubbing contact. 10- to 2,000-G.P.M. capacities; 15- to 150-ft. heads, and higher. If you want highest efficiency in handling acids, corrosives, hot liquids and mild abrasives, WILFLEY is the pump to buy. Write for complete details.

A. R. WILFLEY & SONS, Inc.

DENVER, COLORADO, U. S. A. NEW YORK OFFICE: 1775 BROADWAY, NEW YORK CITY



Offset shaft, single reduction, 20 sizes, ratios 2 to 10:1, 1 to 1000 H.P. Offset shaft, double reduc- tion, 13 sizes, ratios 10 to 72:1, 1 to 400 HP.





Straight line drive, double reduction, 13 sizes, ratios 10 to 72:1, 1 to 400 HP.

Catalogs are available containing complete engineering data, advantages, weights and prices.



SPEED REDUCERS

MEET THE DEMANDS AND REQUIREMENTS OF INDUSTRY

The great load carrying capacity, the very high efficiency and the continued performance of D.O. James Generated Continuous-**Tooth Herringbone Gear Reducers** proves the engineering soundness of their design and manufacture.

These units are the product of an organization with over a halfcentury of gear making experience and have a wide use in many different industries.

D. O. JAMES MANUFACTURING CO. 1140 W. MONROE STREET, CHICAGO, ILL.

FOR 55 YEARS MAKERS OF ALL TYPES OF GEARS AND GEAR REDUCERS

NEW HOUDRY PROCESS CAN:

Speed up development of super engines by providing

super fuels now !

Step up the quality of present aviation gasolines!

In this war, no greater scientific discovery has been made than the Houdry Adiabatic Cracking Process.

It is the latest development of Houdry catalytic research, which has already played leading parts in America's aviation gas and synthetic rubber programs.

The new process can produce a super-aviation fuel of such unheard-of high quality, that today's aircraft engines are incapable of using its full possibilities. Therefore, its most important immediate value will be as a blending agent, to raise the quality of present aviation fuels.

Better performance for today's planes

Even when used in this manner, as a reenforcer only, this super-aviation fuel will tremendously improve the performance of aircraft of current design. It will give our flyers a priceless edge in combatin speed, range, power, maneuverability.

The ultimate benefits of the new process will not be realized until aircraft engines of radically new design are created. Engines that can utilize a fuel as far superior to current aviation fuels as they in

turn are superior to a third-grade motor gasoline. Even that comparison understates the potentialities of the new Houdry Adiabatic Process.

First adiabatic plant now in operation

A semi-commercial unit is now producing superaviation fuel by the new Houdry process. It is a large-scale proving plant with a charging capacity of 600 gallons an hour. Completed in two months time, it demonstrates the further advantages of the process from the standpoint of simplicity and inexpensiveness of plant construction, savings in time and critical materials.

Complete details of its operation and of the process itself cannot, for military reasons, be published. Qualified inquiries are invited and will be satisfied to the extent permitted by military authorities.

The new Houdry Adiabatic Process, like all Houdry processes, is available to any and all American manufacturers without restriction, under license arrangements subject to approval by the United States Government.



THE HOUDRY PROCESS CORPORATION, Wilmington, Delaware

HOUDRY FIRSTS: First to develop and commercially pioneer catalytic cracking. 16 plants in operation today, many others building. ~ First to provide catalytically cracked automobile gasoline of superior quality. More than a billion gallons a year have been produced by Houdry Process. ~ First to produce catalytically cracked base for aviation gasoline. Last year Houdry plants produced more than 90% of all catalytically cracked aviation gas made in the world. ~ First cracked gasoline to meet U.S. Army specifications was made by Houdry Process.



Offset shaft, single reduction, 20 sizes, ratios 2 to 10:1, 1 to 1000 H.P. Offset shaft, double reduc- tion, 13 sizes, ratios 10 to 72:1, 1 to 400 HP.





Straight line drive, double reduction, 13 sizes, ratios 10 to 72:1, 1 to 400 HP.

Catalogs are available containing complete engineering data, advantages, weights and prices.



SPEED REDUCERS

MEET THE DEMANDS AND REQUIREMENTS OF INDUSTRY

The great load carrying capacity, the very high efficiency and the continued performance of D.O. James Generated Continuous-**Tooth Herringbone Gear Reducers** proves the engineering soundness of their design and manufacture.

These units are the product of an organization with over a halfcentury of gear making experience and have a wide use in many different industries.

D. O. JAMES MANUFACTURING CO. 1140 W. MONROE STREET, CHICAGO, ILL.

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FOR 55 YEARS MAKERS OF ALL TYPES OF GEARS AND GEAR REDUCERS

NEW HOUDRY PROCESS CAN:

Step up the quality of present aviation gasolines!

Speed up development of super engines by providing super fuels now !

In this war, no greater scientific discovery has been made than the Houdry Adiabatic Cracking Process.

It is the latest development of Houdry catalytic research, which has already played leading parts in America's aviation gas and synthetic rubber programs.

The new process can produce a super-aviation fuel of such unheard-of high quality, that today's aircraft engines are incapable of using its full possibilities. Therefore, its most important immediate value will be as a blending agent, to raise the quality of present aviation fuels.

Better performance for today's planes

Even when used in this manner, as a reenforcer only, this super-aviation fuel will tremendously improve the performance of aircraft of current design. It will give our flyers a priceless edge in combat in speed, range, power, maneuverability.

The ultimate benefits of the new process will not be realized until aircraft engines of radically new design are created. Engines that can utilize a fuel as far superior to current aviation fuels as they in turn are superior to a third-grade motor gasoline. Even that comparison understates the potentialities of the new Houdry Adiabatic Process.

First adiabatic plant now in operation

A semi-commercial unit is now producing superaviation fuel by the new Houdry process. It is a large-scale proving plant with a charging capacity of 600 gallons an hour. Completed in two months time, it demonstrates the further advantages of the process from the standpoint of simplicity and inexpensiveness of plant construction, savings in time and critical materials.

Complete details of its operation and of the process itself cannot, for military reasons, be published. Qualified inquiries are invited and will be satisfied to the extent permitted by military authorities.

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LaBour Type Q, a new design cen-trifugal for lasting efficiency where priming ability is not required.



LaBour Type DPL, the centrifugal pump that primes itself.

Making explosives, like making high-octane gasoline and so many other items demanded for war, is a chemical process involving large quantities of corrosive liquids. Acids must be manufactured, loaded and unloaded, transferred from tank to vat. Those corrosive liquids must be moved quickly, safely, dependably . . . if there are to be bombs for Berlin and TNT for Tokyo.

FORE THESE

HAPPEN

HINGS CAN

The fact that LaBour Pumps are doing the major portion of that moving job in American chemical plants is important to the future buyer of chemical pumps only because today's performance is a positive test of inbuilt quality. LaBours are making good under the toughest conditions it is possible to impose. That is why LaBour facilities are devoted completely to the war effort; that is why manufacturers of civilian chemicals cannot get LaBour Pumps now.

Out of this severe period of test will come even better LaBour Pumps for tomorrow, for we never stop learning. In the competitive business world that will come with peace, efficient pumping of chemicals will be at a premium just as today—and LaBours will do the job with the same economy and dependability that mark their performance in war.

THE LABOUR COMPANY, Inc. Elkhart, Indiana, U. S. A.

LABOUR PUMPS


The Case of the Corroded Propeller Shaft

A^{SK} an engineer on our new wooden ships where he most hates corrosion, and he'll whip back the two words, "propeller shaft." He knows lost time in drydock and expensive reconditioning swiftly follow the formation of rust on that giant driving rod.

Yet, until recently, the engineer of the wooden ship was resigned to propeller shaft corrosion. The reason: the shaft on such ships bears an extraordinarily heavy voltage of electricity. Against this severe and ceaseless electrical attack, protective coatings of even the highest quality soon broke down.

A coating company working with Thiokol* synthetic rubber had an idea. Could we, they asked, supply a brine-



SYNTHETIC RUBBER "America's First" proof material having extremely high insulating properties — a powdery material which would fuse on metal and form a hard, resilient continuous film? It turned out we could. As applied by the coating company (name on request), that Thiokol material solved the case of the corroding propeller shaft, and is today helping to keep precious ships out of drydock and on their Victory jobs. Thiokol Corporation, Trenton, N. J.

*Thiokol Corporation, Trademark Reg. U.S. Pat. Off.

""ON PRODUCTS: "THIOKOL" MOLDING POWDERS ... "THIOKOL" WATER DISPERSIONS FOR COATING

INDUSTRIAL AND ENGINEERING CHEMISIRY



Micromax is easily tuned to the furnace's needs-all settings are made at the front of the panel.

TO DEFEAT TEMPERATURE SWINGS Make MICROMAX the Operator's Helper

Every setting and resetting of its temperature controller which any standard type fuel-fired furnace or oven could require is supplied with the Micromax Control equipment shown above.

We do not even have to know how much load-swing you anticipate, or how much lag; many users do send us such facts, but the Controller is completely adjustable to any such problem...the limits of satisfactory control, if there are limits, being determined by factors outside the Pyrometer.

Just tell us, when you specify Micromax, the make, size and type of valve; the fuel and air pressures; the type of thermocouple if you have preference; the range of temperature to be controlled; the amount of wire needed between couple, Micromax and valve; and whether you want to have the equipment mounted on panel as shown. The resulting installation will help you secure control of unsurpassed sensitivity, accuracy and dependability.

If a Catalog will answer your needs, ask for N-00A, Micromax Electric Control; our new, compact, fully illustrated 30-page description of this equipment.



Hastelloy Alloys

are Strong and Tough!-and Highly Resistant to Corrosive Media

Hastelloy alloys—types A, B, C, and D—combine outstanding corrosion resistance with excellent physical properties. Each was especially developed to withstand the action of one or more of the common mineral acids or other strongly corrosive agents over a wide range of temperatures and concentrations. Alloys A, B, and C compare in tensile properties to high-strength steels, while alloy D possesses high hardness and wear resistance.

Shown below is a condensed table of mechanical properties of the Hastelloy alloys. For more com-

plete information on mechanical and physical properties, penetration test results, available forms and methods of fabrication, send for the 40-page booklet, "Hastelloy High-Strength Alloys."



MECHANICAL PROPERTIES OF HASTELLOY ALLOYS							
	Hastelloy Alloy A		Hastelloy Alloy B		Hastelloy Alloy C		Hastelloy Alloy D
	Cast Metal	Rolled Metal Annealed	Cast Metal	Rolled Metal Annealed	Cast Metal	Rolled Metal Annealed	Cast Metal
Ultimate Tensile Strength, lb. per sq. in.	69,000- 77,500	110,000- 120,000	75,000- 82,000	130,000- 140,000	72,000- 80,000	115,000- 128,000	36,000- 40,500
Yield Point, lb. per sq. in.	42,500- 45,000	47,000- 52,000	55,000- 57,000	60,000- 65,000	45,000- 48,000	55,000- 65,000	
Elongation in 2 in., per cent	8-12	40-48	6-9	40-45	10-15	25-50	0
Reduction of Area, per cent	16-18	40-54	10-13	40-45	11-16		0
Hardness, Rockwell Brinell	B 85-94 155-200	B 94-97 200-215	B 92-99 190-230	B 96-100 210-235	B 89-97 175-215	B 84-95 160-210	C 50-55
Izod Impact Strength, ftlb.	25-35	62-77	11-16	68-78	9-14	34-40	
Erichsen Value, Depth in mm.		10-11		10-11		8-9	
Transverse Breaking Load, 12-in. span, lb. deflection, in. Modulus of Rupture,	Note: The values given are averages and average ranges obtained with a limited number of specimens. They will serve as a reason- able guide for the engineer or designer planning equipment of Hastelloy alloys.						5,000 0.070-0.080
lb. per sq. in.							- 78,000
Modulus of Elasticity, lb. per sq. in.	27,00	00,000	30,750,000		28,500,000		28,850,000



HAYNES STELLITE COMPANY

Unit of Union Carbide and Carbon Corporation

New York, N. Y. Men Kokomo, Ind.

Chicago-Cleveland-Detroit-Houston-Los Angeles-San Francisco-Tulsa

HIGH-STRENGTH NICKEL-BASE ALLOYS FOR CORROSION RESISTANCE

The word "Hastelloy" is a registered trade-mark of Haynes Stellite Company.

for N-004, hact, fully nt.

DOW CAUSTIC SODA

Getting there first with the most

Air transport is dependent upon the high octane fuel which is being produced faster, today, than some of the lower octane gasolines common to American motorists.

One thousand four-motored planes in flight would require about 1,250,000 gallons of high test gasoline for a three-hour operation. Dow is supplying refiners with huge quantities of Caustic Soda to assist in the production of this vital fuel. This important industrial chemical is used as a reagent to remove sulphur from petroleum products, as a refining and sweetening agent for gasoline.

Refining is only one branch of industry that finds Dow Caustic Soda indispensable. Producers of rubber, textiles, soap, plastics and more than half a hundred other industries depend on Dow for their supply of this essential industrial chemical. Recent additions to facilities for production make Dow Caustic Soda readily available to industry in all parts of the United States.

THE DOW CHEMICAL COMPANY, MIDLAND, MICHIGAN New York City Chicago St. Louis Houston San Francisco Los Angeles Seattle



HIGH PRESSURE CONTAINEBS

War needs have greatly broadened the field of usefulness of high-pressure gases and liquids. And Walter Kidde & Company has kept pace with that development by providing containers in an everwidening variety.

Kidde cylinders are available in many sizes and shapes for the storage of carbon dioxide and other gases. Special-purpose valves and release mechanisms have been devised by Kidde engineers.

If you need help in solving a high pressure container problem, why not get the benefit of Kidde's experience? Our engineers will be glad to advise you. Just drop us a line-there is no obligation.

Walter Kidde & Company, Inc. Belleville, N. J. **530 Main Street**



LIGHTER WEIGHTS





SHATTER-PROOF



Available in Quantity ACID SILICIC

A UNIQUE PRODUCT COMBINING EXCEPTIONAL PURITY with UNUSUAL BULK

This special grade of Silicic Acid offers interesting possibilities as a

CATALYST CARRIER ADSORBENT

or a starting material for the manufacture of

Silicate Phosphors

If you use silica gel

—as a flatting agent
—in pharmaceuticals

you may find this Special Bulky Silicic Acid worthy of investigation. We are also prepared to supply other grades and solicit the opportunity to consider your specific needs.

Samples sent upon request.



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MALLINCKRODT CHEMICAL WORKS

Mallinckrodt Street, St. Louis, Mo. CHICAGO • PHILADELPHIA

Characteristics Acid Silicic Special Bulky

Fine White Powder; Active Adsorbent

Bulk . . . about 8 lbs./cu.ft. Low Alkali . . . not over 0.10%

Iron not over 0.001%

Other Heavy Metals not over 0.0005%

Chlorides not over 0.01% H₂O not over 15%

SiO₂ not less than 85%

74 Gold Street, New York, N. Y. LOS ANGELES • MONTREAL



YEARS OF SERVICE TO CHEMICAL USERS

A Complicated



Produced by

JOHNSON CITY, TENNESSEE

Builders of Anything in IRON or STEEL Not Already Produced as a Specialty

Note the size of the special three-way "Y", alongside man of normal size. It was fabricated by the "Jay-Cee" organization in Johnson City, Tennessee, which specializes in difficult assignments for the chemical and allied industries.

The "Y" unit shown above was fabricated of 8" and 12" diameter standard steel pipe, with light plate flanges. It is part of a complete system of spouting used to transfer raw materials from storage hoppers to screw conveyors in a plant manufacturing carbon products for the Victory Effort.

The "Jay-Cee" organization was established in 1883 — sixty years ago—and is well manned and equipped to offer you a complete organization service.





Here's a place where Activated Alumina is of prime assistance in the production of warimportant petroleum products—as an efficient, certain drying agent.

Pneumatic controls are used in the Houdry system to permit fine, even modulation in the control of all operations. But there dare not be any moisture in the air lines or valves to clog or freeze and upset the entire system. That's where Alorco Activated Alumina takes a hand, freeing this air of every trace of moisture.

Alorco Activated Aluminas are drying air, gases, and organic liquids to dew points below -110° F., on all kinds of war work. Yields and recoveries are thereby increased; constant quality is maintained; corrosion is eliminated. When the Activated Alumina becomes moisture-laden, it is reactivated by heating, and is restored to its original high efficiency. Standard equipment is available which performs these functions.

In many cases, Activated Alumina may have a place in your plant or processes. Tell us your drying problems. ALUMINUM COMPANY OF AMERICA (Sales Agent for ALUMINUM ORE COMPANY) 1911 Gulf Building, Pittsburgh, Pennsylvania.



ALORCO

PRODUCTS





(*Above*) This is what acid does to ordinary drain pipe. (*Below*) Duriron Bell and Spigot pipe is recommended for waste lines and drainage; Duriron Split-Flanged pipe for most industrial uses. Standard sizes, 1" to 8". Larger sizes made on request.



25 YEARS.

Nothing man-made is everlasting. But Duriron pipe and fittings, which have handled salt-acetic acid solutions for 25 years, would almost qualify for that designation.

The installation pictured above is only one. There are many other examples. Some are handling sulphuric, nitric, in fact almost all organic and inorganic acids at various strengths and temperatures. Durichlor is recommended for HCl and Cl solutions, showing remarkable records in these services.

Remember these important attributes of Duriron (or Durichlor) pipe and fittings:

- 1—They are made of the less critical materials.
- 2—They are extremely hard and resistant to scouring from abrasives carried in suspension.
- 3—They are inherently corrosion-resistant . . . no protective coating is needed.
- 4—They are easily installed.

If you are tired of fighting repairs to your piping, why not let us quote you on a completely trouble-free Duriron installation?

THE DURIRON COMPANY, INC. DAYTON, OHIO

what every plant operator should know about **GLASS PIPING!**

Do you have a tough corrosion problem like this?

The war plant in which this picture was taken had the problem of handling a 4% HNO3 solution, containing heavy metal salts, at a temperature over 200°F. That was last July. And Pyrex Piping has been doing the job ever since—without a penny for maintenance. This line is expected to give trouble-free service for years.

Wherever hot or corrosive liquids or gases are conveyed . . . wherever products must be protected from contamination . . . wherever it is important to know what is happening inside a line . . . there PYREX Piping gives you its most profitable service. See photo.

Chemical plants use it to eliminate corrosion problems, because it resists all hot or cold acids (except HF). Food and beverage manufacturers like it because it's easy to keep clean, either by simple flushing or with steam or strong hot cleaning solutions. It helps to produce a purer product.



EASY TO INSTALL

Plant workmen find it easy to make installations themselves. Recently, green plant mechanics have done first-rate installations with PYREX Piping.

You may install from one piece to a whole system-for PYREX Piping may be joined to existing metal lines and equipment. And it is hung and supported much like other types of piping. We do recommend that hangers and supports be padded, to minimize scratching.



STANDS UP MECHANICALLY

PYREX Piping is recommended for working pressures up to 100 lbs. p.s.i. But glass in this form is not as strong as metal. So, care must be taken to avoid installation strains or sharp impact. Nearly 20 years of service under all kinds of plant conditions have proved that only simple common sense and reasonable care are required to handle PYREX Piping without trouble. The glass itself is very hard-about twice as resistant to abrasion as ordinary plate glass. Thus, the piping is particularly suitable for abrasive, corrosive slurries. You can install and use PYREX Piping with confidence.



AVAILABLE NOW

Glass-making materials are fairly plentiful. We do need priority ratings that enable us to get accessories (flanges, gaskets), to assign

Glass Works Corning New York



necessary labor, and to establish your order in our production line. With such priorities we have been making 6 to 8-week deliveries.

Available sizes and lengths: 1", 11/2", 2", 3", and 4" diameters; any length from 6 inches to 10 feet (longer lengths on special request). There are corresponding ells, tees, return bends, and reducers.

Accessories: Compression type joints-with conical pipe ends compressed to a self-centering gasket by metal flanges and clamping bolts. We supply gaskets of materials suited to the liquid or gas you want to convey.

in



LOW COST

The initial cost of PYREX Piping (accessories included) is about the same or less than the cost of full-weight copper or brass piping, in comparable sizes, and is considerably less than the cost of stainless steel.

And because PYREX Piping does not wear out under acid attack, it gives long trouble-free service, with resultant low long-time cost.

WATCH FOR CORNING ADVERTISEMENTS!

Watch this magazine for more information in Corning's adver-tisements headed "What every plant operator should know about Glass Piping." And write for PYREX Piping Bulletin No. 814. Industrial Division, Corning Glass Works, Corning, N. Y. Branch Offices: New York, 718 Fifth Ave.; Chicago, Merchandise Mart

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Pyrex Industrial Glass

BLAW-KNOX builds <u>complete</u> PROCESS PLANTS

Distillation	Evaporation
Ges Absorption	Crystallization
Solvent Extraction	Drying
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Heat Transfer	Organic Synthesis
Furnacing	Emulsification
Cracking	High Pressure Processing
Kilning and Calcining	Impregnating
Polymerizing	Gas Cleaning and others

Complete plants for any of the process industries—from idea to operation. Blaw-Knox single control does the whole job. Research, engineering, fabrication, design and erection of buildings in cooperation with customer's architect and contractor, initial operation — all under one guarantee.

BLAW-KNOX DIVISION OF BLAW-KNOX CO. 2081 FARMERS BANK BUILDING • PITTSBURGH, PA. OFFICES AND REPRESENTATIVES IN PRINCIPAL CITIES 50

for POWER

SOUTHERN COLORADO POWER COMPANY Pueblo, Colo.

90,000 lbs. steam per hour Vogt LE type bent tube boiler with underfeed stoker. Water walls and economizer. Design pressure 525 lbs. Total steam temperature 750 degrees F.

PROCESS

IN A LARGE MID-WESTERN STEEL MILL

Two 105,000 lbs. steam per hour Vogt LE type bent tube boilers with chain grate stokers and economizers. Design pressure 225 lbs. Total steam temperature 550 degrees F.

HEATING

CRIMINAL COURTS BUILDING AND JAIL New York City

Four Vogt sectional header type boilers of 47,000 lbs. steam per hour capacity, oil fired. Design pressure 200 lbs.

HENRY VOGT MACHINE CO. LOUISVILLE, KENTUCKY Branch Offices: NEW YORK CLEVELAND CHICAGO PHILADELPHIA DALLAS

BENT TUBE AND SECTIONAL HEADER TYPES



Illustrated here is Рното-SWITCH LEVEL CONTROL Series P15NX. Designed for hazardous location mounting, directly on the tank, this modern electronic control operates signals or programs pumps to maintain constant levels in the handling of explosive liquids, and to de-tect water in tanks of oil or gasoline.

A THOUSAND TIMES MORE NSITIVE THAN HUMAN TOUCH

The electronic fingers of PHOTOSWITCH—the FLOATLESS LEVEL CONTROL—actually "feel" liquids or powders and maintain levels electronically.

PHOTCLWITCH operates on the simplest and most efficient principle yet devised for controlling the level of any material—liquid or powder— correstive or combustible Only the metal probe—the "electronic finger"— contacts the material under control. There are no moving parts to year out—nothing to fail in operation. PHOTOSWITCH has an unlimited life—is low in cost—simple to install—provides dependable maintenance-free operation—ends wartime replacement problems.

Today throughout industry modern PHOTOSWITCH installations:

- Control pumps to maintain constant liquid level Provide high and low level safeguards
- · Maintain interface between two liquids
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- Govern pump programming operations
- Detect water accumulation in tanks of gasoline or oil and in transformers.

• Provide complete boiler feedwater control.

There is a Photoswitch Level Control to meet every need. Write for complete catalogue information.

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For information on electronic timing, photoelectric smoke density indication, counting, automatic inspection, conveyor control, machinery safeguards, and similar applications, consult Photoswitch Incorporated, specialists in photoelectric and electronic controls for industry.

PHOTOSWITCH INCORPORATED

PHOTOELECTRIC & ELECTRONIC CONTROLS FOR EVERY INDUSTRIAL PURPOSE

CAMBRIDGE, MASS. · District Offices IN ALL PRINCIPAL CITIES

Have you a turbidity control problem? Write for details on the new Photoswitch photoelectric turbidity control-continuously indicates minute density changes invisible to the human eye.



The reason for Marblehead's recognized high efficiency in chemical processes, is the power of its high chemical energy, ready for release immediately to do the job in hand.

This store of pent-up energy is the accumulation of centuries of buildup in the extensive Marblehead limestone quarries, where the bones of prehistoric monsters and the shells of tiny fossils have combined to produce limestone of unusually high calcium content.

Manufactured from this choice limestone by modern methods, under strict technical control, Marblehead Chemical Lime brings you this vast fund of pure, high chemical activity to apply to your process — to help turn out more product at less cost — to assure you thorough action — to help maintain your fixed formulae — to prevent delays and interruptions in your production.

In addition, Marblehead possesses valuable physical characteristics, even more important in some processes than the chemical gualities soft, fine texture — of fast or slowsettling nature — quick slaking freedom from grit.

Used throughout industry, for

STEELMAKING - PAPER & BOX-BOARD — LEATHER — WIRE DRAWING — CHEMICALS PAINT & VARNISH - BRICKS PRODUCTS - WATER FOOD TREATMENT - SEW-AGE DISPOSAL, ETC.

LIME CO.



Marblehead Chemical Lime Is used in open hearth steel manufacture as a basic flux to remove acid elements and impurities from the molten mass.

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MARBLEHEAD

High Calcium

CHEMICAL LIME



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Laboratory Corrosion Data

ON ENDURO STAINLESS STEEL

Republic ENDURO Stainless Steel is highly resistant to corrosion—but more so in the presence of certain chemical media than when subjected to the attack of others.

LABORATORY CORROSION RATA

To help chemists and engineers anticipate the resistance of ENDURO under various conditions, Republic offers laboratory results showing the reaction of Types 18-8, 18-8-SMo and AA to 226 substances. Many of these chemical agents are shown in scaled percentages of concentration and at different temperatures.

This useful information occupies three pages of a

REPUBLIC

28-page booklet, which will also bring you data on physical, mechanical, electrical, heat-treating, heatresisting, welding, machining, drawing and stamping qualities of the popular ENDURO analyses—plus other interesting and informative matter.

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Write today for a copy of ENDURO Booklet No. 361. And keep in mind that if you can qualify with the proper priority, Republic is ready to supply the stainless steel you need for essential production.

REPUBLIC STEEL CORPORATION

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Interesting Compounds that can be supplied now

in limited commercial quantities

TETRAETHANOLAMMONIUM HYDROXIDE N(C₂H₄OH)₄OH

... as commercially supplied, is a 40 to 41 per cent solution of the hydroxide in water and methanol. It is a strong base approaching the fixed alkalies in alkalinity. Although its water solutions are stable at ordinary temperatures, they decompose on heating to form weakly basic polyethanolamines. Thus it has value where it is desirable to destroy a strong base that has been useful at lower temperatures. It is an excellent solvent for certain types of dyes. but is not a solvent for cellulose.

DIETHYL "CELLOSOLVE" C2H5OCH,CH,OC,H5

... is a colorless medium-boiling (121.4°C.) liquid with a slight ethereal odor. Since it dissolves both oils and water, it is an excellent mutual solvent. It is a solvent for nitrocellulose, and this solubility is increased by the presence of alcohol. In colloidal systems, such as detergents or wetting agents of limited water solubility, it permits dilution with water with less tendency to gel or cloud. A stable compound, it may be used as an inert reaction medium.

METHYLDIETHANOLAMINE CH₃N(C₂H₄OH)₂

... is an amine-odored, colorless liquid, miscible with water and benzene. It is suggested as an intermediate in the manufacture of textile auxiliaries, insecticides, emulsifying agents, and corrosion inhibitors. It shows some evidence of selective action in the absorption of acidic gases. Its physical properties include boiling point (at 4mm.), 121°C. and equivalent weight, 119.

The booklet "Chemicals Available in Research Quantities" describes more than 30 new chemicals now available for research study. Write for a copy.





For information concerning the use of these chemicals, address:

CARBIDE AND CARBON CHEMICALS CORPORATION Unit of Union Carbide and Carbon Corporation **30 East 42nd Street**

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New York, N. Y.

INDUSTRIAL AND ENGINEERING CHEMISTRY

PUBLISHED BY THE AMERICAN CHEMICAL SOCIETY . WALTER J. MURPHY, EDITOR

EDITORIALS_

Young Technologists and the Draft

THE introduction of Manning Tables and Replacement Schedules seems to have convinced the executives directing many of our war industries that they cannot hope to retain the services of young chemists and chemical engineers. In too many instances these executives file 42A forms on these young men in a very perfunctory manner and, if the local board classifies such registrants in 1A, the executives accept such action as final and allow the ten-day period for appeal to lapse without further action.

A somewhat similar situation occurs infrequently in some companies which find themselves temporarily overstaffed with chemists and chemical engineers. Instead of frankly advising the young men to seek employment with concerns which are short of technical personnel, the management solves its problem of oversupply by doing nothing, with the result that the young men are inducted. The management feels very patriotic and the war effort suffers.

Such practices by management are contrary to the principle upheld by Selective Service headquarters. Very often a young technologist becomes acquainted with the method followed by his employer only after he has been placed in 1A and the ten-day appeal period has passed.

Such an individual should establish contact immediately with the occupational adviser in Selective Service headquarters of his state or the nearest U. S. Employment Office. He may expect to receive assurance from the occupational adviser that he will be given an opportunity to connect with a war industry needing his particular kind of services and may even receive suggestions as to what concerns may need him. Meanwhile, induction will be stayed. As soon as appropriate employment is found, the new employer should file Form 42A, thus reopening the case with the local board.

When industry includes chemists and chemical engineers in the Manning Tables, it should be made perfectly clear that such men are, like doctors and dentists, practically irreplaceable, for it takes from four to seven years to train a chemist and a chemical engineer.

In his straight-from-the-shoulder talk on the manpower problem before the AMERICAN CHEMICAL So-CIETY in Detroit last month, Fowler V. Harper, Deputy Chairman of the War Manpower Commission, made it quite plain that those who are administering this law have an intelligent and realistic viewpoint and understanding of the needs of industry. We must have active and intelligent cooperation by industry to prevent chaotic conditions arising in the next twelve months.

Ask the Baruch Committee

THE spectacle of Undersecretary of War Patterson, Secretary of the Interior Ickes, and OWI Director Elmer Davis, on the one hand, and Rubber Director Jeffers, on the other, conducting "The Battle of Washington" is very disconcerting and must provide much comfort if not downright aid to our enemies.

The American public has every right to know the truth. It should be given the facts concerning the output of high-octane gasoline. It should be told whether or not it is true, as Patterson and Ickes charge, that Jeffers is weakening American air strength by shrinking combat supplies of high-octane gasoline in order to coddle civilian motorists. The public wants the facts, not from Dorothy Thompson and other columnists, but from somebody technically qualified to pass judgment on the merits of these charges. It does not want either the Gillette Committee or the Truman Committee to mix into this mess. The one group it does have confidence in is the Baruch Committee.

Revise the Specifications

A MONTH ago the country was startled to learn that steel plate had been shipped from a plant of a United States Steel subsidiary which failed to comply with the physical and chemical specifications as prescribed by the Government. The "affair" of the substandard plates was eagerly seized upon by a number of individuals and groups seeking publicity and a new "angle" to discredit industry's war effort.

It now becomes increasingly evident that while the specifications were not met the steel was perfectly sound for the purpose for which it was used. Chemists, physicists, and other technologists should not be placed in the intolerable position of necessarily omitting detailed analyses and tests in order to maintain production. Many specifications have been drawn without proper consideration being given to the end use of the material and the practical conditions under which it must be manufactured in huge quantities in the stress of war conditions. Very definitely the purpose of such specifications should be to determine the minimum satisfactory quality, certainly not to force upon industry a wholly unnecessary burden. Where such conditions exist technical men have every reason to request revisions. For their own personal protection they should be very insistent that changes be made without delay. No chemist wants to slow up the war effort, nor does he wish to run the risk of being held up to ridicule and his profession given the proverbial "black eye".

Gages of Research

CHEMICAL ABSTRACTS has often served as an indicator of trends in chemical research. Two recent analyses of its content are suggestive.

Editor Crane points out, in Little C. A., that the number of contributions of different nations to the content of Chemical Abstracts indicates the changing emphasis each has placed on research. The 1913 volume showed Germany as the source of 34.4 per cent of all papers abstracted. Following in order were: the United States (20.7 per cent), British Empire (14.4 per cent), France (13.0 per cent), Italy (4.7 per cent), Russia (2.5 per cent), and Japan (0.37 per cent). By 1939, the relative order was: United States (27.7 per cent), Germany (18.7 per cent), British Empire (14.1 per cent), Russia (11.1 per cent), France (9.1 per cent), Japan (4.4 per cent), and Italy (3.0 per cent). The changes these figures suggest may not be pictured with the utmost accuracy but certainly they are approximately true.

Another interesting compilation appears in a recent issue of *Science* over the signature of Edward Thomas. Mr. Thomas deals with the numbers of abstracts published in each volume of *Chemical Abstracts* from 1907 through 1942. The figures reveal an amazing uniformity in the rate of increase in each year of peace. From 1907 through 1913, the average increase in number of papers abstracted was 1858 per year. From 1918 through 1938 the average increase was 1832 per year. When the differences between the two periods are considered, the close agreement is striking. Indeed, the agreement of the figures suggests that some cause other than the productivity of research may be the controlling factor.

During World War I (1913-1918) the number of abstracts published diminished an average of 1948 per year. The average decrease has been 3859 per year to date during World War II (1938-1942).

One is tempted to conclude from these figures that research is suffering from war. That is, of course, true in some fields, particularly in pure or fundamental research as contrasted with applied research. But other evidence clearly indicates that never have research workers been so busy as now. The pace of research is quickened and its objectives changed by war. Teams, not individuals, conduct today's investigations. Publication takes the form of military offensives and not scientific papers. Experience, much of it grim, is being accumulated in individuals, rather than in printed papers, to be loosed at war's end in tangible developments that will help build a better world, not simply a more bulky literature.

"Our Change of Address"????

A TLONG last Elmer Davis and his Office of War Information have stopped feuding with Rubber-Czar Jeffers sufficiently to grant us the necessary permission to disclose the sad news that the AMERICAN CHEMICAL SOCIETY has been forced by the exigency of modern warfare to move its quarters. We are established with a fair degree of comfort in the same block with the Mills Building which was the home of this Society several years ago.

Some time ago our beautiful building at 1155 Sixteenth Street, N. W., Washington, was seriously bombed and a portion of our records was destroyed. Our good friends in the United States Bureau of Mines very graciously offered us asylum for a few months at College Park, Md., until the necessary repairs could be made. Unfortunately, within a very brief space of time, we were again visited by high-explosive bombs dropped by enemy raiders flying up the Potomac and it became necessary to find temporary quarters once more-this time in the comparatively safe atmosphere of Williamsburg, Va. Regretfully we must report that hardly were repairs made and our building made partially tenantable when we were advised that the overflow of lawyers and economists in Prentiss Brown's Office of Price Administration was moving in for the duration and we must seek offices elsewhere.

Bewildered reader, this is not an attempt to out-do Orson Welles! As we pen these words we momentarily lift our eyes to gaze upon the beautiful vista of Sixteenth Street, and, while enjoying once again the sight of the rebirth of Nature coaxed by a strong spring sun, we contemplate an editorial in the March issue of our British contemporary, *Chemistry & Industry*, entitled "Our Change of Address". We are attempting in a very amateurish manner to visualize what the experiences of all-out total war are really like. Suddenly the purchase of a war bond each month-end and a two-hour trick once a week as a plane spotter seem like pitifully inadequate personal contributions to the war effort.

So far we have been spared the horrors of bombing. Our homes and our institutions are intact. If we are attacked at some future time may your Editor have the intestinal fortitude to write as did Stephen Miall in *Chemistry & Industry* two months ago:

The war has caused us undoubtedly some little inconvenience, but nothing by comparison with the disasters that have befallen many societies, so we have every reason to be thankful.

In the not too distant future a maniacal ex-Austrian paperhanger will discover, as did Emperor Wilhelm and Napoleon, that a nation so universally gifted in the role of the art of understatement as sharp invective is not to be trifled with.



THE NINTH ANNUAL

SYMPOSIUM COMMITTEE

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CHEMICAL ENGINEERING SYMPOSIUM

Division of Industrial and Engineering Chemistry

American Chemical Society

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The papers not received in time to be included in this issue will be printed later. The pictures on pages 501 and 502 are reproduced through courtesy of E. I. du Pont de Nemours & Company, Inc., and Chicago Bridge and Iron Company, respectively.

The Symposium Committee of the Division of Industrial and Engineering Chemistry undertook its 1912 assignment with special interest, since the topic of Industrial Reaction Rates seemed sufficiently important to justify study during the war period. Despite the interest of chemical engineers in the release of industrial data on the applications of reaction rate principles to reactor design, the committee soon found that contributions were not readily forthcoming. The extra burden of war assignments was one reason. In most instances the rate data resulting from pilot plant studies were not organized for publication.

The last twenty years have seen extensive developments in the theory of chemical reaction kinetics, but most of them have involved such advanced scientific concepts as to discourage attempts at industrial application. However, the time now seems opportune to translate these scientific developments into engineering terms and to develop a special literature in the applications of rate data. The techniques required in acquiring rate data and in interpreting the results to design and operation should result in reducing the time and cost of process development. Many of the customary repeated and extensive pilot plant investigations might be eliminated by more complete understanding of the principles involved. The subject Industrial Reaction Rates had been frequently suggested in past years by members of the division, and the present committee inherited the correspondence of D. B. Keyes on this matter. The committee brought together two groups of investigators, those engaged in the more theoretical developments of chemical kinetics and those experienced in the interpretation of pilot plant rate data to process design. In the field of theoretical chemical kinetics the committee was fortunate in securing such authorities as Henry Eyring, Farrington Daniels, and P. H. Emmett. The committee tried to avoid a local selection of papers but was driven to a preponderance of University of Wisconsin contributions to fill vacancies in the program left by last-minute withdrawals.

The Symposium Committee wishes to acknowledge the services of Harry McCormack in making local arrangements and the active support and encouragement of the Division Committee, particularly its officers, L. W. Bass, R. N. Shreve, T. H. Chilton, and Whitney Weinrich.

In an early postwar year another symposium on the same subject should be timely and bring forth remarkable developments resulting from wartime activities.

is.

Prediction of REACTION RATES

Farrington Daniels UNIVERSITY OF WISCONSIN, MADISON, WIS.

Examination of about thirty recently published, accurate unimolecular gas-phase reactions shows that the simple Arrhenius equation,

$$\mathbf{k} = \mathbf{a}\mathbf{e}^{-\mathbf{Q}/\mathbf{RT}}$$

is applicable. Sixty per cent of these reactions have frequency factors, a, of 10^{12} to 10^{14} corresponding to RT/Nh. Larger frequency factors suggest chain reactions and smaller values often indicate that there may be an appreciable entropy of activation. The kinetics of the rearrangement of certain allyl groups illustrates the fact that the requirement of an improbable

I NORDER to react, chemical substances must first be activated by the introduction of energy. In ordinary thermal reactions this energy comes from collisions with rapidly moving molecules—those which have energy in the range from about 10,000 to 100,000 calories per mole. The well known distribution of energy in a group of molecules is indicated in Figure 1. The proportion of these fast molecules is exceedingly small, but their presence accounts for the progress of chemical reactions. The number of rapidly moving molecules increases exponentially as the temperature is increased, and in a rough way the quantitative application of this relation explains the empirical approximation that the rates of many chemical reactions at room temperature double or treble for a 10° C. rise in temperature.



These activated molecules may be regarded as definite complex molecules and are called by Eyring the "activated complex". It is necessary to supply energy to crowd the reactants together into an activated complex with suitable intershape in the formation of the activated molecule decreases the entropy.

Empirical and theoretical rules for predicting reaction rates are examined and illustrated, including the Eyring equation:

$$\mathbf{k} = \mathbf{K} \frac{\mathbf{RT}}{\mathbf{Nh}} \mathbf{e}^{\frac{\Delta \mathbf{S}}{\mathbf{R}}} \mathbf{e}^{\frac{-\Delta \mathbf{H}}{\mathbf{RT}}}$$

In checking these rules it is important to look for "hidden" constants and to avoid disturbing factors such as trace catalysts, dissolved air, moisture, light, and wall effects. Rate measurements which depend on a nonspecific property, such as total gas pressure, may be unreliable.

atomic distances before new products can be formed. The course of a bimolecular reaction is indicated in Figure 2. Such complexes have only a brief existence, surviving sometimes for about 10^{-13} second, but their properties can be calcu-



Figure 2. Bimolecular Reaction, Showing Formation of Activated Complex

lated indirectly even if they cannot be isolated and measured. There is an equilibrium concentration of these activated molecules which can be calculated by the ordinary rules of thermodynamics:

$$\Delta F^{\circ} = -RT \ln K \tag{1}$$

$$\Delta F^{\circ} = \Delta H - T \Delta S \tag{2}$$

$$K = e^{\frac{\Delta S}{R}} e^{\frac{-\Delta H}{RT}}$$
(3)

We cannot measure equilibrium constant K for activated molecules any more than we can measure K for the equi-

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librium between benzene, carbon, and hydrogen at room temperature; but we can calculate it from heat content ΔH and entropy ΔS by formulas 1, 2, or 3 just as we do for benzene.



We cannot measure ΔH calorimetrically because we are unable to isolate the fleeting activated complex, but we can calculate it as we calculate ΔH thermodynamically by plotting the logarithm of equilibrium constant K against 1/T and taking the slope of the line. In kinetics we plot the logarithm of the specific reaction rate, k, against 1/T and calculate the heat of activation from the slope of the line. This heat of activation usually bears no relation to the heat of reaction, which is concerned with the difference in energy between reactants and products without reference to intermediate stages (Figure 3).

A successful formula for predicting reaction rates is now available. Eyring's equation (6) follows directly from statistical mechanics:

$$k = \mathbf{K} \frac{RT}{Nh} e^{\frac{\Delta S^*}{R}} e^{\frac{-\Delta H^*}{RT}}$$
(4)

It is usually assumed that the probability constant K is not far from unity, and the evaluation of the heat of activation ΔH^* and the entropy of activation ΔS^* becomes the important task of theoretical kinetics. Before exploring this equation further, it will be profitable to consider the empirical Arrhenius formula which preceded it:

$$k = a \ e^{\frac{-Q}{RT}} \tag{5}$$

Here the activation energy, Q, is usually obtained by determining the specific rate constant k at several temperatures and taking the slope of the line obtained by plotting $\ln k$ against 1/T. The frequency factor a has the same dimensions as k, since $e^{-Q/RT}$ is dimensionless. In unimolecular reactions it often has values of about 10¹³, which is of the order of magnitude of the vibration frequencies of atoms in a molecule. This formula has served well in recording simply and accurately the influence of temperature on the specific rate of most chemical reactions whether in the gas phase or in solution.

An empirical equation can always be improved by introducing more constants, and so a term p was introduced into the Arrhenius equation which allowed for orientation at collision—a lock-and-key effect:

$$k = p \ a \ e^{\frac{-Q}{RT}} \tag{6}$$

Examining Equation 4 (from Eyring), it is seen that RT/Nh has a value at room temperature of

$$1 \times \frac{8.3 \times 10^7 \times 300}{6.0 \times 10^{33} \times 6.5 \times 10^{-3}}$$

or about 10^{13} and that $e^{\Delta S^*/R}$, representing the entropy of activation, is really a probability factor which can be connected with spatial arrangement. The factors $K(RT/Nh)e^{\Delta S^*/R}$ are grouped together and called the "frequency factor". In bimolecular reactions the value of the frequency factor is not far from the number of collisions. It varies with the molecular weight and with the temperature but is usually in the neighborhood of 10^{11} , when the concentrations are expressed in moles per liter.

In many unimolecular gas-phase reactions there is little change in entropy on going into the activated state, so that $e^{\Delta S/R}$ is nearly unity. Then the frequency factor is about 10¹³. In most unimolecular reactions one of the molecular bonds simply breaks without having to form a complex with another molecule, so there is no change in shape and not much need for a probability term.

There are, however, a few exceptions. One which we believe to be fairly typical (4) is the rearrangement of 1-cyclohexenyl allyl malonitrile which can be followed easily with refractive index measurements. It is a beautiful first-order reaction in which

$$k = 6.31 \times 10^{10} e^{-26,160/RT}$$

Substituting into Equation 4,

$$6.31 \times 10^{10} = e^{\frac{\Delta S^*}{R}} \frac{RTe}{Nh}$$

Solving this equation, the entropy of activation ΔS^* is -11.7entropy units. This decrease in entropy on activation is in agreement with the fact that the reaction seems to call for a special spatial arrangement. In other words, some of the degrees of freedom are frozen in the formation of the activated complex. Apparently the rearrangement is accomplished by the formation of an internal ring as shown in Figure 4. Several other malonitriles and related compounds with similar rearrangements show the same decrease in entropy of activation. The difference in rearrangement rates of the different compounds depends chiefly on the heat of activation;



Figure 4. Unimolecular Rearrangement of 1-Cyclohexenyl Allyl Malonitrile, Showing That the Formation of the Activated State Involves a Change of Shape and a Decrease in Entropy



Figure 5. Contour Map Showing Energy at Different Interatomic Distances as Molecule AB Approaches Molecule CD and Reacts to Give DB

Cross section shows Franck-Condon curve.

but there is a parallelism between heat of activation and entropy of activation, an increase in heat of activation being accompanied by an increase in entropy of activation.

If the reaction involves chains, the over-all reaction will go too fast for its normal activation energy, and the frequency factor will be too large. The existence of chains is fairly common at higher temperatures, and a chain reaction may still look like a first-order reaction. For example, in the decomposition of a hydrocarbon, the reaction may go through free radicals in the following manner (9):

(1)	$C_3H_8 \rightarrow CH_3 + C_2H_5$
(2)	$\mathrm{CH}_3 + \mathrm{C}_3\mathrm{H}_8 ightarrow \mathrm{CH}_4 + \mathrm{C}_3\mathrm{H}_7$
(3)	$C_8H_7 \rightarrow CH_8 + C_2H_4$
(2 a)	$CH_3 + C_3H_8 \rightarrow CH_4 + C_3H_7$, etc
(4)	$CH_3 + C_3H_7 \rightarrow C_4H_{10}$

When a large supply of reactants is present and a steady state is reached.

$$\frac{dc_{C_{1}H_{7}}}{dt} = k_{1}c_{C_{1}H_{8}} - k_{2}c_{C_{H}} c_{C_{4}H_{8}} + k_{3}c_{C_{2}H_{7}} - k_{4}c_{C_{H}} c_{C_{1}H_{7}} = 0$$

$$\frac{dc_{C_{4}H_{7}}}{dt} = k_{2}c_{C_{1}H_{8}} c_{C_{H}} - k_{3}c_{C_{2}H_{7}} - k_{4}c_{C_{H}} c_{C_{3}H_{7}} = 0$$

From these rate expressions it can be shown that, since the first reaction is slow compared to the other reactions which involve free radicals,

$$\frac{-d c_{C_{2}H_{8}}}{dt} = k_{1}c_{C_{2}H_{8}} \sqrt{\frac{k_{2}k_{3}}{2k_{1}k_{4}}} = kc_{C_{2}H_{8}}$$
(7)

This is the equation for a first-order reaction.

ACTIVATION ENERGIES

The difficulties in calculating frequency factors in the Arrhenius equation are bad enough, but the difficulties in calculating activation energies are much more serious because even a small change in Q makes an enormous difference in k. The exponential character of the equation greatly magnifies any error in the activation energy. Theoretically, if we know the energies of the reacting molecules at all possible interatomic distances before and after passing through the activated complex, we can find the minimum value of energy required to bring about the change. This is the activation energy. The energy contour lines for a process similar to that shown in Figure 2 are indicated in Figure 5. Molecules ABand CD approach each other, form an activated complex, and separate into AC (not shown) and BD. The activation energy is the height of the lowest "energy pass" between the two valleys which correspond to the stable configurations of the reactants and the final products. This procedure gives us the desired means for predicting reaction rates if only we can find a way to draw in correctly these energy-contour lines, particularly in the region of the energy "pass". The means for calculating these energies are quite unsatisfactory.

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One approach is the semiempirical calculation of Eyring. In this calculation there are four assumptions:

It is assumed that a molecule, more particularly the activated complex, behaves as if it were made up of several atom

pairs. 2. Energy-distance curves are calculated for each pair of atoms. These Franck-Condon curves can be calculated em-pirically by the Morse equation. They are of the general type shown in cross section at B (Figure 5). They are calculated from three known constants. The heat of dissociation of the atomic Shown in closes sector at B regimes D. The heat of dissociation of the atomic pair is obtained from calorimetric measurements or from spectro-scopic measurements; the distance between atoms in the normal molecule is obtained from electron diffraction or x-rays; and the vibration frequency is obtained from Raman, infrared, or band spectra. But the equation is empirical at best and is likely to be in error by thousands of calories in the neighborhood of the dis-sociation energy. Errors in these calculations together with an improved formula have been discussed (8). 3. All the attractions between atomic pairs, taken two at a time, are combined with the help of first-order perturbation calcu-lations. Even for four atoms with six possible atomic pairs, the computation is approximate and tedious. Fortunately, it is not necessary to cover the whole mountainside with contour lines; they are needed only in the region of the lowest pass between the two valleys. With a little practice the amount of calculation can be greatly reduced.

be greatly reduced.

It is possible also to do a good job of calculation with nomo-graphs (1, 7), six sliding steel rulers with projections of the ener-gies marked at different distances along the scale. A setting is made and the energies are added up. After perhaps thirty set-tings it is possible to find the one which gives the lowest total

energy—namely, the activation energy. 4. All pairs of atoms are held together both by homopolar or quantum mechanical attraction (the kind of attraction associated with the electron pair), and also by ionic or electrostatic attraction. In some molecules the homopolar force is the greater, in others the ionic binding is greater. The Morse curves are for homopolar attractions. How can we tell which fraction of the attraction is due to homopolar binding and which is due to elec-trostatic binding? Hudroren is such a simple melecule that it is trostatic binding? Hydrogen is such a simple molecule that it is possible to make reliable, though tedious, calculations on the dif-ferent types of attraction. In the hydrogen molecule it turns out that 86 per cent of the total attraction is homopolar and 14 per cent in distinct the Lyne cent applies. cent is electrostatic; Eyring assumed that the 14 per cent applies to all atom pairs. This extension is not very safe, but no better approach has yet been offered. If the true value is 10 or 20 per cent instead of 14, serious errors will be introduced into the calculation of specific rate constant k.

The uncertainties in the calculation of activation energies by Eyring's semiempirical method are sufficiently great to justify simpler rules, even though they rest on less secure foundations and can be regarded only as empirical. In the Morse curves the largest factor is the heat of dissociation of the atom pair, the other two factors being relatively less important. Let us neglect them entirely. However, we cannot take all the heat of dissociation of the broken bonds because, in the activated complex, some new bonds are formed too, and the energy of their formation in the complex must be

considered. Turning to the reaction $H_2 + I_2 \rightarrow 2HI$, which seems to be our best known bimolecular reaction, Hirschfelder (7) finds that about 0.28 of the energy required to break the bonds gives the known energy of activation, and he assumes that this 28 per cent can be carried over to all reactions:

$$AB + CD \rightarrow AC + BD$$

$$\Delta H_{\text{activation}} = 0.28 \left(D_{AB} + D_{CD} \right) \tag{8}$$

where D_{AB} , D_{CD} = energies required to dissociate reacting molecules AB and CD into atoms

These dissociation heats of atom pairs are subject to considerable uncertainty as one tries to assign a definite bond energy to them, irrespective of the molecule in which they are found. Nevertheless, they are useful for approximate estimates; a few of these estimates are included in Table I.

TABLE	I.	APPROX PAIRS IN	IMATE HEAT	rs of Calori	Dissociation ies per Mole	OF	Атом
C—H C—Cl C—Br C—I C—C		92 79 58 44 77	С=С С=С H—H 0—H N—H	122 200 102 113 96	= N - N = C - O C = O Br - Br		33 82 188 45

In molecules which can have several different electronic configurations, such as exist when conjugated double bonds are present, the phenomenon of resonance occurs and the heat of dissociation may deviate largely from that calculated by Table I.

According to Hirschfelder (7) in the still simpler case of atom reactions of the type,

$$A + BC \rightarrow AB + C$$
 (exothermic) (9)

the heat of activation is equal to 5 per cent of the energy of breaking the bond:

$$\Delta H_{\rm activation} = 0.05 D_{BC}$$

The activation heat is quite small anyway, so that a close calculation is not significant. All these methods seem to be fairly satisfactory in the dozen or so cases where it is now possible to check them with experimentally determined activation energies such as in the following reactions (7): $H_2 + I_2$; $H_2 + Br_2$; $I_2 + Cl_2$; $Br_2 + C_2H_4$, etc.

According to another useful relation for making estimates of activation energies the activation energy in endothermic reactions must be at least as great as the endothermic heat of reaction. It may, of course, be much greater.

According to a recent article (δ) the activation energy may be calculated by the formula,

$$Q = 2.8581 \ \tilde{\nu} \ \frac{(35.5 - 900.45 \ \tilde{\nu})}{D_e}$$
(10)

where the spectroscopic heat of dissociation, D_{ϵ} , of a bond in a molecule undergoing unimolecular decomposition is related to a frequency of vibration, $\tilde{\nu}$, and the thermochemical bond energy, D_0 , by the relation:

$$D_e = 1.429 \,\tilde{\nu} + D_0 \tag{11}$$

A nomograph for solving Equations 10 and 11 is available (11).

In general, there are two ways of testing the theories involved in the prediction of reaction rates. First, they may be checked for very simple systems such as

$$H + H_2$$
 ortho $\rightarrow H_2$ para + H

where all the computations can be made rigorously even though laboriously. This type of reaction is usually too simple to be of much practical interest in chemistry. Secondly, the theories may be checked through a statistical study of the large number of reaction rate determinations recorded in the literature.

It may appear simple to check the calculations of activation energies by reference to the literature, but it is not simple. Unfortunately, the reaction rate data are so inaccurate and the mechanisms so complicated that much recalculating and discarding of complicated data and evaluating of experimental accuracy are necessary to determine whether the theories are in agreement with experimental facts. The greatest need now in chemical kinetics is for accurate data on uncomplicated unimolecular and bimolecular reactions over wide temperature intervals.

The difficulties inherent in the experimental determination of activation energies are due to inadequate technique and to incomplete methods of calculation. These points may now be elaborated.

EXPERIMENTAL METHODS

Activation energies are evaluated by determining the rate constants at different temperatures. Unfortunately, in gas reactions (which are sometimes thought to be the simplest) most of the reaction rates have been followed by measuring the total gas pressures at frequent time intervals. This is a nonspecific method in which a certain reaction is assumed to take place; on the basis of this assumption the amount of original material decomposed is calculated from the total pressure. Sometimes this method gives correct results, but if there are competing reactions or adsorptions on the wall or if the reaction does not always proceed as assumed, there may be



serious errors, particularly when the measurements are carried down to low pressures. It is possible that the progress of chemical kinetics has been handicapped because the experimental results were more complicated than they needed to be—complicated by inadequate methods of measurement rather than by the nature of the chemical reactions themselves. One example may be cited. For fifteen years it has been accepted that photosynthesis in the growing plant is an efficient process requiring something less than four quanta per atom of carbon produced in the plant. It is now known that the value is about ten instead of four. Apparently the difficulty lay in the fact that in the earlier measurements the total pressure was measured, and it was assumed that the increase in pressure was due to the evolution of oxygen, but under the special conditions of the experiment an unexpected evolution of carbon dioxide took place also.

If measurements of total pressure are to be used in rate measurements, they must be checked by chemical analysis. Specific methods for determining the concentration of just one of the reactants or products are much needed. Physical methods which do not disturb the reacting system are best, such as the absorption of light by one of the substances present and the application of Beer's law. This method can be extended to the infrared and the ultraviolet. New analytical tools which are specific for a single compound are eagerly sought. Such an instrument is the dropping mercury electrode or polarograph which, by previous calibration, gives simple galvanometer readings proportional to the concentration of one of the reactants or products.

The removal of samples followed by quick chilling is not a bad method for following the course of the reaction, if the reaction is going so slowly and the chilling with solid carbon dioxide or other means is so rapid that there is no appreciable change in concentration during sampling. In another satisfactory technique several small bulbs of reacting material are started together, and each is chilled quickly and analyzed after a different time interval.

Again, flow methods can often be recommended. It is true that the calculation of the time a given molecule stays in the heated chamber may be complicated, but often this difficulty may be less than the difficulties involved in the other methods. This method has the advantage that it is possible to accumulate sufficient quantities of material for satisfactory chemical analysis.

In measuring reaction rates it is necessary to be on constant guard against superficial influences which may affect seriously

the course of the reaction. Among them may be counted walls, moisture, air, and light. The wall effects in gas reactions may be so serious as to disqualify the argument that gas-phase reactions are the simplest to interpret and the best for testing theories of chemical kinetics. There may be a considerable contribution by a heterogeneous reaction on the walls; or free radicals from intermediate stages in the decomposition may be trapped by the walls. If activation energies are to be calculated, it is particularly important to have the conditions of the walls always the same at all temperatures-either scrupulously clean or deeply coated. Traces of moisture may give profoundly altered effects due to the presence of polar molecules on the walls in gas reactions, or to the presence of an ionizing solvent in nonpolar organic solvents. Again the presence of hydrogen ions may cause appreciable catalysis, and it is likely that some cases of catalytic behavior of salts such as calcium chloride and zinc chloride are really due to hydrogen ions produced by hydrolysis with traces of moisture. Oxygen of the air can cause many difficulties. It reacts readily with free radicals and can be responsible either for inhibiting a reaction or for accelerating it. For example, the photobromination of cinnamic acid in carbon tetrachloride

is speeded up more than tenfold by simply drawing out the dissolved air with an aspirator. The effects of the catalysts or inhibitors may be greatly magnified in the case of chain reactions. Daylight in an ordinary laboratory is sometimes sufficient to cause appreciable reaction when chain reactions are involved. ST

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DIFFICULTIES OF CALCULATION

Most laboratory reactions are mixed reactions, complicated with competing reactions, consecutive reactions, or reverse reactions; and it is not easy to determine the extent of these complications. Only a few of these complex reactions are simple enough to permit calculation of the over-all rate by integration of the differential equations involved. A mechanical integrator would often be helpful. Unfortunately one cannot be sure that a given solution is a unique solution. There may be several different combinations of reactions that will give the same over-all rate.

Many reaction rate data have been oversimplified by forcing the data to fit a simple first- or second-order equation or by taking the measurements over too short a time interval. It is true that, after a reaction is three fourths completed, the calculational errors involved in determining the rate constant become very large, and the situation may become seriously complicated by the accumulation of decomposition products. However, if the rate measurements are carried over only a short fraction of the total reaction time, the conclusions may be entirely inadequate and the calculation of the apparent activation energy may be seriously in error.

The difficulty of calculating significant activation energies for mixed reactions is evident. The graph obtained by plotting log k for the over-all mixed reaction against 1/T may be a straight line, and the apparent activation energy obtained from its slope is useful in predicting the influence of temperature on the mixed reactions, but the activation energy thus obtained is not significant in checking theories of chemical kinetics, or in studying the influence of molecular structure or



Figure 7. Graph for Estimating Specific Reaction Rates Slanting lines give values of k for simple unimolecular reactions, assuming frequency factor to be 10¹¹.

substituting groups or solvents on the rate of the reactions. If the observed over-all reaction involves the summation of two separate reactions I and II, then the apparent activation energy includes the activation energy of both I and II. Often I is much slower than II, and the activation energy of II then becomes negligible in comparison with the activation energy of I. Only in such cases does the observed activation energy possess theoretical significance. A check of the frequency factor with theoretical values is a helpful criterion as to whether or not the reaction is simple and the calculated activation energy applicable to an uncomplicated reaction.



Figure 8. Possible Reactions Involving Ethylene and a Halogen

The apparent frequency factor as well as the apparent activation energy may be subject to complications which prevent significant comparison with theory. In unimolecular reactions the units of concentration cancel out, but in bimolecular reactions the numerical values of k and a depend on the units and the standard state chosen. Most of the data so far recorded in the literature have been expressed in concentrations of moles per liter or moles per cc. The former seems preferable as being closer to normal experimental conditions. It must be remembered that the frequency factor is a catch-all for "hidden constants" as well as for experimental errors in the determination of the activation energy.

One of the commonest examples of these hidden constants is found in reactions, sometimes called "pseudo-unimolecular", such as hydrolysis reactions, in which the solvent water reacts with a substance A, but because water is present in such large excess (55 moles per liter), its concentration does not appear to change. The reactions are really bimolecular and should have a frequency factor of the order of 10^{11} instead of 10^{13} so often found in unimolecular reactions, but into the experimentally observed frequency factor has been absorbed the term giving the concentration of water. Thus,

$$\frac{-dc_A}{dt} = kc_{\rm H10} \ c_A = k \ (55) \ c_A \ \text{mole, liter}^{-1}, \ \text{sec.}^{-1}$$

$$k_{\rm obsvd.} = kc_{\rm H10} = k \ (55) = a_{\rm obsvd.} \ e^{\frac{-Q}{RT}}$$

$$k = \frac{a_{\rm obsvd.}}{\frac{6}{56}} e^{\frac{-Q}{RT}}$$
(12)

SURVEY OF LITERATURE

With a broader realization of all the factors involved, it is worth while to examine the literature for checks on the significance of the activation energy and the accuracy of its determination. Just the simplest cases can be reviewed here i. e., unimolecular reactions. The entropy changes in these reactions are usually small, and the gas reactions are free from solvation effects which sometimes complicate either the activation energy or the frequency factor or both.

Chemical Abstracts from 1936 to 1941 contain about 2500 items on reaction velocity; of these, 400 or 500 will be interesting from the standpoint of chemical kinetics, and about 200 will have utilizable data. There are perhaps 300 different reactions with easily discernible Arrhenius equation constants. (In some cases there will be constants for several different reactions in a single article.) Of these 300, less than 100 will have simple clean-cut data. Among this group, the 28 unimolecular gas reactions shown in Figure 6 were selected. Most of them were determined by measurements of total pressure.

In a survey of first-order reactions, one is impressed with the large number in which the solvent takes a direct part in the chemical reaction. As already explained, they are really bimolecular reactions with frequency factors appropriate for bimolecular reactions, but they are classified as first order. Reactions of this type have been responsible in part for a failure to realize how well the theory of unimolecular reactions agrees with experimental facts. In Figure 6 most of these gas-phase unimolecular reactions give a frequency factor from 10^{12} to 10^{14} corresponding to RT/Nh, and show that in all probability: (a) The activation energies have been reliably measured; (b) the reaction measured is not a mixed reaction with several different steps contributing to the observed overall reaction rate; (c) the entropy change is small when the molecule is converted into a molecule of the "activated complex". In the few reactions with a higher value of the frequency factor, there may be chain reactions which lead to an abnormally rapid reaction.

The importance of the entropy term $e^{\Delta S^*/B}$ was slow to be realized because it was hidden in the observed frequency factor. The experimentally determined value of the frequency factor was so inaccurate that any abnormalities went unnoticed.

Another cause for abnormal frequency factors in bimolecular reactions is a failure to express the reactants in terms of their standard states, such as moles per liter or moles per cc. It may happen that the real reactants are intermediates which are present only in very low concentrations. The specific rate constants may be reproducible enough and the activation energies correct, but perhaps the observed frequency factor should include a large term to convert the reactants into standard states. The entropy term calculated from the observed activation energy and the observed frequency factor may then be entirely wrong.

PRACTICAL APPLICATIONS

The best equation for predicting reaction rates is:

$$k = \frac{RT}{Nh} e^{\frac{\Delta S^*}{R}} e^{\frac{-\Delta H^*}{RT}} = a e^{\frac{-Q}{RT}}$$
(13)

For most unimolecular gas-phase reactions, a may be taken as 10^{13} unless a chain reaction is involved or unless there is a considerable change in the shape of the molecule. The graph of Figure 7 is obtained on this assumption. The slanting lines represent first-order specific reaction rate constants, k, expressed in seconds, and the activation energy Q is plotted against the absolute temperature.

From Figure 7 it is easy to estimate that the decomposition of nitrogen pentoxide with an activation energy of 25,000 calories per mole will have, within the range 0° to 100° C., specific reaction rates k between 10^{-1} and 10^{-6} . Values of 10^{-1} to 10^{-6} sec.⁻¹ correspond roughly to half-lives varying from seconds to months, which covers the practical range of most measure-

ments in chemical kinetics. Ethyl bromide, which is known to decompose with easily measurable rates (perhaps 10^{-3}) at 400° C. into ethylene and hydrobromic acid, must have an activation energy of about 55,000 calories. These estimates are in good agreement with experimental facts.

Two more illustrations of Figure 7 may be offered. Referring to Table I and realizing that the activation energy in an endothermic reaction must be at least as great as the heat of reaction, it is expected that the decomposition of ethyl chloride will require a temperature between 500° and 600° C. Again, any process involving a direct rupture of the carbon hydrogen bond at a cost of 92,000 calories per mole must have a slow, limiting step which will require a still higher temperature. Such reactions can be completely neglected at ordinary temperatures. Even though these estimates of reaction rates are rough, they are particularly helpful in eliminating the corresponding reactions from consideration when a number of competing reactions are present.

The calculations of Figure 7 are still less satisfactory for unimolecular reactions in solution. A distribution curve of a large number of first-order reactions recorded in the literature similar to that of Figure 6 still shows a maximum in the neighborhood of 10¹¹ to 10¹⁵ but it is much flatter and broader. Combination with the solvent may easily change the constants of the equation by large amounts.

For bimolecular reactions, $e^{\Delta S^*/R}$ is not negligible as it often is in unimolecular reactions, and a no longer has the value of about 10^{13} which is equivalent to RT/Nh. The two terms together come out to be of the order of the collision frequency between molecules. When concentrations are expressed in moles per liter, the term a in many bimolecular reactions often has a value in the neighborhood of 10¹⁰ or 10¹¹. However, this short cut for estimating constant a as 10¹¹ in a bimolecular reaction is not very satisfactory. The activation energy for the bimolecular reactions can be estimated roughly from heats of dissociation as given in Equations 8, 9, and 10 or from the semiempirical calculation of Eyring.

In general, it is safer to predict relative values than absolute values, and the estimation of differences in reaction rates is more reliable than the estimation of the actual rate. Some of the errors due to inadequate data or mathematical approximations are the same in each of the reactions being compared, and they tend to cancel out.

The separation of isotopes may be taken as an example in which nearly all the factors except those depending on mass cancel out, at least to a certain extent. Using the semiempirical method of Eyring it can be calculated (3) that the activation energy for rupturing the carbon-carbon bond, C^{12} — C^{12} , is 29 gram-calories less than that required to rupture the C¹²-C¹³ bond. This leads to a ratio of the two velocity constants $k_{c^{12}-c^{12}}/k_{c^{12}-c^{13}}$ of 1.05. Preliminary experiments on the fractional fermentation of sugar seem to be in accord with this calculation. If these measurements are later confirmed, they will constitute a strong support for the semiempirical calculation.

The addition of the different halogens to a given unsaturated compound provides another opportunity for making predictions of reaction rates under conditions where some of the uncertainties tend to cancel out. A halogen may add to ethylene in a number of different ways, as shown in Figure 8. The halogen may add directly or it may react by a free radical chain of the type:

$X_2 \rightarrow 2X$

$$X + CH_2 = CH_2 \rightarrow CH_2 - CH_2X$$

$$X_2 + CH_2 - CH_2 X \rightarrow CH_2 X - CH_2 X + X$$

With the semiempirical calculations it is possible to calculate the activation energy in each of the several reactions for both direct addition and for the atom chain (10). When the activation energy is considerably less for one reaction than for the other possible reactions, it may be concluded that this reaction will predominate. For example, reaction a (Figure 8) with an activation energy of 25,000 calories will take place in preference to reaction c with an activation energy of about 50,000 calories per mole. Furthermore, there seems to be little difference in these two cases between the activation energy for direct addition and for the atom chain. In reaction b, however, the calculated activation energy with chlorine is 80,000 calories by the bimolecular reaction and 57,000 calories by the atom chain. Although the chain mechanism predominates in the decomposition of the chloride, both mechanisms seem equally possible for the decomposition of the iodide.

Many ionic reactions are so fast that their rates cannot be measured. The ion itself may be regarded as being in an activated state. Some ionic reactions are slow and here the theories of Brønsted (2) and Bjerrum are useful, not for calculating absolute rates, but in predicting the effect of electrolytes and other factors on the reaction rate.

In photochemical reactions a knowledge of the quantum yield (molecules acting per quantum absorbed) enables one to calculate the reaction rate when the intensity of the photochemically active light is known. In some reactions, where reversal of the reaction occurs or competing reactions are present, the quantum yield may be considerably less than unity: in chain reactions it is greater than unity. Some of these quantum yields may be estimated by analogy when they have not been recorded in the literature. As in the case of thermal reactions, catalytic impurities may seriously affect the rates of the reaction.

The fact that most reactions are complex and contain intermediate reaction products suggests that rapid chilling of a reacting system should provide a chemical means for obtaining certain desired products. Applications of this technique have not yet been fully explored.

Although most chemical reactions are complicated with competing, consecutive, and reverse reactions, and thus lead to fractional orders in the rate equation and to time lags and changes in the rate expression during the course of the reaction, the realization that all chemical reactions take place in simple unimolecular and bimolecular (and occasionally termolecular) steps leads to simplification in predicting reaction rates. The formulas for estimating the rates of the separate unimolecular and bimolecular reaction steps are not yet satisfactory and the mathematical calculations are often extremely complicated, but the problem is clearly defined.

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ORGANIC REACTIONS

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The rate of a chemical reaction is calculated from the fundamental physical properties of the molecules. The nature of the approximations involved in the usual application of this formula is discussed critically. The usefulness of the theory as a framework within which to correlate empirical knowledge is emphasized. Evidence is presented for the predominance of polar or ionic binding over homopolar binding in the activated state for many organic reactions. Ionic activated states are shown to account for catalyzed cis-trans isomerization and



Equipment Used by Woburn Degreasing Company to Change the Molecular Structure of Castor Oil to form Drying Oil for Paints and Varnishes

polymerization of substituted olefins by the "singlet" mechanism, addition to double bonds, intramolecular rearrangements, alkylation catalysis by aluminum chloride and by acids, as well

S IMPLE analysis of the physical processes involved in a chemical reaction leads to a simple fundamental formula for the rate of reaction. Chemical reaction always involves a reorganization of the stable configurations of a particular set of atoms. For example, when a collection of two hydrogen atoms and a deuterium atom change from a configuration in which the deuterium atom is far away from the two hydrogen atoms, which vibrate and rotate about their common center of gravity, to a configuration in which one of the hydrogen atoms is far away and the deuterium atom vibrates and rotates about its common center of gravity with the other hydrogen atom, we say that the reaction

$$H_2 + D \longrightarrow H + HD$$
 (1)

has taken place. In like manner, with greater complexity,

as many aspects of surface catalysis. Dehydration and dehydrogenation on metal oxide surfaces are shown to be consistent with an ionic activated complex on the surface.

every chemical reaction can be described as a change in the configuration of some set of atoms from one stable configuration to another. Using the ideas of classical mechanics, we can represent any configuration of this set of atoms by a point in many-dimensional space whose coordinates are the internuclear separations of the set. In general, for a set of N atoms, there will be 3N-6 internuclear separations, and the configuration of the set will be represented by a point in a space of 3N-6 dimensions, called "configuration space". The change from one configuration to another is then represented by the motion of this point from one part of configuration space to another. If we know the laws of force which operate between the various atoms of our reacting set, to be called the "reaction complex", we can calculate, in principle at least, how this point will move. It can be

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shown that by properly choosing the coordinate system the equations of motion of this point can be made identical with those for the motion of a single particle of suitable mass whose potential energy for each position is equal to the potential energy of the reaction complex in the configuration which corresponds to that position of the representative point. For the simple example of two hydrogen atoms and a deuterium atom, configuration space has only two dimensions if the three atoms stay on the same line throughout their motion, and we can plot contour lines of constant potential energy. This surface, called the "potential energy surface" for the reaction, has the general shape of two long valleys connected by a pass. If a marble of the proper mass is rolled down one of these valleys, its motion nearly corresponds to that of the representative particle in reaction 1.

Using the ideas of quantum mechanics, the set of N atoms, or the reaction complex, is represented not by a moving point, but by a wave function in configuration space, which can be determined as the solution of the Schrödinger equation for the reaction complex. Only for special values of the energy, E, can solutions be found which satisfy the Schrödinger equation. These eigenfunctions can be designated by subscripts which indicate the quantum numbers of the system. A complex system has as many quantum numbers as there are classical degrees of freedom. The value of Ecorresponding to a given eigenfunction-i. e., the energy level of the state having the specified quantum numbers-is expressed as a function of these numbers. The exact solution of the Schrödinger equation is difficult and has been accomplished only for simple cases. However, the solutions can often be well approximated in different regions of configuration space. For example, the eigenfunction for the HHD complex in the region where we have essentially $H_2 + D$ is well approximated by the product of an H_2 eigenfunction with that of a free deuterium atom.

FORMULATION OF RATE THEORY

We can now formulate the rate of a chemical reaction from the idea that it consists of the rate at which complexes pass from one region of configuration space to another. Let C_{n_i} be the concentration of reaction complexes in the initial region of configuration space, where j stands for the whole set of quantum numbers which specify the internal vibrations of the system, and n stands for the quantum number which corresponds to the classical degree of freedom along which the representative particle moves as it passes from the region of configuration space corresponding to reactants to that corresponding to products. Let ν_{n_i} be the frequency with which a reaction complex in the n_j th quantum state approaches the energy barrier separating initial and final states. Let κ_{nj} be the probability that the complex succeeds in crossing the barrier on any one attempt. Then the number of systems crossing is given by

$$\frac{-dc}{dt} = \sum_{nj} C_{nj} \nu_{nj} \kappa_{nj}$$
(2)

where C = total number of complexes in initial state at any time t

This formula is valid for all kinds of reactions under all conditions, whether the reaction be proceeding at equilibrium rate or not. However, it is not yet possible to evaluate all three of the factors involved under these general conditions. C_{ni} is usually calculated for the equilibrium case where equal numbers of reaction complexes pass across the barrier in the forward and backward direction. This is not a serious restriction, since activated complexes are isolated from one another in space, and the origin of one activated complex is not closely connected with the disappearance of another.

STATISTICAL EQUILIBRIUM THEORY

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To calculate the concentration of activated complexes C_{*i} in the state nj, it will be convenient to consider the following system (7): System A consists of one or many atoms or molecules in thermal equilibrium with s oscillators. Suppose the total energy E, possessed by the combined system of A and the s oscillators, be kept constant. What is the probability that A will have energy ϵ in some unique state? Since any distribution of energy E in a unique way is as likely as any other, the probability of A having energy ϵ in a definite state is proportional to the number of ways the remaining energy $(E-\epsilon)$ can be distributed among the s oscillators. Taking $h\nu$ as the size of one quantum of energy of the oscillators, the problem is then in how many ways, N., can the n quanta $[n = (E-\epsilon)/h\nu]$ be distributed among the s oscillators. If there is but one oscillator (s = 1), the *n* quanta must all be given to it—i. e., $N_1 = 1$. For s = 2 we have $N_2 =$ (n+1)/2. For s oscillators the result is $N_* = (n+1)^{s-1}/s!$ with sufficient accuracy. This is easily seen if it be supposed that n quanta are arranged in a line from right to left with one oscillator always kept on the extreme right. Each of the remaining s-1 oscillators may then be introduced in any of the n + 1 positions to the left of the first oscillator and adjacent to one or more of the quanta. The quanta between two adjacent oscillators are then supposed to belong to the one on the right. The s-1 oscillators can then be introduced into the line in $(n + 1)^{s-1}$ ways. This counts as distinct those arrangements arising from permutation of the order of the oscillators. This is corrected by dividing by s! to give $N_s = (n + 1)^{s-1}/s!$ for the number of ways of distributing the n quanta among the s oscillators:

$$N_{\bullet} = \frac{1}{s!} \left(\frac{E - \epsilon + h\nu}{h\nu} \right)^{\epsilon - 1} = \frac{1}{s!} \left(\frac{E + h\nu}{h\nu} \right)^{\epsilon - 1} \left(1 - \frac{\epsilon}{E + h\nu} \right)^{\epsilon - 1} = a' \left(1 - \frac{\epsilon}{E + h\nu} \right)^{\epsilon - 1}$$
(3)

By selecting oscillators with low enough frequencies, we know experimentally that the average energy of an oscillator is equal to kT down to as low temperatures as are desired as well as at high temperatures. Thus, when s is very large compared with the number of degrees of freedom in A, and if E is large, no appreciable error is made in Equation 3 by taking $E + h\nu = skT$.

Thus $N_s = a'(1-\epsilon/skT)^{s-1}$. Expanding by the binomial theorem,

$$N_{s} = a' \left[1 - (s - 1) \frac{\epsilon}{skT} + \frac{(s - 1)(s - 2)}{s^{2}} \frac{1}{2} \left(\frac{\epsilon}{kT} \right)^{s} - \frac{(s - 1)(s - 2)(s - 3)}{s^{3}} \frac{1}{3!} \left(\frac{\epsilon}{kT} \right)^{s} + \dots \right]$$
(4)

but for very large s this becomes

$$N_{e} = a' e^{-\frac{e}{kT}} \tag{5}$$

If this energy ϵ corresponds to the *i*th state of A, we can call it ϵ_i and have for the probability p_i that A is in the state *i*:

$$J_{\bullet} \sim p_i = a \exp\left(-\epsilon_i/kT\right)$$
 (6)

If the system is known to lie in one of a certain set of states, we obtain by summing p_i in Equation 6 over these states,

$$\sum_{i} p_{i} = a \sum_{i} \exp((-\epsilon_{i}/kT)) = 1$$
$$a = 1/\sum_{i} \exp(-\epsilon_{i}/kT)$$

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$$p_i = \frac{\exp\left(-\epsilon_i/kT\right)}{\sum \exp\left(-\epsilon_i/kT\right)}$$
(7)

Thus, returning to the reaction rate problem, we take p_{nj} equal to the ratio of the number of systems, n_{nj} in the njth state to the number of systems, n, in all states; that is,

$$p_{nj} = \frac{n_{nj}}{n} = \frac{\exp\left[-(\epsilon_n + \epsilon_j)/kT\right]}{\sum_{nj} \exp\left[-(\epsilon_n + \epsilon_j)/kT\right]}$$
(8)

where ϵ_n and ϵ_i are the energies associated with the *n*th and *j*th quantum levels, respectively. If on both sides of Equation 8 we divide both numerator and denominator by the volume, V, we have the expression for

$$C_{nj} = \frac{n_{nj}}{V} = \frac{n}{V} \frac{\exp((-\epsilon_{nj}/kT))}{V} / \sum_{nj} \frac{\exp((-\epsilon_{nj}/kT))}{V}$$

In a bimolecular reaction between A and B we have $n = n_A n_B$ since every pair, AB, constitutes a reaction complex. In this case Equation 8 becomes:

$$\frac{n_{nj}}{n_A n_B} = \frac{\exp\left(-\epsilon_{nj}/kT\right)}{\sum_{i=1}^{n} \exp\left(-\epsilon_{nj}/kT\right)}$$
(8A)

Dividing the numerator on both sides by V and the denominators by V^2 ,

$$C_{nj} = C_{A}C_{B} \frac{\exp\left(-\epsilon_{nj}/kT\right)}{V} / \frac{\sum_{nj} \exp\left(-\epsilon_{nj}/kT\right)}{V^{2}}$$
(8B)

The frequency, ν_{ni} , now requires further consideration. In a unimolecular reaction it will be easily defined as the frequency of the bond which breaks in the reaction. There will then be a discrete set of possible values of ν_{nj} ; for some of them there will be a high probability of reaction, which we express by saying that κ_{n_1} is large for these frequencies. For bimolecular reactions, the frequencies ν_{nj} are very low and closely spaced. In fact, as the potential energy surface for H-H-H shows, the frequency of approaching the barrier is simply the frequency with which systems travel down the energy valley. If a system does not cross the barrier but is reflected, it will not return until it has suffered a reversal in velocity by collision with another atom or molecule, when it (or some other molecule) repeats the performance. It is then possible to think of the energy valley as a very long box, partially closed at one end by the energy barrier, and at the other by interaction with a third molecule. We can then express the frequency of the reaction complex in this degree of freedom by the quotient of its velocity divided by the length of path it travels between approaches to the barrier. If this degree of freedom is the one designated by the quantum number n, the energy of the system will be given closely by

$$\epsilon_{nj} = \epsilon_j + \frac{n^2 h^2}{8\mu l^2} = \epsilon_j + \epsilon_n \tag{9}$$

where μ = effective mass

2l = distance traveled between approaches to barrier

Its velocity is then easily calculated:

$$v_{nj} = \sqrt{\frac{2\epsilon_{nj}}{\mu}} = \frac{nh}{2\mu l}$$

Its frequency results upon dividing by 2l:

$$_{nj} = nh/4\mu l^2 \tag{10}$$

The rate of reaction, Equation 2, can now be written:

$$-\frac{dc}{dl} = \frac{c \sum_{nj} \kappa_{jn} e^{-\epsilon_j/kT} \frac{e^{-\frac{\epsilon_n}{kT}}}{V} \frac{nh}{4\mu l^2}}{\sum_{nj} \exp\left[-(\epsilon_n + \epsilon_j)/kT\right]/V^2}$$
(11)

To carry the calculation farther, we must know something about how κ_n depends on j and n. The exact calculation of κ_{nj} is a difficult problem in quantum mechanics and has been carried out so far only for a few highly idealized energy surfaces (9). In these cases it has been shown that κ_{in} is a rapidly fluctuating function of both n and j—i. e., both of the energy of reaction coordinate and of other degrees of freedom. However, the average value of the transmission coefficient varies only slowly with the average energy of the molecules in a reacting system, so that for all practical purposes κ_{in} can be replaced by an average value $\bar{\kappa}_n$. This average value is very close to that predicted by classical mechanics. Thus, we should expect no transmission of those complexes whose total energy is less than the energy necessary to surmount the barrier, except for "tunneling", which is negligible in almost all observed reaction rates. Moreover, those complexes whose total energy is sufficient to surmount the potential energy barrier will nearly all do so. This is the more true, the less regular the energy surface is in the neighborhood of the barrier. Any asymmetry or curvature in the energy surface tends to bring the probability of transmission closer to the value to be expected on purely classical particle mechanics. Therefore, $\bar{\kappa}_n$ is very small when n is less than n_0 , the quantum number for the translational energy level of the same energy as the top of the barrier. For levels above the top of the barrier we can define a mean value κ averaged over all values of $\overline{\kappa}_n$ for $n > n_0$. This average κ , which in many cases will approach unity, is then taken outside the sum. In reactions which involve passing from one energy surface to another, κ will usually be much smaller than unity. This is the case in certain ab-normally slow reactions of the double bond to be discussed below.

Putting the average value of κ into Equation 11, the rate equation becomes

$$-\frac{dc}{dt} = \left[c \sum_{jn}^{jn_{\theta}} \frac{e^{-\frac{\epsilon_j}{kT}}}{V} e^{-\frac{n^2\hbar^2}{8\mu l^2 kT}} \frac{n\hbar}{4\mu l^2} \kappa_{jn} (n < n_0) + \\ \kappa c \sum_{jn_{\theta}}^{\infty} e^{-\frac{\epsilon_j}{kT}} e^{-\frac{n^2\hbar^2}{8\mu l^2 kT}} \frac{n\hbar}{4\mu l^2}\right] / \sum_{n_j}^{\infty} \frac{e^{-\frac{(\epsilon_j + \epsilon_n)}{kT}}}{V^2} \quad (12)$$

The values $\epsilon_n = n^2 \hbar^2 / 8\mu l^2 kT$ are very closely spaced when l is large, as it is in the bimolecular case we are considering; therefore it is permissible to replace the summation over n by integration for purposes of evaluating Equation 12. We have then for the reaction rate term which does not involve leakage through the barrier,

$$V_{2} = c\kappa \sum_{j} \frac{e^{-\frac{\epsilon_{j}}{kT}}}{V} \frac{kT}{h} \int_{n_{0}}^{\infty} e^{-\frac{n^{2}h^{2}}{8\mu l^{2}kT}} \frac{n^{2}h^{2}}{4\mu l^{2}kT} dn \bigg/ \frac{e^{-\frac{(\epsilon_{n} + \epsilon_{j})}{kT}}}{V^{2}}$$
(13)

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The factor multiplying the exponential in the integrand is simply its derivative, so that the integral is immediately evaluated to give

$$V_2 = c\kappa \left[\sum_{i} \frac{e^{-\frac{\epsilon_j}{kT}}}{V} e^{-\frac{\epsilon_0}{kT}} \frac{kT}{h} \right] / \sum_{nj} \frac{e^{-\frac{(\epsilon_n + \epsilon_j)}{kT}}}{V^2}$$
(14)

where we have written $\epsilon_0 = n_0^2 \hbar^2 / 8\mu l^2$ for the energy of the top of the barrier.

The factor $\kappa (kT/h)$ in Equation 14 is the average frequency with which reaction complexes cross the barrier, and the remaining factor,

$$\frac{c\sum_{i} e^{-\frac{\epsilon_{i}}{kT}} e^{-\frac{\epsilon_{0}}{kT}} / V}{\sum_{n_{i}} e^{-\frac{(\epsilon_{i} + \epsilon_{n})}{kT}} / V^{2}} = c \frac{F^{\ddagger}}{F} e^{-\frac{\epsilon_{0}}{kT}}$$
(15)

can be interpreted as the ratio of the partition function, F^{\ddagger} , for complexes at the top of the barrier to the partition function, F, for systems in the initial state, multiplied by their concentration. It gives the equilibrium concentration of reaction complexes which are at the top of the barrier. Such complexes will be called "activated". The usefulness of this interpretation depends, as we have seen, upon the possibility of assuming the transmission coefficient to have an average value κ for all levels above a certain level. The height of this level above which transmission becomes appreciable determines the "top" of the barrier at which the equilibrium calculation gives the correct number of reaction complexes. Hence there is no exact relation between this height and the height of the energy barrier. But in most cases we can expect them to be identical for practical calculations. If there is much discrepancy, it will be necessary to include in Equation 14 terms in $n < n_0$ for which κ_{in} is appreciable but not unity. It will be recognized that Equation 14 is the one derived by Eyring (11) from somewhat different considerations. Trimolecular and higher reactions involve no new features since the ultimate step preceding reaction will be motion along some particular reaction coordinate.

It is now clear to what extent we are justified in speaking of an "equilibrium" between initial and activated states. Furthermore, it is evident that the assumption of equilibrium is not essential to the calculation, but can be justified and corrected where necessary by consideration of the transmission coefficient κ_{m} . On the other hand, it is convenient and fruitful to be able to employ the methods of equilibrium theory and thermodynamics with the assurance that in all cases they will furnish a first approximation to the rate, and usually a sufficient one. Thus the expression for the rate for a reaction of any order is

$$-\frac{dc_1}{dt} = c_1 c_2 \dots c_n \kappa \frac{kT}{h} \frac{F^{\ddagger}}{F} e^{-\frac{\epsilon_0}{kT}} = c_1 c_2 \dots c_n k'$$
(16)

where $F = \sum_{nj} e^{-\frac{\epsilon_n + \epsilon_j}{kT}} V^{-n}$

k' = specific reaction rate constant, given by

$$k' = \kappa \, \frac{kT}{h} \frac{F}{F} e^{-\frac{\kappa}{kT}} \tag{17}$$

The concentration of activated complexes may be expressed in terms of the equilibrium constant for activation, K^{\ddagger} ,

$$K^{\ddagger} = \frac{c^{\ddagger}}{c_1 c_2 \dots c_n} = \frac{F^{\ddagger}}{F} e^{-\frac{a}{kT}}$$
(18)

where c^{\ddagger} = equilibrium concentration of activated complexes

The specific reaction rate, k', is then given by

$$k' = \kappa \, \frac{kT}{h} \, K^{\ddagger} \tag{19}$$

We can now define a free energy and an entropy of activation, so that Equation 19 can be written:

$$\kappa' = \kappa \frac{kT}{h} e^{-\frac{\Delta F \ddagger}{RT}} = \kappa \frac{kT}{h} e^{-\frac{(\Delta H \ddagger - T\Delta S \ddagger)}{RT}}$$
(20)

$$k' = \kappa \frac{kT}{h} e^{\frac{\Delta S^{\ddagger}}{R}} e^{-\frac{(\Delta E^{\ddagger} + P\Delta V^{\ddagger})}{RT}}$$
(21)

This formula for the specific reaction rate may be compared with the familiar Arrhenius formula

$$\varepsilon' = A e^{\frac{-E}{RT}}$$
(22)

The frequency factor, A, contains the entropy of activation and the transmission coefficient, as well as the standard frequency of crossing the barrier kT/h. The energy of activation, E, is given by the standard enthalpy of activation and is consequently slightly dependent on temperature. The barrier height, ϵ_0 , is exactly equal to the energy of activation only at absolute zero. It might be written $\epsilon_0 = \Delta H_*^*$ to denote the extrapolated value of the standard enthalpy of activation at absolute zero.

The effect of pressure on the specific reaction rate constant, k', is easily seen by considering Equation 20. From thermodynamics,

$$\left(\frac{\partial \Delta F^{\ddagger}}{\partial p}\right)_{T} = \Delta V^{\ddagger}; \left(\frac{\partial \Delta F^{\ddagger}}{\partial T}\right)_{p} = -\Delta S^{\ddagger}$$
(23)

Using the first of these relations,

$$\left(\frac{\partial \ln k'}{\partial p}\right)_T = -\frac{\Delta V^{\ddagger}}{RT}$$
(24)

It is evident that the change in volume on forming the activated state is the determining factor in the effect of pressure on the specific rate constant. If the activated complex has a smaller volume than the initial state, the specific rate constant will increase with increasing pressure. This is usually the case in bimolecular reactions. In unimolecular reactions, however, the volume of the complex increases slightly. Hence we should expect increased pressure to have a slight decelerating effect on the rate constant. This is borne out by the meager data on rates at high pressures (34).

The effect of pressure can be expressed conveniently in terms of the change in temperature required by a given change in pressure to preserve a constant specific reaction rate (12). Differentiating Equation 20,

$$\left(\frac{\partial \ln k'}{\partial T}\right)_{p} = \frac{1}{T} + \frac{\Delta F^{\ddagger}}{R T^{2}} - \frac{1}{RT} \left(\frac{\partial \Delta F^{\ddagger}}{\partial T}\right)_{p}$$
(25)

Using Equation 23, this becomes:

$$\left(\frac{\partial \ln k'}{\partial T}\right)_{p} = \frac{\Delta H^{\ddagger} + RT}{RT^{2}}$$
(26)

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With Equation 24 this gives

$$\left(\frac{\partial p}{\partial T}\right)_{\text{in } k'} = \left(\frac{\partial \ln k'}{\partial T}\right)_{p} \left(\frac{\partial \ln k'}{\partial p} \right)_{T} = -\frac{\Delta H^{\ddagger} + RT}{T \Delta V^{\ddagger}}$$
(27)

a relation reminiscent of the Clausius-Clapeyron equation.

Although it is not often possible at present to evaluate the necessary quantities in the foregoing rate expressions from fundamental physical data, such as spectroscopic frequencies, the concepts to which they lead are fruitful. The activated complex has most of the properties of an ordinary molecule except for an unstable vibrational degree of freedom which will lead to consummation of the reaction. Thus it is possible to speak of a free energy of activation and to apply all the usual thermodynamic treatment to the activated state. This leads us to classify rate processes according to the type of activated complex involved in the rate controlling step. There are three such types.

TYPES OF ACTIVATED COMPLEX

In certain processes only the weaker secondary bonds between molecules, but no valence bonds, are broken. Viscous and plastic flow and diffusion are examples of this type of process. They were discussed in a previous paper (30).

There are two types of activated complexes which involve rupture of valence bonds in molecules. In the first the bonds in the activated state are predominantly the homopolar or shared-electron type. Thus when a hydrogen molecule approaches an iodine molecule, an activated complex of two hydrogen and two iodine atoms is formed in which all the bonds are essentially the same as those in H₂ or I₂. Similarly, three hydrogen atoms form an activated complex in ortho-para hydrogen conversion in which the bonds are covalent or homopolar bonds. This type of activated complex was the first to be treated theoretically and is the one to which the semiempirical scheme of calculating activation energies applies (13). In this type of activated state, the valence electrons cannot be said to be associated with one atom any more than with another. Another example of this type of activated complex is found in those unimolecular reactions which proceed through dissociation into neutral radicals, such as the thermal cracking of hydrocarbons (29). Thus ethane dissociates to form an ethyl radical and a hydrogen atom. In the activated complex, the C-H bond will be lengthened, but each atom will have nearly a normal electron density around it. Thus the proton can be pictured as about to depart with its electron. The activated complex represents incipient radical formation.

The second type of activated complex represents incipient dissociation into ions. The bonds between the atoms are predominantly polar, or ionic, in character. This means that the electrons are more closely associated with one of the bonded atoms than the other. The extreme case of this sort is represented by alkali halide crystals, in which the sodium and chlorine exist as separate ions. However, all degrees of polarity exist, from the almost completely homopolar bond such as H₂ to the extremely polar bonds of the alkali halides. For convenience, those bonds in which polar configurations play a major role will be called "ionic" although this is not to be construed as implying "dissociated into ions". Thus even so ionic a compound as sodium chloride dissociates into atoms in the gas phase, although it reacts with water to yield ions in solution. The activated complexes into which this and similar substances enter will be termed "ionic", since the binding is better represented by ionic structures than by homopolar ones.

IONIC REACTION MECHANISMS

Ionizations in solution afford a major class of reactions which must proceed through an ionic activated state, and many of the features of the energy surfaces for ionic reactions may be most readily studied in this class. Acid strengths and relative rates of reactions involving ionic activated complexes (e.g., nitration of benzene) afford important information on the influence of substituents on the strength of the unstable bond in the activated complex. One method is to correlate acid strengths (31) and rates of nitration of substituted benzenes with activated complexes in which the substituent group is assigned a fractional charge to account for the inductive effect of the substituent through the carbon chain. The induced charge on each carbon atom is reduced by a fixed amount on each atom in the chain through which the induction is transmitted. The resulting charge distribution accounts for the dipole moment of the substituted molecule as well as for the change in strength of the critical bond as the substituent is varied. The activated complex is thought of as intermediate between a completely homopolar and a completely polar structure. The differences in activation energy are assigned to differences in the initial states of the molecules. Another method (38) is to calculate the energy required to furnish an electron at the spot of attack in the molecule. That is, for attack by an ion, the energy of a completely polar activated complex is calculated, supposing the substituent affects the energy of the activated state. This method is equally successful in predicting relative rates and acid strengths, and neither is sufficiently advanced to do more. The ease of ionization has been empirically correlated with the "negativity" of the substituent (16), and several empirical electronegativity scales of the elements have been devised (28).

The chief structural features that enter into the ease of excitation of an ionic state are the following:

3. Great differences in the electronegativities of the two groups favor dissociation into ions, since the electrons are then located nearer to one of the groups than to the other, even in the initial state.

Actual dissociation into ions does not usually occur in the absence of solvent, even though the molecule may exist in a polar electronic state. The power of the solvent to dissociate a molecule depends largely upon its ability to form coordination compounds with the ions formed—i. e., to solvate them. Substances which can accommodate unshared electrons from the negative ion or which have unshared electrons to fill the available orbitals of the positive ion are good ionizing solvents. Water is such a substance. It owes its solvating power to the unshared electron pairs of its oxygen, which are free to bond the H₂O to any ion having an unoccupied orbital—i. e., a positive ion. In addition, the proton can often form hydrogen bonds with negative ions and thus give water the power to solvate both positive and negative ions.

^{1.} Dissociation into symmetrical ions is highly improbable since there is normally no tendency for the electrons to be localized in any one part of a symmetrical bond.

^{2.} Large resonating substituents, such as conjugated systems or aromatic groups, favor ion formation, since the larger the number of resonance structures possible for the ion, the greater will be its stabilization. Thus triphenyl methyl chloride forms conducting solutions in cresol and in liquid sulfur dioxide. Bent and co-workers (4) studied reactions of the type Na + R \rightarrow Na⁺ + R⁻ for radicals, R, of the triaryl methane type. The free energies of these reactions in ether solution are all about -20 kg,-cal. per mole. The free energies of the reactions R₄ \rightarrow 2R are all about +10 kg,-cal. for the same radicals; the stabilizing power of the resonating group for the ionic reaction is evident.

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The ionizing power of a solvent can often be enhanced by addition of a substance (such as anhydrous aluminum chloride) which can coordinate one or both of the ions formed. The aluminum has an available empty orbital, lacking two electrons to complete an octet. Hence, it can bond negative ions readily and would be expected to promote ionization. Alcohol solutions of triphenyl methyl chloride which are nonconducting become conductors when aluminum chloride is added (16). Even alkyl halides in which aluminum chloride is dissolved exhibit conductivity which increases with the length of the carbon chain (37); this is evidence of both a solvent and a substituent effect. Addition of benzene increases the conductivities. Thus it is apparent that ionization accompanies reactions in which aluminum chloride is involved. Concentrated sulfuric acid dissociates according to the equation,

$$2H_2SO_4 \longrightarrow H_3SO_4^+ + HSO_4^-$$

in which the solvated proton $H_3SO_4^+$ has an orbital available for bonding with negative ions. Strong acids catalyze many of the same reactions as aluminum chloride—e.g., alkylation and isomerization. The effect of boron trifluoride may be attributed to the same sort of action. Anhydrous hydrogen fluoride is an ionic molecule and would likewise be expected to furnish protons readily which can catalyze condensations.

INTRAMOLECULAR REARRANGEMENT

Ten years ago Whitmore (39) proposed that all alkyl chain rearrangements proceed through the formation of carbonium ions. Considerable qualitative and quantitative evidence has been presented in support of this view. These reactions are almost invariable concomitants of alkylations which are catalyzed either by strong acids such as hydrofluoric and sulfuric or by Friedel-Crafts catalysts such as boron fluoride and aluminum chloride. There is good reason, therefore, to attribute the same activated state to each type of reaction. However, in the absence of kinetic data it is impossible to state what is the slowest step of the mechanism.

That intramolecular rearrangements should occur easily via positive ions is evident from consideration of the simple cases of H_3 and H_3^+ , which have been studied theoretically (18). It has been shown that the H_3 molecule is most stable in the linear configuration, whereas H_3^+ is most stable in a triangular configuration. Thus the proton in other positive ions when bound to both the nuclei is probably stable.

For example, the ion
$$CH_{sC}$$
-CCH_s can exist in the form H +

$$H_{3C}$$
 H_{4C} H_{C} H_{3C} H_{C} H_{3C} H_{C} H_{3} H_{C} H_{3} H_{C} H_{3} H_{C} H_{3} H_{1} H_{1}

activation energy. If the methyl finally shifts to the middle carbon, the system will have rearranged. This mechanism is reminiscent of that proposed by Egloff (10) and others, who supposed two hydrogen atoms to be removed from the hydrocarbon with a resulting triangular free radical. However, there is reason to think the triangular configuration is much less stable than the linear one for neutral radicals (18). For rearrangement to occur, it is not necessary that the charged fragments of the molecule separate completely, although conductivity measurements seem to indicate that in some cases they do. All that is required is that the positive group be sufficiently free to rotate as a nearly independent unit. Since electrostatic forces are much longer range than covalent bond forces, this freedom to rotate may be attained prior to complete dissociation into ions.

ALKYLATION AND FRIEDEL-CRAFTS CATALYSTS

Alkylation of benzene with normal alkyl halides in the presence of aluminum chloride leads to a large degree of branched-chain products under conditions such that alcohols give unrearranged products (35). Moreover, alkylation of benzene with olefins in the presence of aluminum chloride leads to much less isomerization than in the presence of concentrated sulfuric acid (22). The reaction with alcohols requires the presence of hydrochloric acid in addition to aluminum chloride, whereas that with alkyl halides does not. All these facts are consistent with the following mechanism. Aluminum chloride has great power to form complexes with substances which can furnish a pair of electrons to occupy the available low-energy orbital on the aluminum. Halogen in alkyl and acyl halides, oxygen in carbonyl, and, to a lesser extent, labile hydrogen (as hydride ion) and double bonds are good electron donors. The resulting complexes are highly ionic in nature. For example, ethyl bromide and aluminum bromide yield the complex $[C_2H_{\delta}^+ (A|Br_{\ell})^-]$ in which the two ions (8) are nearly independent. This is evident experimentally from the rapid exchange of radioactive bromine between aluminum bromide and ethyl bromide (14). The positive ethyl is then free to attack the unsaturation electrons in benzene with the displacement of hydrogen. Acid chlorides have two electron donors, the chloride and the carbonyl oxygen. This accounts for the fact that the addition of aluminum chloride in excess of the acyl halide yields much greater catalysis than the first equivalent of catalyst added. It is also borne out by the fact that a mixture of alkyl chloride, benzene, and acetic anhydride in the presence of aluminum chloride yields the alkylated acetophenone directly if more than one mole of aluminum chloride is used, whereas acylation alone takes place if less than one mole is used (36). Similarly, hydrohalogen acids form ionic complexes with aluminum chloridee. g., H⁺ (AlCl₄)⁻. It has been found that the conductivity of solutions of aluminum bromide in toluene is increased over a thousand times upon addition of hydrogen bromide (26). This indicates considerable dissociation of the complex. Thus we should expect the presence of protons in solutions of aluminum chloride, hydrochloric acid, and alcohols. The proton has a greater polarizing effect on the C-O bond in ROH than has aluminum chloride, but it is improbable that dissociation into ions takes place. Rather

the $\begin{bmatrix} H \\ R-C-OH \\ H \end{bmatrix}^+$ complex has an electrostatic bond be-

tween oxygen and carbon which is too strong to permit sufficient freedom for the alkyl group to rearrange. The difference in rearranging power between sulfuric acid, which also furnishes protons according to the scheme, $2H_2SO_4 \rightarrow$ $H_{3}SO_{4}^{+} + HSO_{4}^{-}$, and aluminum chloride can be similarly understood. In this case since sulfuric acid is much more soluble in the reaction mixture than aluminum chloride, it furnishes a more highly ionizing solvent; consequently there is greater loosening and perhaps even dissociation of the complex which allows rearrangment of the alkyl radical. The fact that rearrangement does occur in alkylation with secondary and tertiary alcohols (21) is in accord with the usual view of the weakening of the C-O bond by the electronrepellent influence of adjacent alkyl groups. This explanation will account for the difference in rearranging powers when benzene is alkylated with olefins (22). The complex (e. g., H_2C — CH_2^+ in the case of ethylene) is then similar to

that proposed by Roberts and Kimbail (32) for bromination. The mechanism presented here is essentially that of Fairbrother (15) who gives as additional evidence of complex formation the large increase in molar polarization when ethyl bromide is added to a solution of aluminum bromide in cyclohexane. In contrast, addition of bromobenzene in place of ethyl bromide gives a polarization of the solution which is the sum of those of the separate components; this indicates little or no complex formation and may be evidence as to why aryl halides react very slowly in Friedel-Crafts reactions. Complex formation might be supposed to inhibit reaction by stabilizing the initial state. However, if as in the case of alkyl halides the activated state of the complex is stabilized even more than the initial state, the activation free energy will be lowered. Since polar or internally ionized substances make better bonds with electron-seeking reagents such as aluminum chloride than do homopolar substances, the observed facts indicate that the activated state in these reactions is extremely polar.

DOUBLE BOND REACTIONS

There are also specific catalysts for radical formation. Introduction of free radicals or atoms into the system will favor this type of reaction. The two cases can be compared in the reactions of olefinic double bonds. It has been pointed out (24) that the cis-trans isomerizations and the polymerizations of substituted ethylenes fall into two distinct kinetic classes. In one group are those reactions in which the frequency factor is about 10¹² and the activation energy is about 45,000 calories per mole. The other group contains those reactions in which the frequency factor is very low (105) and the activation energy is only 23,000 calories per mole. The first group is catalyzed by such compounds as aluminum chloride, ferric chloride, and sulfuric acid; the second group is catalyzed by O₂, benzoyl peroxide, atoms (Br, Na, etc.) Some reactions exhibit both types of kinetics, depending upon the temperature. This general behavior can be well correlated with the electronic structure of the double bond. Mulliken (25) discussed the electronic states of ethylene by considering the energy states of a single electron moving in the average potential field of C2H4++ in which the bonds are considered to be disposed as follows:

Hence, the electron density in ethylene can be inferred to a first approximation by considering the juxtaposition of two CH₂⁺ ions. In the free methylene the electrons are not distributed about the carbon with spherical symmetry, but are localized in three mutually perpendicular pear-shaped orbitals, which lie along the coordinate axes. These orbitals, or wave functions, whose absolute value is a measure of the electron density in the molecule, are usually denoted as [x], [y], and [z], respectively. The axes are so chosen that the [z] orbitals overlap when two methylenes join to form an ethylene; the [y] orbitals lie in the plane of the CH₂ and serve to overlap the spherically symmetric hydrogen orbitals to form the C-H bonds. The [x] orbitals project perpendicular to the plane of the methylenes. Thus the [z] orbitals combine to form one of the two bonds of the double bond, whereas the [x] orbitals form the other and the weaker of the two. Each orbital can be occupied by two electrons at most, according to the Pauli exclusion principle. Hence in $C_2H_4^{++}$ there are orbitals available for two electrons, which make up the second of the two bonds in the double bond. It is these electrons which are most significant in determining the chemical behavior of the double bond.

In the ground state of ethylene, the methylenes lie in the same plane. The [x] orbitals are superposed to approximate the orbitals for ethylene. Two different combinations are possible—viz., $[x_a + x_b]$ and $[x_a - x_b]$. In the first (bonding) orbital, the wave functions of the separate methylenes are added; hence a bonding orbital corresponds to a greater electron density between the carbons than that calculated simply by adding the electron densities of two methylenes. The orbital $[x_a - x_b]$ is called "antibonding" since it corresponds to a smaller electron density in the region between the two carbons than the sum of the two methylene densities. In the ground state both electrons are in the bonding orbital, and the antibonding orbital is unoccupied. This means that the electrons occupy [x] methylene orbitals which overlap-i. e., have like sign on the same side of the molecule plane. The lowest excited state is one in which one electron occupies the bonding orbital and the other the antibonding orbital. Since the electrons occupy different orbitals, their spins need not be paired, and there will be two states, a singlet and a triplet, with somewhere near the same energy. However, when the excited singlet state is written out, it corresponds to both electrons occupying the same methylene orbital—i. e., to the structures CH_2^+ — CH_2^- and $CH_2^--CH_2^+$ of internally ionized ethylene. The excited triplet state corresponds to a homopolar state in which the electrons are on different carbon atoms.

Now as one methylene is rotated about the C—C bond in the ground state, the bonding [x] orbitals overlap less and less as the rotation proceeds and the bond becomes correspondingly weaker. As it approaches the position in which the planes of the methylenes are perpendicular to each other, the [x] orbitals are forced closer and closer to the [y] orbitals on the opposite methylene, with which they cannot combine. Hence there is an increasing repulsion as the methylene rotates, so that the perpendicular configuration of ethylene has a higher energy than the planar configuration. The exchange energy in the second C—C bond becomes less and less as the methylene rotates, and somewhere near 45° becomes actually a repulsion. In the perpendicular configuration the lowest energy state is one in which the electrons are on different carbons with unpaired spins, a triplet state.

When the methylene has rotated by 180°, the sign of the [x] orbital on that methylene is reversed, and both electrons are in antibonding orbitals of very high energy. Thus if $[x_a]$ indicates the [x] orbital on methylene A, a wave function which is a bonding molecular orbital is given by $[x_a + x_b]$, whereas the antibonding orbital is $[x_a - x_b]$. As methylene B is rotated by 180°, $[x_b]$ changes sign, and bonding orbitals become antibonding upon rotation by 180°. Thus the activated state for the singlet mechanism will be represented by a linear combination of the wave functions $[x_a + x_b]$, $[x_a + x_b]$, and $[x_a - x_b]_1$. Adding and multiplying give the wave function

$$[x_a]_1[x_a]_2 + [x_b]_1[x_b]_2$$
(28)

Subtracting gives

$$[x_a]_{,}[x_b]_{,} + [x_b]_{,}[x_a]_{,}$$
(29)

The first excited singlet state has the wave function

$$[x_a + x_b]_1 [x_a - x_b]_2 + [x_a + x_b]_2 [x_a - x_b]_1$$

in which only one electron is in the antibonding orbital. Multiplying gives

$$[x_a]_1[x_a]_1 - [x_b]_1[x_b]_1$$
(30)

The activated singlet state is some linear combination of states 28, 29, and 30. States 28 and 30 are polar (i. e., both

electrons are situated on the same carbon atom) whereas state 29 is a completely homopolar state, with one electron on each carbon. The initial ground state is $[x_a + x_b]_1$, $[x_a + x_b]_2 = [x_a]_1 [x_a]_2 + [x_b]_1 [x_b]_2 + [x_a]_1 [x_b]_2 + [x_b]_1 [x_a]_2 - i. e., a mixture of polar and homopolar.$



Figure 1. Potential Energy as a Function of Angle for Rotation about a Double Bond

In view of the catalytic effect of aluminum chloride, boron fluoride, and similar substances with strong electron affinities, it is clear that the catalyst lowers the energy of the activated state more than it lowers the energy of the initial state. Thus, the activated state is more readily polarized than the initial state. This means that, in the presence of the catalyst at least, the activated state which resonates between the structures indicated by formulas 28, 29, and 30 contains little of homopolar structure 29.

In cis-trans isomerization, if a symmetrically substituted ethylene retains its electronic configuration with antiparallel spins (singlet state), it must pass through an energy maximum as it rotates (Figure 1). Moreover, since this maximum is greater than the energy of the triplet state, the energy surface for reaction in the singlet state crosses that for reaction in the triplet state (full lines of Figure 1). If the magnetic interaction between these states is considered, the surfaces do not actually cross but approach very close to each other (dotted lines of Figure 1). It is now evident why double bond reactions should exhibit two activation energies. The lower energy is that for the triplet surface; the higher is that for the singlet surface. When two energy surfaces nearly touch, the chance that a system will jump from one to the other is great. This probability decreases with the separation of the surfaces, increases as the speed of the system increases, and increases as the angle increases through which a noncrossing particle must turn to avoid jumping. Hence, although the activation energy for the triplet surface is lower, only infrequently will systems be able to shift from the initial singlet surface as they pass through the crossing region. Most of the systems will jump the small gap between the surfaces and proceed by the higher energy singlet mechanism. This accounts for the low frequency factor of the triplet mechanism. However, the presence of an atom or radical with its odd electron allows the formation of an activated state in which there are three electrons in three orbitals and greater resonance energy,

so that the two energy surfaces are separated much more widely. The gap is then too wide for any except very fast systems to jump; most go by what, for two electrons, was the triplet mechanism. Thus polymerization of styrene, which in the absence of catalyst proceeds with a frequency factor of 10^5 , retains the same activation energy but has an increased frequency factor of $10^{10}-10^{12}$ when benzoyl peroxide or triphenylmethylazobenzene is added (33). 言語

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The normal and abnormal additions (23) of hydrobromic acid to olefin can also be explained on the basis of the electronic structure. Normally, the HBr is ionized and H+ adds first to the double bond. Ortho-para directing groups for benzene, when adjacent to the ethylenic double bond, tend to form a double bond with the new carbon and thus release the two electrons of the original double bond to the far carbon atom. Thus, although by analogy to Br+ (32) the incoming H⁺ ion can be considered to add to both carbons, it is bound more strongly to the least substituted one. The bromide ion then subsequently adds to the positive carbon. When peroxides are present, however, bromine atoms are formed by the peroxide (23). An incoming neutral bromine atom is not influenced by the charge distribution in the olefin, and forms the activated state in such a way as to give it the largest entropy and lowest energy (least steric hindrance). Since entropies are mainly determined by moments of inertia, and these are greatest for molecules in which the heavy atoms and groups are symmetrically placed, we should expect the bromine atom to add to the least substituted carbon atom, in contrast to the behavior of the bromide ion.

While most of the evidence that organic reactions proceed by ionic mechanisms is inferential, it is becoming increasingly clear that such mechanisms are very common. The most thoroughly investigated case is that of the hydrolysis of alkyl halides in neutral and basic media, which has been studied kinetically by Hughes, Ingold, and others (20). They have amassed an impressive array of evidence for their proposed mechanism of the first-order hydrolysis. The hypothesis that the slow step is a reversible ionization of RCl into $R^+ + Cl^-$ leads to predictions of the effects on the hydrolysis rate of change of substituent, change of solvent, and change of ionic strength which are in excellent agreement with the experimental data. There seems to be little room for doubt in this case. In basic solutions and for light halides, such as CH₃Cl and C₂H₅Cl, the rate of hydrolysis is second order, indicating a bimolecular mechanism. From the structure it is reasonable to suppose that CH₃Cl will not ionize readily, since it has none of the favoring conditions outlined above.

To summarize, an ionic mechanism will be favored over a radical mechanism whenever the reactant readily forms a complex with the catalyst which is more easily polarized in the activated than in the initial state. Alkyl halides and olefinic double bonds are outstanding examples of reactants which form such complexes with electron-accepting catalysts such as aluminum chloride and concentrated sulfuric acid.

HETEROGENEOUS REACTIONS

Reactions on surfaces can be treated in a similar fashion, where the atoms in the surface enter into the activated complex. This binding may be either polar or homopolar or intermediate between the two. Since metal oxides form ionic crystal lattices, it is probable that activated complexes which involve them are predominantly polar. Thus catalytic alkylations and isomerizations on alumina can be explained in much the same way as when they are catalyzed by acids or aluminum chloride. The aluminum ions in the crystal surface are electron acceptors and favor incipient ionization
in the activated complex. In many cases the charged fragments may actually separate sufficiently to allow one of them to rotate freely in the field of the other and thus to undergo rearrangement. In such cases it is convenient to think of the surface as a polar solvent, and the reactants as forming a reasonably mobile two-dimensional ionic solution. The adsorbed negative ions move on a checkerboard of positive ions in the surface, and the adsorbed positive ions move over the negative ions in the surface. There is thus the possibility that, for some reactions, diffusion on the surface may be rate controlling. This does not appear to have been observed, however, except possibly in the case of sulfur dioxide oxidation (6). The measurement of the surface conductivity of catalyst surfaces would give information as to the mobility of the adsorbed ions on the surface. The importance of ionic mechanisms in catalysis was emphasized by Nyrop from a different point of view (27)

Of special interest is the large class of reactions on surfaces which are capable of simultaneously dehydrating and dehydrogenating an alcohol acid or ester. That both reactions proceed simultaneously at measurable rates indicates that their free energies of activation can differ by no more than 1 or 2 kg.-cal. Since this is true for a wide variety of surfaces (40) and for many different molecules, it is evidence that the strengths of the critical bonds in the activated complexes for these reactions do not depend strongly on the nature of the surface. This would be the case in an ionic activated complex where the change in bond strengths when the surface is changed depends mainly on the change in the radii of the ions in the surface. Thus, suppose ROH is adsorbed as R⁺ OH⁻ on the surface of ions Zn⁺⁺ and O⁻⁻ in the reaction leading to dehydration. The bonding energy with the surface will then be:

$$E_{\text{lonie}} = \frac{Ze^2}{(r_{\text{R}}^* + r_0^{--})} + \frac{Z'e^2}{(r_{\text{OH}}^- + r_{\text{Zn}}^{*+})}$$
(31)

where

Z = effective charge on surface anion

Z' = effective charge on metal ion

Alternatively, for dehydrogenation, suppose ROH is adsorbed as RO^- and H^+ . The bonding energy with the surface is then:

$$E_{\text{ionic}}' = \frac{Ze^2}{(r_{\text{R}}^* + r_0^{--})} + \frac{Z'e^2}{(r_{\text{RO}}^- + r_{\text{Zn}}^{*+})}$$
(32)

The activation energies for dehydration and dehydrogenation will differ by the amount,

$$E' - E = \frac{Ze^{2}(r_{\rm R}^{*} - r_{\rm H}^{*})}{(r_{\rm R}^{*} + r_{\rm O}^{--})(r_{\rm H}^{*} + r_{\rm O}^{--})} + \frac{Z'e^{2}(r_{\rm RO}^{-} - r_{\rm OH}^{-})}{(r_{\rm RO}^{-} + r_{\rm Zn}^{*+})(r_{\rm OH}^{-} + r_{\rm Zn}^{*+})} + \frac{\delta E \text{ (independent of surface)}}{\text{of surface)}} (33)$$

where the radii are O^{--} for the activated state. Since most of the charge in RO^{-} is located on the oxygen, $r_{RO^{-}}$ and r_{OR}^{-} will be nearly equal and the second term will be small. Neglecting r_{R}^{+} in comparison with the other radii, the first term becomes $Ze/(r_{O}^{--} + r_{O}^{2}^{--}/r_{R}^{+})$. The value of $r_{O^{--}}$ is 1.4 Å. so that for $r_{R}^{+} > 2$ Å., this term too will be small. When the metal is changed, it is evident that E' - E will not change greatly. If the activated state consists of an ion pair about to desorb as a neutral molecule, the surface will have little influence on the activation energy.

A catalyst may greatly accelerate an over-all process without itself being a constituent of the activated complex of the rate determining step. To do this it must have so speeded up, or circumvented, some previously rate-determining process as to make the rate-determining step an earlier or later one in which the catalyst is not involved.

If two competing reactions are both speeded up in this way by each of a group of catalysts, the relative rates of the processes will be independent of the catalyst. Whenever relative yields of competing reactants are independent of or only slightly dependent on the catalyst, one suspects that the new rate-determining activated complexes make no bonds or only weak ones with the catalyst. The meager kinetic data available indicate that desorption of products is probably the slowest step in the above reactions. The variations in relative rates of dehydration and dehydrogenation on different surfaces and for different molecules represent relatively minor variations in the free energy of activation. These minor changes are of primary importance in selecting a catalyst, but at present they are not sufficiently well understood experimentally to permit more than speculation concerning them.

The numerous experiments of Adkins and co-workers (δ) on simultaneous dehydration and dehydrogenation of alcohols, acids, and esters over alumina, thoria, and titania catalysts indicate the main features of the reaction mechanism. Ethyl acetate reacts on an alumina surface to yield ethylene, carbon dioxide, acetic acid, and acetone, with smaller quantities of ethanol, hydrogen, and ethane. The following mechanism explains the facts. Ester cleavage can occur at either C—O bond (3). On the surface both of these cleavages occur, yielding positive and negative adsorbed ions. The oxide ion in the surface adsorbs the positive ion and the metal ion in the surface adsorbs the negative ion:

$$CH_{3}COOC_{2}H_{5} - (Al_{2}O_{3}) \rightarrow CH_{3}C = O^{+} + OC_{2}H_{5}^{-}$$
(34)

$$CH_{a}C \longrightarrow O^{-} + C_{2}H_{b}^{+}$$
(35)

There are then two reactions competing for the acetate ion:

$$CH_{3}CO^{+} + CH_{3}C \longrightarrow (CH_{3})_{2}CO + CO_{2}$$
(36)

$$CH_{3}C \longrightarrow O^{-} + C_{2}H_{5}^{+} \longrightarrow CH_{3}COOH + C_{2}H_{4}$$
(37)

The ethyl ion adsorbed on the oxide ion in the surface undergoes further reaction. A molecule of ethylene may be desorbed, leaving a proton on the surface:

$$C_2H_5^+ \longrightarrow C_2H_4 + H^+ \tag{38}$$

Similarly, the ethylate ion adsorbed on the metal ion in the surface may desorb acetaldehyde, leaving a hydride ion on the surface which combines with the proton from reaction 38 to give H_2 or with an ethyl ion to give ethane:

$$C_{2}H_{5}O^{-} \longrightarrow CH_{3}CHO + H^{-}$$
 (39)

$$\mathrm{H}^{+} + \mathrm{H}^{-} \longrightarrow \mathrm{H}_{2} \tag{40}$$

$$H^{-} + C_2 H_{\delta}^{+} \longrightarrow C_2 H_{\delta}$$
(41)

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Alternatively, the ethylate may desorb ethylene, leaving a hydroxyl ion on the surface which combines with its proton to give water:

$$C_2H_5O^- \longrightarrow C_2H_4 + OH^-$$
(42)

$$H^+ + OH^- \longrightarrow H_2O$$
 (43)

Or the ethylate may combine with the proton from reaction 38 to give ethanol:

$$C_2 H_b O^- + H^+ \longrightarrow C_2 H_b O H \tag{44}$$

All of these substances occur in the decomposition products of ethyl acetate in proportions which vary with the catalyst and with its mode of preparation. One series of fourteen alumina catalysts is reported (2) in which ethane and hydrogen production is very small (2-3 per cent of the gaseous product). In this case, reactions 39, 40, 41, and 44 can be neglected.

The remaining equations formulate a mechanism leading to specific stoichiometric consequences which can be checked on Adkins' data. Since all the ethyl ions are changed to ethylene, the amount of ethylene produced is independent of the amounts of carbon dioxide, acetone, and acetic acid formed. This result is reported by Adkins (2). Furthermore, since all the acetate ion results in either carbon dioxide or acetic acid, and all the acetyl results in acetone, the ratio of the number of moles of ester decomposing by reaction 34 to the number decomposing by reaction 35 is given by the ratio of acetone to carbon dioxide plus acetic acid:

 $\frac{[\text{molecules decomposing by Equation 35}]}{[\text{molecules decomposing by Equation 34}]} = \frac{[\text{CO}_2] + [\text{CH}_3\text{COOH}]}{[\text{CO}_2]} \quad (45)$

But every molecule of acetone comes from an acetyl (Equation 36); hence the number of moles of acetone must equal the number of moles of carbon dioxide if there are no side reactions. Consequently, the total number of moles of ethyl acetate decomposed must equal twice the number of moles of carbon dioxide plus the number of moles of acetic acid:

$$2[CO_2] + [CH_3COOH] = [CH_3COOC_2H_5] = [C_2H_4]$$
(46)

where the brackets refer to the number of moles of the respective substances. For experiments on fourteen different catalysts the average value, taken without regard to sign, of the expression:

$$[C_{2}H_{4}] - 2[CO_{2}] - [CH_{2}COOH] = D_{1}$$
(47)

is $0.0411 \ [C_2H_4]$, and the average value of

$$[CH_{3}COOC_{2}H_{5}] - 2[CO_{2}] - [CH_{3}COOH] = D_{2}$$
 (48)

is 0.0331 [CH₃COOC₂H₅]. The smallness of the deviations D_1 and D_2 thus supports Equation 46 and therefore the postulated mechanisms. In seventeen other cases where deviation of more than 10 per cent occurs, appreciable amounts of ethane and hydrogen are also noted in the products. This results from Equations 39, 40, and 41. Since the other products were not analyzed quantitatively, stoichiometric checks cannot be made in these cases.

The ratio $[CH_3COOH]/[CO_2]$ varies from 0.365 to 4.43 (over twelvefold) in this series of experiments; whereas the

values of D_2 vary from 0.5 to 9.3 per cent of the ester decomposed. Experiments on eleven other alumina catalysts (1) prepared in various ways, mainly by hydrolysis of aluminum alkoxides, yielded unmeasured quantities of ethanol (Equation 44) and consequently check Equation 46 less well.

Ethanol undergoes similar reactions at an oxide surface. This can be explained by a preliminary adsorption of ethanol in two analogous ways:

C₂H₃OH

$$\sim C_2 H_5^+ + O H^-$$
 (49)

$$>C_{2}H_{3}O^{-} + H^{+}$$
 (50)

The negative ion is always adsorbed on the metal ion in the surface. Reactions 38 to 41, inclusive, complete the steps of the mechanism. Hoover and Rideal (19) studied the reactions of ethanol at 297° to 326° C. on precipitated thoria. Since very little ethane was produced under these conditions, reaction 41 can be neglected in comparison with 38. The activation energy for hydrogen production is given as 24 kg.-cal. per mole whereas that for ethylene production is given as 30. Since almost equal volumes of hydrogen and ethylene are produced in unit time, this difference in heat of activation, if real, must be made up by a corresponding difference in the entropy of activation. This would indicate that the slowest step of dehydration involves an activated state with more rotational and translational freedom than does the activated state for dehydrogenation. This condition is satisfied if the activated state for dehydration consists in the detachment of a water molecule, formed by Equation 43, from the surface, whereas that for dehydrogenation consists in the detachment of acetaldehyde to leave a hydride ion adsorbed on the surface (Equation 39). The dehydration-activated complex then has the additional entropy of a practically free water molecule.

The effect of added gases can also be explained by this mechanism. Hoover and Rideal report that small amounts of added water vapor inhibit the production of ethylene more than the production of hydrogen, whereas added chloroform works in the opposite direction. Water ionizes on the surface to give H⁺ and OH⁻, and chloroform ionizes to give H⁺ and CCl₃⁻. If the adsorbed ions are somewhat free to move on the surface, a surface phase equilibrium would be expected in reactions 49 and 50 since they are not the slowest steps of the reactions. If, then, additional H⁺ and OH⁻ ions are furnished in equal amounts, straightforward calculation shows that, of reactions 49 and 50, the one with the larger equilibrium constant will be reversed most. Hence the concentration of ethyl ion will be reduced more than that of ethoxide ion, if Equation 49 has a larger equilibrium constant than 50; the result would be a decrease in the rate of production of ethylene relative to hydrogen. On the other hand, when chloroform is added, the only common ion is the proton which shifts the equilibrium so that the concentration of ethoxide ion is reduced relative to that of ethyl, and the production of ethylene is enhanced relative to hydrogen. The absolute rates of both reactions are reduced by either water or chloroform since they reduce the number of sites available for adsorption of alcohols.

A similar effect explains the action of water in raising the ratio of carbon dioxide to ethylene in ethyl acetate decomposition (5). The additional hydroxyl ions from the water use up the ethyl ions in Equation 37 to form ethanol and thus decrease the amount of ethylene obtainable from ethyl acetate. Data are not available to check the stoichiometry in this case, but the above assumption is at least a plausible one and is analogous to the ethanol case. Acetone also raises the ratio of carbon dioxide to ethylene (5). This can be understood by an increase in the concentration of acetyl ions which are available to displace carbon dioxide from acetate by Equation 36, since acetone would ionize on the surface to give CH₃CO⁺ and CH₁⁻ ions. The slight effect of added phenol in lowering the ratio of carbon dioxide to ethylene can be explained in the same way as the effect of chloroform on ethanol, since phenol would give C₆H₅O⁻ and H⁺ ions on the surface. The additional protons compete with the acetyl ions for acetate in Equations 36 and 37, and thus increase the acetic acid and ethylene production at the expense of carbon dioxide and acetone. That the effect is only slight is evidence of the weakness of phenol as an acid.

A third reaction of this same type is the decomposition of formic acid on zinc oxide (17). The competing reactions are:

$$HCOOH = H_2O + CO$$
(51)

$$\rightarrow H_2 + CO_2$$
 (52)

In this case the molecule is so simple that the mechanism is quite straightforward, consisting only of analogies to reactions 34 and 35:

$$HCO^+ + OH^-$$
(53)

HC00H ← H⁺ (54)

 $HCO^+ \longrightarrow CO + H^+$ (55)

 $HCOO^- \longrightarrow CO_2 + H^-$ (56)

 $H^+ + H^- \longrightarrow H_2$ (57)

$$H^+ + OH^- \longrightarrow H_2O \tag{58}$$

The activation energy for the production of hydrogen is given as 28 kg.-cal. per mole and that for the production of water as 16.8 kg.-cal. per mole. Again the rates of production of H₂O and H₂ are nearly equal, so that this difference in heat of activation, if real, is balanced by a difference in entropy of activation of about 20-25 entropy units in favor of the production of hydrogen. This is in contrast to the case of ethanol, where the entropy of activation for the production of water was greater. In formic acid decomposition, the activated state for hydrogen production would then have the greater entropy. This would be the case if it consisted of hydrogen being desorbed from the surface, whereas that for water production consisted of the desorption of CO from HCO⁺ leaving a proton on the surface. The difference in heats then would represent the difference in the heats of desorption of hydrogen and water.

The general features of surface reactions may be summarized as follows: Metal oxide surfaces adsorb reactants as ions, the metal ion adsorbing a negative reactant ion. The resulting reactant ions are in many cases sufficiently mobile on the surface so that equilibrium can be established between the ionized and un-ionized forms. The surface then acts essentially as a polar solvent. In all cases the slow step is either the adsorption in which ions are formed, or the desorption in which the ions recombine with the old or with new partners. In either case the reactants in the activated complex make weak bonds with the surface; they are either just beginning to make a bond or just on the point of breaking a bond. The result is that, if two processes such as hydrogenation and dehydration go at about the same rate on one catalyst, the relative free energies of activation are only slightly shifted by a new catalyst. The theory of the activated complex is helpful in interpreting the observed kinetic data and the effects of poisons so as to build a unified picture of the mechanism of an important class of catalyzed organic reactions.

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Principles of Reactor Design

GAS-SOLID INTERFACE REACTIONS

David M. Hurt

E. I. DU PONT DE NEMOURS & COMPANY, INC., WILMINGTON, DEL.

A method of correlating the performance of small-scale with large-scale reactors has been developed. This method, limited to gas-solid interface reactions, has proved useful for the rational design of plant-scale reactors from small-scale test data.

Over-all reaction rates have been shown to be a function of surface reaction rates and diffusional, or mass transfer, rates and these component factors have been individually correlated with their respectively important variables. The new concepts of

THE central problem in the development of any chemical process is the rational design of the reactor or the equipment in which the chemical changes involved in the process take place. In contrast to unit operations such as heat transfer, absorption, distillation, etc., there has been little progress in developing general principles of design for reactors. Plant-scale reaction equipment has reached a high degree of perfection for many specific reactions, but in many cases this has been accomplished largely by trial-and-error methods on relatively large-scale equipment. On the other hand, there are many plant-scale reactors in use today which are, in effect, nothing more than hundreds or even thousands of small-scale reactors arranged for parallel flow.

The problem of correlating the performance of small-scale and large-scale reactors is obviously more complex than for unit operation equipment involving physical changes only. A review of previous work on this problem will serve to illustrate the inherent difficulties as well as the general background from which the specific solution given here was developed.

WORK OF OTHER INVESTIGATORS

Literature references on this general subject are not numerous. Damköhler $(4, \delta, 6)$ made a generalized mathematical analysis of this problem by the theory of dimensional similitude; although interesting, his work does not particularly advance the art, except perhaps in a negative sense by demonstrating and proving the inherent limitations. For the general case of fluid reactants in a continuous reactor, he started with the interrelations be-tween the different variables as governed by the following funda-mental laws: Newton's law of motion, Fourier's law of heat conduction, Fick's law of diffusion, conservation of mass, and conservation of energy; he then derived five dimensionless parameters, given in nonmathematical terms below, which must be respectively equal in both large and small reactors for com-plete similarity: Literature references on this general subject are not numerous. plete similarity:

Inertia force (Reynolds number) I. Viscous force

H. R. U. (height of over-all reaction unit) and H. C. U. (height of catalytic unit or surface reaction unit) have been introduced as measures of over-all reaction rate and surface reaction rate, and used in conjunction with a conventional gas-film H. T. U. as a measure of mass transfer rate.

New data on gas-film H. T. U. values, covering particle sizes and shapes normally used as catalysts, are presented. Data for the oxidation of sulfur dioxide on platinum catalysts are given to illustrate the method.

- Moles generated per second due to chemical reaction II. Moles accumulating per second due to flow
- Moles generated per second due to chemical reaction III. Moles accumulating per second due to diffusion
- Heat generated per second chemically IV. Net heat brought in per second by flow
- Heat generated per second chemically V. Net heat brought in per second by conduction

Thus for a chemical reaction taking place in a model and its prototype, equality of I (Reynolds number) is necessary for dynamic similarity, equality of II and III for reaction-kinetic similarity, and equality of IV and V for thermodynamic simi-larity. However, attempts to apply this analysis to practical design problems showed that complete similarity for two reactors of dissimilar size was impossible of atteinment. But predicting of dissimilar size was impossible of attainment. By neglecting certain of the above groups, the conditions for partial similarity could be derived, but since the relative importance of the dimensionless groups disregarded cannot be accurately predeter-

mined, this leaves the results open to considerable doubt. Laupichler (10), for the catalyzed water-gas reaction, intro-duced the concept of total reaction resistance as the sum of conversion resistance and diffusion resistance. He showed that the influence of diffusion resistance on over-all reaction rate was negligible for the catalyzed water-gas reaction with the specific catalyst, temperature range, and flow rate which he investigated. However, Laupichler's work gives no method of predicting the relative importance of diffusion resistance and conversion resistance for other flow rates, other temperatures, other catalysts, or on other reactions.

Edgeworth-Johnstone (?) reviewed the previous work on the general subject of the transference of chemical processes from small- to large-scale operation, and summarized the general factors of importance for similarity of results when either chemi-cal resistance is controlling, or when dynamic resistance is con-trolling. For conditions where both resistances are important, he states that there is no estimated of pradicting largehe states that there is no satisfactory method of predicting largescale performance from small-scale tests. The above references, although of no particular value for actual problems of reactor design, serve to illustrate the inherent

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difficulties encountered in previous attempts to correlate the performance of reactors. For example, Damköhler's work proved that similarity of over-all performance for two reactors of dissimilar size is obtainable only through various combinations of dissimilar values for the essential dimensionless groupings of the fundamental variables. (Obviously, increase in capacity without change in unit reactor size is always possible by increasing the number of units in direct ratio to the desired capacity increase, but this simple method is either impractical or uneconomic in most cases.) It follows that progress can be made in this field only by breaking down over-all reaction rates into two or more component factors and correlating these factors individually with their respective variables.

CORRELATING PLANT-SCALE WITH SMALL-SCALE PERFORMANCE

The general problem of principles of reactor design has been limited here to gas-solid interface reactions in continuoustype reactors. The solution developed for this field consists of evaluating over-all reaction rates as a function of mass transfer rate and surface reaction rate, and then determining the relation between these component factors and their respective variables that will give satisfactory correlation for reactors or converters of widely different capacity.

Since most solid catalysts are employed as packed beds of irregular particles and their actual surface is difficult to determine, we have utilized the familiar H. T. U. concept to represent a measure of the difficulty of the desired performance, with respect to both over-all performance and its component factors. We have retained the gas-film H. T. U. (height of packed bed which gives a change in partial pressure equal to the mean driving force across the gas film) as a measure of mass transfer rate; and we have introduced the new concepts of H. R. U. (height of a reaction unit or depth of catalyst bed which gives a change in partial pressure of reactant equal to the mean over-all driving force), and H.C.U. (height of a catalytic unit, or surface reaction unit, of similar meaning but referred to surface reaction driving force) as measures of over-all reaction rate and surface reaction rate, respectively. Thus the driving forces are $(y - y^*)$ for H. R. U., $(y - y_i)$ for H. T. U., and $(y_i - y^*)$ for H. C. U. The equations of definition, in differential form, follow for these terms:

$$\frac{dZ}{H_{\mathcal{R}}} = \frac{dy}{(y^* - y)} \qquad (1)$$
$$\frac{dZ}{H_{\mathcal{T}}} = \frac{dy}{(y_i - y)} \qquad (2)$$
$$\frac{dZ}{H_{\mathcal{C}}} = \frac{dy}{(y^* - y_i)} \qquad (3)$$

For the simplified conditions of steady state, unpoisoned catalyst surface, and firstorder reaction, the relation of H. R. U. to its component parts may be readily derived. The derivation is made for "point conditions", or for a point in the catalyst bed where the mole fraction of reacting gas is y, and for equimolar counterdiffusion (no volume change).

Eliminating (dZ/dy) from Equations 1 and 2,

$$H_R = H_T \frac{(y^* - y)}{(y_i - y)}$$
(4)

$$\frac{(y^* - y)}{(y_i - y)} = \frac{y^* - y_i + y_i - y}{(y_i - y)}$$
(5)

$$= 1 + \frac{(y^* - y_i)}{(y_i - y)}$$
(6)

Substituting Equation 6 in 4,

$$H_R = H_T + H_T \frac{(y^* - y_i)}{(y_i - y)}$$
(7)

Eliminating (dZ/dy) from Equations 2 and 3,

$$H_C = H_T \frac{(y^* - y_i)}{(y_i - y)}$$
(8)



Equipment for Contact Conversion of Carbon Monoxide in Water Gas with Steam to Produce Carbon Dioxide and Hydrogen at One of the Plants of E. I. du Pont de Nemours and Company, Inc.

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A method of correlating the performance of small-scale with large-scale reactors has been developed. This method, limited to gas-solid interface reactions, has proved useful for the rational design of plant-scale reactors from small-scale test data.

Over-all reaction rates have been shown to be a function of surface reaction rates and diffusional, or mass transfer, rates and these component factors have been individually correlated with their respectively important variables. The new concepts of

THE central problem in the development of any chemical process is the rational design of the reactor or the equipment in which the chemical changes involved in the process take place. In contrast to unit operations such as heat transfer, absorption, distillation, etc., there has been little progress in developing general principles of design for reactors. Plant-scale reaction equipment has reached a high degree of perfection for many specific reactions, but in many cases this has been accomplished largely by trial-and-error methods on relatively large-scale equipment. On the other hand, there are many plant-scale reactors in use today which are, in effect, nothing more than hundreds or even thousands of small-scale reactors arranged for parallel flow.

The problem of correlating the performance of small-scale and large-scale reactors is obviously more complex than for unit operation equipment involving physical changes only. A review of previous work on this problem will serve to illustrate the inherent difficulties as well as the general background from which the specific solution given here was developed.

WORK OF OTHER INVESTIGATORS

Literature references on this general subject are not numerous. Damköhler (4, δ , δ) made a generalized mathematical analysis of this problem by the theory of dimensional similitude; although interesting, his work does not particularly advance the art, except perhaps in a negative sense by demonstrating and proving the inherent limitations. For the general case of fluid reactants in a continuous reactor, he started with the interrelations be-tween the different variables as governed by the following funda-mental laws: Newton's law of motion, Fourier's law of heat conduction, Fick's law of diffusion, conservation of mass, and conservation of energy; he then derived five dimensionless parameters, given in nonmathematical terms below, which must be respectively equal in both large and small reactors for com-plete similarity: plete similarity:

Inertia force (Reynolds number) I.

Viscous force

H. R. U. (height of over-all reaction unit) and H. C. U. (height of catalytic unit or surface reaction unit) have been introduced as measures of over-all reaction rate and surface reaction rate, and used in conjunction with a conventional gas-film H. T. U. as a measure of mass transfer rate.

New data on gas-film H. T. U. values, covering particle sizes and shapes normally used as catalysts, are presented. Data for the oxidation of sulfur dioxide on platinum catalysts are given to illustrate the method.

- Moles generated per second due to chemical reaction II. Moles accumulating per second due to flow
- Moles generated per second due to chemical reaction III. Moles accumulating per second due to diffusion
- Heat generated per second chemically IV. Net heat brought in per second by flow
- Heat generated per second chemically v. Net heat brought in per second by conduction

Thus for a chemical reaction taking place in a model and its prototype, equality of I (Reynolds number) is necessary for dynamic similarity, equality of II and III for reaction-kinetic similarity, and equality of IV and V for thermodynamic simi-larity. However, attempts to apply this analysis to practical design problems showed that complete similarity for two reactors of discipling the size that the size of attributes the size of th of dissimilar size was impossible of attainment. By neglecting certain of the above groups, the conditions for partial similarity could be derived, but since the relative importance of the dimensionless groups disregarded cannot be accurately predeter-mined, this leaves the results open to considerable doubt.

Laupichler (10), for the catalyzed water-gas reaction, intro-duced the concept of total reaction resistance as the sum of con-version resistance and diffusion resistance. He showed that the influence of diffusion resistance on over-all reaction rate was negligible for the catalyzed water-gas reaction with the specific catalyst, temperature range, and flow rate which he investigated. However, Laupichler's work gives no method of predicting the relative importance of diffusion resistance and conversion resistance for other flow rates, other temperatures, other catalysts, or on other reactions.

Edgeworth-Johnstone (7) reviewed the previous work on the general subject of the transference of chemical processes from small- to large-scale operation, and summarized the general factors of importance for similarity of results when either chemi-cal resistance is controlling, or when dynamic resistance is con-trolling. For conditions where both resistances are important, he states that there is no entisfector method of readiating large he states that there is no satisfactory method of predicting largescale performance from small-scale tests.

The above references, although of no particular value for actual problems of reactor design, serve to illustrate the inherent

Part Int

difficulties encountered in previous attempts to correlate the performance of reactors. For example, Damköhler's work proved that similarity of over-all performance for two reactors of dissimilar size is obtainable only through various combinations of dissimilar values for the essential dimensionless groupings of the fundamental variables. (Obviously, increase in capacity without change in unit reactor size is always possible by increasing the number of units in direct ratio to the desired capacity increase, but this simple method is either impractical or uneconomic in most cases.) It follows that progress can be made in this field only by breaking down over-all reaction rates into two or more component factors and correlating these factors individually with their respective variables.

CORRELATING PLANT-SCALE WITH SMALL-SCALE PERFORMANCE

The general problem of principles of reactor design has been limited here to gas-solid interface reactions in continuoustype reactors. The solution developed for this field consists of evaluating over-all reaction rates as a function of mass transfer rate and surface reaction rate, and then determining the relation between these component factors and their respective variables that will give satisfactory correlation for reactors or converters of widely different capacity.

Since most solid catalysts are employed as packed beds of irregular particles and their actual surface is difficult to determine, we have utilized the familiar H. T. U. concept to represent a measure of the difficulty of the desired performance, with respect to both over-all performance and its component factors. We have retained the gas-film H. T. U. (height of packed bed which gives a change in partial pressure equal to the mean driving force across the gas film) as a measure of mass transfer rate; and we have introduced the new concepts of H. R. U. (height of a reaction unit or depth of catalyst bed which gives a change in partial pressure of reactant equal to the mean over-all driving force), and H.C.U. (height of a catalytic unit, or surface reaction unit, of similar meaning but referred to surface reaction driving force) as measures of over-all reaction rate and surface reaction rate, respectively. Thus the driving forces are $(y - y^*)$ for H. R. U., $(y - y_i)$ for H. T. U., and $(y_i - y^*)$ for H. C. U. The equations of definition, in differential form, follow for these terms:

$$\frac{dZ}{H_{E}} = \frac{dy}{(y^{*} - y)}$$
(1)
$$\frac{dZ}{H_{T}} = \frac{dy}{(y_{i} - y)}$$
(2)
$$\frac{dZ}{H_{C}} = \frac{dy}{(y^{*} - y_{i})}$$
(3)

For the simplified conditions of steady state, unpoisoned catalyst surface, and firstorder reaction, the relation of H. R. U. to its component parts may be readily derived. The derivation is made for "point conditions", or for a point in the catalyst bed where the mole fraction of reacting gas is y, and for equimolar counterdiffusion (no volume change).

Eliminating (dZ/dy) from Equations 1 and 2,

$$H_R = H_T \frac{(y^* - y)}{(y_i - y)}$$
(4)

$$\frac{(y^* - y)}{(y_i - y)} = \frac{y^* - y_i + y_i - y}{(y_i - y)}$$
(5)

$$= 1 + \frac{(y^* - y_i)}{(y_i - y)}$$
(6)

Substituting Equation 6 in 4,

$$H_R = H_T + H_T \frac{(y^* - y_i)}{(y_i - y)}$$
(7)

Eliminating (dZ/dy) from Equations 2 and 3,

$$H_C = H_T \frac{(y^* - y_i)}{(y_i - y)}$$
(8)



Equipment for Contact Conversion of Carbon Monoxide in Water Gas with Steam to Produce Carbon Dioxide and Hydrogen at One of the Plants of E. I. du Pont de Nemours and Company, Inc.

Substituting Equation 8 in 7,

$$H_R = H_T + H_C \tag{9}$$

With appropriate correction factors Equation 9 is also applicable to reactions involving a change in volume or reactions reversibly poisoned by product, reactant, or impurity. Change in volume affects mass transfer rate by inducing gas flow in a direction normal to the solid surface and, thus, the magnitude of H_T . This correction factor can, in general, be neglected without appreciable error since it lies between $(1 - y)/(1 - y)_f$ and unity for volume decrease, or between $(1 - y)_f/(1 - y)$ and unity for volume increase.

Temporary or reversible poisoning of an active solid surface is often a factor of major importance in determining over-all reaction rates. The noncumulative poisoning of a solid catalyst by a gaseous impurity is fairly well known, but the equally important and similar self-poisoning by a reactant or a product is not so evident, although its effect must likewise be evaluated before correlation of over-all performance for different conditions can be expected. When the poisoning agent is a product, a reactant, or an impurity present in approximately constant concentration, the effect may be treated as steady-state conditions. Although the exact mechanism of poisoning is not always known, its magnitude can be evaluated most conveniently in terms of the fraction of total catalyst surface not poisoned. Previous unpublished work of the writer showed that this fraction is represented by the dimensionless factor $1/[1 + k_1(p_p)]$ where, for the given surface, k_1 varies with temperature only. Thus, the value of H_R for poisoned reactions is given by¹:

$$H_R = [1 + k_1(p_p)](H_T + H_c)$$
(10)

The above development therefore is applicable to true first-order reactions, pseudo first-order reactions, or reactions of no definite order which may be classed as pseudo firstorder reactions poisoned by a product or reactant. Furthermore, it may be used for second-order reactions without appreciable error when one reactant is always used in large excess. It covers, therefore, the majority of the reactions encountered in practice.

¹ Based on purely theoretical reasoning, the correct form of Equation 10 should be

$H_R = (1 + k_1 p_p)^z H_T + (1 + k_1 p_p) H_C$

where x would be somewhat less than unity and would vary with the fraction of the aurface poisoned and with the relative magnitudes of the gas film thickness and the diameter of poisoned areas. For simplicity, we have used the form in the text above. Since this same equation has been used both in evaluating small-scale tests and calculating large-scale performance, any minor errors thus introduced cancel out to a large extent. To consider the individual correlation of H. T. U., H. C. U., and k_1 with their respectively important operating variables, the method used is to set up the most probable relations, as based upon specific knowledge, analogy, or deduction, and then test these assumptions by means of existing performance data on reactors covering a wide range in capacity. Specifically, the initially assumed relations are as follows: d suph

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H. T. U. is independent of the specific reaction or type of catalyst, is practically independent of temperature and pressure, but varies with flow conditions as defined by Reynolds number, with shape and size factors of the solid particles, and with physical properties of the gas mixture as defined by some function of the dimensionless group $(\mu/\rho D_{\tau})$. H. C. U. is specific for the specific reaction and the statement of the specific reaction.

H. C. U. is specific for the specific reaction and the shape, size, and type of catalyst, is independent of Reynolds number, varies directly with mass velocity, is independent of pressure, but varies widely with temperature.

Coefficient k_1 is specific for the specific reaction and type of catalyst, is independent of Reynolds number, varies with temperature, and is independent of total pressure when the poison concentration is expressed as partial pressure in atmospheres.

DETERMINATION OF GAS-FILM H. T. U.

In the application of this method of correlating test data on reactors, it was necessary to determine the values of H. T. U. independently before values for H. C. U. could be calculated, since any one specific test gives only a value for the over-all reaction rate under those conditions. The only data available for transfer rates to packed beds were those of Ahlberg (1) on water vapor absorption by silica gel particles and those of Furnas (8, 9) on heat transfer to packed beds. These data covered only a narrow range of particle size and mass velocities; moreover, there was a possibility of appreciable resistances within the solid so that the over-all transfer rates would not give true gas-film H. T. U. values. The experimental measurement of gas-film H. T. U. was undertaken for the various sizes and shapes of solid particles normally used as catalysts.

Various types of systems were investigated to determine the simplest and most accurate system for measuring gasfilm H. T. U. The general method was limited to steadystate conditions in all cases, since this permitted the direct evaluation of the results and eliminated the necessity of resorting to Schumann's involved method (11) of evaluating unsteady-state data.

The specific systems tried were: adsorption of water vapor from moist air by silica gel particles, adsorption of water vapor from moist air by particles coated with phosphorus pentoxide, adiabatic humidification of air by wetted particles (measuring both heat and mass transfer rates), evaporation

TABLE I. HEAT AND MASS TRANSFER FACTORS FOR VAPORIZATION OF WATER INTO AIR IN A PACKED TOWER WITH $3/8 \times 3/8$ Inch Cylindrical Wetted Pellets

(Height of	packing 2 in	nches, total	pressure 1	atmosphere.	$(c\mu/k)^{2/2}$	$= 0.83. (\mu/\mu)$	$(D_n)^{2/3} = 0.3$	72)		
Run No.	6	7	8	9	10	11	10	10	14	15
Mass velocity, lb./(hr.)(sq. ft. cross section) 526	895	895	1180	335	205	12	13	14	710
Temperature, ° C.			000	1100	000	200	205	102	715	110
Inlet air	23.23	26.90	26 90	26 00	27 00	97 05		0.1 =0		
Top layer pellets	(Av.)	13.88	14 70	14 05	12 97	27.00	12.00	24.78	26.61	20.85
Bottom laver pellets	11.13	13 68	13 80	12 65	12.27	14.20	13.99	12.31	14.70	14.30
Exit air	13.25	16 45	16 47	16 49	15.22	13.35	13.40	12.18	13.80	13.30
Partial pressure of water vapor, atm.		101.10	10.11	10.42	10.44	15.44		13.52	16.37	16.07
Inlet air	0.0047						0.0010			
Exit air	0.0117						0.0048			
Vanor pressure of water at surface temp	atm.						0.0136			
Top laver	(Av.)									
Bottom laver	10.0131						0.0155	111		
$(t_1 - t_2)/\Delta t_m$	1.75	1.62	1 54	1 54	1 09		0.0150			
HT heat transfer, in.	1.14	1 23	1 30	1.0%	1.83	2.08		2.25	1.54	1.52
$HT/(c\mu/k)^{2/3}$, in.	1.36	1 48	1 57	1.30	1.09	0.96		0.89	1.30	1.32
$(m - m)/\Lambda m$	1.75		x.01	1.01	1.31	1.15		1.07	1.57	1.60
HT mass transfer, in.	1.14						2.04			
$H_T/(\mu/aD_r)^{2/3}$ in.	1.59						0.98			
Modified Reynolds No.	374	630	620	840	1010		1.35			
		000	000	840	240	145	145	72	505	50

of naphthalene into air from naphthalene particles, and evaporation of naphthalene into hydrogen from naphthalene particles.

In all cases the beds of solid particles were contained in small cylindrical towers with a wire screen support for the packed section. The tower diameter employed was not less than ten particle diameters in any case, so as to minimize any "wall effects". The gas flows were measured by calibrated sharp-edge orifices. The packed bed depth was regulated to keep the change in gas composition in the range from about 50 to 80 per cent approach to equilibrium; thus the magnification of any small errors in the measurement of exit gas or equilibrium composition was prevented. The same size and shape of particles (3/8) inch diameter \times $^{3}/_{8}$ inch thick, cylindrical) were maintained for the various systems investigated, and the preferred method only (evaporation of naphthalene into air) was utilized for the other sizes and shapes subsequently measured.

The first system investigated was the direct absorption of water vapor from moist air on silica gel particles. In an attempt to obtain steady-state conditions, the time of the runs was limited to 2 to 4 minutes so that the equilibrium partial pressure of water vapor from the gel would still be

negligible at the end of the runs. The water contents of the inlet and exit air were determined by continuous sampling and analysis, and the weight increase of the gel determined as a material balance check. The results were reproducible but showed an unexpectedly high H. T. U. of 10 inches for a mass velocity of 600 [or $H_T/(\mu/\rho D_r)^{3/\epsilon} = 13.8$ inches for $D_pG/\mu = 425$, with particles $^{3}/_{8}$ inch in diameter $\times ^{3}/_{8}$ inch, and a bed 3.3 inches in diameter $\times 2$ inches]. This indicated that a major difference between equilibrium vapor pressure and interface vapor pressure must have developed during these short runs.

In an attempt to eliminate the "solid film" effect encountered in adsorbing water on silica gel, the silica gel particles were coated with a layer of phosphorus pentoxide, and mass transfer rates were measured by the same method as for the silica gel. In these runs the maximum time for a run was such that the total water adsorbed (or reacted) was only a fraction of its stoichiometric equivalent to the phosphorus pentoxide present. This system gave an H. T. U. value of 2.5 inches at a mass velocity of 600 [or $H_T/(\mu/\rho D_{\bullet})^{*/\bullet} = 3.5$ inches for $D_pG/\mu = 425$, with particles */* inch in diameter $\times */*$ inch, and a bed 3.3 inches in diameter $\times 2$ inches]; while of the expected order of magnitude, this value still left some doubt as to its exact accuracy as a measure of the true gas-film H. T. U.

Adiabatic humidification, where the heat of evaporation is supplied by the gas stream, was next investigated as a means of eliminating the solid film effect. Partially dried air was passed over silica gel pellets wetted with water. The surface temperature of the wetted pellets was checked by fine-wire thermocouples embedded in two pellets placed in the top and bottom layers of the packed bed, and the inlet and exit water vapor concentrations were measured by sampling through



Figure 1 (Above). Heat and Mass Transfer Rates between Gas Streams and Packed Beds of $\frac{3}{8} \times \frac{3}{8}$ Inch Cylindrical Particles

Figure 2 (Below). Mass Transfer Rates between Gas Streams and Packed Beds of Various Particle Sizes and Shapes

> tubes packed with phosphorus pentoxide. Inlet and exit gas temperatures were taken, and heat transfer rates were calculated as a check against mass transfer rates. All measurements were made under steady-state conditions. Steady state (to the nearest 0.1° C.) was reached in about 5 minutes with this system and lasted about 5 to 20 minutes (depending on gas flow rate), at which time the surface of the pellets started to dry. This method gave H. T. U. values somewhat lower than the preceding method, and these values are believed to be the true gas-film H. T. U. with a probable accuracy of about ± 10 per cent. The mass transfer and heat transfer rates as obtained check closely when correlated by the method of Chilton and Colburn (3), which would not be expected if there were any appreciable error in this method of determining the true surface temperature and surface vapor pressure. The experimental data are summarized in Table I and correlated in Figure 1.

The above method was satisfactory for a somewhat limited range of gas velocities only, since at high velocities steadystate conditions lasted too short a time for accurate tests, and at low velocities adiabatic conditions could not be maintained. Therefore H. T. U. values for the total velocity range desired were determined by measuring the evaporation rate of solid naphthalene particles into air or into hydrogen. At room temperatures naphthalene has such a low partial pressure that the cooling effect of evaporation is negligible as compared to the heating effect of the gas stream, and thus the surface temperature of the naphthalene (and its consequent vapor pressure) could be accurately determined, since it could vary less than 0.1° C. from the gas stream temperature. In this method the naphthalene vapor concentration in the exit gas was not measured directly but was calculated from the gas flow rate, time of run, and loss in weight

										ΗT	
Run No.	Mass Velocity, Lb./(Hr.) (Sq. Ft.)	Packed Height, Inch	Time of Run Min.	Temp., °C.	Naphthalene Vaporized, Gram	$p C_{10}H_{s}$ in Exit Gas, Atm. $\times 10^{2}$	Surface Vapor Pressure, Atm. × 10 ³	$\frac{(p_1 - p_2)}{\Delta p_m}$	<i>HT</i> , Inches	$\frac{\left(\frac{\mu}{\rho D_v}\right)^{1/2}}{\text{Inches}}$	Reynold No.
				2/1 × 2/2 Ir	ch Cylindrical	Particles. Air.	$D_p = 0.38 \text{Ir}$	nch			
16 17 18 19 20 21	950 458 226 81 40.4 21.7	1 1 1 1 1	2 4 6 10 14 20	26.3 26.5 26.9 27.5 27.9 28.1	0.153 0.176 0.159 0.137 0.115 0.108	0.040 0.048 0.059 0.086 0.101 0.124	0.169 0.171 0.175 0.184 0.187 0.191	0,270 0,350 0,408 0,630 0,758 1,05	3.70 3.03 2.45 1.59 1.32 0.95	2.00 1.64 1.33 0.87 0.72 0.52	670 324 160 57.2 28.5 15.3
			3/2	$\times \frac{3}{8}$ Inch	Cylindrical Par	ticles, Hydro	gen, $D_p = 0.3$	8 Inch			
22	4.8	I	10	27.0	0.159	0.115	0.175	1,11	0.90	0.36	7.0
				3/16 × 3/16 I	nch Cylindrical	Particles. Ai	$D_n = 0.17$	nch			
23 24 25 26 27 28	945 455 226 81 40.4 21.7	1 1 1 1 1	1.50 2 4 6 10 12	27.8 27.4 27.6 28.4 28.6 29.0	0.254 0.186 0.205 0.137 0.130 0.095	0.090 0.102 0.112 0.143 0.162 0.182	0.185 0.182 0.184 0.193 0.196 0.203	0.657 0.825 0.935 1.33 1.72 2.22	1.52 1.21 1.07 0.75 0.58 0.45	0.83 0.66 0.58 0.41 0.315 0.245	300 145 72 26.8 12.8 6.9
				3 to 4 Me	sh Irregular P	articles, Air, L	$D_p = 0.22$ Incl	1			
29 30 31	945 455 226	1 1 1	2 2 3	26.5 27.0 27.2	0.320 0.189 0.160	0.084 0.103 0.117	0.170 0.175 0.179	0.675 0.893 1.07	1.48 1.12 0.935	0.80 0.61 0.51	395 190 94
				4 to 6 Me	sh Irregular Pa	articles, Air, L	$D_p = 0.16$ Inch	1			
32 33 34 35 36 37	735 459 226 81 40.4 21.7	1 1 1 1 1	2 2 3 6 10 15	27.4 27.4 28.0 28.0 28.0	0.351 0.231 0.183 0.154 0.135 0.117	0.120 0.126 0.135 0.159 0.168 0.178	0.182 0.182 0.182 0.189 0.189 0.189 0.189	1.07 1.17 1.35 1.82 2.17 2.85	0.935 0.855 0.74 0.55 0.46 0.35	$\begin{array}{c} 0.51 \\ 0.465 \\ 0.385 \\ 0.30 \\ 0.25 \\ 0.19 \end{array}$	$222 \\ 139 \\ 68.5 \\ 24.5 \\ 12.2 \\ 6.6$
				6 to 8 M	esh Irregular P	article, Air, D	v = 0.11 Inch				
38 39	455 226	1	2 3	29.0 29.0	0.280 0.221	0.154 0.166	0.201 0.201	1.43 1.73	0.70 0.58	0.38 0.315	95 47
10				8 to 10 M	esh Irregular P	articles, Air, J	$D_p = 0.08$ Inc	h			
40 41	318 193	0.80 0.80	3 4	28.5 28.8	0.283 0.240	$\begin{array}{c} 0.149 \\ 0.152 \end{array}$	0.196 0.198	1.40 1.48	0.57 0.54	0.31 0.295	46 29.2

Mass Transfer Factors for Vaporization of Naphthalene into Air or Hydrogen from Solid Naphthalene Particles in a Packed Tower TABLE II.

(Total pressure 1 atmosphere, tower diameter $3^{4}/_{16}$ inches, $(\mu/\rho D_{p})^{2/4} = 1.84$ for $C_{10}H_{5}$ -air or 2.54 for $C_{10}H_{5}$ -hydrogen)

of naphthalene particles. For this purpose a special tower of low gross weight made of thin-gage aluminum tubing was used so that the loss in weight of the packed bed of naphthalene particles could be accurately determined without removal from the tower.

This method was used in extending the measurements to the various sizes and shapes of particles normally used as catalysts. The sizes and shapes covered were $3/8 \times 3/8$ inch and $3/16 \times 3/16$ inch cylindrical particles and irregular broken solids of the following size ranges: 3 to 4 mesh, 4 to 6 mesh, 6 to 8 mesh, and 8 to 10 mesh. The experimental data are summarized in Table II and shown graphically in Figures 1 and 2.

For the same size and shape of solid particles, data for the various systems measured were correlated by plotting $H_T/(\mu/\rho D_{\bullet})^{*/*}$ for mass transfer, or $H_T/(c\mu/k)^{*/*}$ for heat transfer against the modified Reynolds number $D_p G/\mu$. For different size particles of similar shape no satisfactory correlation of the data into a single curve could be obtained. The data are, accordingly, presented as separate curves for each size and shape investigated. The slopes of these curves in the turbulent and viscous regions do not differ so widely as do the curves of pressure drop for flow through granular solids (2), where the slope of the friction factor-Reynolds number plot is -1 below a value of about 40, and about -0.2 above this value. The relative positions of the curves show that H. T. U. decreases, in general, as particle diameter decreases, but that this effect is diminishing rapidly at the lowest values of D_p employed.

CORRELATION OF EXISTING DATA

In order to demonstrate their application and as a general test of their validity, the methods developed were applied to existing processes for which sufficiently detailed data on both small-scale and large-scale reactors are available. Previous unpublished work of the writer covering an extensive investigation of the reaction rates for oxidation of sulfur dioxide over platinum catalysts for equipment sizes ranging from laboratory scale up to full plant scale has been thus correlated. This reaction is reversibly poisoned by the reaction product sulfur trioxide, so that for this case:

$$H_R = (1 + k_1 p_{SO_s})(H_T + H_c) \tag{11}$$

Values of k_1 vs. temperature for two types of platinum catalyst for this reaction are shown in Figure 3, and H_c is plotted against temperature for the same catalysts in Figure 4. Values of H. T. U. are as shown in Figure 2, the value of $(\mu/\rho D_v)^{t/s}$ being 1.18 for sulfur dioxide-air. H. C. U. varies

TABLE III. SURFACE	RELATIVE REACTION	IMPORT RATES	ANCE OF AV	of Mass erage P	TRANSFER	ANI
	OPE	RATING	CONDIT	NONS		

	% of Total I	Reaction Time
Reaction	For mass transfer	For surface reaction
$\begin{array}{c} \text{CO} + \text{H}_2\text{O} \longrightarrow \text{H}_4 + \text{CO}, \\ \text{N}_1 + 3\text{H}_2 \longrightarrow 2\text{NH}_4 \\ \text{CO} + 2\text{H}_2 \longrightarrow \text{CH}_4\text{OH} \\ \text{CO} + 3\text{H}_2 \longrightarrow \text{CH}_4 + \text{H}_2\text{O} \end{array}$	60 15 ^a 20 ^a 50	40 85 a 80 a
$\frac{2 \text{CH}_{3}\text{OH} + \text{O}_{2} \longrightarrow 2 \text{HCHO} + 2 \text{H}_{2}\text{O}}{4 \text{NH}_{3} + 5 \text{O}_{2} \longrightarrow 4 \text{NO} + 6 \text{H}_{2}\text{O}}$	80 160 <i>b</i>	20

^a These reactions are known to be reversibly poisoned by the reaction products. However, insufficient data for evaluating the poisoning coeffi-cients were available, and omission of this factor may have appreciably affected the results shown. ^b This indicates that the oxidation of NH₂ on platinum is a chain reaction extending into the gas phase.

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directly with mass velocity, and since the values shown in the plot are specific for G = 600 pounds/(square foot)(hour), H. C. U. values for other mass velocities equal H. C. U. (from plot) $\times G/600$.



Figure 3. Sulfur Trioxide Poisoning Coefficients for Oxidation of Sulfur Dioxide on ³/₈ × ³/₈ Inch Platinum Catalysts

This correlation covers the complete range from laboratory up to full plant scale results, or for catalyst volume from about 100 ml. up to about 100 cubic feet, mass velocities from about 35 to 600 pounds/(square foot)(hour), and inlet gas compositions from 1 to 10 per cent sulfur dioxide. It is estimated that the accuracy is within about 20 per cent, or only slightly less than the average reproducibility of these catalysts.

The plots of k_1 and H. C. U. (in conjunction with appropriate H. T. U. values) completely define the catalyst performance under any conditions. Plots for two representative platinum catalysts (A and B) are included to illustrate the equal slopes of the straight-line plots obtained by using log-reciprocal coordinates. From the slope of the H. C. U. plots the calculated activation energy for this reaction is 25,600 gram-calories per gram mole. Similarly, from the slope of the k_1 plots the heat of adsorption for sulfur trioxide on platinum black is estimated as 12,100 gram-calories per gram mole.

The method of correlating specific test data ranging from laboratory-scale to plant tests by these plots was as follows: The k_1 and H. C. U. plots were drawn from points calculated from laboratory-scale isothermal tests. This required two tests, made under essentially similar conditions except for different average sulfur trioxide concentrations, at each temperature. Obviously any one test gives only a value for H. R. U., with three component parts, under those conditions. But since H. T. U. is independently known, two tests permit the evaluation of k_1 and H. C. U. by the method of simultaneous equations. These plots were then used to calculate the performance of pilot or full-scale plant under adiabatic conditions. This was done by a stepwise calculation with a sufficient number of steps to reduce the error, owing to assumption of isothermal conditions and constant poisoning factor in each step, to negligible amount. Comparison of actual with calculated results then indicated the accuracy of the correlation.

A number of other gas-solid interface reactions have been reviewed from the standpoint of similarly breaking down the over-all reaction rates to permit the correlation of smalland large-scale data. The approximate relative importance of mass transfer rate and surface reaction rate for various commercial reactions under average plant-scale conditions is shown in Table III. No major discrepancies between small- and large-scale results were found when analyzed by this method, although the data in most cases were much less complete than for sulfur dioxide oxidation.

DISCUSSION

In all of this work the conditions necessary for attainment of thermodynamic similarity have been intentionally neglected for the following reasons. Laboratory or small-scale tests are inherently isothermal, whereas large-scale tests are inherently adiabatic or at least nonisothermal. Therefore, complete thermodynamic similarity, although perhaps possible, is in general impractical of attainment or leads to economically unfeasible types of equipment. We therefore preferred to correlate surface reaction rates with the nonindependent variable, temperature. This necessitates the use of stepwise calculations in evaluating performance data obtained under nonisothermal conditions or, conversely, when calculating performance under dissimilar nonisothermal conditions.



Figure 4. Surface Reaction Rates for Oxidation of Sulfur Dioxide on $\frac{1}{8} \times \frac{3}{8}$ Inch Platinum Catalysts

Figures 1, 3, and 4 show that all three component factors have an important effect on the over-all reaction rate for the oxidation of sulfur dioxide on platinum. However, their relative magnitude will vary greatly with specific conditions as to mass velocity, temperature, and partial pressure of

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sulfur trioxide. Thus for catalyst B, with a mass velocity of 600 pounds/(hour)(square foot), the height of a mass transfer unit would remain constant at 2.0 inches while the height of a catalytic unit would vary from 0.22 inch at 575° C. to 33 at 375°, and the sulfur trioxide poisoning factor would vary from 1.04 (for 0.01 atmosphere sulfur trioxide and 575° C.) to 5.3 (for 0.1 atmosphere and 375°). For the same catalyst but a mass velocity of 50 (comparable to small-scale test conditions) H_T would be constant at 0.95 inch, H_C would vary from 0.02 inch at 575° C. to 2.75 at 375°, while the poisoning factor would be the same as for the higher flow. At high temperatures, therefore, the over-all reaction rate is largely controlled by mass transfer rate, while at low temperatures surface reaction rate is most important when sulfur trioxide pressure is low, or sulfur trioxide poisoning is most important when sulfur trioxide pressure is high.

Table III shows that mass transfer rate is an important contributing factor (and in some cases largely controlling) for the over-all reaction rate for many industrial reactions. The small amount of published performance data on specific catalysts would scarcely confirm this conclusion. However, in general, the more active the catalyst, the greater the relative importance of mass transfer to over-all reaction rate, and few if any chemical companies publish performance data for their most active catalysts.

This work should find its major application in connection with the development of new products or processes, in that it should permit more accurate design of the initial pilotplant equipment and full-scale equipment. It also permits quantitative evaluation of the factors governing economic type or size of equipment from small-scale data, and thus development work can be concentrated on the specific type of equipment which is most feasible economically for the specific reaction. For existing processes the same methods can be used for determining the economic justification for changing type or size of existing converters. In general, the work to date indicates that laboratory-scale test data made under approximately isothermal conditions, when correctly interpreted, give a more accurate indication of plant-scale performance than can be obtained from semiworks-scale tests, where accurate control and measurement of conditions are more difficult.

The various factors affecting optimum type and size of reactor from the economic standpoint are so numerous, and the relative magnitude of these factors varies so widely for different reactions, that any generalizations attempted would be limited in applicability. However, the general type of equipment to be preferred for any specific reaction can often be predicted from general knowledge or experience. For example, reactions with unfavorable equilibrium constants require either recycling or several reactors in series with intermediate removal of product in order to secure satisfactory over-all yield; reactions with satisfactory equilibrium constants but high reaction heats require continuous or intermittent removal of heat or dilution with an excess of inerts or one reactant; while those with favorable equilibrium values and low reaction heats may be satisfactorily carried out in single-stage adiabatic systems.

Therefore, for some reactions the general type of equipment necessary can be determined by inspection. However, in many cases the choice is not obvious and must be based on economic comparisons. For example, in the oxidation of sulfur dioxide, it is evident that adiabatic converters, which are cheapest to construct, are least efficient from standpoint of catalyst performance; on the other hand, internal heat-exchange types designed for decreasing temperatures in direction of gas flow, or lowest catalyst temperatures at the exit end, will be most expensive but most efficient. Converters giving approximately isothermal conditions come somewhere between these two extremes. Thus qualitative knowledge is not sufficient to determine the respective over-all merits, and it is necessary to use quantitative data of the type shown. From them the optimum performance and specific size and cost can be accurately estimated for each general converter type, and the ultimate choice as to equipment can be based on over-all economic considerations.

The same general procedure applies to pilot-plant design as for full-scale plant design. The preferred type of full-scale equipment should be determined before the pilot plant is designed so that the pilot plant may more nearly resemble scaled-down plant equipment than scaled-up laboratory equipment.

The major purpose of this work was to develop means for reducing or eliminating trial-and-error development methods with actual equipment. It is believed that this can be accomplished through the quantitative methods developed here for predicting performance of a given type and size of reactor. It is not implied that pilot-plant scale equipment is to be outmoded, but rather that the function of the pilot plant may be confined to confirmation of reaction rates, confirmation of materials of construction, and evaluation of economic catalyst life under commercial operating conditions.

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NOMENCLATURE

- specific heat at constant pressure, P. c. u./(lb.)(°C.)
- D, =
- D_p =
 - = =
- diffusivity, sq. ft./hr. particle diameter, ft. superficial mass velocity, lb./(hr.)(sq. ft.) height of catalytic (or surface reaction) unit, H. C. U., in. H_{C} height of over-all reaction unit, H. R. U., in. height of transfer unit (gas film), H. T. U., in. thermal conductivity, P. c. u./(hr.)(sq. ft.)(° C./ft.) coefficient of catalyst poisoning, 1/atm.
- $H_R =$
- H_T = =
- k_1
 - = partial pressure of diffusing component, atm.
- terminal values of p $p_1, p_2 =$
- partial pressure of poisoning component, atm. $p_{\mathbf{p}}$ mean partial pressure driving force across gas film, atm. $\Delta p_m =$
- absolute temperature, °K. T
- temperature,
- $t_1, t_2 =$ terminal values of t
- mean temperature driving force across gas film, ° C. mole fraction of reacting gas in gas stream mole fraction of reacting gas at gas-solid interface $\Delta t_m =$
- U
- $\frac{y_i}{y^*}$ = log mean of (1 - y) and $(1 - y_i)$ = height of packed bed, in. = viscosity, lb./(hr.)(ft.) = density, lb./(cu. ft.)
- ==
- $-\frac{y}{Z}_{f}$
- μ
- ρ

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SOLID CATALYSTS and REACTION RATES General Principles

Based on the theory of activated adsorption, general rate equations are developed for chemical reactions catalyzed by solids. Consideration is given to the differences in equation forms resulting from control of the rate by different types of activated steps. Quantitative expressions are proposed for the effects of adsorption, catalyst activity, particle size, porosity, flow conditions, poisons, and diluents as well as temperature, pressure, and concentration. Experimental procedures for the evaluation of the constants of the equations are discussed. A general method is outlined for integration of rate equations in the design of commercial reactors.

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S A BASIS for the development of rate equations, it is postulated that when catalyzed by a solid, a liquidor gas-phase chemical reaction actually occurs on the surface of the catalyst and involves the reaction of molecules or atoms which are adsorbed by activation on the active centers of the surface. From this viewpoint the catalyst increases the rate of reaction through its ability to adsorb the reactants in such a form that the activation energy necessary for reaction is reduced far below its value in the uncatalyzed reaction. These principles are extensively discussed in the periodical literature and in theoretical treatises on catalytic rate phenomena (4, 7). The purpose of this paper is to develop from these principles equations which may be applied to the interpretation and extension of rate data and to point out experimental procedures best adapted to the complete evaluation of such equations from a minimum of data. Methods are also developed for the use of such equations in the design of industrial reactors.

In order that a reactant in the main fluid phase may be converted catalytically to a product in the main fluid phase, it is necessary that the reactant be transferred from its position in the fluid to the catalytic interface, be activatedly adsorbed on the surface, and undergo reaction to form the adsorbed product. The product must then be desorbed and transferred from the interface to a position in the fluid phase. The rate at which each of these steps occurs influences the distribution of concentrations in the system and plays a part in determining the over-all rate. Because of the differences in the mechanisms involved, it is convenient to classify these steps as follows when dealing with catalysts in the form of porous particles:

1. The mass transfer of reactants and products to and from the gross exterior surface of the catalyst particle and the main body of the fluid.

2. The diffusional and flow transfer of reactants and products in and out of the pore structure of the catalyst particle when reaction takes place at interior interfaces. The activated adsorption of reactants and activated desorption of products at the catalytic interface.
 The surface reaction of adsorbed reactants to form acti-

4. The surface reaction of adsorbed reactants to form activation-adsorbed products.

It is evident that the rates of these four types of operations are dependent on widely different factors in addition to the concentrations or concentration gradients involved. Type 1 is determined by the flow characteristics of the system, such as the mass velocity of the fluid stream, the size of the particles, and the diffusional characteristics of the fluid. Type 2 is determined by degree of porosity of the catalyst, the dimensions of the pores, the extent to which they are interconnected, the size of the particles, the diffusional characteristics of the system, and the rate at which the reaction occurs at the interface. Type 3 is determined by the character and extent of the catalytic surface, and by the specific activation energies required for the adsorption and desorption of each of the components of the fluid. Type 4 is determined by the nature and extent of the catalytic surface and by the activation energies required for the reaction on the surface.

The relative importance of these four operations in determining the over-all rate varies widely. Type 1 is important only when dealing with rapid reactions or where flow conditions are unfavorable. Since the rate of this operation is little affected by temperature, its relative importance tends to vary for a particular system; it is frequently negligible at low and highly important at high temperatures. Type 2 is frequently negligible for catalysts of low activity in small particles with large interconnected pores, and ceases to be a factor for nonporous catalysts having no internal surface. However, in the general case of an active catalyst in moderately large particles having large internal surfaces with restricted capillarity it may be of major importance.

Operations of types 3 and 4 are chemical phenomena generally involving relatively large activation energies and are therefore highly sensitive to temperature. The actual chemical transformations frequently proceed by several successive stages, each with its own characteristic rate. This is particularly true where several molecules are involved. Since chemical rates vary over wide ranges, it is improbable that the rates of any two steps of types 3 and 4 will be of equal order in any given system. For this reason in many cases it is permissible to consider only the slowest single step of types 3 and 4 and assume that equilibrium is maintained in all other steps of these types. Under such conditions the slowest activated step may be termed the "rate-controlling step", and the over-all rate is determined by consideration of it in combination with the physical steps of types 1 and 2.

ACTIVATED ADSORPTION

Activated adsorption, as differentiated from ordinary van der Waals adsorption and capillary condensation, is a highly specific reaction between the adsorbate and the surface, and possesses the characteristics of a reversible chemical reaction. Since this concept was introduced by Taylor in 1930, much attention has been devoted to it in the literature, recently summarized by Taylor (7), Emmett (7), and Glasstone, Laidler, and Eyring (4).

It may be assumed that a unit area of catalytic surface contains L' active centers on which activated adsorption can take place and that all of these centers behave similarly. Frequently the active centers are not uniform, and as adsorption proceeds, the remaining centers are progressively less active; the results are an increase in energy of activation and a decrease in heat of adsorption. In the present discussion the energy of activated adsorption will be assumed the same for all spots, or an average value will be assumed to represent the entire surface.

The rate of adsorption of a component, \mathbf{A} , from a fluid in contact with the surface is then proportional to its activity a_{At} in the fluid at the interface and to the concentration c'_i of vacant active centers per unit area of surface. A surface concentration of c'_A adsorbed \mathbf{A} molecules per unit area will result.

In the development of rate equations for application to industrial processes, it is convenient to express rates r in moles per unit time per unit mass of catalyst at uniform conditions. The total volume occupied by the catalyst particles, including interstices between particles, is related to the mass of the catalyst by the bulk density, ρ_b , as contrasted to the density of the individual pellets, ρ_p , and the true density of the catalytic solid ρ_c . Similarly, it is convenient to express surface concentrations in moles per unit mass of catalyst. Thus, if A is the catalytic area per unit mass,

- $L = AL'/N_0$ = maximum molal adsorption capacity per gram of catalyst with one molecule per active center
- $c_A = A c'_A / N_0$ = moles of adsorbed A per unit mass of catalyst $c_i = A c'_i / N_0$ = molal adsorption sites unoccupied per unit mass of catalyst

Expressing the rate of adsorption, r, in moles per unit time per unit mass of catalyst:

$$\cdot = k_A a_{Ai} c_l \tag{1}$$

Since activated adsorption is a reversible phenomenon, component \mathbf{A} is also desorbed from the surface at a rate proportional to the concentration of adsorbed molecules on the surface. Thus the rate of desorption is expressed by:

$$r = k'_A c_A \tag{2}$$

When adsorption equilibrium is reached, the rates of adsorption and desorption become equal. Equating (1) and (2),

$$k_A a_{Ai} c_l = k_A c_A$$

$$\Gamma \frac{c_A}{a_A e_l} = \frac{k_A}{k'_A} = K_A \tag{3}$$

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If component A is in admixture with other components B, R, S, and I which are also adsorbed on active centers of the same type, rate and equilibrium equations similar to 1, 2, and 3 may be written for each component. Then,

$$c_{I} = L - (c_{A} + c_{B} + c_{R} + c_{S} + c_{I}...)$$
 (4)

At equilibrium conditions each of the adsorbate concentration terms in Equation 4 may be replaced by an expression similar to that obtained by solving Equation 3 for c_A :

$$c_{l} = L - c_{l}(a_{Ai}K_{A} + a_{Bi}K_{B} + a_{Ri}K_{R} + a_{Si}K_{S} + a_{Ii}K_{Ii}...) \quad (5)$$

$$c_{l} = \frac{1}{(1 + a_{Ai}K_{A} + a_{Bi}K_{B} + a_{Ri}K_{R} + a_{Si}K_{S} + a_{Ii}K_{I}...)}$$
(6)

An expression for the equilibrium surface concentration of **A** in terms of interfacial fluid activities is obtained by combining Equations 3 and 6:

$$e_{A} = \frac{a_{A;}K_{A}L}{(1 + a_{A;}K_{A} + a_{B;}K_{B} + a_{R;}K_{R} + a_{S;}K_{S} + a_{I;}K_{I}...)}$$
(7)

Similar equations may be written for the equilibrium surface concentrations of the other components of the mixture.

SURFACE REACTIONS

Surface reactions may be assumed to take place either between an absorbed reactant molecule and a molecule in the fluid phase or between adsorbed molecules on adjacently situated active centers. With the latter mechanism a reaction proceeds at rates proportional to the concentrations of adjacently adsorbed reactants. Thus, if adsorbed molecule A reacts with adsorbed molecule B, the rate of the reaction is proportional to the number of pairs of adjacently adsorbed A and B molecules per unit area of surface. Similarly, if in a monomolecular reaction, adsorbed molecule A is reacting with a vacant active center to form a complex which subsequently breaks down to form two adsorbed product molecules, the rate of the reaction is proportional to the number per unit area of A molecules adsorbed adjacent to vacant active centers.

It is assumed that the active centers of the surface are distributed in a regular geometrical pattern determined by the lattice structure such that each individual center is surrounded by s other centers equidistant from it. Thus, if the pattern is rectangular with the active centers forming the corners of squares, s = 4. If the pattern is such that the centers form the corners of equilateral triangles, s = 6.

An average adsorbed molecule of **A** has adjacent to it $s\theta_i$ vacant centers, where θ_i is the fraction of the total centers which is vacant. Similarly, $s\theta_B$ molecules of **B** are adjacent to each adsorbed **A** molecule, where θ_B is the fraction of the total centers which is occupied by adsorbed **B** molecules. Then the surface concentration of **A** molecules and vacant active centers adjacent to each other becomes $1/2sc'_A\theta_i$, and the concentration of **A** molecules and **B** molecules adsorbed in adjacent positions becomes $1/2sc'_A\theta_B$. The factor 1/2 results from the fact that, in the summation represented by the product of the concentration and fractional adsorption terms, each pair of adjacent molecules and centers is counted twice.

Since θ_l equals c'_l/L' and θ_B equals c'_B/L' ,

$$c'_{Al} = \frac{8}{2L'} c'_{A}c'_{l} \tag{8}$$

$$c_{AB}' = \frac{8}{2L'} c_A c_B' \tag{9}$$

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where $c_{Al} =$ surface concentration of pairs of adsorbed A molecules and vacant centers in adjacent positions

 c'_{AB} = surface concentration of pairs of adsorbed **A** and **B** molecules in adjacent positions

Equations 8 and 9 may be similarly written with concentrations in moles per unit mass.

The rate of a monomolecular surface reaction involving interaction of an adsorbed A molecule and a vacant active center then becomes:

$$r = kc_{Al} = k \frac{s}{2L} c_A c_l \tag{10}$$

Similarly, for a surface reaction between adsorbed A and B molecules:

$$r = kc_{AB} = \frac{ks}{2L} c_A c_B \tag{11}$$

OVER-ALL SURFACE RATE EQUATIONS

On the basis of the theory outlined above, a general equation may be developed for the following surface reaction:

$$\mathbf{A} + \mathbf{B} \rightleftharpoons \mathbf{R}$$

In the general case the system will include inert components in the fluid phase represented by I....

The net rate of the forward reaction is the difference between the rates of the forward and reverse reactions which are represented by Equations 11 and 10, respectively. Thus,

$$r = \frac{s}{2L} \left(k c_A c_B - k' c_R c_l \right) \tag{12}$$

The surface concentrations may be expressed in terms of the activities in the fluid at the interface from Equations 1 and 2. Thus, the net rate of adsorption of component \mathbf{A} is equal to

the over-all rate of reaction. This net adsorption rate is the difference between the rates of adsorption and desorption, or

$$r = k_A a_{Ai} c_l - k'_A c_A = k'_A (K_A a_{Ai} c_l - c_A)$$

$$c_A = K_A a_{Ai} c_l - r/k_A$$
(13)

Similar expressions may be written for the other reactant and product adsorptions, and substituted in Equation 12:

$$r = \frac{s}{2L} \left[k \left(K_A c_{Ai} c_l - \frac{r}{k'_A} \right) \left(K_B a_{Bi} c_l - \frac{r}{k'_B} \right) - k' \left(K_R a_{Bi} c_l + \frac{r}{k'_R} \right) c_l \right]^{(14)}$$

The concentration of vacant centers also may be expressed in terms of fluid-phase activities at the interface:

$$c_{l} = L - (c_{A} + c_{B} + c_{R} + c_{I}...) + r\left(\frac{1}{k_{A}} + \frac{1}{k_{B}} - \frac{1}{k_{R}}\right) + r\left(\frac{1}{k_{A}} + \frac{1}{k_{B}} - \frac{1}{k_{R}}\right) = \frac{L + r\left(\frac{1}{k_{A}} + \frac{1}{k_{B}} - \frac{1}{k_{R}}\right)}{(1 + K_{A}a_{Ai} + K_{B}a_{Bi} + K_{R}a_{Ri} + K_{I}a_{Ii...})}$$
(15)

Combining Equations 15 and 14 yields a complete expression for the rate of reaction in terms only of activities in the fluid at the interface and the constants of the system. If the constants were all evaluated, the equation could be solved graphically for the rate at specified conditions. However, in general this complete equation involving the rates of all adsorption steps as well as the rate of the surface reaction is so cumbersome as to be of little value.

As previously mentioned, in many cases it is satisfactory to assume that the rate is controlled by a single slow step and that all other steps are so fast that equilibrium may be as-



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Bank of Catalytic Cracking Units to Produce Gasoline Stock

sumed. The slow step may be either the surface reaction or the adsorption of any one reactant or the desorption of any product. Simplified useful equations may be developed on this basis.

SIMPLIFIED EQUATIONS FOR MONOMOLECULAR SURFACE REACTIONS

Two mechanisms may be postulated for reversible surface reactions which are monomolecular in both directions, such as isomerization reactions. The reaction might proceed through an adsorbed molecule, acquiring sufficient energy to cause it to react and form a product molecule (all the time confined to a single active center). In the other mechanism an adsorbed molecule becomes sufficiently energized to form a complex with an adjacent active center, which then decomposes to form an adsorbed product molecule.

If the first mechanism is followed, the rate of reaction is proportional to the concentration of adsorbed reactant molecules:

$$r = kc_A \tag{16}$$

If the second mechanism is correct, the rate of reaction is proportional to the concentration of pairs of adsorbed molecules and adjacent vacant active centers. This rate is expressed by Equation 10.

Assuming that only a single activated step is rate controlling, simplified over-all equations may be derived according to either mechanism for the reaction:

 $A \rightleftharpoons R$

Surface Reaction Controlling. If the surface reaction is rate controlling, it is assumed that all adsorption steps are in equilibrium, and the surface concentration terms in Equations 10 and 16 may be replaced by Equations 6 and 7:

MECHANISM 1

$$r = \frac{kL}{1 + a_{Ai}K_A + a_{Ri}K_R + a_{Ii}K_I \dots} \left(a_{Ai}K_A - \frac{a_{Ri}K_R}{K'} \right)$$
(17)

where K' = surface equilibrium constant = k/k

At equilibrium the net rate becomes zero and

$$\frac{a_{Ri}}{a_{Ai}} = \frac{K_A}{K_R} K' = K \tag{18}$$

Substituting Equation 18 in 17,

$$r = \frac{kLK_A}{1 + a_{Ai}K_A + a_{Ri}K_R + a_{Ii}K_{I\dots}} \left(a_{Ai} - \frac{a_{Ri}}{K} \right)$$
(19)

MECHANISM 2

$$\tau = \frac{ksLK_A}{2(1 + a_{Ai}K_A + a_{Ri}K_R + a_{Ii}K_{I} \dots)^2} \left(a_{Ai} - \frac{a_{Ri}}{K}\right) \quad (20)$$

The essential difference between Equations 19 and 20 is the squared term in the denominator. According to these equations the initial rate, when $a_{Ri} = 0$, of a reaction following mechanism 1 is progressively increased by increased activity of the reactant in the fluid phase. If mechanism 2 is followed, the initial rate may increase with increased activity of **A** at low activities, reach a maximum corresponding to an optimum activity, and then diminish as the activity of **A** is further increased. Effects of this type have been experimentally observed in varying the pressure on monomolecular catalytic reactions.

Adsorption of Reactant Controlling. If the adsorption of the reactant is the rate-controlling step, it is assumed that the surface reaction and the other adsorption steps are in equilibrium. The rate is expressed by Equation 1:

$$r = k_A a_{Ai} c_l - k'_A c_A \tag{21}$$

In the application of Equation 21 all surface concentrations may be expressed in terms of the equilibrium of Equation 3, with the exception of c_A . This surface concentration must be arrived at from the condition of equilibrium in the surface reaction:

$$A = \frac{c_R K_A}{K K_R} = \frac{a_{Ri} c_l K_A}{K}$$
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$$c_{l} = L - (c_{A} + c_{B} + c_{I...}) = L - c_{l}(a_{Ri}K_{A}/K + a_{Ri}K_{R} + a_{Ii}K_{I...})$$

$$c_{l} = \frac{L}{1 + a_{Ri}K_{A}/K + a_{Ri}K_{R} + a_{Ii}K_{I}...}$$
 (23)

Combining Equations 22 and 23 with 21,

$$\tau = \frac{k_A L}{1 + a_{Ri} K_A / K + a_{Ri} K_R + a_{Ii} K_{I...}} \left(a_{Ai} - \frac{a_{Ri}}{K} \right) \quad (24)$$

Equation 24 is independent of the mechanism of the surface reaction.

Comparing the form of Equation 24 with 19 and 20, it will be noted that, when adsorption of the reactant is controlling, the initial rate (where $a_{Ri} = 0$) is directly proportional to the activity of the reactant; if the surface reaction is controlling, the initial rate will increase less than in proportion to increased activity of the reactant.

Another characteristic of reactions controlled by adsorption is evident by consideration of the net rate of the reverse reaction of Equation 24. If the over-all equilibrium constant K is small, the net rate of the reverse reaction becomes independent of the activity of **A**. This behavior is characteristic of reactions in which the rate is controlled by the rate of desorption of the product.

BIMOLECULAR-MONOMOLECULAR REACTION

The class of reaction which is bimolecular in one direction and monomolecular in the other may be represented by the equation:

$$\mathbf{A} + \mathbf{B} \leftrightarrows \mathbf{R}$$

If it is assumed that the reaction takes place between adjacently adsorbed molecules, it is necessary that the monomolecular reverse reaction follow the mechanism expressed by Equation 10. By the same procedures followed in the preceding section, the following rate equations are developed:

SURFACE REACTION CONTROLLING

$$= \frac{k_{s}LK_{A}K_{B}}{2(1 + a_{Ai}K_{A} + a_{Bi}K_{B} + a_{Ri}K_{R} + a_{Ii}K_{I}...)^{2}} \times \left(a_{Ai}a_{Bi} - \frac{a_{Ri}}{K}\right) \quad (25)$$

Adsorption of A Controlling

$$= \frac{k_A L}{1 + a_{Bi}K_B + \frac{a_{Ri}K_A}{a_{Bi}K} + a_{Ri}K_R + a_{Ii}K_I + \dots}} \times \left(a_{Ai} - \frac{a_{Ri}}{a_{Bi}K}\right) (26)$$

Adsorption of R Controlling

$$= \frac{k_R L K}{1 + a_{Ai} K_A + a_{Bi} K_B + a_{Ai} a_{Bi} K_R K + a_{Ii} K_I + \dots} \times \left(a_{Ai} a_{Bi} - \frac{a_{Ri}}{K}\right)$$
(27)

In Equation 25 the initial rate of the reaction is increased by increased activity of component **B**; in Equation 26 increasing the activity of **B** reduces the initial rate where the activity of **R** is zero. Thus, it is characteristic of a bimolecular reaction in which the rate is controlled by the adsorption of a re-

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actant that the initial rate is reduced by increased activity of the other reactant.

In Equation 25 the over-all equilibrium constant of the reaction appears in both the numerator and denominator of the multiplying fraction. Under conditions favorable for the forward reaction where K is large, the rate becomes independent of the activity of the product and may approach $k_R L/K_R$, independent of the activities of both reactants and product.

If the reaction on the surface occurs between an adsorbed **A** molecule and an unabsorbed **B** molecule in the fluid phase, the rate is proportional to the product of the surface concentration of **A** and the interfacial fluid activity of **B**. Equations similar to 25, 26, and 27 resu't, except that the adsorption equilibrium constant of **B** does not appear. If the surface reaction is controlling, the term s/2 does not appear, and the denominator group enters as the first power instead of the square.

REACTIONS BIMOLECULAR IN BOTH DIRECTIONS

Reactions of this type are represented by the following equation:

$$\mathbf{A} + \mathbf{B} \rightleftharpoons \mathbf{R} + \mathbf{S}$$

By extension of the methods demonstrated above, the following rate equations may be derived, assuming the surface reaction to take place between adjacently adsorbed molecules:

SURFACE REACTION CONTROLLING

$$r = \frac{k_{s}LK_{A}K_{B}}{2\left(1 + a_{Ai}K_{A} + a_{Bi}K_{B} + a_{Ri}K_{R} + a_{Si}K_{S} + a_{Ii}K_{I} + \ldots\right)^{2}} \times \left(a_{Ai}a_{Bi} - \frac{a_{Ri}a_{Si}}{K}\right) \quad (28)$$

ADSORPTION OF A CONTROLLING

$$r = \frac{\kappa_A L}{1 + \frac{a_{Ri} a_{Si} K_A}{a_{Bi} K} + a_{Bi} K_B + a_{Ri} K_R + a_{Si} K_S + a_I K_I + \dots} \times \left(a_{Ai} - \frac{a_{Ri} a_{Si}}{a_{Bi} K}\right)$$
(29)

ADSORPTION OF R CONTROLLING

$$\tau = \frac{k_R L K}{1 + a_{Ai} K_A + a_{Bi} K_B + \frac{a_{Ai} a_{Bi} K_R K}{a_{Si}} + a_{Si} K_S + a_{Ii} K_I + \dots} \times \left(\frac{a_{Ai} a_{Bi}}{a_{Si}} - \frac{a_{Ri}}{K}\right) \quad (30)^{-1}$$

Comparisons between Equations 28, 29, and 30 are similar to those between 25, 26, and 27. A reaction whose rate is controlled by the adsorption of a reagent is characterized by an adverse effect on initial rate resulting from an increase in activity of the other reactant. A reaction whose rate is controlled by adsorption of a product is characterized by the initial rate being independent of reactant activities under conditions of large over-all equilibrium constants and negligible reverse reaction.

REACTIONS INVOLVING MORE THAN TWO MOLECULES

The adsorption theory of catalysis does not preclude reactions involving the simultaneous interaction of several molecules, and no highly improbable mechanism such as the simultaneous collision of all molecules is involved. The rates of such reactions should be proportional to the concentration of groups of the required number of molecules adsorbed on adjacent active centers. Rate equations might be built up by extension of the procedures used in developing Equations 10 and 11 and the following relations.

It would be expected that the rates of such reactions would be low because of the low concentrations of properly adsorbed groups except in the case of one reactant molecule or atom A reacting with several other molecules or atoms B, all of the same species. In such a case high rates are obtained with a catalyst which strongly absorbs reactant B so that the majority of the surface is covered with adsorbed B molecules or atoms, and most of the A molecules or atoms which are adsorbed are surrounded by the requisite number of B units on adjacent centers.

ADSORPTION WITH DISSOCIATION

Although other mechanisms are possible, Glasstone, Laidler, and Eyring (4) suggest that, where a molecule is dissociated during adsorption, it is commonly first adsorbed on a dual adsorption site consisting of two adjacent active centers. This adsorbed molecule then decomposes, and the atoms jump to two vacant active centers. Thus, if A_2 is a molecule which dissociates into two A atoms and l_2 is a dual adsorption site,

$$\begin{array}{l} \mathbf{A}_2 + l_2 = \mathbf{A}_2 l_2 \\ \mathbf{A}_2 l_2 + 2 l = 2 \mathbf{A} l + l_2 \end{array}$$

It is believed that the first step is rate controlling and that equilibrium is maintained in the second. Then if r is expressed in moles of A_{2} ,

$$\tau = k_{A_2} a_{A_2} c_{l_2} - k'_{A_2} c_{A_3 l_2} \tag{31}$$

Since the second step maintains equilibrium,

$$c_{A_2 l_2} = \frac{c_{Al}^2 c_{l_2}}{K'_A c_l^2} \tag{32}$$

The concentration of dual adsorption sites is expressed by an equation similar to 8 and 9:

$$c_{l_1} = \frac{s}{2L} c_l^* \tag{33}$$

Combining 31, 32, and 33,

$$r = \frac{s}{2L} \left(k_{A1} a_{A1} c_i^2 - k'_{A1} \frac{c_{A1}^2}{K'_A} \right)$$
(34)

At equilibrium,

$$\frac{c_{Al}^2}{a_{A1}c_l^2} = \frac{k_{A1}K'_A}{k'_{A1}} = K_{A1}$$
(35)

$$c_A = c_{Al} = c_l \sqrt{a_{A_l} K_{A_l}} \tag{36}$$

If A_2 is adsorbed with dissociation from a mixture also containing components **B**, **R**, and **I**, an expression similar to Equation 7 may be developed for adsorption equilibrium conditions:

$$c_A = \frac{\sqrt{a_{A_2}K_{A_2}}L}{1 + \sqrt{a_{A_1}K_{A_2}} + a_BK_B + a_RK_R + a_IK_I + \dots}$$
(37)

Effect of Dissociation on Reaction Rate Equations. From Equation 37 it is evident that, where a molecule dissociates as it is adsorbed, the square root of the product of its activity times its adsorption equilibrium constant appears in all adsorption equilibrium expressions in place of the first power of this product. Thus, Equations 19, 20, 25, and 28, in which all adsorption steps are at equilibrium, may be modified to apply where a component is dissociated and one half molecule participates in the reaction merely by raising to the one half power the activity and adsorption equilibrium constant of the component which is dissociated wherever either appears in the equation.

The effects of dissociation where adsorption rate is controlling may be demonstrated by consideration of the effect on Equation 29 of the dissociation of **B** first and then **A**. If A is not dissociated the rate is expressed by Equations 1 and 2:

$$r = k \left(a_A c_l - \frac{c_A}{K_A} \right) \tag{38}$$

If **B** is dissociated and only $1/{}_{B}$ molecule enters into the reaction, an expression for c_{A} is derived from the equilibrium of the surface reaction:

$$c_{A} = \frac{c_{R}c_{S}}{c_{1/2B}K'} = \frac{c_{l}a_{Ri}K_{R}a_{Si}K_{s}}{\sqrt{a_{Bi}K_{B}}K'} = \frac{c_{l}a_{Ri}a_{Si}K_{A}}{\sqrt{a_{Bi}}K}$$
(39)

$$c_{i} = \frac{L}{1 + \frac{a_{Ri}a_{Si}K_{A}}{\sqrt{a_{Bi}K}} + \sqrt{a_{Bi}K_{B}} + a_{Ri}K_{R}a_{Si}K_{Si}a_{I}K_{I} + \dots}$$
(40)

Substituting Equations 39 and 40 in 38,

$$r = \frac{k_{A}L}{1 + \frac{a_{Ri}a_{Si}K_{A}}{\sqrt{a_{Bi}}K} + a_{Bi}K_{B} + a_{Ri}K_{R} + a_{Si}K_{Si} + a_{Ii}K_{I} + \dots} \left(a_{Ai} - \frac{a_{Ri}a_{Si}}{\sqrt{a_{Bi}}K}\right)$$
(41)

Comparing Equations 41 and 29, if the component whose adsorption rate is controlling is not dissociated, the rate equations are modified for application where a component is dissociated and only one half molecule enters the reaction, by raising the activity and adsorption equilibrium constant of the dissociated component to one half power wherever they appear in the equation.

If component A of Equation 29 is dissociated and only one half molecule enters the reaction, it is necessary to express the rate of reaction by Equation 34. From the equilibrium of the surface reaction,

$$c_{1/2A} = \frac{c_R c_S}{c_B K'} = \frac{c_l a_{Ri} a_{Si} \sqrt{K_A}}{a_{Bi} K}$$
(42)

$$c_{l} = \frac{1}{1 + \frac{a_{Ri}a_{Si}\sqrt{K_{A}}}{a_{Bi}K} + a_{Bi}K_{B} + a_{Ri}K_{R} + a_{Si}K_{S} + a_{Ii}K_{I} + \dots}$$
(43)

Substituting Equations 42 and 43 in 34,

$$r = \frac{sLk_A}{2\left(1 + \frac{a_{Ri}a_{Si}\sqrt{K_A}}{a_{Bi}K} + a_{Bi}K_B + a_{Ri}K_R + a_{Si}K_S + a_{Ii}K_I + \dots\right)^2} \times \left[a_A - \left(\frac{a_{Ri}a_{Si}}{a_{Bi}K}\right)^2\right]$$
(44)

This equation is quite different in form from Equation 29, and it is also dependent on the mechanism assumed for the adsorption and dissociation of A. By assuming a different mechanism (4), an equation can be obtained in which the initial rate is proportional to the one half power of the activity of A instead of the first power of Equation 44.

Effect of Temperature. Each of the equilibrium constants appearing in the rate equations is expressed as a function of temperature by the following equation applicable to both chemical and adsorption equilibria:

$$K = e^{\frac{-\Delta g^{\circ}}{RT}} = e^{\frac{-\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R}}$$
(45)

Although in general ΔG° varies greatly with temperature, it is frequently satisfactory to assume ΔH° and ΔS° to be independent of temperature at average values.

According to the Eyring theory of absolute reaction rates (4), any reaction may be considered as proceeding in two steps, first the formation of an activated complex and then the decomposition of this activated complex into the final products. It is assumed that the concentration or activity of the activated complex molecules maintains thermodynamic equilibrium with the activities of the reactants. The rate of reaction is, then, the rate of decomposition of the activated complex molecules into products which in turn is proportional to the concentration of activated complex molecules according to a relation which was derived (4) from the principles of statistical mechanics. Thus, for the surface phenomena under discussion in which rates are expressed in moles per unit mass,

$$k = \frac{\mathbf{k}T}{\mathbf{h}} K^{\ddagger} = \frac{\mathbf{k}T}{\mathbf{h}} e^{-\frac{\Delta H^{\ddagger}}{RT} + \frac{\Delta S^{\ddagger}}{R}}$$
(46)

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where k = reaction velocity constant, moles per unit time per unit mass of catalyst

 ΔH^{\ddagger} , ΔS^{\ddagger} = molal standard enthalpy and entropy changes accompanying formation of activated complex

Equation 46 applies both to activated adsorptions and surface reactions.

Since in all the rate equations the reaction velocity constant is multiplied by either L or sL/2, it is convenient to group the constants together:

$$L \text{ or } \frac{ksL}{2} = C'Te^{\frac{-\Delta H^{\ddagger}}{RT} + \frac{\Delta S^{\ddagger}}{R}}$$
(47)

where constant C' is a function of the nature and extent of the catalytic surface.

To extend the catalytic rate equations to all temperatures, the expressions of Equations 45 and 47 are substituted for all equilibrium and velocity constants, respectively. The resultant equations become cumbersome and it is preferable to consider the temperature variation of the individual constants separately with the aid of simplifying assumptions which will be discussed later.

POISONS

The term "poison" has been loosely used to denote any material which retards the rate of a catalytic reaction. Thus, the products of the reaction are sometimes referred to as poisons because increasing their concentration reduces the rate. However, it is believed more logical to eliminate all reactants and products from classification as poisons and reserve the term for other components which retard the reaction by reducing the number of active centers available for the reactants. Such poisons may be classified as either temporary or permanent.

From inspection of the rate equations it is evident that any inert component, I, which is adsorbed on the active centers promoting the reaction, serves as a poison; the extent of the retardation depends on the concentration of the inert and its adsorption equilibrium constant. If the adsorption of the inert is reversible with a moderate equilibrium constant, the poisoning effect quickly reaches a constant value which is temporary and is eliminated by removal of the component from the reactant fluid. Thus, the nitrogen in air might serve as a temporary poison in a catalytic oxidation. The effects of such inerts are included in the rate equations.

Another type of poisoning frequently encountered results from the permanent, substantially irreversible adsorption of components present in small quantities in the reactant fluid. The effect of this type of poisoning is progressively to reduce L', the number of active centers per unit area, as the catalyst continues in service. The frequently observed loss of activity of a catalyst in service may result from poisoning of this type, from structural changes affecting the area and L, or from physically coating the active surface with a solid or semisolid material either present in the reactants or formed by secondary reactions. In high-temperature organic reactions, catalysts

Right. Panel Board on One-Gallonper-Hour Catalytic Cracking Unit

Below. Commercial Catalytic CodimerGasolineUnitatRight; Thermal Unit at Left; Receiver House in the Center

Courtesy, Universal Oil Products Company

are frequently coated with high-molecular-weight compounds approaching pure carbon in composition. Such coatings may be looked upon as reducing the effective concentration of active centers L.

LIMITATIONS OF SURFACE RATE EQUATIONS

The rate equations derived above are ideal forms involving several assumptions which are not rigorous. The derivation implies that all active centers on the catalytic surface behave similarly while there is evidence that this is not the case. Frequently the energy of activation gradually increases as active centers are progressively occupied. It is well known that surface activity depends upon spatial arrangement of active centers which may not be uniform over the entire surface. Also it is assumed that each component is adsorbed independent of interaction between the adsorbed molecules of like or unlike species. Again there is evidence that such is not the case, and corrections were developed (4) for such interaction effects in simple systems. Interaction between adsorbed molecules tends to reduce the loss in enthalpy ordinarily accompanying activated adsorption.

Although numerous attempts have been made to establish more rigorous adsorption relations, there is little evidence that their use is justified in rate equations for complex reaction systems. It is believed more generally satisfactory to use the equations developed above and evaluate the constants from direct reaction rate measurements at conditions representing the ranges of interest of the variables. Constants directly evaluated from experimental data in this manner represent average apparent or effective values over the range considered, and the resultant equations cannot be expected to be entirely rigorous.

As in all theoretical rate calculations, the form of the relation is dependent on the mechanism. This situation is entirely different from that encountered in thermodynamic

equilibrium calculations in which the mechanism is immaterial. Furthermore, the correct mechanism cannot be selected by consideration of stoichiometric equations but must be determined by comparison of the trends of experimental data with the trends manifested in the various rate equations.

EFFECT OF CATALYST POROSITY

To obtain large catalytic areas and still have a catalyst form which may be easily handled and will produce good flow distribution, many industrially important catalysts are used in relatively large particles having a high degree of porosity. In such particles the gross external area of the particle is negligible in comparison to the large internal area of the pores, and the total catalytic area per unit mass is practically independent of particle size.

In the derivation of the basic rate equations it has been implied that the activities of the reactants and products in the fluid phase at the catalytic interface are constant throughout the catalyst mass. However, where finite reaction rates are produced, concentration gradients exist within a catalyst particle because of the diffusion and flow of reactants into the inner pores and the diffusion and flow of products out to the main fluid stream at the particle surface. It is evident that the reaction rate per unit surface may vary widely from a maximum at the exterior to a minimum at the center of the



Figure 1. Catalytic Effectiveness Factors

particle. In such a case the over-all rate of reaction is less than would result if the interfacial fluid concentrations were constant throughout at the exterior values.

The ratio of the actual reaction rate obtained per unit mass of catalyst to the rate which would result if no concentration gradients existed within the particles may be termed the "effectiveness factor" of the particle and designated by E_A .

It is evident that the effectiveness factor of a catalyst is a function of the particle size, the pore dimensions and the extent to which the pores are interconnected, the catalytic activity, and the diffusional characteristics of the reactants and products. The relations between these factors were developed by Thiele (9) for several simple cases which, with the aid of reasonable simplifying assumptions, could be handled mathematically. Rigorous equations of this type involving complex rate equations would be difficult to develop and cumbersome to use.

It is suggested that an empirical method for taking into account variations in effectiveness factor be based on the curve developed by Thiele for spherical particles catalyzing a first-order irreversible reaction. The effectiveness factor is expressed as a function of a modulus $D'_p \sqrt{(k/4r_p D_r)}$ by Figure 1, plotted from Thiele's equation (9). The effective diameter D'_p is defined as the diameter of a sphere having the same surface area per unit volume as the particle. Thus $D'_p = 6/A_p \rho_p$. The reaction velocity constant in the modulus was defined as the proportionality factor relating reaction. However, the same expression results if k is defined as the proportionality factor rate and the difference between the reactant concentration and the equilibrium value in a reversible reaction.

Application of Figure 1 to other than first-order reactions involves the assumption of a linear relation between reactant concentration and reaction rate. Although by no means generally rigorous, this is a fair approximation in many cases. Further complications are introduced where a change of volume occurs in the reaction, resulting in definite flow as well as diffusion in the pores. However, Thiele's studies indicate that these effects do not greatly affect the over-all form of the relation, and it is believed that Figure 1 is a useful approximation for general application, particularly if the constants of the modulus are empirically determined at conditions in the range of operating interest.

For use as an empirical approximation, the square root terms of Thiele's modulus may be combined into a single factor which, for a given catalyst and reaction system, may be assumed to be a function only of temperature, represented by the usual exponential relation. The modulus may then

be written as $D'_{p}a'e^{-T}$, and

$$Z_A = f(m) = f\left(\frac{D'_p a' e}{D'_p a' e}\right)$$
(48)

with the function represented by Figure 1.

All the preceding rate equations should include the effectiveness factor E_{\perp} as a multiplier on the right-hand side, when applied to porous catalysts for which the external area of the pellet is negligible as compared to the internal area.

MASS TRANSFER TO PARTICLE SURFACE

The rate equations in the preceding sections are all expressed in terms of activities in the fluid phase at the catalytic interface, which, through the incorporation of the effectiveness factor in the equation, are taken as the same as the activities in the fluid phase at the gross exterior surface of the catalyst particle. These interfacial activities are less or greater than the activities in the main stream of fluid surrounding the particles by the amounts of the activity gradients necessary to maintain diffusion. Thus, if a_A is the activity of **A** in the main fluid stream,

$$A_i = a_A - \Delta a_A \tag{49}$$

Similarly, for a product, S, diffusing away from the surface,

$$a_{Si} = a_S + \Delta a_S \tag{50}$$

The activity differences Δa_A and Δa_S are functions of the rates of diffusion and the flow characteristics of the system, which may be calculated with satisfactory accuracy for many gaseous systems and may be empirically evaluated by similar methods for other systems.

Chilton and Colburn (2), analyzing the mass transfer and diffusional problems in gas absorption and distillation, introduced the concept of the "transfer unit"; it may be defined as the length or height of contacting zone required to produce a unit concentration change in the main body of a fluid stream in the directions of flow as the result of a diffusional driving force producing the transfer of unit concentration difference. The contacting characteristics of a system are conveniently expressed in terms of the height of such a transfer unit, H. T. U., a factor having the dimension of length. Chilton and Colburn pointed out that for a given packing material the H. T. U. is a function of the modified Reynolds number, D_pG/μ , and the Schmidt number $\mu/\rho D_s$. In terms of this concept the drop in partial pressure of gaseous component A as a result of mass transfer may be represented by the following equations:

For equimolal counterdiffusion of the two components in a binary system,

$$\Delta p_A = \left(\frac{r}{A_p}\right) \frac{M_m \pi a}{G} (\text{H. T. U.})$$
(51)

For diffusion in a binary system resulting in removal of component A, the other component remaining,

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$$\Delta p_{A} = \left(\frac{r}{A_{p}}\right) \frac{M_{m} p_{qf}}{G} a(\text{H. T. U.})$$
(52)

where $p_{of A} = \log \text{mean of } (\pi - p_A) \text{ and } (\pi - p_{Ai})$

Rigorous treatment of the simultaneous diffusion of several components, particularly when volume changes are involved at the interface, leads to complicated and cumbersome expressions (6, 8). As an approximation it is suggested that concentration differences resulting from diffusion in complex reacting systems be evaluated by direct application of Equation 51 where no change in volume results from the reaction. For determination of the terms in the Schmidt group, each component is considered as diffusing in a binary system composed of itself and of all the other components of the mixture in the average proportions in which they appear in the diffusional film. On this basis diffusion coefficients may be evaluated from the correlation developed by Gilliland (5). It should be noted, however, that the algebraic sum of the partial pressure differences of all the components involved must equal zero.

Where a volume change accompanies the reaction, the effect of a mass flow in the direction of the volume decrease is superimposed on the diffusional effects that would be calculated from Equation 51. This effect reduces the concentration difference necessary to maintain diffusion in the direction of the volume decrease and increases the concentration differences for diffusion in the opposite direction.

As an approximation, arrived at by comparison of Equations 51 and 52, it is suggested that where a change of volume accompanies the reaction, Equation 51 be used as described above and the result corrected by the multiplying factor f_{D} :

$$f_D = \left(\frac{p_{gf}}{\pi}\right)^{-\Delta n} \tag{53}$$

where $\Delta n =$ change in number of moles per mole of reaction

Concentration differences of reactants are multiplied by f_D while those of products are divided by f_D .

Fortunately the corrections expressed by Equation 53 are generally not large, and errors involved cancel to some extent if a consistent method of calculating diffusional effects is adhered to both in the experimental evaluation of the constants in the rate equations and in their application. Greatly simplified procedures are possible in particular cases; in many cases where conversion rates are low and mass velocities high the concentration differences may be neglected entirely.

Gamson, Thodos, and Hougen (3) evaluated the dimensionless group a(H. T. U.) in terms of the Reynolds and Schmidt numbers for the flow of gases through granular solids, and established a unique relation independent of the size, density, porosity, and composition of the solid. This relation was found to hold for different shapes, provided the particle diameter D_p was based upon the diameter of a sphere having the same gross area as the particle. Thus for a cylinder,

$$D_p = \sqrt{D_c H + \frac{D_c^2}{2}}$$

where
$$D_c$$
 = diameter of cylindrical surface
 H = height of cylinder



Figure 2. Diffusional Mass Transfer in Gases Flowing through Granular Solids

	n	Mesh size		a, Sq. 1	Ft./Cu. Ft	
Inch 0.50 0.40 0.30 0.20 0.10 0.05 0.01	Foot 0.0417 0.0333 0.0250 0.0167 0.00833 0.00417 0.000833	opening (Tyler) 2.5 3.5 7-8 12-14 60	26% " 107 133 178 266 533 1066 5330	30% 101 126 168 252 504 1008 5040	40% 86.4 108 144 216 432 864 4320	50% 72 90 120 180 360 720 3600
		8				

• Per cent void space = 100 $(1 - \frac{b}{\rho_n})$.

The resulting correlation is plotted in Figure 2. From this diagram values of a(H. T. U.) are readily determined for any system of known dimensions and physical properties.

The effective diameter D_p is not the same as the D'_p used in the Thiele modulus. For example, for a right cylinder of height equal to diameter $D'_p = D_c$, whereas $D_p = \sqrt{3/2} D_c = \sqrt{3/2} D'_p$. The values of a(H. T. U.) obtained from Figure 2 are restricted to conditions where the total gross external area of the particle is available for heat and mass transfer.

EVALUATION OF RATE EQUATION CONSTANTS

Each of the equilibrium and velocity constants of the rate equations is a function of temperature expressed by Equation 45 or 46. The incorporation of 46 in a rate equation is simplified by combining all the multiplying constants into an over-all rate constant, C. Since the entropy changes may be taken as independent of temperature, they may also be included in the over-all constant. Thus for Equation 28,

$$C = \frac{\frac{\Delta S^{\ddagger} + \Delta S^{a}_{A} + \Delta S^{b}_{B}}{R}}{h2}$$

and this equation, including the effectiveness factor, may be written:

$$r = \frac{\frac{-\Delta H^{\circ}}{RT}}{\left(1 + a_{Ai}K_A + a_{Bi}K_B + a_{Ri}K_R + a_{Si}K_S + a_IK_I + \ldots\right)} \times \left(a_{Ai}a_{Bi} - \frac{a_{Ri}a_{Si}}{K}\right)$$
(54)

where $\Delta H^{\circ\prime} = \Delta H^{\ddagger} + \Delta H^{\circ}_A + \Delta H^{\circ}_B$

The over-all chemical equilibrium constant, K, can ordinarily be evaluated from thermodynamic data. Experimental evaluation is required for the effectiveness factor, the over-all rate constant, the over-all standard enthalpy change, and the various apparent adsorption equilibrium constants.

Constants in complex equations of this type are best determined by a differential reactor containing a bed of catalyst so shallow that relatively small changes of composition are obtained. Such apparatus should be designed to produce the smallest composition changes that permit accurate evaluation of the rate of reaction with the available analytical methods. Because of the exponential influence of temperature it is desirable that the differential bed be at as uniform temperature as possible, requiring a small diameter reactor with good heat transfer provisions in the walls of the container.

In a differential reactor the average activity of each component may be taken as the arithmetic average of the inlet and outlet values for small changes or, better, derived from the logarithmic mean of the differences between the activities at the inlet and the outlet for the reactants. The mean activity of a product, R, may be taken as a_{R_e} minus the log mean value of $(a_{R_e} - a_R)$ at the terminal conditions where a_{R_e} is the activity of R when the reaction proceeds to equilibrium. Then by calculating the diffusional activity differences from Equations 51 and 53, the interfacial activities are obtained, corresponding to the measured average rate. The use of log mean activities is merely an improved approximation, which in many cases is not satisfactory except where concentration changes are small.

Effectiveness Factor. This factor is evaluated as a function of temperature by differential rate measurements with two widely different particle sizes at each of two different temperatures, holding the activities constant at each temperature. At each temperature the ratio of the rates, $r_{1/T_2} = E_{A_1}/E_{A_2}$ corresponding to the particle sizes D_{p_1} and D_{p_2} , is determined. The Thiele modulus may be read directly from Figure 3, derived from Figure 1. From two values of the modulus at different temperatures the constants a' and b of Equation 48 may be calculated, completely evaluating E_A as a function of particle size and temperature.

Where this factor proves to be of considerable importance, it may be desirable to investigate a series of several particle sizes to verify the form of the relation expressed by Figure 1.

Adsorption Equilibrium Constants. These constants, appearing in the rate equations, might be independently determined by adsorption measurements on the individual components. Such measurements may prove to be a valuable adjunct to direct catalytic rate measurements but are open to question because of the interaction effects and variability of active centers previously mentioned. Until these relations are better understood, these constants in the rate equations are best determined in the specific reaction under study by making rate measurements over a wide range of concentrations.

To minimize tedious algebraic solutions of simultaneous equations, it is desirable in complex systems to determine the effective average value of the absorption equilibrium constant of each component by a constant-temperature series of three differential rate measurements in which the activity of that component is varied over a wide range while holding the ac-



Figure 3. Determination of Effectiveness Factor Modulus

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tivities of all other components constant. A convenient procedure is to make an initial run with the activity of each component at approximately the middle of the range of interest. Additional series of two runs each are then made in which the activity of each component is varied from a minimum value in one to a maximum in the other while holding the activities of all other components constant. This procedure may require two or more trials at some of the conditions with interpolation in order to obtain satisfactory constancy of the grouped activities but is not difficult with a flexible differential reactor apparatus which permits wide variation in feed rates and depths of catalyst bed.

Once the adsorption equilibrium constants are all evaluated, each single rate measurement permits calculation of the group $-\Delta \mu^{\circ'}$

Ce RT

Effect of Temperature. Each adsorption equilibrium constant is a function of temperature expressed by Equation 45. For a complete experimental evaluation of the standard enthalpy and entropy changes in adsorption under reaction conditions, it is necessary to repeat at a different temperature the evaluation of the individual average adsorption equilibrium constants as described above. Such measurements completely evaluate the equation with determination of C and $\Delta H^{\circ'}$.

Where such complete data are not available, the standard entropy change accompanying adsorption at one atmosphere may be roughly approximated by assuming a loss of 23.0 entropy units. Such an assumption is somewhat similar to Trouton's rule. Entropies of adsorption also may be derived from activated adsorption equilibrium measurements for the individual components on the catalyst. It is believed that entropy changes determined in this manner may be satisfactorily used in rate equations, whereas the corresponding enthalpy changes may be of little value.

If standard entropy changes in adsorption are approximated or measured, a single determination of the equilibrium constant permits evaluation of the standard enthalpy change and complete expression of the constant as a function of temperature. If these functions are evaluated for all components, C and $\Delta H^{\circ\prime}$ may be evaluated from any two rate measurements at different temperatures. In this procedure errors in the temperature coefficients of the equilibrium constants are adsorbed in calculation of $\Delta H^{\circ\prime}$ and may have relatively little effect on the over-all accuracy of the equation.

Activated Adsorption Measurements. It has been assumed that the correct mechanism and equation was established. This may be done by qualitative analysis of the effects of varying the activities of the components as previously discussed. However, it is believed that much useful information along these lines may be obtained by measurements of activated adsorption rates and equilibrium constants of the individual components on the catalyst, even though the resulting constants cannot be substituted directly into the final rate equation.

Adsorption measurements will serve to establish the relative magnitudes of the equilibrium constants, detect dissociation during adsorption, and permit calculation of the entropy change in adsorption. Further investigation is necessary before the full value can be established of such measurements in supplementing direct rate determinations.

INTEGRATION OF RATE EQUATIONS

The principal value of a rate equation is to determine the volume of reactor required to produce a specified catalytic conversion. The extent of conversion may be designated by x_A , the moles of reactant A converted per mole of total



Figure 4. Diagrammatic Variation of Activities (Temperature, Pressure, and Rate) in a Cooled Reactor for an Exothermic Reaction (r Defined by Equation 54)

feed. Through the stoichiometry of the reaction and the relations between mole fractions and activities, the activity of each component in a given reactor feed may be evaluated as a function of x_A and plotted in curves such as Figure 4. Where the reaction is at constant pressure and activities are equal to mole fractions or partial pressures, this calculation is simple and yields linear relations if no volume change occurs.

From the relationship between x_A and activities, the reaction rate r for an isothermal or adiabatic reaction at constant pressure may be calculated as a function of x_A by means of the rate equation. When working with an adiabatic reactor, temperature must be expressed as a function of conversion from the thermal properties of the system. Such a relation is plotted in Figure 4 for a more complex case; the upper rate curve is based on the assumption that interfacial activities are equal to the activities in the main stream of fluid.

If activity differences due to diffusion are important, a trial-and-error calculation is required in all except the most simple cases. The effect of these differences on the initial rate is determined by assuming an initial rate slightly lower than read from the upper curve of Figure 4 and calculating the diffusional concentration differences from Equations 51 and 53. Using these differences to obtain interfacial activities, a corrected initial rate is determined. If this rate is seriously different from that originally assumed, the calculation should be repeated. Where diffusion is a controlling factor, it may be necessary to repeat such trial-and-error calculations throughout the reactor as the integration proceeds. However, in many cases the complete rate curve based on true interfacial activities is satisfactorily established by the following approximation:

$$r = r' - (r'_{\bullet} - r_{0}) \frac{r' dr' / dx_{A}}{r'_{\bullet} dr'_{\bullet} / dx_{A}}$$
(55)

where r, r_0 = corrected rate, based on true interfacial activities corresponding to conversion x_{\perp} and initial con-

$$r', r'_{\bullet}$$
 = corresponding rates, neglecting diffusional effects

In this manner the lower rate curve of Figure 4 may be approximated from a single trial-and-error calculation at the initial conditions.

In an elementary cross section of catalyst bed, having a volume dV, a conversion dx_A is produced. From the definition of r,

$$Fdx_A = r\rho_B dV \tag{56}$$

Since r is a function of x_A expressed by the curve of Figure 4, this equation may be written:

$$dV = \frac{F}{\rho_B} \frac{dx_A}{f(x_A)}$$

or $V = \frac{F}{\rho_B} \int_0^{x_A} \frac{dx_A}{f(x_A)}$ (57)

It is common practice to express correlations of catalytic conversion data in terms of the space velocity, S,, which is defined as the volumes of feed, measured at standard conditions, per unit time per volume of catalyst. Equation 57 may be rewritten to express the relation between space velocity and conversion:

$$S_{\bullet} = \frac{FM_f}{V_{\rho_f}} = \frac{\rho_B M_f}{\rho_f \int_0^{x_A} \frac{dx_A}{f(x_A)}}$$
(58)

The integral is readily evaluated by plotting the reciprocal of the corrected rate curve of Figure 4 and measuring the area under it.

Although the above procedure is not particularly tedious, considerable simplification is possible under ideal conditions involving simple forms of rate equations or where $f(x_A)$ satisfactorily approximates a straight line.

In the general case, frequently encountered in process design problems, the integration of the rate equation may be complicated by significant pressure drop in the reactor and temperature conditions which are neither isothermal nor adiabatic, but correspond to some specified rate of heat transfer to or from the reactor. Under these conditions the curves of Figure 4 may be developed by a progressive series of trialand-error calculations starting from the reactor inlet. A further complication is introduced by the transverse temperature gradients resulting from the heating or cooling of the reactor walls and temperature differences between the fluid and the adjacent catalyst surfaces. The temperature curves of Figure 4 represent the effective average temperatures across any transverse section of the catalyst bed. Reactors are generally designed to keep these transverse temperature differences small. The temperature difference between the fluid and the catalyst is given by the following equation (3) if no volume change accompanies the reaction:

$$\Delta T = \frac{\Delta p_A \Delta H_A}{1.076\pi C p_m} \left(\frac{c_p \mu}{k_h}\right)^{*/*} \left(\frac{\rho D_*}{\mu}\right)^{*/*} \tag{59}$$

Where a volume change occurs, ΔT of Equation 59 is divided by f_D of Equation 53.

A small increment of conversion, x_{A1} is selected in which the average values of all variables may be assumed to be the

arithmetic mean of the terminal values. An average rate r'for this increment is assumed generally somewhat lower than the initial rate r'_0 calculated from the initial activities. Based on this assumed value of r', the diffusion corrections are calculated and the corresponding value of the corrected average rate, r_{av} , evaluated. The volume of catalyst corresponding to the selected increment of conversion is then $F \Delta x_{A1} / \rho_B r_{av}$. Using this volume, the pressure drop (1, 3) and temperature change in the increment are calculated from the flow and thermal characteristics of the system after approximation values of t_1 and p_1 have been established from which the activities corresponding to x_{A1} are calculated. Using the average activities and average temperature of the incremental section, a second value of the average rate is calculated. If this value differs greatly from that initially assumed, the calculation is repeated. After satisfactory values for the average and terminal conditions of the first increment are established, the procedure is repeated for a second increment, Δx_{A1} , and these stepwise calculations are continued until the desired conversion x_{At} is reached. The total reactor volume is then the sum of the incremental volumes, and the temperature and pressure variations throughout the reactor will have been evaluated. This procedure is not unduly tedious because with experience the various curves can be extrapolated from increment to increment with sufficient accuracy to make second approximations rarely necessary.

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CONCLUSIONS

The foregoing equations and methods have been developed in the belief that a fundamentally sound approach will greatly minimize the amount of pilot plant experimentation ordinarily employed in evaluating the effects of the operating variables of catalytic systems and arriving at optimum reactor designs. In ideal cases a few differential rate measurements will obviate the need of a pilot plant and permit immediate design of large-scale reactors for optimum results. However, it must be recognized that the theoretical treatment is idealized and in its simple form does not take into account secondary and side reactions which may accompany the main reaction. Furthermore, in the extension of equations to conditions far different from those at which the constants are evaluated, serious errors may result from the assumptions of constancy for such variable factors as enthalpy changes in activated adsorption. Careful consideration of such limitations with considerable discretion must be used in the application of these methods until the basic principles have been more thoroughly explored and tested.

ACKNOWLEDGMENT

The work reported here was made possible by the financial support of the Wisconsin Alumni Research Foundation and the sponsorship of the University Research Committee. The helpful suggestions and criticisms of J. O. Hirschfelder are gratefully acknowledged.

NOMENCLATURE

= gross external area of catalyst particles/unit of total catalyst volume including interstices a'= empirical constant

 a_A , a_B , etc. = activities of components **A**, **B**, etc., in main fluid phase

- a_{Ai} , a_{Bi} , etc. = activities of components **A**, **B**, etc., at catalytic interface A
 - = component A
- = total interfacial area/unit mass of catalyst A Ap = gross external area of catalyst particles/unit mass of catalyst
 - = empirical constant
- $b \\ \mathbf{B}$ = component **B**
- c_A , c_B = surface concentrations of adsorbed A and B, moles/unit mass of catalyst

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- $c_{B} = surface concentration of adsorbed A and B molecules/$ unit catalytic area = concentration of vacant adsorption sites, equivalent a mole/unit mass of catalyst = concentration of vacant adsorption sites/unit area $C_{p_m}^{c_i}$ C_{p_m} D'_p = over-all rate constants = mean molal heat capacity of fluid stream C' = effective average diameter of catalyst particles for Thiele modulus = $6/A_{p\rho_p}$ = effective average diameter of catalyst particles for D_p **Reynolds** number = coefficient of diffusion D, = effectiveness factor E_A = diffusional correction factor (Equation 53) f_D F G = reactor feed rate, moles/unit time = mass velocity/unit total cross section ΔG° = standard free-energy change = Planck constant h ΔH_{A} ΔH° = heat of reaction per mole of A ΔH° = standard enthalpy change $\Delta H^{\circ'}$ = over-all standard enthalpy change ΔH^{\ddagger} = standard enthalpy of activation = inert component = forward and reverse reaction velocity constants \bar{k}, \bar{k}' = Boltzmann constant k_A , k_A , etc. = adsorption and desorption velocity constants of component A thermal conductivity of fluid
 over-all fluid-phase reaction equilibrium constant
 surface reaction equilibrium constant k⊾ K K′ K_A , K_B , etc. = adsorption equilibrium constants of components A and B $L_{L'}$ = total molal adsorption sites/unit mass of catalyst = total active centers per unit area of surface = Thiele modulus m M_f N_o = average molecular weight of reactor feed = Avogadro number = partial pressure of component A in main fluid stream PA
 - partial pressure of component A at particle interface = PAi
 - = log mean of (πp_A) and (πp_A) Pos

- = reaction rate, moles/unit mass of catalyst/unit time
- = reaction rate, neglecting external diffusion gradients
- = average hydraulic radius of catalyst pores
- = gas law constant

 $r_{r'}$

r, R

R

8

S

- = component R = number of equidistant sites adjacent to each active
- center
- = component S
- 4.5° = standard entropy change
- = entropy of activation = space velocity ΔS^{\ddagger} S.
- = moles of A converted/mole of reactor feed XA.
- θ_A, θ_B = fraction of total sites occupied by adsorbed A and B molecules
- = fraction of total adsorption sites unoccupied θι
- viscosity μ = ρ
 - = density of fluid
- = bulk density of catalyst = true density of catalytic solid PR
- ρ
- = density of feed at standard conditions = density of catalyst particle PY
- Pp = total pressure

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(SOLID CATALYSTS and REACTION RATES)

Oxidation of Sulfur Dioxide

The data of Lewis and Ries on the oxidation of sulfur dioxide in a flow system over a platinized asbestos catalyst have been analyzed in accordance with the principles outlined in the preceding paper (page 529). The data are well represented by an equation based on the assumption that the rate controlling step is a surface reaction between activation-adsorbed sulfur dioxide and atomic oxygen. The experimental data show somewhat less deviation from this general equation than from the empirical expression proposed by Lewis and Ries.

TERIFICATION of the applicability of the rate equations developed in the preceding paper (page 529) is difficult because of the almost complete lack of suitable published data. Many catalytic rate measurements have been carried out in static systems in which large diffusional concentration differences were inevitable and controlled by conditions of natural convection which are not subject to generalized analysis. Of the data obtained in flow systems, many are unsuitable because of the large concentration changes accompanying high degrees of conversion intended to simulate the over-all results of commercial reactors.

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Ideally, data should be obtained under flow conditions in a differential reactor containing a bed of catalyst so shallow that relatively small changes of composition occur. Since temperature has an important influence on reaction rate, it is desirable that the differential section be kept at a temperature as uniform as possible. This requires a small-diameter reactor with good heat transfer at the walls.

One of the most thoroughly investigated catalytic reactions is the oxidation of sulfur dioxide over a platinum catalyst. The extensive experimental data obtained by Bodenstein and Fink (3), Knietsch (5), and Taylor and Lenher (7) cannot be used for the development of general rate equations because in each case a static system was employed in which diffusional concentration and temperature differences are difficult to predict. Each of these investigators and Benton (1) proposed empirical expressions representing their own data, but in all cases diffusional effects were neglected and the resultant equations are applicable only over limited ranges of conditions.

Lewis and Ries (6) carried out a series of flow experiments in reactors reasonably approximating differential operation. A platinized asbestos catalyst was used in glass U-tube reactors immersed in a molten metal bath. Although data necessary for the evaluation of diffusional concentration differences are not presented, it seems reasonable to neglect these effects be-



Figure 1. Effect of Sulfur Trioxide Concentration

cause of the conditions of forced flow and the finely divided form of the catalyst. With this assumption the data may be used for the evaluation of a complete rate equation.

FORM OF EQUATION

In the oxidation of sulfur dioxide the following four activated rate influencing steps are possible: activated adsorption of sulfur dioxide, activated adsorption of oxygen, surface reaction between sulfur dioxide and oxygen, and desorption of sulfur trioxide. Since one atom of oxygen must combine with one molecule of sulfur dioxide, it seems reasonable to assume that oxygen is atomically adsorbed on catalysts promoting this reaction. It will also be assumed that one of these four steps is rate controlling, and that the others are relatively so fast that they maintain equilibrium.

If the surface reaction is rate controlling and partial pressures are assumed to equal activities,

$$r = \frac{E_{A}CTe^{\frac{-\Delta H^{\circ}}{RT}}}{(1 + p_{SO_{2}}K_{SO_{2}} + \sqrt{p_{O_{2}}K_{O_{2}}} + p_{SO_{3}}K_{SO_{3}} + p_{N_{2}}K_{N_{2}})^{2}} \times \left(p_{SO_{2}}\sqrt{p_{O_{2}}} - \frac{p_{SO_{4}}}{K}\right)$$
(1)

Similarly, if the adsorption of sulfur dioxide is assumed to be the rate determining step, the following equation is obtained, corresponding to Equation 26 of the preceding paper (page 532):

$$r = \frac{E_{A}CTe^{\frac{-\Delta H^{\circ'}}{RT}}}{(1 + \sqrt{p_{0_{2}}K_{0_{2}}} + \frac{p_{80_{1}}K_{80_{3}}}{\sqrt{p_{0_{1}}K}} + p_{80_{4}}K_{80_{4}} + p_{N_{2}}K_{N_{2}})} \times \left(p_{80_{2}} - \frac{p_{80_{4}}}{\sqrt{p_{0_{2}}K}}\right)$$
(2)

A corresponding equation of similar form may also be written for the case of adsorption of oxygen as the rate determining step.

If the desorption of sulfur trioxide is assumed to be the controlling step, the following equation applies, corresponding to Equation 27 of the preceding paper:

$$r = \frac{E_A C T e^{\frac{-\Delta H^{\circ'}}{RT}}}{(1 + p_{SO_2} K_{SO_2} + \sqrt{p_{O_2} K_{O_2}} + p_{SO_2} \sqrt{p_{O_2}} K_{SO_2} K_{+ p_{N_2} K_{N_2}})} \times \left(p_{SO_2} \sqrt{p_{O_2}} - \frac{p_{SO_3}}{K} \right)$$
(3)

In this case the selection of the proper form of equation is possible by comparison of the qualitative trends of the experimental data with those called for by the various equations. Lewis and Ries found that the rate of initial oxidation was increased by increasing the partial pressure of either the sulfur dioxide or the oxygen. The effect of sulfur dioxide concentration is large and that of oxygen relatively small, but both were definitely indicated. This behavior rules out the selection of Equation 2 as the proper form. If the adsorption of sulfur dioxide were controlling, Equation 2 would require that the initial rate of oxidation be reduced by increased oxygen concentration. Similarly, if adsorption of oxygen were controlling, the rate of initial oxidation would be reduced by increased sulfur dioxide concentration.

The experimental data indicate a strong retardation of the oxidation rate with increased sulfur trioxide concentration over the entire range of conditions investigated. As a result of this behavior, Equation 3 is also eliminated because it requires that the rate of oxidation be independent of sulfur trioxide concentration under conditions where the over-all equilibrium constant K is large.

Thus, Equation 1 represents the most logical expression of the qualitative effects observed. A possible alternate form would result from the assumption that sulfur dioxide is not adsorbed by activation and that activation-adsorbed oxygen atoms react with sulfur dioxide molecules from the gas phase to form adsorbed sulfur trioxide molecules. The resulting equation differs from Equation 1, in that the denominator term appears as a first power instead of a square. Choice between these two forms can be made only as a result of quantitative examination of the data.

The effects of nitrogen and various other inerts were investigated by Bodenstein and Fink (β) with the conclusion that over a considerable range the rate of oxidation was unaffected by the concentration of nitrogen. Accordingly it may be assumed that the adsorption equilibrium constant of nitrogen is negligible, and all terms involving it are dropped from the rate equations.

GENERAL METHOD FOR EVALUATING CONSTANTS

Rearranging Equation 1 and letting
$$E_A CTe^{\frac{-\Delta H^{\circ\prime}}{RT}} = C_i$$
,

$$\sqrt{\frac{p_{SO_2}\sqrt{p_{O_2}} - \frac{p_{SO_1}}{K}}{r}} = \frac{1 + p_{SO_2}K_{SO_2} + \sqrt{p_{O_2}K_{O_2}} + p_{SO_1}K_{SO_2}}{\sqrt{C_i}}$$
(4)

If the over-all gas-phase equilibrium constant K is calculated from thermodynamic data, this equation contains four unknown constants at any given temperature. These constants are readily evaluated if data are available in which the rates are measured while the concentration of one component is varied, holding all others constant. For example, if only the sulfur dioxide concentration is varied, holding all other concentrations constant, Equation 4 may be written:

$$\sqrt{\frac{p_{80_2}\sqrt{p_{0_2}} - p_{80_1}/K}{r}} = p_{80_2}\frac{K_{80_2}}{\sqrt{C_1}} + \frac{d}{\sqrt{C_1}}$$
(5)

where

Thus a plot of
$$\sqrt{\frac{p_{so_2}\sqrt{p_{o_2}}-p_{so_i}/K}{r}}$$
 against p_{so_2} should re-

 $d = 1 + \sqrt{p_{01} K_{02}} + p_{S02} K_{S02}$

sult in a straight line, the slope of which is equal to $K_{SO2}/\sqrt{C_i}$. Similar plots against varying partial pressures of oxygen and sulfur trioxide at the same temperature, in each case holding

(6)



Courtesy, Universal Oil Products Company

Commercial Catalytic Polymer Gasoline Unit

all other partial pressures constant, yield values of $\sqrt{K_{02}}/\sqrt{C_t}$ and $K_{S02}/\sqrt{C_t}$, respectively. These values may be substituted in Equation 4, and the result is an expression containing only C_t as an unknown constant. C_t may then be found by applying this equation to each experimental observation at the temperature under consideration. An average value of C_t is thus obtained, and the deviation of the individual values from the average is a measure of the accuracy of the equation.

This same general method also may be used in cases where it is not feasible to hold all concentrations except one rigorously constant in a series of runs. This case is generally encountered because it is experimentally difficult to vary the concentration of one component over a wide range without some incidental variation of the others. However, if these incidental variations are not too large, the data may be used for accurate evaluation of constants by applying the graphical method described above in successive approximations. Thus, as a first approximation incidental variations from the desired constant compositions are neglected, and the constants of the equation completely evaluated on this basis. This first approximation equation is then used to correct the observed individual rate data to the basis of constant compositions. The corrected data are then used to determine a second set of corrected rate equation constants. Ordinarily, a second approximation will yield values of satisfactory accuracy if reasonable care is used in the experimental work to keep incidental variations at a minimum.

APPLICATION TO LEWIS AND RIES DATA

Lewis and Ries carried out three series of runs, each for the purpose of investigating the effects of varying the concentration of one of the active components of the system. In the A

series the concentration of sulfur dioxide in air was varied considerably in the low concentration range of less than one per cent by volume. Conversions were moderate, and as a result the average sulfur trioxide concentrations were small and the oxygen concentration substantially constant. Series of runs of this type were carried out at four different temperatures.

Since the concentration changes were relatively small, it was assumed in all runs that the average partial pressures were the logarithmic means of the inlet and outlet values for the oxygen and sulfur dioxide. The mean partial pressure of the sulfur trioxide was taken as the difference between the sum of the partial pressures of the entering sulfur dioxide plus sulfur trioxide and the mean partial pressure of the sulfur dioxide.

Data are not included on the weights or volumes of the catalyst in the various reactors used in the experiments, and it is thus impossible to calculate absolute values of r, the rate of oxidation per unit mass of catalyst. However, each series of runs was conducted in a single reactor with a constant weight of catalyst and at a constant rate of gas flow. Accordingly, the reaction rates, r, for each series are based upon this constant weight of catalyst and are taken as proportional to the difference between the mole percentages of sulfur dioxide in the entering and leaving mixtures, since volume changes are negligible with the small concentrations employed. These concentration changes are designated as r/w, where w is a proportionality factor depending on mass of catalyst per unit gas flow and is unknown in all cases and different for different series of runs.

Examination of these data confirm the conclusion of Lewis and Ries that the initial rate of oxidation is directly proportional to the first power of the partial pressure of sulfur dioxide, and a plot of Equation 5 yields a straight line of approximately zero slope. Accordingly it may be assumed that the term $p_{S02}K_{S02}$ in the denominator of the rate equation is negligible in comparison to the other additive terms.

In their B series of runs Lewis and Ries varied the amount of oxygen from 20 to 1 per cent in the mixture of sulfur dioxide, oxygen, and nitrogen entering the reactor. The sulfur dioxide content varied from 0.3 to 0.7 per cent. In the C series of runs sulfur trioxide was added to the mixture entering the reactor, and the percentages of both sulfur dioxide and sulfur trioxide varied over considerable ranges. The oxygen concentration also varied from approximately 17.5 to 21 per cent; this variation is not excessive; and the fluctuation of sulfur dioxide concentration does not interfere with evaluation of K_{02} and K_{803} since the A series showed the adsorption equilibrium constant of sulfur dioxide to be negligible. These two series could be used for the evaluation of K_{02} and K_{803} , respectively, by the general method outlined above except for the fact that the two series were carried out at different temperatures. This situation requires a special simultaneous solution.

For the C series with varying sulfur trioxide concentration, an equation similar to 5 may be written:

$$y_{1} = \sqrt{\frac{p_{30_{2}}\sqrt{p_{0_{1}}-p_{80_{2}}/K}}{r/w}} = \frac{p_{130_{1}}K_{130_{2}}}{\sqrt{C_{t_{1}}}} + \frac{1+\sqrt{p_{10_{2}}}\sqrt{K_{10_{2}}}}{\sqrt{C_{t_{1}}}}$$
(7)

This equation is of the form $y_1 = M_1x_1 + I_1$, where $x_1 = p_{803}$, and permits evaluation of slope M_1 and intercept I_1 from a plot of the data of the series. From Equation 7,

$$\frac{M_1}{I_1} = \frac{K_{180_1}}{1 + \sqrt{p_{10_2}}\sqrt{K_{10_2}}}$$

or $K_{180_2} = \frac{M_1}{I_1} \left(1 + \sqrt{p_{10_2}}\sqrt{K_{10_2}}\right)$ (8)

Similarly for the B series, with varying oxygen concentration,

$$y_{2} = \sqrt{\frac{p_{SO_{2}}\sqrt{p_{O_{2}}} - p_{SO_{2}}/K}{r/w}} = \frac{\sqrt{p_{tO_{2}}}\sqrt{K_{tO_{2}}}}{\sqrt{C_{t_{2}}}} + \frac{1 + p_{3SO_{2}}K_{3SO_{1}}}{\sqrt{C_{t_{2}}}}$$
(9)

If y_1 is plotted against $x_2 = \sqrt{p_{02}}$, and the slope M_2 and intercept I_2 are determined,

$$\frac{M_2}{I_2} = \frac{\sqrt{K_{202}}}{1 + p_{4801} K_{4801}}$$

or $\sqrt{K_{101}} = \frac{M_2}{I_2} (1 + p_{2801} K_{4801})$ (10)

Since the two series are at different temperatures, the adsorption equilibrium constants will differ. Let

$$\sqrt{\frac{K_{101}}{K_{102}}} = \alpha \text{ and } \frac{K_{1801}}{K_{2801}} = \beta$$
 (1)

Combining Equations 8, 10, and 11,

α

$$K_{1SO_2} = \frac{M_1}{I_1} \left[1 + \sqrt{p_{1O_2}} \alpha \frac{M_1}{I_2} \left(1 + \frac{p_{1SO_1} K_{1SO_1}}{\beta} \right) \right]$$
(12)

If α and β are known, Equation 12 may be solved directly for K_{180_2} . By substituting this value in Equations 10 and 11, K_{180_2} and K_{20_2} are also determined.

Expressions for α and β may be derived from Equation 45 of the preceding paper (page 534):

$$= e^{-\frac{\Delta H_{02}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$$
(13)

$$= e^{-\frac{\Delta H_{BO_2}^{\circ}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$$
(14)

The standard enthalpy change of activated adsorption of either component may be evaluated from Equation 45 if a single value of the adsorption equilibrium constant is known at any temperature and if ΔS° is taken as the rough approximation value of -23 recommended in the preceding paper. However, since no values of the equilibrium constants are known initially, Equations 12, 13, and 14 must be solved simultaneously by successive approximations. Approximate values of $\Delta H_{O_1}^{\circ}$ and $\Delta H_{SO_2}^{\circ}$ are first assumed, and the corresponding values of α and β calculated. First approximation values of K_{180} , and K_{20} , are then calculated from Equations 12, 11, and 10. Using these first values of the equilibrium constants, second approximations of ΔH_{so}° and ΔH_{o}° are calculated from Equation 45 of the preceding paper, and the entire calculation is repeated to obtain second approximations of the equilibrium constants.

The above procedure was carried out, first neglecting variations in oxygen concentration in the C series runs and variations in sulfur trioxide concentration in the B series. From the equation thus evaluated, the two series were corrected to constant oxygen and sulfur trioxide concentrations, respectively, and the constants of the equations re-evaluated. The corrected data for the final determinations of M_1/I_1 and M_2/I_2 from Equations 7 and 9 are plotted in Figures 1 and 2.

As pointed out by Lewis and Ries, the data of the C series of runs clearly indicate an over-all gas-phase reaction equilibrium constant of approximately 120, with partial pressures expressed in atmospheres, at 425° C. This value is approximately half that calculated from the recent thermodynamic data of Bichowsky and Rossini (2) and of Kelley (4). This discrepancy might be due to (a) differences between the true reactor temperatures and the bath temperatures measured by Lewis and Ries, (b) slight errors in the determination of small quantities of sulfur dioxide in the presence of large quantities of sulfur trioxide, or (c) possible errors in the thermodynamic data. It is felt that explanation b is the most plausible; accordingly the low values of K corresponding to the observed Lewis and Ries data were used in plotting Figures 1 and 2. However, it is recommended that the thermodynamic values be employed in application of the resultant rate equation.



Figure 2. Effect of Oxygen Concentration

Once the equilibrium constants of Equation 1 are completely evaluated as functions of temperature, it is possible to evaluate $\Delta H^{\circ\prime}$ from the data of the various A series runs at different temperatures by plotting values of $\ln \left(\frac{E_A C e^{-\Delta H^{\circ\prime}}}{RT} \right)$ against 1/T. The slope of this line is equal to $-\Delta H^{\circ\prime}/R$. Average values of the groups of runs at the four different temperatures of the A series are plotted in Figure 3.

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INDUSTRIAL REACTION RATE

The points of Figure 3 do not closely approximate a linear relation and might be interpreted as indicating an optimum temperature of maximum rate above which oxidation rate would be reduced by increased temperature. From theoretical considerations this appears to be an improbable situation, and it is believed that the deviations of the points from the indicated straight line of Figure 3 are not much greater than the probable experimental error of the measurements.

FINAL EQUATION

As a result of the above analysis, the following values are recommended for the terms of the equation:

$$\frac{r}{w} = \frac{\frac{-\Delta H^{\circ'}}{RT}}{(1 + \sqrt{p_{01}K_{01}} + p_{803}K_{803})^2} \left(p_{801}\sqrt{p_{01}} - \frac{p_{803}}{K}\right)$$
$$K_{803} = e^{\frac{21,400}{RT}} - \frac{23}{R}$$
$$K_{01} = e^{\frac{20,360}{RT}} - \frac{23}{R}$$
$$K = e^{\frac{22,980}{RT}} - \frac{19.95}{R}$$
$$\Delta H^{\circ'} = + 3690$$

Evaluation of the group of constants wE_AC will require specific rate data on any particular catalyst under consideration.



Figure 3. Effect of Temperature

The accuracy of this equation is indicated by the deviations of the individual points from the curves of Figures 1, 2, and

3 and by the values in Table I for E_ACTe^{-RT} , calculated for the constant-temperature runs of the C series in which maximum variations of sulfur dioxide and sulfur trioxide concentrations were investigated. For these calculations the over-all equilibrium constant of 120 indicated by Lewis and Ries data was used. For comparison the corresponding constants of the Lewis and Ries empirical equation are also tabulated.

Lewis and Ries did not apply their equation to runs 1 and 2 (Table I) which were close to equilibrium conditions. However, the present equation includes these points with fair agreement, in view of the uncertainty of the experimental values. The average deviation of the equation for all fourteen runs is 18.5 per cent, that for runs 3-14, inclusive, is 15.0 per cent as compared to Lewis and Ries deviation of 17.5 per cent for the same runs.

The data are not sufficiently accurate to demonstrate conclusively whether Equation 1 or the alternate form implying no adsorption of sulfur dioxide is correct. However, it appears that slightly better correlation is obtained with Equation 1 in which the denominator group is squared than when this group enters as the first power.

TABLE I. VALUES OF $E_A CT e^{\frac{-\Delta H^{\circ r}}{RT}}$ at Constant Temperat	
$-\Delta H^{\circ}$	URE
Run No. EACTe 7 7 Deviation Lewis and Ries 7 Deviation from Av. b Values from Av.	8
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	
Av. $19.14 \pm 18.5 0.173 \pm 17.5$	

The over-all standard enthalpy term $\Delta H^{\circ\prime}$ is small as compared to the usual so-called energies of activation calculated for reactions of this type. This results from the considerable effect of temperature on the adsorption equilibrium constants in the denominator of the equation, and also from the fact that $\Delta H^{\circ\prime}$ includes the sum of the standard enthalpies of adsorption of the reactants as well as the enthalpy of activation. The calculated value of $\Delta H^{\circ\prime}$ also would be increased by any corrections applied for the diffusional effects which were neglected entirely in this analysis.

CONCLUSIONS

The proposed form of equation represents the experimental data at least as accurately as the empirical equation developed by Lewis and Ries. It would be expected that the apparent adsorption equilibrium constants and the over-all temperature coefficient term $\Delta H^{\circ\prime}$ evaluated from these data should be roughly applicable to other platinum catalysts for this reaction. However, the $\Delta H^{\circ\prime}$ values are somewhat uncertain because of the limited range of temperatures investigated experimentally, the neglect of diffusional effects, and the values assumed for the standard entropy changes of activated adsorption.

ACKNOWLEDGMENT

The work reported here was made possible through financial support of the Wisconsin Alumni Research Foundation.

NOMENCLATURE

The symbols are those used in the preceding paper (page 540) with the following additions:

- = intercepts of plots to determine adsorption equilib- I_1, I_2 rium constants
- M_1, M_2 = slopes of plots to determine adsorption equilibrium constants
- partial pressure of SO₂, atmospheres p_{so_3} , etc. = proportionality factor relating concentration change to reaction rate r
- ratios of O2 and SO3 adsorption equilibrium con- $\alpha.\beta$ stants at temperatures T_1 and T_2 , respectively

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Cation-Exchange Water Softening Rates

Experiments on the softening of water by cation exchangers and the regeneration of the exchanger by a salt solution have been conducted on sufficiently thin beds to permit the differential rate equations to be established in terms of operating variables. The usual method of conducting tests on thick beds does not allow the differential equations to be obtained. The differential rate equations have been determined and solved for the variable boundary conditions encountered in the changing activity of the stationary bed.

Mathematical equations and charts are given for the performance of commercial beds of zeolite under conditions of variable thickness, rate of water flow, initial hardness of water, and initial base-exchange capacity, particle size, and activity of exchanger.

THE objectives of this investigation were to obtain experimentally the differential rate equations for the softening of water by a cation exchanger and by mathematical treatment to apply the results to the construction of performance charts for the operation of commercial beds of this exchanger.

A sodium aluminum silicate synthetic cation exchanger was selected, of the type extensively used for the rapid removal of calcium and magnesium ions from hard waters. This exchanger has a guaranteed base-exchange capacity of 15,000 grains of calcium carbonate per cubic foot, a density of 28 pounds per cubic foot, and a composition corresponding to John du Domaine, R. L. Swain, O. A. Hougen UNIVERSITY OF WISCONSIN, MADISON, WIS.

the formula $Na_2O.Al_2O_3.SSiO_2$. Tests were conducted on four grain sizes—on 14 mesh, 14 to 20 mesh, 20 to 28 mesh, and 25 to 35 mesh (Tyler screens). Inasmuch as the composition of both water and the exchanger vary from point to point in the bed as well as with time, it is desirable to conduct tests on thin beds to establish instantaneous and point values of reaction rates.

Usually tests are conducted on thick beds, but such tests give integrated results only and do not permit establishment of the differential rate equation or the mechanism of softening except through the highly uncertain procedure of assuming a rate equation which, upon integration, gives the experimental results. A bed thickness of 0.5 inch (1.27 cm.) was used which is sufficiently thin compared to commercial beds (averaging 3 feet or 91.4 cm. in thickness) to permit the use of the arithmetic mean values of entrance and exit stream conditions in establishing mean point values and thus to arrive directly at the desired differential rate equations. A synthetic hard water was made from distilled water and calcium chloride, producing a hardness equivalent to about 200 parts of calcium carbonate per million parts of water. Fresh zeolite from the same lot was used in all tests.

WATER SOFTENING EXPERIMENTS

The experimental apparatus is outlined in Figure 1:

The softener consisted of a glass cylinder, 5.5 inches (14 cm.)in internal diameter. In this cylinder a bed of exchanger of 100 grams (dry basis) about 0.5 inch thick was supported on a brass screen. A perforated plate was set above the bed at the top of the chamber to distribute the water supply and to avoid the disturbance which a single stream would create. The hard water

			Тав	le I. Calcu	LATED DATA	OF SOFTENIN	IG TEST 21			
1 Time, Elapsed y, Min. 0 25 50 75 100 125 150 125 150 175 200	2 Ca in H ₂ O Leaving Bed, u 0.74 1.40 2.00 2.58 3.06 3.42 3.64 3.78 3.54	$\begin{array}{c} 3^{a} \\ \hline Ca & Re-moved from \\ H_{2}O, u_{r} \\ 3.40 \\ 2.74 \\ 2.14 \\ 1.56 \\ 1.08 \\ 0.72 \\ 0.56 \\ 0.36 \\ 0.30 \end{array}$	4 b Av. Ca in H ₂ O, <i>ua</i> 2.44 2.77 3.36 3.60 3.78 3.89 3.99 3.99	5 c Ca Re- moved/Time Interval, <i>ura</i> 0 3.08 2.44 1.84 1.32 0.89 0.60 0.42 0.33	$\begin{array}{c} 6d \\ Accumulated Ca \\ Removed, \\ \Sigma ura \\ 0 \\ 3.08 \\ 5.52 \\ 7.36 \\ 8.68 \\ 9.57 \\ 10.17 \\ 10.59 \\ 10.92 \end{array}$	7 • Ca in Exchanger, $p \times 1000$ 0 0.578 1.038 1.384 1.630 1.800 1.912 1.992 2.054	81 Na Re- moved from Exchanger, vr × 10 ³ 0 0.578 1.038 1.384 1.630 1.800 1.912 1.992 2.054	$\frac{\partial p}{\partial y} = R_1 \times 10^4$ $\frac{2.380}{2.160}$ $\frac{2.634}{1.134}$ 0.814 0.552 0.380 0.272 0.228	$ \frac{1}{p} \frac{\partial p}{\partial y} \times 10^{4} $ $ \frac{1}{p} \frac{\partial p}{\partial y} \times 10^{4} $ $ 0.976 $ $ 0.780 $ $ 0.532 $ $ 0.337 $ $ 0.226 $ $ 0.326 $ $ 0.146 $ $ 0.098 $ $ 0.069 $ $ 0.057 $	116 $\sqrt{\frac{1}{p}} \frac{\partial p}{\partial y} \times 10$ 3.120 2.790 2.310 1.837 1.504 1.209 0.990 0.831 0.755

^a 2.07 minus column 2. ^b Average entering and leaving; for thin bed = (2.07 + column 2)/2. ^c Obtained from Figure 3 as average values in stated time intervals. ^d Cumulative summation of column 5. ^e Calcium adsorbed by zeolite = $(w \Delta y / 10^{\circ}) \times \text{col. 6} = (752 \times 25 \times \text{col. 6})/10^{\circ} = 0.000188 \times \text{col. 6}$. ^f Square root of column 10.

INDUSTRIAL REACTION RATE

was passed downward through the bed. Before a run was started, the air in the exchanger was removed by an upward flow of distilled water. The removal of air was essential to prevent channeling. The time for displacing the initial distilled water content by the hard water supply at the beginning of each run was estimated from the void content and rate of flow. The rate of water flow was measured and controlled by a rotameter accurate to within 0.5 per cent. Hard water was passed until the exchange material was nearly spent. The hardwas nearly spent. The hard-ness of all samples of water was measured by titration with standard potassium palmitate solution according to Suter's modification (2) of the method of Blacher, Grünberg, and Kissa (1).

Interpretation of Experimental Data. The mechanism of softening water consists in the removal of metallic ions from the water in exchange for sodium ions from the exchanger. The reverse reaction predominates in the



Figure 1. Flow Chart for Experiments on Water Softening

regeneration of the spent exchanger with salt solution.

The most plausible theory of the rate of cation exchange consistent with the experimental data is that the instantaneous rate of softening at constant temperature and constant flow rate is proportional to the product of the concentration of available sodium in the exchanger. All the sodium in the exchanger might not be replaceable. Since the bed of exchanger was stationary and the water was passed through in a steady continuous stream, it is simpler mathematically to base the reaction upon the rate of accumulation of calcium ions by the exchanger rather than upon its rate of removal from the water. Because the interchange of sodium and calcium is ionic, it is more convenient to express exchange rates on the basis of gram equivalents rather than upon gram mass.

In this discussion concentrations of sodium and calcium ions in the hard water are expressed as gram equivalents per million grams of water. The sodium and calcium contents of the exchanger are expressed in gram equivalents per gram of exchanger. The rate equations consistent with theory and tests are as follows:

FORWARD REACTION RATE,

$$R_1 = \frac{\partial p}{\partial y} = k_1 \ uv^2 \tag{1}$$

REVERSE REACTION RATE,

$$R_2 = -\frac{\partial p}{\partial y} = k_2 (\gamma q)^2 p \tag{2}$$

NET REACTION RATE.

$$R_{n} = R_{1} - R_{2} = k_{1} uv^{2} - k_{2} (\gamma q)^{2} p$$
⁽³⁾

Typical experimental data for run 21 are given in column 2 of Table I and in Figure 2. About twenty-five softening tests were conducted, but the detailed data are shown only for run 21, selected at random. The initial hardness of the water, u_0 , was 4.14 gram equivalents of calcium per million grams of water; the flow rate was 752 grams per minute, and the temperature 85° F. (29.4° C.). The times recorded in Table I were corrected for the times required to displace the distilled water initially present in the bed. This corrected time was estimated from the void content of the interchanger and the rate of flow of water.

Interpretation of Softening Data. The method of interpreting the experimental data on softening in terms of Equation 1 is illustrated in columns 3 to 11 of Table I. From Equation 1

From Equation 1,

$$\sqrt{\frac{\partial \overline{p}}{\partial y} \frac{1}{p}} = \sqrt{k_1 v} \tag{4}$$

Values of $\sqrt{\frac{\partial p}{\partial y} \frac{1}{p}}$ are plotted against v_r , the sodium removed from the exchanger, in Figure 5. In general, for all runs a straight line most consistently fits the results, even though in Figure 5 a slight curvature better fits the data for this particular run. The intersection of this straight line with the zero ordinate line corresponds to a condition of zero softening rate and indicates that all the available sodium has been removed; hence $v_0 = v_r = 0.00262$ (Figure 5). The slope of this line gives the value of $\sqrt{k_1}$, and the intercept with zero abscissa line gives the initial value of $\sqrt{\frac{\partial p}{\partial y} \frac{1}{p}}$. Thus for run 21, Figure 5: $\sqrt{k_1} = 1.43$, $k_1 = 2.04$, and $v_0 = 0.00262$. In this manner the values of k_1 were obtained for all softening runs covering different mesh sizes and different rates of water flow.

The effects of particle size and rates of water flow are listed in Tables II and III.

Reaction Velocity Constant of Reverse Reaction. To obtain values of the reaction velocity constant k_2 of the reverse reaction, the spent exchanger was regenerated after each softening run by passing salt solution through the bed. The brine samples were analyzed for calcium content and the

TABLE II. EFFECT OF MESH SIZE IN SOFTENING TESTS (100 grams exchanger, water flow rate 752 grams per minute, temperature

B		85° F.)		
Run No.	Mesh Size ^a	Initial Na in Exchanger, 70	Final Ca in Exchanger, P/	Value k_1
41 43	20–28	0.00232 0.00224	0.001864 0.001864	2.24 2.34 Av. 2.29
19 2 21	14-20	0.00196 0.00280 0.00262	0.001508 0.002058 0.002054	2.08 1.86 2.04 Av. 1.99
27	On 14	0.00228	0.001716	1.62
	1 17	Count and a inter (00	25)	tia an average

^a Runs made on the finest mesh size (28-35) were erratic; an average *k* value of 2.86 seemed reasonable.

TABLE III.	EFFECT OF	FLOW RATE ON SOFTENING TESTS	
(14-	20 mesh size,	100 grams exchanger, 85° F.)	

Run No.	Flow Rate, G./Min.	Initial Na in Exchanger, 70	Ca in Exchanger, Pf	Value k_1
4 19 2 21	409 752 745 752	0.00196 0.00196 0.00280 0.00262	0.001574 0.001508 0.002058 0.002054	1.12 2.08 1.86 2.04 Av. 1.99
$ \begin{array}{r} 45 \\ 8 + 39 \\ 29 + 47 \end{array} $	1104 1210 1399	0.00237 0.00264 0.00214	$\begin{array}{c} 0,00186\\ 0,001902\\ 0,00154 \end{array}$	1.77 2.07 2.27

results interpreted in a manner similar to the softening tests. The individual test runs were erratic, but from about twenty tests an average value of 241,000 was obtained for the equilibrium constant:

$$K = k_1/k_2 = 241,000$$

Summary of Results. The net rate equation combining both softening and regeneration can be expressed by Equation 3:

$$R_n = k_1 uv^2 - k_2 p(\gamma q)^2$$

The values of the forward reaction velocity constant k for different particle sizes of zeolite are as follows:

Mesh Size	k1
28-35	2.86 (est.)
14-20 On 14	1.91

As might be expected, the reaction velocity constants based upon unit weight of exchanger increase with increased fineness of particle.

Equilibrium constant K of the reaction was found to be about 241,000. The reverse reaction velocity constant k_2 can thus be obtained from the equilibrium constant.

The effect of water flow rate was inappreciable for either forward or reverse reaction within the range of reproducible results. The variable results obtained are perhaps due to channeling which masked any effect of flow rate.

RATE EQUATION FOR SOFTENING PROCESS

In this development the rate Equation 1 for the forward reaction is integrated. A similar development can be made for the reverse reaction, Equation 2. The net rate Equation 3 was not integrated. The following mathematical development is limited to conditions where the reverse reaction is relatively small. When water is softened by flowing steadily through a bed of cation exchanger, the compositions of both water and exchanger vary progressively with both time and location in the bed. Thus, the variables u, v, p, and q are functions of x and y, and may be denoted more precisely as u(x, y), etc., with initial values $u_0 = u(0, 0)$, etc.

Consider an element of the bed, at depth x, dx cm. thick and 1 sq. cm. in cross section (normal to the direction of water flow). At time y, the concentration of calcium ions in the water entering is u; that in water leaving is $u + (\partial u/\partial x)dx$. In time dy, then, the number of gram equivalents of calcium adsorbed by the exchanger is

$$\frac{1}{10^{\delta}} (G \, dy) \, \left(- \frac{\partial u}{\partial x} \, dx \right) \, = \, (\rho \, dx) \, \left(\frac{\partial p}{\partial y} \, dy \right)$$

and from this equation of material balance Equation 5 is obtained:

$$\frac{\partial u}{\partial x} = -\frac{10^6 \rho}{G} \frac{\partial p}{\partial y} \tag{5}$$

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(12)



Each gram equivalent of calcium ion added to the interchanger is replaced by one gram equivalent of sodium in the zeolite, $\Delta p = -\Delta v$, so that

$$p - p_0 = v_0 - v$$
 (6)

This gives $\partial p/\partial y = -(\partial v/\partial y)$ so that substitution in Equations 1 and 5 results in the system

$$\frac{\partial u}{\partial x} = auv^2$$

$$\frac{\partial v}{\partial y} = buv^2$$

$$(7)$$

where
$$a = -\frac{10^6 \rho k_1}{G}$$
 and $b = -k_1$ (8)

From the nature of the process, system 7 is subject to the following boundary conditions:

$$\begin{array}{l} (0, y) = u_0; & \text{i. e., at } x = 0, \, u = u_0 \text{ for all } y \text{ values} \\ x, 0) = v_0; & \text{i. e., at } y = 0, \, v = v_0 \text{ for all } x \text{ values} \end{array} \right\}$$
(9)

SOLUTION OF DIFFERENTIAL EQUATIONS

The solution of system 7 subject to boundary conditions 9 was accomplished by special devices, designed to fit the particular problem at hand.

Solving each equation of system 7 for uv^2 and equating the right-hand members,

$$\frac{\partial(bu)}{\partial x} = \frac{\partial(av)}{\partial y}$$

This means that av dx + bu dy is an exact differential, so that a function f(x, y) exists such that

$$u = \frac{1}{b} \frac{\partial f}{\partial y} \text{ and } v = \frac{1}{a} \frac{\partial f}{\partial x}$$
 (10)

df

dr.

$$\frac{\partial u}{\partial x} = \frac{1}{b} \frac{\partial^2 f}{\partial x \, \partial y} = auv^2 = a \left(\frac{1}{b} \frac{\partial f}{\partial y}\right) \left(\frac{1}{a} \frac{\partial f}{\partial x}\right)^2$$
$$a \frac{\partial^2 f}{\partial x \partial y} = \frac{\partial f}{\partial y} \left(\frac{\partial f}{\partial x}\right)^2 \tag{11}$$

Integration gives:

or

where $\Phi(x)$ = arbitrary function of x

By Equations 9 and 10, $f(x, 0) = av_0x + C$; substitution of the latter in Equation 12 gives

 $f = -\frac{a}{\frac{\partial f}{\partial x}} + \Phi(x)$

 $\frac{\partial f}{\partial x} = \frac{a}{\Phi(x) - f}$

$$\Phi(x) = av_0 x + C - \frac{1}{v_0}$$

$$\frac{\partial f}{\partial x} = \frac{a}{av_0 x + \left(C - \frac{1}{v_0}\right) - f}$$
(13)

where C = arbitrary constant

The ordinary differential equation corresponding to Equation 13 is:

$$\frac{dF}{dx} = \frac{a}{av_0 x + \left(C - \frac{1}{v_0}\right) - F}$$
(14)

The variables can be separated by letting $G = F - av_0 x - C + (1/v_0)$, and the solution is:

$$F v_0 - \ln\left(F - av_0 x - C + \frac{2}{v_0}\right) = a \text{ constant}$$

It follows that the general solution of Equation 13 is:

$$v_0 - \ln\left(f - av_0 x - C + \frac{2}{v_0}\right) = \psi(y)$$
 (15)

where $\psi(y)$ = arbitrary function of y

By Equations 9 and 10, $f(0, y) = bu_0 y + j$, so that

$$\psi(y) = bu_0 v_0 y - \ln\left(b_0 y + j - C + \frac{2}{v_0}\right) + j v_0 \qquad (16)$$

From Equations 10 and 13, $f = av_0x + C - 1/v_0 + 1/v$. This value is substituted into Equation 15 and the boundary condition $v(x, 0) = v_0$ is made use of to reduce the number of arbitrary constants. This done, Equations 15 and 16 give:

$$\ln\left(\frac{1}{v_0} - \frac{1}{v}\right) = \ln b u_0 y + a v_0^2 x - b_0 v_0 y - \frac{v_0}{v} + k$$
(17)

where $k = cv_0 - jv_0 - 1$

If Equation 17 is differentiated with respect to y, and $\partial v/\partial y$ replaced by buv^2 (from system 7),

$$\frac{u}{u_0} = \left(1 - \frac{v}{v_0}\right) \left(1 - \frac{1}{bu_0 v_0 y}\right) \tag{18}$$

Now $u(0, y) = u_0$, so that v(0, y) can be determined from Equation 18 and this result in conjunction with 17 gives k = 1.

The final solution of system 7 may now be written in the following form:

$$\begin{pmatrix} v_0 \\ v \end{pmatrix} = -b_0 v_0 y e \begin{pmatrix} v_0 \\ v \end{pmatrix} = \begin{pmatrix} v_0 \\ v \end{pmatrix} \begin{pmatrix} v_0 \\ v$$

It has been verified that Solution 19 satisfies system 7 and boundary conditions 9. Furthermore, it follows from the method that the solution is unique.

 $\frac{z_{j}}{\partial y}$

2(

Softening of Water by Ion Exchangers Is Commercially Important in Many Installations Such as Municipal Water-Treating Plants, Laundries and Dye Works, Paper and Textile Mills, Oil Refineries, Breweries, Hospitals, and Industrial Chemical Works. 13

Photographs were supplied through courtesy of American Water Softener Company, Cochrane Corporation, Elgin Softener Corporation, Graver Tank & Mfg. Co., Inc., Infilco, Inc., and National Aluminate Corporation

ARRANGEMENT OF SOLUTION

For simplification, the following new dimensionless variables are introduced:

$$r = av_0^2 x = \frac{10^4 \rho k_1 v_0^2}{G} x$$

$$s = bu_0 v_0 y = k_1 u_0 v_0 y$$

$$z = \frac{v_0}{v} - 1$$
(20)

From Equations 19 and 20,

$$\ln z + z = \ln s + s - r \tag{21}$$

$$\frac{v}{v_0} = \frac{1}{1+z}$$
 (22)

$$\frac{u}{u_0} = \frac{1+1/s}{1+1/z} \tag{23}$$

In any specific problem r and s may be calculated from the given data. Equation 21 may be quickly solved for z by a table of natural logarithms or by a graph of the function $(\ln z + z)$.

Of special interest is the behavior of u/u_0 as y approaches zero $(y \rightarrow 0)$, x being fixed (for the value of u at y = 0 cannot be determined by direct substitution in Equations 19 or 23). Then r is constant and $s \rightarrow 0$, so that by Equation 21, $z \rightarrow 0$. From Equation 17,

$$\lim_{y \to 0} (\ln \frac{z}{s}) = \lim_{y \to 0} (s - z - r) = -r$$

Hence from Equation 23,

$$\lim_{y \to 0} \left(\frac{u}{u_0}\right) = \lim_{y \to 0} \left(\frac{z}{s}\right) \left(\frac{1+s}{1+z}\right) = \lim_{y \to 0} \left(\frac{z}{s}\right) = e^{-r} \quad (24)$$

It should also be noted that for fixed x, u and v are increasing and decreasing functions of y, respectively; for fixed y, u and v are decreasing and increasing functions of x, respectively. Also $u(x, \infty) = u_0$; $v(x, \infty) = 0$; $u(\infty, y) = 0$; $v(\infty, y) = v_0$. Also, u and v are single-valued functions of (positive) x and y. These properties of the solution are as expected.

Comparison with experiment is gratifying. Thus, the data of softening run 21 give $u_0 = 4.14$, $v_0 = 0.00262$, GA = 752, $\rho Ax = 100$, and $k_1 = 2.04$, where A is the surface area of the zeolite bed. These give r = 1.86 and s = 0.0221y. Comparison of observed results (Column 2, Table I) and calculated results follows (see also Figure 2).

y	u observed	u calcd.	¥	w observed	u calcd.
0	0.74	0.64	125	3,42	3.40
25	1.40	1.34	150	3.64	3.58
50	2.00	2.10	175	3.78	3.70
75	2.58	2.70	200	3.84	3.82
00	3.06	3.10			

Other softening runs yield no worse and some give better comparisons.

In softening hard water initially free of sodium, the reverse reaction can for practical purposes be neglected. The relative magnitude of the reverse reaction can now be estimated. The forward and reverse rates are $R_1 = k_1 uv^{\sharp}$ and



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 $R_2 = k_2 p(\gamma q)^2$, respectively. Using the relation $p = r_0 - w$ and $q = u_0 - u$ with Equations 20, 21, and 23, it can be shown that

$$\frac{R_{2}}{R_{1}} = \frac{k_{2} u_{0}}{k_{1} v_{0}} \frac{\left(1 - \frac{z}{s}\right)^{z}}{\left(1 + \frac{1}{s}\right)^{z}} \le \frac{k_{2} u_{0}}{k_{1} v_{0}}$$
(25)

In the typical commercial case illustrated in the following pages, $R_2/R_1 \leq 1.12$ per cent. This maximum value of the reverse rate is attained only at the exit face of the bed when the bed is nearly exhausted. This means that, when hard water which is sodium-free upon entrance flows through a bed of exchanger, the exchanger becomes completely spent, the reverse rate is nearly negligible and under such circumstances of steady flow and initial zero sodium content, chemical equilibrium is not attained.

APPLICATION OF EQUATIONS

The performance of a cation exchanger in softening water can now be calculated for conditions where the rate of the reverse reaction rate is relatively slight. For example, it is desired to know the residual hardness of water after steady operation of a softener for 16 hours, with water flowing through the bed at a rate of 4 gallons per square foot per minute, with a bed 3 feet thick. The initial hardness of the water corresponds to 300 parts calcium carbonate per million parts water. This represents 6.00 pound equivalents of calcium ion per million pounds of water. The initial replaceable sodium content of the exchanger is equivalent to 25,000 grains calcium carbonate per cubic foot. The density of the mineral is 28 pounds per cubic foot and grain size, 14 to 20 mesh. Under these conditions:

$$\rho = 28 \text{ lb./cu. ft.}$$

 $x = 3.0 \text{ ft.}$

 $k_{1} = 1.91 \text{ per min.}$



 $G = 4 \times 8.33 = 33.32$ lb./sq. ft./min.

$$v_{\bullet} = \left(\frac{25,000}{100}\right) \left(\frac{2}{7000}\right) \left(\frac{1}{28}\right) = 0.00255 \text{ lb. equivalent Na/lb.}$$
exchanger

 $u_{\pm} = 6.00$ lb. equivalent Ca ion/million lb. way $y = 16 \times 60 = 960$ min.

From Equation 20,

$$r = \frac{10^{6} \rho k_{1} v_{0}^{2} x}{G} = \frac{(10)^{6} (28) (1.91) (0.00255)^{2} (3)}{33.32} = 31.3$$

$$s = k_{1} u_{0} v_{0} y = (1.91) (6.0) (0.00255) (960) = 28.1$$

From Equation 21,

$$\ln z + z = \ln s + s - r = \ln 28.1 + 28.1 - 31.3 = -0.136$$

hence $z = 0.521$

From Equation 23,

$$\frac{4}{4_0} = \frac{1 + \frac{1}{s}}{1 + \frac{1}{s}} = \frac{1.0356}{2.919} = 0.355$$

Hence u = 0.355 (6.00) = 2.12 pound equivalents of calcium ion in water leaving softener at end of 16 hours.

In this manner, values of residual hardness can be calculated for any time, thickness of bed, rate of water flow, cationexchange capacity of exchanger, and reaction velocity constant.

PERFORMANCE CHARTS

To expedite calculations, performance charts have been constructed expressing the effect of all variables grouped in the dimensionless groups r, s,

r/s, and u/u_0 .

In Figure 6, u/u_0 is plotted against s/r for equal values of r. In Figure 7, values of r are plotted against s for such conditions that the residual hardness of the water leaving the bed is 7 parts calcium carbonate per million (0.41 grain per gallon). Curves are constructed for different values of initial hardness. The problem previously solved algebraically can now be readily solved by using Figure 6. For example, at r = 31.3, s = 28.1, s/r= 0.898, and $u/u_0 = 0.36$ in agreement with calculations. For the particular conditions of this problem, r is constant and s varies only as time. Figure 6 shows that in varying s/r from 0.68 to 0.90 at r = 31.3, the hardness of water leaving rapidly increases from a u/u_0 value of 0.001 to 0.37 or from 0.3 to 111 parts calcium carbonate per million. The values of s are directly proportional to time, for the given condition s = $(28.1 \ y/960) = 0.0292 \ y.$ Thus the hardness of the water leaving the zeolite rapidly changes

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from 0.3 to 111 p. p. m. calcium carbonate as the time elapsed changes from 12.2 to 16.1 hours.

The mineral should be regenerated when the water leaving reaches a hardness of 7 p. p. m. calcium carbonate. From Figure 7 an r value of 31.3 corresponds to an s value of 24.6, or the time elapsed is 24.6/0.0292 = 844 minutes (14.1 hours). The water softened by 3 cubic feet of mineral during this period is $844 \times 4 = 3376$ gallons; the calcium carbonate removed is $(3376 \times 8.34 \times 300-7)/10^6 = 8.24$ pounds calcium carbonate (57,680 grains), or 19,227 grains per cubic foot. The total water softened by one cubic foot of mineral under the above conditions is $(4 \times 844)/3 = 1130$ gallons.

For any particular zeolite values of k_1 , ρ and v_0 are constant. For any particular zeolite it is more convenient to plot x/G against v_0y , instead of r against s as in Figure, 7. where x/G can be expressed in thickness of bed in feet divided by rate of water flow in gallons per square foot per minute, and u_0y can be expressed as initial hardness of water supply in grains calcium carbonate per gallon multiplied by softening time in hours. Such a plot is neither general nor expressed in dimensionless units, but for a particular zeolite it has the advantage of reading directly in commercial terms.

In these calculations the reverse reaction was neglected. However, even in the case where the bed was used until only 60 per cent of the hardness was removed, the reverse reaction reached a maximum ratio of only 1.1 per cent of the forward reaction at the exit side of the bed at the end of 16 hours. For all shorter distances in the bed and for all shorter intervals of time, the reverse rate would be correspondingly less than 1.1 per cent of the forward rate.

REACTION VELOCITY k1 FROM PERFORMANCE DATA

With the kinetic equations established for water softening and its mathematical development, it becomes possible to calculate reaction velocity constant k_1 from the performance of a thick bed as in commercial operation. It is necessary to start either with a fully regenerated or fresh cation exchanger and to know its density, maximum cation-exchange capacity, and thickness of bed. The initial hardness, u_0 , of the water supply, rate of water flow, G, and exit hardness, u, at the end of a given time, y, must be measured.

For example, a bed of exchanger is used which is 3 feet thick, has a density of 28 pounds per cubic foot, and has a maximum cation-exchange capacity of 25,000 grains calcium carbonate per cubic foot. Water having an initial hardness of 300 parts calcium carbonate per million is passed through the exchanger at a rate of 4 gallons per square foot per minute for 14.1 hours when the water leaving has a hardness of 7 parts calcium carbonate per million. These data are similar to previous illustration, but k_1 is now to be calculated. Under these conditions, $u_0 = 6.0$, $v_0 = 0.00255$, G = 33.32 pounds per square foot per minute, $u/u_0 = 0.0233$; y = 846 minutes:

$$\frac{s}{r} = \frac{2(33.32 \times 3.0 \times 846)}{(10^6 \times 28 \times 0.00255 \times 3)} = 0.79$$

From Figure 6 the intersection of s/r = 0.79 with $u/u_0 =$ 0.0233 gives an r value of 32. Thus,

$$k_1 = \frac{rG}{10^6 \rho \ v_0^2 x} = \frac{(32) \ (33.32)}{(10)^6 \ (28) \ (0.00255)^2 \ (3)} = 1.95$$

LIMITATIONS OF EQUATIONS AND PROCEDURE

The actual experimental values reported in this paper are of value only for a particular cation exchanger and a particular type of water. The mathematical treatment is of general value and has been developed for both the forward and reverse reactions but not for the net reaction rate. Where the initial water supply has a high sodium content, the reverse reaction becomes appreciable and the given equations do not strictly apply. It is believed, however, that this general procedure, the mathematical treatment, and the general performance charts presented here can be used to obtain the complete performance characteristics of a bed of cation exchanger with the minimum of experimental data; in general the method should be applicable to any waters for the removal of magnesium as well as calcium. The effects of pH, temperature, and mineral composition of the water, and the effects of grain size, chemical composition, and structure of the mineral can be evaluated by this procedure and the results extrapolated with the minimum of experimental data. The mathematical treatment can also be applied to similar heterogeneous reactions in a batch process where one atom or ion in the fluid phase reacts with two atoms or active spots in the solid phase.

ACKNOWLEDGMENT

Credit is gratefully acknowledged to E. C. Carlson and D. K. Starr for technical services in experimental work; to N. A. Ednie for construction of performance charts; to R. E. Langer for the method of deriving Equation 11 from system 7; to Milton Shoemaker for information on industrial performance; and to the Wisconsin Alumni Research Foundation for financial support.

NOMENCLATURE

- $\begin{array}{rcl} a & = & -(10^{6} \ \rho \ k_{1}) \ /G \\ b & = & -k_{1} \end{array}$
- \overline{b} C = constant
- = mass velocity of water flow, lb./sq. ft./min. G
- k_1 = reaction velocity constant of softening as defined by Equation 1
- = reaction velocity constant of regeneration as defined by k_2 Equation 2
- = equilibrium constant = k_1/k_2 K
- calcium content of exchanger, gram equivalents/gram zeolite, and lb. equivalent/lb. zeolite p =
- q = sodium content of brine, gram equivalents/milliongrams water, and lb. equivalent/million lb. water $r = -w_0^2 x$ (dimensionless group) $R_1 = \text{rate of softening, gram equivalents calcium removed}$
- by zeolite/min./gram exchanger
- R_2 = rate of regeneration, gram equivalents calcium removed from zeolite/min./gram exchanger
- $R_n = \text{net rate} = R_1 R_2$ $s = -bu_0v_0y$ (dimensionless group)
- = calcium ions in water, gram equivalents/million grams water, and lb. equivalents/million lb. water u
- sodium content of exchanger, gram equivalents/ gram exchanger, and lb. equivalent/lb. exchanger v =
- flow rate of water, grams/min. distance in bed, cm. or ft. w
- x
- = time elapsed, min. y
- $(v_0/v) 1$ (dimensionless group) z activity coefficient for sodium ion in solution; at low = γ
- concentrations $\gamma = 1$
- 6 = differential operator
- density ----- $\frac{\rho}{\Sigma}$
- = summation

Subscripts

- a = average
- r = removed
- ra = average removed 0 = initial state

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Catalytic Hydrogenation Rates

EQUIPMENT AND CONTROL

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Unique equipment has been constructed for measuring reaction rates in catalytic vapor phase reactions at high pressures and temperatures in continuous flow systems, in contrast to the laboratory glass equipment used for obtaining kinetic data under static conditions. The equipment lends itself to obtaining data of practical value for process design. Mechanisms for control of temperature and pressure, flow rates, and feed ratios are illustrated. Special features

FOR industrial process design it is desirable to obtain reaction rate data in equipment where conditions simulate the flow conditions of the commercial process, since kinetic data obtained in a static system may not be applicable. In this general study of the mechanism and kinetics of heterogeneous catalytic reactions in flow systems,

¹ Present address, Universal Oil Products Company, Riverside, Ill. ² Present address, Standard Oil Company of California, San Francisco, Calif. are dual-motor-driven needle valves for control of hydrogen flow through capillary glass nozzles and for control of pressure on system by release of hydrogen. Special electrically heated and cooled preheater and reaction chamber of Duronze metal and closures for rendering reactor leakproof under conditions of severe temperature gradients are shown. Electrical relay circuits for temperature and pressure control in operation of motors are described.

the particular system chosen was the vapor-phase hydrogenation of isooctane to isooctane with a nickel catalyst. This process is perhaps no longer of great industrial importance, but it lends itself well to an investigation of the mechanism and rates of a given type of catalytic reaction.

The special design and construction of experimental equipment and control devices are of prime importance in successfully conducting kinetic studies in flow systems. A detailed account of equipment is given here since the particular ap-

paratus and controls constructed are applicable to a great variety of kinetic studies in addition to vapor-phase hydrogenation. The equipment was de.....

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signed and constructed to cover the following: pressures up to 1000 pounds per square inch, temperatures up to 600° C., liquid feed rates from 0.06 to

Figure 1. Assembly of Hydrogenation Equipment and Control Devices







Hydrogen from commercial cylinders, 1, is expanded through a diaphragm-type pressurereducer valve, into two auxiliary tanks, 2. The pressure in these tanks is maintained about 30 pounds per square inch above the operating pressure in the system in order to obtain a low and fairly constant pressure differential across the flow control valve, 3. Hydrogen flows from the auxiliary tanks, 2, through the flow control valve, 3, into the preheater, upper 6, where it is heated and mixed with the vaporized liquid feed. After the mixture has passed through the catalyst bed, lower 6, and condenser, 7, the noncondensable hydrogen is released from the system through the



Figure 2. Flow Controller

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- Figure 2. Flow High-pressure hydrogen supply tank Low-pressure sopply tanks Flow-control needle valve Flow-control manometer Orifice Catalyst chamber and preheater Condenser Liquid receiver

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- 2.40 gallons per hour, hydrogen feed rates from 1 to 40 cubic feet per hour, and catalyst volumes up to 500 cc. Control devices were developed which are capable of holding each variable constant within, roughly, one per cent of any desired value.

ASSEMBLY OF EQUIPMENT

The equipment assembly is shown in Figure 1 and a schematic flow sheet of the hydrogenation process in Figure 2. The heavy white lines with arrows indicate the paths of the hydrocarbon and hydrogen flowing through the apparatus.

The liquid feed, consisting of a mixture of isooctene and isooctane of definite percentage unsaturation, is pumped into calibrated charging tank 14 by a small gear pump, 15. A variable-stroke constant-speed plunger pump, 13, forces the liquid from the tank into the preheater (upper part of 6) where it is vaporized and mixed with the hydrogen before entering the reaction chamber (lower part of 6). The mixture of gases passes through the bed of nickel catalyst where the hydrogen and isooctene react. After leaving the catalyst chamber, the gaseous products enter condenser 7 where the liquid hydrocarbons separate from the noncondensable hydrogen and fall by gravity into liquid receiver 8. The liquid is removed from the system at a constant rate by regulating the flow through the drain valve so that a constant liquid level is maintained in the receiver.

- Water displacement tank Pressure-control needle valve Wet test meter Pressure controller Liquid-proportioning pump Charging tank Liquid supply pump Liquid supply
- 9. 10. 11. 12.
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pressure control valve, 10, where the rate of release of gas is adjusted to maintain a constant pressure on the system. Only those parts of the experimental equipment which are unique in their design and construction are described here.

PREHEATER AND REACTOR

The preheater and reactor consist of a single aluminum bronze block, machined in the form of a cylinder, 4.75 inches o. d., 1.25 inches i. d., and 39 inches long (Figure 3). The upper third of this cylinder is the preheater section, and the lower two thirds the reaction chamber. The preheater



Figure 3. Preheater and Reaction Chamber

section is enclosed by a 2000-volt radiant electrical heater, a small-link brass chain is used as packing material to afford good thermal contact and a high degree of turbulence. The reaction chamber is enclosed by a 20-gage welded stainlesssteel sleeve having an inside diameter 1/s inch greater than the outside diameter of the aluminum bronze cylinder. Air is blown through the annular space between the cylinder and sleeve to remove the heat of reaction and to minimize the temperature gradient in the reaction zone. A 4000watt, 220-volt radiant electrical heater encloses the stainless-steel sleeve. The entire block and heaters are mounted in a 10-inch transite pipe; the annular space is packed with rock wool insulation.

The temperature of the preheater section is maintained constant by a controller which utilizes the difference in the coefficients of expansion of porcelain and aluminum bronze to operate a micro-switch through a lever system. The micro-switch actuates a magnetically controlled mercury switch which opens and closes the heater circuit. The reactor section is maintained at a constant temperature by a controller similar to the one on the preheater section and by regulating the flow of cooling air through the stainless-steel sleeve. The temperatures of the preheater and reactor are measured by iron-constantan thermocouples placed in wells in the aluminum bronze cylinder. In addition, there is one thermocouple in the gas stream immediately below the catalyst bed and another in the gas stream slightly below the top surface of the catalyst bed.

After several attempts to obtain pressure-tight closures on the ends of the aluminum bronze cylinder, the following method proved satisfactory. (Figure 1 was photographed before this final modification of the end closures was made.)





Figure 5. Control Panel

Steel plugs with knife-edge bearing surfaces and standard pipe connections are placed in contact with copper gaskets resting on seats machined in each end of the aluminum bronze cylinder. A welded steel truss supporting four compression coil springs is placed on the upper steel plug. By means of four 5/8-inch tie rods the top surfaces of the coil springs are connected to another welded steel truss bearing against the lower plug. By compressing the springs, the steel plugs are forced against the copper gaskets. The springs are not completely closed when the maximum load is applied; consequently the aluminum bronze cylinder is free to expand and contract with changes in temperature.

HYDROGEN FLOW CONTROLLER

The flow rate of fluid through an orifice is determined by the pressure drop across that orifice; this principle is used to control the rate of flow of hydrogen. Figure 4 shows the

Figure 4. Flow Controller

- 1. By-pass around orifice to allow hydrogen to flow into system with-

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- By-pass around orifice to allow hydrogen to flow into system with-out passing through orifice Glass capillary drawn to fine tip (serves as orifice) Traps to catch any mercury that may be blown out of manometer Electrical contacts to actuate relays Relays operating tandem reversible motor Mercury manometer which moves in response to varying pressure drop across orifice from variations in flow rate of hydrogen through orifice Hydrogen-inlet needle valve for regulating flow rate of hydrogen admitted to system Tandem reversible motor which drives inlet needle valve Variable-gear speed reducer to regulate speed at which valve is driven 7.
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Figure 6. Pressure Controller

Hydrogen-outlet needle valve for regulating the release of Hydrogen-outlet needle valve for regulating the release of hydrogen from system Variable-gear speed reducer to regulate speed at which needle valve is driven Pulley upon which string, connected to mercury switch, is wound as tandem reversible motor operates Tandem reversible motor for driving outlet needle valve Relays which operate tandem reversible motor Mercury switch for governing direction of rotation of tandem reversible motor Bucket containing requisite amount of lead weight to balance any desired system pressure Pulley for rotating piston and thus decreasing static friction in gland packing Piston which moves vertically in response to pressure fluctua-tions in system

- 5.
- 7.
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- ۹. Pinton which moves vertically in response to pressure nuctua-tions in system Cylinder filled with heavy lubricating oil Mercury trap which prevents hydrogen from being absorbed by oil and subsequent frothing when system pressure is reduced Explosion-proof motor ($^1/\epsilon$ h. p.) for rotating piston
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operation of the flow controller. Initially needle valve 7 is closed, and the mercury in the two manometer legs, 6, is at the same level. The two fixed contacts, 4, one 1/16 inch above the other in the right leg of the manometer, are above the mercury; relays 5 are so connected that the tandem reversible motor, 8, is turning to open needle valve 7. As the valve slowly opens, the pressure drop across orifice 2 increases because of the increasing rate of flow of gas through the valve, and the mercury level in the right leg of the manometer steadily rises. When the mercury touches the lower contact, the first relay circuit is completed and the motor opening the valve is stopped.

Because of slight overcontrol, the mercury surface continues to rise and finally reaches the upper contact, which completes the second relay circuit and starts the motor which closes the valve. This motor continues to close the valve, and thus diminishes the flow rate of gas through the orifice and decreases the pressure drop across the orifice until the mercury drops away from the upper contact. When this connection is broken, the relay operates to stop the motor which is closing the valve. If there is still overcontrol, the mercury will fall below the first contact and the cycle will be repeated. After several oscillations the valve will achieve the correct position with neither motor turning. This corresponds to the lower contact being below and the upper contact above the mercury surface.

Each orifice consists of a short length of capillary glass tubing with one end drawn to a fine tip. It is mounted inside a steel fitting and held in place by a rubber compression joint. Orifices of various diameters are used to vary the flow rate over wide ranges. The final small adjustment to attain any desired rate is made by moving the contacts in the right manometer leg. The control panel is shown in Figure 5.

PRESSURE CONTROLLER

The pressure in the apparatus is controlled by regulating the release of hydrogen from the system. The device used for this purpose is shown in Figure 6. It consists of a needle valve geared to a tandem reversible motor. The direction of rotation of the motor is governed by a pair of relays which are operated by a mercury switch attached to a pressure indicator, similar in construction to a dead-weight pressure gage tester.

Let us assume that piston 9 and bucket assembly 7 remain stationary. Pulley 3 is mounted on the motor shaft which turns at one revolution per minute. As the motor turns counterclockwise, it unwinds the string from the pulley and lowers mercury switch 6 to the on position; this energizes the relays and reverses the direction of rotation of the motor.



Now the string is wound up on the pulley which raises the switch to the off position; this deactivates the relays and again causes the motor to turn counterclockwise. The cycle takes about 10 seconds and results in an oscillating motion of the valve about some mean position.

If the bucket were to drop a small distance and then remain stationary at the new point, the valve would oscillate about a new mean position which would be closer to shutoff than the former setting.

If the bucket were to rise a short distance and then remain stationary at the new point, the valve would oscillate about another mean position which would be farther from shutoff than the initial position. Hence the position of the bucket governs the mean position of the valve because of the intervening string linkage.

In actual operation the vertical movement of the bucket in response to slight variations in pressure is utilized to adjust the mean position of the valve; the rate of release of hydrogen is thus controlled so that the system pressure will remain practically constant. Since even a slight displacement of the piston will result in a change in the main setting of the valve, the variations in pressure in the apparatus are small.

ACKNOWLEDGMENT

Credit is acknowledged for suggestions and information received from G. B. Zimmerman, R. L. Smith, C. D. Lowry, Jr., and K. M. Watson, and for equipment and support of research assistants received from the Wisconsin Alumni Research Foundation and the Universal Oil Products Company. The latter organization also initiated the project and established the first research fellowship for it.

INTERPRETATION OF RESULTS

Procedures for studying rates of catalytic hydrogenation are outlined, together with precautions in purification of reactants, activation of catalyst, and analysis of product. Experimental data seem to indicate that the controlling step in this process is the rate of surface reaction, that the mass transfer step is negligible, and that adsorption equilibrium is maintained between the gas phase and adsorbed components. Reaction rate equations are developed, including the effects of activated adsorption and surface reaction expressed in terms of concentrations for two catalysts. Further work is underway at various total pressures, temperatures, and catalyst sizes to evaluate these additional effects and to improve the present interpretation.

S STATED by Anderson and Rowe (page 554) the system chosen for studying the rates of catalytic hydrogenation was the reaction of hydrogen with isooctene to form isooctane in the vapor phase in a continuous flow process. Adequate nickel catalyst was obtained to ensure uniformity of supply for a large number of tests. The catalyst pellets were cylinders $\frac{1}{8} \times \frac{1}{8}$ inch and, as received, contained nickel in an oxidized state supported on kieselguhr. This catalyst is commonly used for hydrogenation of unsaturated hydrocarbons. Its exact composition and chemical analysis were not disclosed by the producer. Before use the catalyst was activated by reduction and heating for 4 hours in a stream of hydrogen at 300° C. and 5 atmospheres pressure. The hydrogen was flowed at a rate of 2.64 cubic feet per hour (at standard conditions) through a catalyst bed $1^{1}/_{4}$ inches in diameter.

To ensure uniformity of isooctene for all tests, an initial supply of 550 gallons was made available, and to dilute the feed, 100 gallons of isooctane were also placed in storage. Both stocks were commercial grade. Because of the sensitivity of the nickel catalyst to poisoning, it was necessary to remove even small traces of sulfur, polymers, and peroxides. Polymers and peroxides formed upon storage so that the stock required purification just prior to use.

The vaporized feed stock was passed through an activated bed of catalyst in the absence of hydrogen, and this catalyst was not used for rate studies. This treatment was adequate to remove the permanent poisons such as sulfur. To eliminate polymers and peroxides, the stock was steam-distilled and dried before each use; the feed so treated was satisfactory for 4 or 5 days before repurification became necessary.

RATE STUDIES

The experimental procedure was outlined in detail by Anderson and Rowe. Successive tests were made on the same batch of catalyst until its activity decreased. To detect this decline, a

R. B. Beckmann, A. E. Pufahl, O. A. Hougen

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standard run was repeated during each series of experiments. No general conclusions can be made regarding the life of the catalyst because the process variables differ in each series of tests and because each process variable affects the catalyst life in a singular manner.

when the first runs were made, the liquid feed was undiluted isooctene, and no special means were provided for removing the heat of reaction. Operation under these conditions resulted in temperature gradients in the catalyst bed as high as 150° to 200° C. At first a 10-inch bed was used, but to ensure better temperature control and to attain lower changes in concentration, the thickness was reduced to 1.5 inches using 30 cc. of catalyst. To decrease the temperature gradients and make the operation more nearly isothermal, a cooling jacket was added to the reactor block. However, even with a blast of cold air passing through the jacket, operation was still far from isothermal. The amount of heat liberated in the initial portion of the bed, where the greatest part of the reaction occurs, was too great to be dissipated without setting up temperature gradients of 20° to 30° C. To decrease further the temperature gradients, the isooctene feed was diluted with isooctane. This reduced the concentration of reactants entering the catalyst bed and supplied a material of high heat capacity to absorb some of the heat liberated. It was found that the temperature could be kept within reasonable limits by use of a feed containing not more than 50 per cent olefin. The liquid feed stock was mixed in 50-gallon lots.

in 50-gallon lots. ANALYTICAL PROCEDURE. The analyses of the feed stock and the product require a method for determining the olefin content in a mixture of paraffins and olefins. Bromination, hydrogenation, and refractive index were used. In the bromination method, the concentration of unsaturated hydrocarbons is determined by the amount of bromine necessary to combine with the double bonds, as described by Thomas, Bloch, and Hoekstra (3). Hydrogenation is carried out statically in a high-pressure bomb according to the method of Adkins (1). The degree of unsaturation of a hydrocarbon mixture is measured by determining the amount of hydrogen necessary to saturate the sample completely. In the third method the concentration of unsaturated hydrocarbons is determined by the refractive index of the mixture.

The bromination method gives accurate, reproducible results if the unsaturation is less than 30 per cent, but the procedure is lengthy and does not permit rapid and immediate analysis of the product as the run progresses. The refractometer, calibrated with mixtures of isooctene and isooctane of known degrees of unsaturation as determined by a static bomb hydrogenation as a primary standard, permits the rapid analysis of the products and gives accurate results over the entire range of composition. The refractive index method is dependable as long as the feed stock is free of polymers and peroxides. The effect of composition upon the index of refraction of isooctene-isooctane solutions at 24° C. is shown in Figure 1.

PRELIMINARY TESTS. In tests conducted over several months it was found difficult to secure reproducible results. The catalyst rapidly lost its activity and required frequent replacement. When tests were conducted over a wide temperature range, the anomalous situation was encountered in having the rate of reaction reach a maximum at 220° C. and then decline. At first it was thought this effect might be due to a reverse or secondary reaction. Tests were conducted for detecting reversal of reaction by passing pure isooctane through the catalyst at atmospheric pressure and 300° C., with and without hydrogen. These tests were repeated with a mixed feed. In no case was a dehydrogenation effect noted. Later thermodynamic calculations support the observation and show that no reverse reaction is possible at these low temperatures. Indeed, the reverse reaction is scarcely evident at 400° C. The temperature reversal effect noted was finally found to be due to localized reaction and poisoning in a thick bed which resulted in faulty temperature observations. That is, the reaction was not taking place at the thermocouple locations. This situation was corrected by using smaller beds and purifying the feed just before each run both by sulfur removal in the vapor phase and by steam distillation of the liquid.

and putity ing the test just before each run both by simily removal in the vapor phase and by steam distillation of the liquid. Score or Tesrs. The tests were conducted at temperatures varying from 175° to 275° C., for molal ratios of hydrogen to isooctene from 0.5 to 2.0, for mass velocities from 30 to 900 pounds per hour per square foot of total fluid stream, and for space velocities of isooctene from 1.7 to 32 pound moles per hour per cubic foot of catalyst. Fairly wide variations in average partial pressures of hydrogen, isooctene, and isooctane resulted from variations in the composition of the entering feed and in the variable reaction rates obtained. Two different catalysts were used representing different batches supplied by the manufacturer. The two catalysts were supposed to be alike, but one was found to be much more active than the other. The total pressure was not varied. It was found at the end of this investigation that to obtain more reliable measurements of some of the constants in the rate equation, tests should be conducted at wide variations in the total pressure applied to the system. This procedure is planned for future tests. Table I lists the experimental data taken on two catalysts at 250° C. and 5.0 atmospheres pressure.

INTERPRETATION OF DATA

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From the tests made at 250° C. at a total pressure of 5 atmospheres, the rates of production were measured in pound moles of isooctene converted per cubic foot of catalyst per hour. From the composition of the entering stream, flow rate, and conversion rate, the composition of the leaving stream was computed. The average partial pressure of each component gas in the reactor was taken as the logarithmic mean value of the entering and leaving conditions for both hydrogen and isooctene. For the isooctane the average partial pressure was taken as the total pressure less the sum of the average partial pressures of the two reactants. Tests were rejected where the changes in partial pressures from inlet to outlet were greater than 3 to 1 because of the uncertainty in the method under such conditions. A correct average partial pressure could be obtained by integrating the final rate equation and then repeating all calculations. This more accurate method did not seem to be justified at this time. For the



Figure 1. Refractive Indices of Commercial Isooctene-Isooctane Solutions

time being all tests were eliminated where calculations of average partial pressures were uncertain. By plotting the average gas composition for each run at constant total pressure on a triangular plot and expressing the partial pressures of the three component gases in atmospheres as the three coordinates of the plot, lines connecting equal production rates were established. By this method it was found that under conditions of constant temperature and constant total pressure the rate of production increased with increases in both the partial pressures of isooctene and hydrogen. Variable space velocity had no noticeable effect on this plot. The relation of reaction rate to the product of the concentrations of hydrogen and isooctene was not linear, but indicated that the reaction was retarded by covering of the active spots of the catalyst by the reactants as well as by the product. This observation is in accordance with principles outlined by Hougen and Watson (page 529) and indicates that the rate controlling step is the surface reaction between adsorbed hydrogen and adsorbed isooctene. It was also demonstrated that the transfer of reactants to the catalyst interface was not a rate determining step and that the reverse reaction rate was negligible. This latter statement is in agreement with thermodynamic calculations. These observations also preclude the rate of adsorption of any component as a rate determining step. If the adsorption of hydrogen had been a rate determining step, the reaction rate would not have increased with increase in the partial pressure of isooctene. Conversely, if the adsorption of isooctene had been the rate determining step, the rate would not have been influenced favorably by increase in hydrogen concentration. If the desorption of isooctane had been the rate determining step, the rate of production would not have been influenced favorably by an increase in either hydrogen or isooctene concentration.

In agreement with these observations, the most plausible reaction rate equation is the following, in accordance with the principles outlined by Hougen and Watson (page 529):

$$r = \frac{k_{s}LK_{A}K_{B}a_{Ai}a_{Bi}}{2(1 + a_{Ai}K_{A} + a_{Bi}K_{B} + a_{Bi}K_{R})^{2}}$$
(1)

In this system activities may be replaced by partial pressures in atmospheres, and values of the main stream properties have been established equivalent to values at the interface. Constants k, s/2, and L can be combined as a single constant, k'. Thus Equation 1 becomes:

$$T = \frac{k'K_{A}K_{B}p_{A}p_{B}}{(1 + K_{A}p_{A} + K_{B}p_{B} + K_{R}p_{R})^{2}}$$
(2)

If the reaction required the dissociation of molecular hydrogen to atomic hydrogen, the above equation would be modified to the extent of replacing values of K_A and p_A by their square root values; but the experimental results did not warrant this interpretation.

EVALUATION OF CONSTANTS

The constants in Equation 2 were evaluated after converting it to the following form:

$$a = \sqrt{\frac{p_A p_B}{\rho_{BT}}} = a + bp_A + cp_B + dp_R$$
(3)

where R = parameter as defined by Equation 3

 $a = 1/\sqrt{k'K_AK_B}$ $b = aK_A$ $c = aK_B$ $d = aK_R$ $\rho_B = \text{bulk density of catalyst} = 86.4 \text{ lb./cu. ft.}$

Constants a, b, c, d should ordinarily be evaluated by solving four simultaneous Equations 3 taken from a set of four experimental values under various partial pressures. However, since the total pressure was held constant in these experiments, this method would permit determination of only three constants, since of the four equations only three would be truly independent. Fortunately the adsorption coefficient for hydrogen was found to be nearly negligible relative to that of either isooctene or isooctane so that only three constants need be evaluated. This does not imply that hydrogen is not actively adsorbed but only that its equilibrium adsorption constant is relatively small. The evaluation of the constants a, c, and d by the use of simultaneous equations or by determinants did not prove satisfactory because of the insufficient variation in partial pressures, combined with probable errors of 10 per cent in some individual runs. The following graphical method of evaluating constants was therefore resorted to. The method of simultaneous equations and least squares can be used after the most reliable values are first selected by the graphical method. Values of p_A , p_B , and p_R at a given total pressure of 5 atmospheres were plotted on a triangular plot for equivalent values of parameter R (Figure 2). Straight and parallel lines could be constructed for isometric values of R, and isometric lines for the two catalysts were parallel but not coincident for the same values of R. The equation of these lines can be written:

$$p_A = \alpha p_B + \beta \tag{4}$$

where for catalyst 1:

$$\alpha = 1.257$$
 and $\beta = 0.022$ for R = 0.753

for catalyst 2:

Cataly

$$\alpha = 1.257$$
 and $\beta = 0.250$ for R = 0.521

 β was calculated from all tests made at 250° C. and 5 atmospheres pressure. These values of β were plotted against the corresponding values of R, and the following were obtained:

Catalyst 1:
$$R = -0.044\beta + 0.75 = -0.044p_A + 0.056p_B + 0.75$$
 (5)

st 2:
$$R = -0.079\beta + 0.54 = -0.079p_A + 0.099p_B + 0.54$$
 (6)

At 5 atmospheres pressure, $p_A = 5 - p_B - p_R$. Hence for:

Catalyst 1:
$$R = 0.53 + 0.10p_B + 0.044p_R$$
 (7)

Catalyst 2:
$$R = 0.145 + 0.178p_B + 0.079p_R$$
 (8)

Referring to Equation 3, for catalyst 1, at 250° C.:

a = 0.53 =
$$\frac{1}{\sqrt{k'K_AK_B\rho_B}}$$
 or $k'K_AK_B = \frac{3.56}{\rho_B} = 0.052$



PARTIAL PRESSURE OF ISO-OCTANE IN ATMOSPHERES

c = 0.10 =
$$aK_B$$
 or $K_B = \frac{0.1}{0.53} = 0.189$
d = 0.044 = aK_R or $K_R = \frac{0.044}{0.53} = 0.083$

For catalyst 2, at 250° C.:

$$a = 0.145 = \frac{1}{\sqrt{k'K_AK_B\rho_B}} \text{ or } k'K_AK_B = \frac{47.0}{\rho_B} = 0.695$$

$$c = 0.178 = aK_B \text{ or } K_B = \frac{0.178}{0.145} = 1.227$$

$$d = 0.079 = aK_R \text{ or } K_R = \frac{0.079}{0.145} = 0.545$$

Comparison of the two catalysts shows that the ratio K_B/K_R remained the same for both (namely, 2.25) and that the adsorption of hydrogen was negligible in comparison. However, the absolute values of K_B , K_R , and $k'K_AK_B$ were much greater for catalyst 2 than for catalyst 1:

At 250° C.	Catalyst 1	Catalyst 2	Ratio
k'KAKB	0.052	0.695	$13.4 \\ 6.5 \\ 6.5$
KB	0.189	1.227	
KR	0.083	0.545	

Experiments at temperatures other than 250° C. were not extensive enough in variations of partial pressures to permit accurate evaluations of the adsorption equilibrium constants.

The resultant rate equations for catalysts 1 and 2 may be summarized as follows at conditions of 250° C. and 5 atmospheres total pressure.

Catalyst 1:
$$r = \frac{0.0412 p_A p_B}{(1 + 0.189 p_B + 0.083 p_R)^2}$$
 (9)

Catalyst 2:
$$r = \frac{0.551p_A p_B}{(1 + 1.227p_B + 0.54p_R)^2}$$
 (10)

A comparison of results calculated from Equations 9 and 10 compared with experimental results are listed in Table I. The equations agree with the experimental results, on the average, within ± 2 per cent.

EFFECT OF MASS TRANSFER ON REACTION RATE

The rate of transfer of reactants up to the surface of the catalyst and of the products back into the main fluid stream can be treated as separate operations in the over-all reaction rate mechanism. In the present instance the gradient in the partial pressure of the reactants necessary to account for the observed rates of reaction was found to be negligible. Partial pressure drops due to mass transfer are likely to be important in reactions catalyzed by solid surfaces only for extremely high reaction rates accompanied by low mass velocities of the fluid through the catalyst bed.

The rate of mass transfer of any component gas from a fluid stream to a granular solid may be expressed by the following:

$$r_B = \frac{GA_p \Delta p_B}{a(\text{HTU})M_m p_{al}} \tag{11}$$

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		TABLE I.	Hydroge	NATION	OF ISOOCT	ene* at 5 Atm	OSPHERE	s and 250	° C.			
D		Mass		-Partial	Pressure of	Component Gas	es, Atm					realed.
No.	C.	(Hr.) (Sq. Ft.)	PA	PB	PR	<i>p</i> _A	PB	p_R		Texptl.	realed.	rexptl.
					Catalyst N	umber 1						
86 87 88 99 91 92 93 95 96 97 98 99 101 102 103 104 107 108 109 110 111 114	248 247 250 251 250 249 249 249 249 250 250 251 251 254 252 249 252 249 252 249 250	$\begin{array}{c} 156.64\\ 195.29\\ 300.23\\ 374.64\\ 157.08\\ 195.73\\ 244.77\\ 254.47\\ 315.47\\ 156.45\\ 139.62\\ 174.09\\ 76.32\\ 155.75\\ 156.07\\ 105.58\\ 104.24\\ 156.06\\ 155.77\\ 166.06\\ 130.28\\ 602.19\\ 483.43\\ \end{array}$	$\begin{array}{c} 1,890\\ 1,637\\ 1,891\\ 1,637\\ 2,161\\ 1,890\\ 1,639\\ 1,883\\ 1,637\\ 1,757\\ 1,890\\ 1,637\\ 1,892\\ 1,143\\ 1,453\\ 1,892\\ 1,892\\ 1,443\\ 1,163\\ 1,443\\ 1,637\\ 1,637\\ 1,892\\ 1,$	$\begin{array}{c} 1.513\\ 1.637\\ 1.613\\ 1.633\\ 1.381\\ 1.515\\ 1.638\\ 1.517\\ 1.638\\ 1.513\\ 1.637\\ 1.573\\ 1.513\\ 1.536\\ 1.513\\ 1.536\\ 1.536\\ 1.731\\ 1.867\\ 1.731\\ 1.637\\ 1.637\\ 1.513\\ 1.536\end{array}$	$\begin{array}{c} 1.597\\ 1.726\\ 1.596\\ 1.727\\ 1.457\\ 1.595\\ 1.723\\ 1.600\\ 1.726\\ 1.665\\ 1.597\\ 1.726\\ 1.595\\ 1.595\\ 1.821\\ 1.595\\ 1.826\\ 1.970\\ 1.826\\ 1.726\\ 1.726\\ 1.726\\ 1.726\\ 1.595\end{array}$	$\begin{array}{c} 1.5330\\ 1.3320\\ 1.6920\\ 1.4600\\ 1.4600\\ 1.8760\\ 1.6100\\ 1.3720\\ 1.6514\\ 1.4340\\ 1.3940\\ 1.5250\\ 1.3055\\ 1.3055\\ 1.316\\ 0.7795\\ 1.073\\ 1.424\\ 1.428\\ 1.061\\ 0.8102\\ 1.060\\ 1.198\\ 1.525\\ 1.770\end{array}$	$\begin{array}{c} 1.0990\\ 1.3320\\ 1.2850\\ 1.4600\\ 0.9940\\ 1.1830\\ 1.2520\\ 1.4340\\ 1.1880\\ 1.0890\\ 1.3070\\ 0.8093\\ 1.634\\ 1.385\\ 0.9732\\ 0.9594\\ 1.385\\ 1.389\\ 1.389\\ 1.389\\ 1.198\\ 1.526\\ 1.377\end{array}$	$\begin{array}{c} 2.3680\\ 2.3360\\ 2.0230\\ 2.0230\\ 2.0800\\ 2.1300\\ 2.2070\\ 2.2560\\ 2.1320\\ 2.4180\\ 2.3865\\ 2.4180\\ 2.3875\\ 2.5420\\ 2.5865\\ 2.5420\\ 2.5928\\ 2.6126\\ 2.5928\\ 2.6510\\ 2.5918\\ 2.5510\\ 2.6040\\ 1.9490\\ 1.8530\end{array}$		$\begin{array}{c} 3.224\\ 3.048\\ 3.850\\ 3.722\\ 3.220\\ 3.389\\ 3.429\\ 3.699\\ 3.524\\ 3.008\\ 2.914\\ 2.902\\ 2.100\\ 2.600\\ 2.600\\ 2.600\\ 2.600\\ 2.600\\ 2.600\\ 2.600\\ 2.600\\ 2.600\\ 2.600\\ 2.600\\ 3.950\\ 3.950\\ \end{array}$	$\begin{array}{c} 3.042\\ 3.022\\ 3.889\\ 3.616\\ 3.565\\ 3.426\\ 3.202\\ 3.698\\ 3.492\\ 3.902\\ 3.900\\ 2.902\\ 3.900\\ 2.908\\ 1.957\\ 1.955\\ 1.955\\ 2.537\\ 2.494\\ 2.417\\ 2.002\\ 2.412\\ 2.412\\ 2.455\\ 3.939\\ 4.179\end{array}$	$\begin{array}{c} 0.944\\ 0.991\\ 1.010\\ 0.972\\ 1.107\\ 1.011\\ 0.932\\ 1.002\\ 0.991\\ 0.965\\ 1.030\\ 1.030\\ 1.030\\ 0.933\\ 0.968\\ 0.976\\ 0.933\\ 0.968\\ 0.916\\ 0.928\\ 0.916\\ 0.916\\ 0.958\\ 1.058\\ \end{array}$
***	200	200.20			Catalyst N	Jumber 2						
$\begin{array}{c} 116\\ 117\\ 118\\ 120\\ 122\\ 123\\ 124\\ 125\\ 126\\ 127\\ 128\\ 130\\ 131\\ 133\\ 135\\ 136\\ 138\\ 139\\ 142\\ 143\\ 144\\ 146 \end{array}$	$\begin{array}{c} 248\\ 249\\ 245\\ 248\\ 247\\ 250\\ 250\\ 250\\ 250\\ 250\\ 250\\ 250\\ 251\\ 251\\ 251\\ 251\\ 251\\ 250\\ 250\\ 251\\ 250\\ 250\\ 250\\ 250\\ 250\\ 250\\ 250\\ 250$	$\begin{array}{c} 469.08\\ 656.84\\ 137.76\\ 171.80\\ 141.21\\ 139.92\\ 156.64\\ 195.29\\ 266.68\\ 311.40\\ 206.43\\ 177.93\\ 155.52\\ 85.31\\ 152.71\\ 190.19\\ 155.83\\ 155.84\\ 156.01\\ 156.21\\ 156.38\\ 156.78\\ \end{array}$	$\begin{array}{c} 1.892\\ 1.892\\ 1.892\\ 1.637\\ 1.892\\ 1.892\\ 1.892\\ 1.637\\ 1.637\\ 1.637\\ 1.637\\ 1.892\\ 1.637\\ 1.892\\ 1.637\\ 1.235\\ 1.899\\ 1.889\\ 1.637\\ 1.235\\ 1.393\\ 1.669\\ 1.714\\ 1.983\\ \end{array}$	$\begin{array}{c} 1.513\\ 1.513\\ 1.513\\ 1.637\\ 1.513\\ 1.513\\ 1.637\\ 1.513\\ 1.637\\ 1.513\\ 1.637\\ 1.513\\ 1.637\\ 1.513\\ 1.637\\ 1.835\\ 1.637\\ 1.835\\ 1.755\\ 1.675\\ 1.832\\ 1.755\\ 1.675\\ 1.839\\ 1.468\\ \end{array}$	$\begin{array}{c} 1.595\\ 1.595\\ 1.595\\ 1.595\\ 1.726\\ 1.595\\ 1.595\\ 1.726\\ 1.595\\ 1.726\\ 1.595\\ 1.726\\ 1.595\\ 1.726\\ 1.595\\ 1.726\\ 1.595\\ 1.726\\ 1.595\\ 1.726\\ 1.933\\ 1.852\\ 1.761\\ 1.687\\ 1.549\end{array}$	$\begin{array}{c} 1.643\\ 1.728\\ 1.2665\\ 1.123\\ 1.321\\ 1.321\\ 1.354\\ 1.63\\ 1.254\\ 1.589\\ 1.183\\ 1.393\\ 0.463\\ 1.216\\ 1.331\\ 1.240\\ 0.750\\ 0.776\\ 0.867\\ 1.025\\ 1.150\\ 1.423\\ \end{array}$	$\begin{array}{c} 1.244\\ 1.326\\ 0.835\\ 1.123\\ 0.817\\ 0.819\\ 0.865\\ 1.259\\ 1.163\\ 1.259\\ 1.163\\ 1.183\\ 0.917\\ 1.743\\ 0.659\\ 0.835\\ 1.140\\ 1.470\\ 1.470\\ 1.470\\ 1.470\\ 1.451\\ 1.002\\ 0.730\\ \end{array}$	$\begin{array}{c} 2.113\\ 1.946\\ 2.8985\\ 2.754\\ 2.862\\ 2.860\\ 2.781\\ 2.664\\ 2.634\\ 2.634\\ 2.634\\ 2.634\\ 2.634\\ 2.634\\ 2.720\\ 2.774\\ 3.125\\ 2.834\\ 2.834\\ 2.834\\ 2.824\\ 2.824\\ 2.824\\ 2.824\\ 2.847\\ \end{array}$		$\begin{array}{c} 6.931\\ 7.131\\ 3.944\\ 4.006\\ 4.315\\ 4.241\\ 4.918\\ 5.640\\ 4.348\\ 4.660\\ 4.348\\ 4.660\\ 2.709\\ 4.315\\ 4.268\\ 2.610\\ 3.144\\ 3.154\\ 4.357\\ 6.3576\\ 3.997\\ 4.700\\ \end{array}$	$\begin{array}{c} 7.234\\ 8.063\\ 3.906\\ 4.018\\ 4.081\\ 4.081\\ 4.391\\ 4.297\\ 4.999\\ 4.750\\ 1.779\\ 3.121\\ 4.186\\ 4.136\\ 4.136\\ 3.165\\ 3.663\\ 3.865\\ 4.377\\ \end{array}$	$\begin{array}{c} 1.044\\ 1.131\\ 1.003\\ 1.019\\ 1.008\\ 1.020\\ 1.018\\ 1.020\\ 1.013\\ 1.016\\ 1.177\\ 1.021\\ 1.019\\ 0.917\\ 1.153\\ 0.970\\ 0.969\\ 1.076\\ 1.133\\ 1.007\\ 1.013\\ 0.967\\ 0.931\\ \end{array}$

- where $\Delta p_B = \text{drop in partial pressure of component gas, atm.}$ $r_B = \text{rate of mass transfer, lb. moles component B/hr./lb. catalyst}$
 - $p_{gf} = \log \text{ mean partial pressure of gases other than component } \mathbf{B} \text{ in gas film}$

$$p_{gf} = \frac{(p - p_{Bg}) - (p - p_{Bi})}{\ln \frac{p - p_{Bg}}{p - p_{Bi}}}$$
(12)

Values of a(HTU) were determined by Gamson, Thodos, and Hougen (2), expressed in terms of the modified Reynolds number, $D_p G/\mu$, and the Schmidt number, $\mu/\rho D_r$. The value of a for $1/8 \times 1/8$ inch cylinders is 252 square feet per cubic foot, the bulk density ρ_B is 86.4 pounds per cubic foot (void space 60 per cent), and the value of A_p is 252/86.4 or 2.92 square feet per pound mass.

For the particular system under study the Schmidt number of the gas mixture varied from 0.3 to 0.4, covering the entire range of compositions and temperatures investigated. The Reynolds number varied from 35 to 137 and the reaction rates from 0.011 to 0.045 pound mole of isooctene converted per hour per pound mass of catalyst. Values of Δp_B for isooctene were calculated for these extreme conditions from Equation 11 and are compared with the average value of the partial pressure of isooctene available for transfer, p_B , in Table II.

These calculations show that the drop in partial pressure of isooctene due to mass transfer never exceeded 3.3 per cent of the maximum pressure drop available. Inasmuch as the accuracy of the rate data is ± 5 per cent, any possible effects of mass velocity were submerged and considered negligible.

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EFFECT OF MASS TRANSFER ON PARTIAL PRESSURE DROP TABLE II. Δp_B $\left(\frac{\mu}{\rho D_{\Psi}}\right)^{2/3}$ D_pG $\frac{\mu}{\rho D_{v}}$ $\Delta p B$ p_B Mm TB aAp p_R Run No. HTU p_B p_A pos a(HTU) G 0.0091 0.0318 0.0246 0.0326 μ 0.011 0.041 0.036 0.0353 2.2730 1.6920 1.4600 1.0490 $\begin{array}{c} 1.517 \\ 2.023 \\ 2.0800 \\ 2.902 \end{array}$ 70.89 81.78 86.08 94.10 $\begin{array}{c} 1.2100 \\ 1.2850 \\ 1.4600 \\ 1.0490 \end{array}$ 3.750 3.7150 3.540 3.951 $\begin{array}{c} 0.00667\\ 0.01050\\ 0.01188\\ 0.00380\end{array}$ $1.682 \\ 2.649 \\ 2.994 \\ 0.957$ 0.944 3.85 3.722 2.387 154.2 300 374.6 95.3 55.22 108.9 137.3 34.9 0.384 0.329 0.316 0.316 $0.528 \\ 0.4768 \\ 0.4640$ 81 88 89 100 0 4640

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NOMENCLATURE

 $a_A, a_{Ai}, \text{etc.} = \text{activity of component gas in main fluid phase}$ a, b, c, d = constants in Equation 3 a(HTU) = dimensionless unit for mass transfer

- = gross outside area of catalyst pellets, sq. ft./cu. ft.

- $= \text{ component } \mathbf{B}$ = av. diameter of catalyst particle
- _D, D, G, k, k' = diffusivity
- = mass velocity of fluid flowing, lb./(sq. ft.)(hr.) = forward reaction velocity constant
- = forward reaction velocity constant
- \mathbf{K} = adsorption equilibrium constant L = total molal adsorption sites per unit mass of catalyst \mathbf{M}_{\bullet} = mean molecular weight of gases in main fluid stream
- p_A , p_B , etc. = partial pressure of component gas in main fluid stream
- = gas law constant
- R R R = parameter as defined by Equation 3
- = component \mathbf{R} = reaction rate, lb. moles isooctene converted/lb. catalyst/hr.

number of equidistant sites adjacent to each active center
 constant in Equation 4

α

= variable in Equation 4 B

- ${}^{
 ho}{}_{B}$
- = density of fluid = bulk density of catalyst, lb./cu. ft. = viscosity

Subscripts

s

- = component A (hydrogen) = component B (isooctene)
- $\stackrel{\pmb{A}}{B}$
- $R = \text{component } \mathbf{R}$ (isooctane)
- = interface i
- = gas a

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Conduction, Convection and Heat Release in

CATALYTIC CONVERTERS

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EAT transfer considerations form an important part of a catalytic converter design. The productivity of a continuous converter depends greatly upon provisions for removing the exothermic heat of reaction or, in the case of an endothermic reaction, for supplying it. An increased efficiency in heat transfer generally permits a larger output of product per unit volume of catalyst. Heat transfer also is essential in maintaining a temperature uniformity within the catalyst bed. The rates of heat generation in the catalyst granules must be balanced by corresponding rates of heat removal such that the point-to-point temperatures in the bed as a whole will lie within specified limits. In extreme cases these limits may be as narrow as $10-20^{\circ}$ C. When the thermal balance is not properly arranged by design or is disturbed by faulty operation, an excessive and local rise or fall in temperature will result. In the former case an excessive "hot spot" may lead to the destruction of the catalyst or to by-product formation; in the latter, cooling the bed may lead to a stoppage of the reaction. Thus, from the viewpoint of efficiency and control, some measure of heat exchange is essential in a catalytic reactor.

This paper deals with the solutions of differential thermal equations for cylindrical and slab-shaped catalyst beds. The specific solutions deal with conditions in the catalyst cross section, and relate point and average catalyst temperature with (a) the temperature of the gas, (b) the average temperature of the catalyst at the periphery of the bed, (c) the rate of heat release by the chemical reaction, and the rates of heat transfer both (d) by transverse conduction through the solid

catalyst and (e) by convection through the gas film between the catalyst and the flowing gas stream. Since the rate of reaction (and of heat release) is a function not only of temperature, but also of concentration of reactants and time of contact, this rate will vary down the length of the catalyst bed. The temperature of the gas stream, which is assumed uniform at any cross section, will also vary along the catalyst bed. Thus, a complete reactor design involves a step-bystep analysis in the direction of gas flow from one cross section to the next with the aid of heat and material balances. By this means the following items may be computed for beds of different dimensions:

- Catalyst and gas temperatures at any point in the bed. Transverse heat flow rates at any cross section. Product formation in a volume of catalyst per unit of time.
- 3.

The following fundamental information is required for the computations:

1. Variation of rate of reaction with temperature, reactant concentrations, and time of contact, usually obtained from pilot plant data.
2. Molar heat of reaction.
3. Thermal conductivity of the catalyst-gas system.
4. Gas-film heat transfer coefficient in broken solids of catalyst size as a function of flow conditions and gas properties.
5. Thermal properties of the gas stream.

The following design variables must be set:

1. Catalyst wall temperature from point to point. (This will involve trial-and-error methods such that the rate of transverse

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(2)

heat transfer from the catalyst bed at a given cross section equals the rate of its removal by the heat transfer medium.)

- Catalyst bed diameter or thickness.
 Length of catalyst bed.
- 4. Inlet gas composition, flow rate, and temperature.

It is also suggested that the thermal equations presented afford opportunities for obtaining better insight to the complexity of converter variables through analysis of the effect of variations of the major variables, taken singly. Moreover, the equations are not limited to heat release by chemical reaction, but may be applied to electrical heating problems or any other cases for which the assumptions listed below are valid. Furthermore, they may be applied to a combination involving any two of the three basic rates—conduction, convection, and heat release. Thus, conduction and convection alone, for example, would apply to cross-sectional conditions $k_0 e^{\frac{-E}{R_1 T}} \approx \epsilon + m t = k'$

Equation 1 may therefore be rewritten:

$$\frac{q}{V_{\text{ref}}} = C_0 + C_1 t \tag{3}$$

$$a = (C_0 + C_1 t) dV_{cat}$$
(4)

here
$$C_0 = \varphi[\epsilon, Q, \Theta, C]$$

 $C_1 = \varphi[m, Q, \Theta, C]$

 C_0 and C_1 vary with longitudinal position in a catalyst bed, but within a thin cross-sectional slice they may be assumed constant. Equation 3 therefore expresses the linear variation of heat release with temperature in a catalyst cross section.

Solutions are presented for thermal equations involving the rate of heat generation in cylindrical and slab-shaped catalyst beds, the rate of heat removal by convection between solid and gas, and its removal by conduction through the catalyst and gas in a direction perpendicular to the gas stream. Point temperatures in any catalyst cross section, the integral mean temperature of the section, and the rate of heat transfer through the periphery of the bed have been related to the diameter or thickness of bed, outer bed temperature, gas temperature, catalyst activity, temperature coefficient of heat generation, thermal conductivity of catalyst, and convection coefficient.

The functions are plotted in dimensionless form

in a packed heat exchanger, and also to certain disk and stripfin heat exchanger problems (4).

The present analysis and computations based upon it are on an a priori basis and are subject to experimental check.

The problem of heat transmission in a catalyst bed has been extensively discussed with qualitative conclusions by Damkoehler (1). Paterson (5) presented a mathematical treatment for the conduction of heat in an infinite or semi-infinite medium generating heat. Problems relating to the measurement of gas and solid in a catalyst bed were pointed out by Jakob (3), and temperature differences between catalyst and gas were measured under various conditions for the hydrogenation of ethylene. Convection heat transfer coefficients in beds of subdivided solids in the catalyst range have recently been measured over a wide range of conditions and correlated by Hougen, Gamson, and Thodos (2).

ASSUMPTIONS

1. The rate of heat release at any point in a catalyst bed is a function of catalyst activity k_0 , catalyst temperature e^{-E/R_1T} , heat of reaction Q, time of contact Θ , and reactant concentration C. Thus the rate of heat release per unit volume of catalyst is:

$$\frac{q}{V_{cat.}} = \varphi \left[\frac{-E}{R_1 T}, Q, \Theta, C \right]$$
(1)

Over the limited range of temperatures of interest in a catalyst bed the specific reaction rate may be expressed as a linear function of temperature as in Equation 2.

in terms of a temperature variable,
$$\frac{1 - t_R}{t_R + \frac{C_0 + ht_g}{C_1 - h}},$$

a rate variable, $R \sqrt{\frac{C_1 - h}{k}}$, and a position variable,

r/R. Major assumptions include uniform gas temperature at every cross section and small longitudinal solids temperature gradient compared with the transverse gradient.

A catalytic reactor design procedure involving analysis by successive small increments in the direction of gas flow is suggested. Sample computations are presented of thermal gradients in a eatalyst bed. Applications to packed heat exchangers and fin exchanger problems are indicated.

2. Temperatures at all points in the catalyst are constant with respect to time. Heat released or absorbed by the reaction at any point is removed or introduced by heat conduction and convection. Radiation is neglected.

3. Heat transfer by conduction through solid catalyst and gas is entirely in a direction perpendicular to gas flow. (This transfer is essentially independent of longitudinal gas velocity.) Temperature gradients and heat flow rates in a longitudinal direction are considered negligibly small and are not included.

4. Because of mixing, the temperature of the gas within any thin cross-sectional slice of catalyst bed is uniform and constant.

CYLINDRICAL CATALYST BED SECTION

Temperature Distribution. Consider an elementary ring in a catalyst section having an outer radius R and thickness Δl (Figure 1). The ring with radius r, width dr, and thickness Δl will have a volume:

$$dV_{cai} = 2\pi \Delta lr dr \tag{5}$$

Combine with Equation 4 to obtain rate of heat release:

$$dq = (C_0 + C_1 t)(2\pi \Delta lr)dr$$
(6)

The rate of heat release by an exothermic reaction in a disk having a radius τ and thickness Δl is:

$$q_1 = \int_0^r (C_0 + C_1 t) (2\pi r \,\Delta t) dr \tag{7}$$

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The rate of heat loss from the disk by radial conduction through the area $2\pi \tau \Delta l$ is a function of the thermal conductivity of the solid and the temperature gradient. It may be expressed:

$$q_2 = - 2\pi r \Delta lk \, \frac{dt}{dr} \tag{8}$$

In the above, positive heat is expressed as flow from higher to lower temperature.

The rate of heat loss from the disk by convection transfer between solid and gas is a function of a temperature difference between these two, of a volumetric transfer coefficient, and of the disk volume, thus:

$$q_{3} = \int_{0}^{r} 2\pi r \,\Delta lh(t - t_{g}) \,dr \tag{9}$$

A heat balance may be expressed in terms of the heat flow rates given in Equations 7 through 9. Thus $q_1 = q_2 + q_3$ and

$$\int_0^T (C_0 + C_1 t) (2\pi r \Delta t) dr = -2\pi r \Delta t k \frac{dt}{dr} + \int^T 2\pi r \Delta t h (t - t_g) dr \quad (10)$$

All possible heat balances for exothermic and endothermic reactions yield equations convertible into 10. Thus the solution of this equation will be a general solution. Cancel $2\pi \Delta l$, differentiate with respect to r, divide through by

Cancel $2\pi \Delta l$, differentiate with respect to r, divide through by rk in Equation 10, and the following equation is obtained:

$$\frac{d^2t}{dr^2} + \frac{1}{r}\frac{dt}{dr} + \frac{(C_0 + ht_p)}{k} + \frac{(C_1 - h)t}{k} = 0$$
(11)

Define
$$n = (C_0 + ht_g), \quad p = (C_1 - h), \quad t' = t + (n/p)$$

Then

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$$\frac{dt}{dr} = \frac{dt}{dr}; \quad \frac{d^2t}{dr^2} = \frac{d^2t}{dr^2}$$

Substitute in Equation 11:

$$\frac{d^2t'}{dr^2} + \frac{1}{r}\frac{dt'}{dr} + \frac{p}{k}t' = 0$$
(12)

Equation 12 is a standard form of Bessel's equation; its general solution, when p/k is positive, is:

$$t' = NJ_0\left(r\cdot\sqrt{\frac{p}{k}}\right) + MY_0\left(r\cdot\sqrt{\frac{p}{k}}\right)$$
(13)

N and M are constants of integration and J_0 and Y_0 are Bessel functions of the zero order.

Express Equation 13 in terms of original variable, t:

$$t = \left[NJ_0\left(r \sqrt{\frac{p}{k}}\right) + MY_0\left(r \sqrt{\frac{p}{k}}\right) \right] - \frac{n}{p}$$
(14)

BOUNDARY CONDITIONS. Let radius to outer limit of catalyst section be R. The temperature at R is t_R . Then at r = R, t =

 t_{R} ; at r = 0, $dt/d\tau = 0$. Differentiate Equation 14 with respect to r:

$$= -N \sqrt{\frac{\bar{p}}{\bar{k}}} J_1\left(r \sqrt{\frac{\bar{p}}{\bar{k}}}\right) - M \sqrt{\frac{\bar{p}}{\bar{k}}} Y_1\left(r \sqrt{\frac{\bar{p}}{\bar{k}}}\right)$$
(15)

Figure 1. Elementary Ring in a Catalyst Section

Setting r = 0 and dt/dr = 0,

 $\frac{dt}{dr}$

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$$N \sqrt{\frac{p}{k}} J_1(0) + M \sqrt{\frac{p}{k}} Y_1(0) = 0$$

But $J_1(0) = 0$; therefore $M \sqrt{\frac{p}{k}} Y_1(0) = 0$. Since $Y_1(0)$ is infinite, M = 0 and the term containing this constant in Equation 14 is eliminated. Setting r = R and $t = t_R$ in Equation 14:

$$t_{R} + \frac{n}{p} = NJ_{e}\left(R \sqrt{\frac{p}{k}}\right); \ N = \frac{t_{R} + \frac{n}{p}}{J_{o}\left(R \sqrt{\frac{p}{k}}\right)}$$

Substituting N in Equation 14 yields a particular solution:

$$t = \left(t_R + \frac{n}{p}\right) \left[\frac{J_0\left(r \sqrt{\frac{p}{k}}\right)}{J_0\left(R \sqrt{\frac{p}{k}}\right)} \right] - \frac{n}{p}$$
(16)

Rearranging Equation 16 into dimensionless variables,

$$(t - t_R) = \left(t_R + \frac{n}{p}\right) \left[\frac{J_0\left(r \sqrt{\frac{p}{k}}\right)}{J_0\left(R \sqrt{\frac{p}{k}}\right)} \right] - \left(\frac{n}{p} + t_R\right)$$

Dividing through by t_R and expressing radius as r/R

$$\frac{t-t_R}{t_R} = \left(1 + \frac{n}{pt_R}\right) \left[\frac{J_0\left\{\left(R \sqrt{\frac{p}{k}}\right)\left(\frac{r}{R}\right)\right\}}{J_0\left(R \sqrt{\frac{p}{k}}\right)} - 1 \right]$$
$$\frac{t-t_R}{t_R + \frac{n}{p}} = \frac{J_0\left\{\left(R \sqrt{\frac{p}{k}}\right)\left(\frac{r}{R}\right)\right\}}{J_0\left(R \sqrt{\frac{p}{k}}\right)} - 1 \qquad (1)$$

This function was evaluated and is plotted as a series of solid lines in Figure 2. The dimensionless variables are called x, y, and z, and are defined as follows:

$$x = R \sqrt{\frac{C_1 - h}{k}}$$
$$y = r/R$$

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$$z = \frac{t - t_B}{t_B + \frac{C_0 + ht_g}{C_1 - h}}$$

The solution of Equation 12 when p/k is negative follows immediately from the Bessel relation:

$$J_{\theta}(ix) = I_{0}(x) \tag{18}$$

Substituting Equation 18 in 16 when p/k is negative, the following particular solution is obtained:

$$= \left(t_{R} + \frac{n}{p}\right) \left[\frac{I_{0}\left(r \sqrt{\frac{p}{k}}\right)}{I_{0}\left(R \sqrt{\frac{p}{k}}\right)} \right] - \frac{n}{p}$$
(19)

In dimensionless form, Equation 19 becomes:

P

$$\frac{t-t_R}{t_R+\frac{n}{p}} = \frac{I_0\left\{\left(R\sqrt{\frac{p}{k}}\right)\left(\frac{r}{R}\right)\right\}}{I_0\left(R\sqrt{\frac{p}{k}}\right)} - 1$$
(20)

Figure 3 is a plot of function 20 in terms of the dimensionless

variables x, y, z. As the values of functions 16 and 19 approach zero, the evalua-tion of temperatures by the function becomes indeterminate. Therefore, an alternate solution as $\pm (p/k) \rightarrow 0$ is required. Start with Equation 10 and simplify into the following:

$$\int_0^T (n+pt)rdr + rk \frac{dt}{dr} = 0$$
(21)

The solution of Equation 21 yields:

$$t = t_R + \frac{n}{4k} \left(R^2 - r^2 \right) \tag{22}$$

which is a parabolic solution.

Integral Mean Temperature. A true average cross-section temperature is of value for catalyst design computations. The following is a derivation of an integral mean temperature ob-tained by dividing the volume of the temperature dome (formed by plotting catalyst temperature at any cross section) by the area of the section:

$$= \frac{\int_{0}^{r} = \mathcal{R}}{\frac{\int_{0}^{r} 2\pi r t dr}{\pi R^2}}$$
(23)

Substitute Equation 16 for t in 23 and integrate. The solution in dimensionless form is:

$$\frac{t_{m}-t_{R}}{t_{R}+\frac{n}{p}}=\frac{2}{R\sqrt{\frac{p}{k}}}\left[\frac{J_{1}\left(R\sqrt{\frac{p}{k}}\right)}{J_{0}\left(R\sqrt{\frac{p}{k}}\right)}-1\right]=\left[\frac{J_{2}\left(R\sqrt{\frac{p}{k}}\right)}{J_{0}\left(R\sqrt{\frac{p}{k}}\right)}\right](24)$$

Equation 24 has been evaluated and is presented as a dotted line in Figure 2. The solution for Equation 24 when the value of p/k is negative is as follows:

$$\frac{t_{\bullet} - t_{B}}{t_{B} + \frac{n}{p}} = \frac{2}{R \sqrt{\frac{p}{k}}} \left[\frac{I_{1}\left(R \sqrt{\frac{p}{k}}\right)}{I_{0}\left(R \sqrt{\frac{p}{k}}\right)} - 1 \right] = \left[\frac{I_{t}\left(R \sqrt{\frac{p}{k}}\right)}{I_{0}\left(R \sqrt{\frac{p}{k}}\right)} \right] (25)$$

This equation has been evaluated and is presented as a dotted line in Figure 3. The range of this solution is limited, however, by the available I_2 tables.



Courtesy, Weiss and Downs Catalytic Converter for Oxidation of Naphthalene and Benzene

The integral mean temperature when $\pm (p/k) \rightarrow 0$ may be found by substituting t from Equation 22 in Equation 23 and integrating:

$$t_m = t_R + \frac{nR^2}{8k} \tag{26}$$

Total Heat Generated. The total heat of reaction released per unit of time in the total volume of a thin catalyst section is of interest in design computations. It may be expressed:

$$\frac{q}{\pi R^2 \Delta l} = C_0 + C_1 t_m \tag{27}$$

SLAB-SHAPED CATALYST BED SECTION

Temperature Distribution. The following derivation deals with a thin section sliced from a slab-shaped catalyst bed in a direction perpendicular to the gas stream (Figure 4). The thickness of the slab is 2B, the length l, and the height β . There are no temperature gradients along the height of the slab. The walls of a heat transfer system are in contact with the sides of the slab.

Because of symmetry, the analysis of heat transfer relations in the thin section is based upon the center line as the line of reference

The thin section has a width B, thickness Δl , and height β . Within this thin section consider an elementary strip at a dis-tance b from the center, with a width db, a thickness Δl , and height β . The volume of this strip will be:

$$V_{cal} = \beta \Delta l db$$
 (28)

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Combine with Equation 4 to obtain rate of heat release:

d

$$a' = (C_0 + C_1 t) \beta \Delta l db \tag{29}$$

The rate of heat release by an exothermic reaction in a section having a width b is:

$$q'_{1} = \int_{0}^{b} (C_{0} + C_{1}t) \beta \Delta l db \qquad (30)$$

The rate of heat loss from the section by outward conduction through the area $\beta \Delta l$ is given by:

$$q'_{\mathbf{a}} = -\beta \,\Delta lk \,\frac{dt}{db} \tag{31}$$

The rate of heat loss from the section by convection transfer between solid and gas follows:

$$q'_{\mathbf{s}} = \int_0^b \beta \,\Delta lh \, (t - t_{\mathbf{o}}) \, db \tag{32}$$

The general steady-state heat balance involving any combination of Equations 30 through 32 is as follows:

$$\int_{0}^{b} (C_{0} + C_{1}t) \beta \Delta l db = -\beta \Delta lk \frac{dt}{db} + \int_{0}^{b} \beta \Delta lh (t - t_{\theta}) db (33)$$

Keeping the same definitions of n and p used in the cylindrical catalyst bed case, the particular solution of Equation 33 is:

$$t = \left(t_B + \frac{n}{p}\right) \left[\frac{\cos\left(b\sqrt{\frac{p}{k}}\right)}{\cos\left(B\sqrt{\frac{p}{k}}\right)}\right] - \frac{n}{p}$$
(34)

The solution in dimensionless form is:

$$\frac{t-t_{B}}{t_{B}+\frac{n}{p}} = \frac{\cos\left\{\left(B\sqrt{\frac{p}{k}}\right)\left(\frac{b}{B}\right)\right\}}{\cos\left(B\sqrt{\frac{p}{k}}\right)} - 1$$
(35)

Equation 35 has been evaluated for positive values of p/k and is presented as a series of solid curves in Figure 5. The solution for Equation 33 when p/k is negative is:

$$t = \left(t_{B} + \frac{n}{p}\right) \left[\frac{\cosh\left(b \sqrt{\frac{p}{k}}\right)}{\cosh\left(B \sqrt{\frac{p}{k}}\right)}\right] - \frac{n}{p}$$
(36)

or

$$\frac{t - t_B}{t_B + \frac{n}{p}} = \frac{\cosh\left\{\left(B\sqrt{\frac{p}{k}}\right)\left(\frac{b}{B}\right)\right\}}{\cosh\left(B\sqrt{\frac{p}{k}}\right)} - 1$$
(37)

Equation 37 appears as a series of solid lines of variable b/B in Figure 6. The solution for Equation 34 or 35 as $\pm (p/k) \rightarrow 0$ is:

$$t = t_B + \frac{\pi}{2k} \left(B^2 - b^2 \right) \tag{38}$$

Integral Mean Temperature. The derivations for integral mean temperature for a slab parallel those presented for the cylindrical case. Consequently, only the final solutions will be given.

Integral mean slab temperature with positive p/k is:

$$t_{\rm m} = \frac{t_B + \frac{n}{p}}{B\sqrt{\frac{p}{k}}} \tan\left(B\sqrt{\frac{p}{k}}\right) - \frac{n}{p} \tag{39}$$

In dimensionless form this equation is:

$$\frac{t_{-} - t_B}{t_B + \frac{n}{p}} = \frac{\tan\left(B\sqrt{\frac{p}{k}}\right)}{B\sqrt{\frac{p}{k}}} - 1$$
(40)

Equation 40 is plotted as a dotted line in Figure 5.

When p/k is negative, the integral mean slab temperature becomes:

$$u_m = \frac{t_B + \frac{n}{\bar{p}}}{B\sqrt{\frac{p}{k}}} \tanh\left(B\sqrt{\frac{p}{\bar{k}}}\right) - \frac{n}{\bar{p}}$$
(41)

Thus,

$$\frac{t_m - t_B}{t_B + \frac{n}{p}} = \frac{\tanh\left(B\sqrt{\frac{p}{k}}\right)}{B\sqrt{\frac{p}{k}}} - 1 \tag{42}$$

The integral mean temperature in the slab as $\pm (p/k) = 0$ is:

$$t_m = t_B + \frac{nB^2}{3k} \tag{43}$$

Total Heat Generated. The equation for the total heat re-leased per unit of time in the total volume of the thin section is similar to that for a cylindrical catalyst bed (Equation 27):

$$\frac{q}{2B\beta\,\Delta l} = C_0 + C_1 t_m \tag{44}$$

CYLINDRICAL CATALYST BED WITH A LIMITING ASSUMPTION

Previous derivations and all computed examples which follow this section are based on assumption 4; i. e., the temperature of the gas within any thin cross-sectional slice of catalyst bed is uniform and constant. Another limiting assumption that can be made, however, is that the gas temperature at any cross section follows the solid temperature, point by point, with a constant difference between them:

$$t - t_{\sigma} = \sigma \tag{45}$$

The difference, σ , would be constant in any cross section, but would vary and even change sign at different sections along the bed. The differential equation for this case is:

$$\int_0^r (C_0 + C_1 t) (2\pi r \,\Delta t) dr = -2\pi r \,\Delta t k \,\frac{d}{dr} + \int_0^r 2\pi r \,\Delta t h \sigma dr \quad (46)$$

The solution is the same as that for the derivation of temperature distribution in a cylindrical catalyst bed section (page 564), when C_0 and C_1 are truly constant. Figures 2 and 3 may then be used for the values of x, y, and z:

$$x = R \sqrt{\frac{\overline{C_1}}{k}}$$

$$y = \frac{r}{\overline{R}}$$

$$z = \frac{t - t_R}{t_R + \frac{C_0 - h\sigma}{C_1}}$$
or $z = \frac{t_m - t_R}{t_R + \frac{C_0 - h\sigma}{C_1}}$

However, to postulate a constancy of C_0 and C_1 when the gas temperature is assumed to vary over the cross section is un-doubtedly not valid. At constant pressure, concentration would have with temperature of the pressure of the pr vary with temperature and also complete mixing could no longer be assumed (as is in assumption 4). Since C_0 and C_1 are func-tions of the concentration, they would no longer be constant throughout a sumption the sum of the constant throughout a cross section.

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DISCUSSION

For reasons of precision, Equations 17 and 20 for the cylindrical catalyst case have been plotted to different scales in Figures 2 and 3. The same is true for the corresponding equations and plots for the slab-shaped bed. Actually $\frac{t - t_R}{t_R + \frac{C_0 + ht_r}{C_1 - h}}$, the temperature group, is a smooth function for

real and imaginary values of the rate group, $R\sqrt{(C_1 - h)/k}$, corresponding to positive and negative values of $(C_1 - h)/k$.

heat release, conduction, and convection. Since the functions are general, they are applicable to any combination of two rates, or to all three. Thus we may consider the following four combinations.

System Involving Only h and k ($C_1 = 0$). In this case $R\sqrt{-h/k}$ is always imaginary and the solution lies entirely in the lower half of Figure 8. The cross-sectional temperatures of a packed heat exchanger would be an example. Certain thin-fin heat transfer problems may also be solved in this manner.



Figure 2. Solution for Temperatures in Cylindrical Catalyst-Bed Cross Section for Positive Values of $(C_1 - h)/k$

This is shown in Figure 7, a rectilinear plot of the variables. The curves for real values of the rate group and positive values of the temperature group lie in the first quadrant. They run smoothly through the origin and branch in the third quadrant for imaginary and negative values. The computation of temperature becomes indeterminate as the functions pass through the origin, and in this region the use of parabolic Equations 22 and 38 is essential.

The functions reach definite limits. For example, as $R\sqrt{(C_1 - h)/k}$ approaches 2.4, the temperature group approaches infinity; and as the temperature group approaches -1, $R\sqrt{(C_1 - h)/k}$ approaches imaginary infinity. The meaning of this becomes clear in Figure 8, where the temperature group is plotted against the dimensionless group (r/R) at parameters of the rate group. As the rate group approaches 2.4, the temperature rise becomes extremely large and the thermal situation becomes unstable. For imaginary values of the rate group (i. e., $(C_1 - h)/k$ is negative) the temperature group tends toward a stable limit.

The equations developed relate the rise of temperature in a bed cross section, among other variables, with the three rates: System Involving Only C_1 and k (h = 0). If the rate of heat release is independent of h (which is not probable in a chemical reaction), the solution for an exothermic reaction lies in the upper half of Figure 8, and that for an endothermic reaction, in the lower half, because C_1 changes sign with type of reaction. This solution may be of interest in electrical heating problems.

System Involving Only C_1 and h (k = 0). In $R\sqrt{(C_1 - h)/k}$ as $k \to 0$, the imaginary value of the group approaches infinity and $-\frac{t - t_R}{t_R + \frac{C_0 + ht_g}{C_1 - h}} = 1$. This may be

rearranged to give

 $C_0 + C_1 t = h(t - t_g)$

which is the expected heat balance.

System Involving C_1 , h, and k. For an endothermic reaction C_1 is numerically negative and the solution involves only the imaginary values of $R\sqrt{(C_1 - h)/k}$. For an exothermic reaction either the real or imaginary solution may occur, depending upon the relative magnitudes of C_1 and h.

CONVERTER DESIGN

Two types of information are required in the design of a catalytic converter: heat transfer equations supported by the necessary thermal data, and kinetic equations (or graphical correlations) and corresponding data. The former are supplied by Equations 17, 20, 21, 24, 25, 26, 27, and Figures 2 and

$$\frac{ln_e}{d\Theta} = \frac{(\epsilon + ml_m)n_a^2}{V_i} = \frac{(\epsilon + ml_m)n_a^2 P}{n_i R_1 T_g}$$
(48)

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but
$$\Theta = \frac{V_{cat}}{V_t} = \frac{AlP}{n_t R_1 T_g}$$
 and $d\Theta = \frac{AP}{n_t R_1 T_g} dl$ (49)



Figure 3. Solution for Temperatures in Cylindrical Catalyst-Bed Cross Section for Negative Values of $(C_1 - h)/k$

3 for a cylindrical catalyst bed, and by Equations 35, 37, 38, 40, 41, 43, and Figures 5 and 6 for a slab-shaped bed); within the stated limitations, they are general in nature. The latter must be determined experimentally. It is apparent that numerous combinations of design procedure will result from the use of the thermal equations with the various functions for zero-, first-, and second-order reactions. Purposes of illustration, however, may be served well by a second-order reaction of the form:

$$A + B \longrightarrow C + D$$

The following equations are developed for this reaction in a continuous catalytic flow system.

For A = B,

$$\frac{dC_e}{d\theta} = k'C_a^2 = k_0 e^{\frac{-E}{R_1T}} C_a^2 = (\epsilon + mt_m)C_a^2$$
(47)
range

Substitute for $d\Theta$ in Equation 48:

$$\frac{dn_e}{Adl} = \frac{dn_e}{dV_{cat}} = (\epsilon + mt_m) \left(\frac{n_a P}{n_t R_1 T_g}\right)^2 = (\epsilon + mt_m)(a - n_c)^2 \left(\frac{P}{n_t R_1 T_g}\right)^2 \quad (50)$$

Or since $n_e = af$,

$$\frac{df}{Adl} = (\epsilon + mt_m) \frac{(a - af)^2}{a} \left(\frac{P}{n_t R_1 T_g}\right)^2 \tag{51}$$

Now, to introduce heat quantities,

$$q = n_e Q$$
 and $dn_e = dq/Q$ (52)

Substitute for dn. in Equation 50:

$$\frac{dq}{dV_{cat}} = Q (\epsilon + mt_m)(a - n_c)^2 \left(\frac{P}{n_t R_1 T_g}\right)^2 = Q (\epsilon + mt_m)(a - af)^2 \left(\frac{P}{n_t R_1 T_g}\right)^2$$
(53)

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$$\frac{dq}{dV_{eqt}} = C_0 + C_1 t_m \tag{54}$$

(55)

where

or

$$C_0 = Q \epsilon (a - af)^2 \left(\frac{P}{n_t R_1 T_g}\right)^2$$

$$C_1 = Q \ m \ (a \ -af)^2 \left(\frac{P}{n_t R_1 T_g}\right)^2$$
(56)

Computational Steps. The following are the computational steps based upon the above equations, upon Figures 2, 3, 5, or 6 and upon heat balances.

I. At the bed entrance C_0 and C_1 may be computed through Equations 55 and 56; t_o , t_R , and R are design variables which must be set; and h(2) is calculable through the Reynolds number. Knowing these, the value of t_m may be determined from Figure 2 or 3 for the catalyst in the cylindrical bed.

II. The rate of heat release per volume per unit of time at the bed entrance is:

$$C_0 + C_1 t_m$$

III. The rate of heat transfer per volume per unit of time from solid to gas is:

$$t_m - t_g)$$

IV. The rate of heat loss by conduction is:

$$(C_0 + C_1 t_m) - [h(t_m - t_g)]$$

V. The radial rate of heat transfer through the catalyst wall in heat units per unit area per unit time is:

$$\frac{C_0 + C_1 t_m - [h(t_m - t_o)]}{2\pi R}$$

This value must balance with the exchanger coefficients when the wall temperature is tR.

VI. Write a heat balance for the heat received by the gas along the bed:

$$GC_{o}Adt_{g} = hA(t_{m} - t_{g})dl$$

Substitute dl from Equation 51 in the above:

$$dt_g = \frac{h (t_m - t_g)a (n_t R_1 T_g)^2}{GC_p A k_{t_m} (a - af)^2 P^2} dj$$

VII. Carry out computations in terms of Δt_{σ} and Δf :

$$\Delta l_{g} = \left[\frac{\Delta f(t_{m} - t_{g})T_{g}^{2}}{(a - af)^{2}k_{t_{m}}}\right] \left[\frac{(n_{l}R_{1})^{2}a}{AP^{2}}\right] \left(\frac{h}{C_{p}G}\right)$$

VIII. Assuming a very small value of Δf (especially at the entrance of the bed), compute Δt_{q} as follows:

- $(t_m t_g)$ is assumed constant over the 1. interval and is set equal to its value at the beginning of the interval.
- Guess at an average value of $T_{m_{av}}$ and $T_{\sigma_{av}}$ for the interval.

- 3. Using an average $f = f + (\Delta f/2)$ compute Δt_{g} over the total interval Δf , since all other terms in equation of step VII are known. Also calculate t_{g} at end of interval (= t_{g} +
- Δt_{g}). Check conjectured value of T_{g} in step 2 and correct if 4 necessary
- necessary. Compute C_0 and C_1 with the aid of Equations 55 and 56 at $f = f_0 + \Delta f$ and at T_o from step 4. Knowing C_0, C_1, h, k , t_o (from 3), R, and t_R , compute the value of t_m with aid of Figures 2 and 3. If the average of t_m at the beginning of the interval and t_m^* at the end of the interval equals the assumed value of an average t_{max} in step 2, the operation is completed, and computational steps starting at I are repeated for the next Δf . If the average is not that assumed, a new guess of t_m must be made in step 2. 5.

IX. Previous steps lead to estimated values of t_m and t_o , rate of heat release, and radial heat transfer rate as a function of the fraction conversion f. It is of greater interest to relate these to the length of catalyst bed, l. This may be done by graphically integrating Equation 51.

SAMPLE CALCULATION

Problem. On the basis of the assumptions which follow, compute the mean and maximum solids temperatures, the gas temperature, the fraction conversion, and the radial rate of heat flow through the catalyst periphery as a function of bed length.

Assumptions. The quantities which are design variables are marked with an asterisk *.

CATALYST BED:

- *Length = 3 ft. *Diameter = 3 in.

 - *Diameter of packing = 0.0167 ft. (Tyler mesh 7-8) Void space = 40%
- *Outside bed temperature = 360° C. (boiling mercury bath) Maximum allowable temperature in bed = 440° C. (80° rise) *Over-all space velocity = 5000 (cu. ft. inlet gas at S. T. P.)/
- (hr.)(cu. ft. catalyst bed) Av. thermal conductivity of catalyst and support at bed conditions = 0.001 C. h. u./(ft.)(sec.)(°C.) = 3.6 B. t. u./ (hr.)(ft.)(°F.)

GAS PROPERTIES AT BED CONDITIONS: Specific heat $C_p = 0.33$ C. h. u./(lb.)(° C.) Viscosity $\mu = 0.018$ centipoise Prandtl group $= C_p \mu/k = 0.8$ Molecular weight $M_2 = 30$



Figure 4. Thin Section Sliced from a Slab-Shaped Catalyst Bed

REACTION:

Heat of reaction = 28,000 C. h. u./pound mol. (exothermic) Energy of activation = 21,000 C. h. u./pound mol. Kinetically second order, and of the general form

 $A + B \rightarrow C + D$

Reaction rate constant $k' = 3.9 \times 10^{10} e^{-E/R_1 T}$

- REACTION CONDITIONS IN BED: Feed *1. 360° C. at bed entrance *2. Stoichiometric proportions = a moles each of A and B

 - *3. Inerts = 0%Pressure throughout bed is nearly constant and approximately equal to 1 atm.

Calculations. To evaluate the constants in the approximate equation $k' = \epsilon + mt_m$, plot the function k'against temperature, from $k' = k_0 e - E/R_1 T$, over the range desired. (A maximum temperature rise of 80° C. means an average temperature rise of approximately 50° C.) For greater precision in later calculations, define a new temperature scale, using the centigrade degree, but with a displaced zero point such that 0° S. on the new scale = 350° C.

Draw the best straight line through the curve from 10° to 60° S. The linear function becomes:

$$k' = 737 + 105.3 t_m$$

Similarly
$$C_1 = 426,200 \left(\frac{1-f}{T_g}\right)^2$$

CALCULATION OF h. According to Hougen, Gamson, and Thodos (2),

:101

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$$G = \frac{\overline{(\overline{SV})}(l_T)(M_1)}{(3600)(359)} = \frac{(5000)(3)(30)}{(3600)(359)} = 0.3485 \,\text{lb./(sec.)(sq. ft.)}$$

Modified Reynolds number $= \frac{D_p G}{\mu} = \frac{(0.0167)(0.3485)}{(0.018)(0.000672)} = 481.0$

From Figure 9 in reference 2:

$$j = 0.0847 = \frac{h'}{C_p G} \left(\frac{C_p \mu}{k}\right)^{3/3}$$

where h' =surface heat transfer coefficient

$$\bar{h}' = \frac{(0.0847)(0.33)(0.3485)}{(0.8)^{3/3}} = 0.0113$$

Also for $D_p = 0.0167$ ft. and voids = 40 per cent, the ratio of catalyst surface to catalyst volume = 216 sq. ft./cu. ft. = a. Therefore:

$$h = ah' = 2.440$$
 C. h. u./(sec.)(cu. ft.)(° C.)



Figure 5. Solution for Temperatures in Cross Section of Slab-Shaped Catalyst Bed for Positive Values of $(C_1 - h)/k$

CALCULATION OF C_0 AND C_1 . From Equations 55 and 56 calculate C_0 and C_1 as functions of f and T_{g} . Since $n_t = 2a$,

CALCULATION OF BED TEMPERATURES. At f = 0.00, $t_{g} = 10^{\circ}$ S. (360° C.) and $t_{R} = 10^{\circ}$ S. Substituting $T_{g} = 633^{\circ}$ K.:

$$C_{0} = \frac{Q\epsilon (1-f)^{2}}{4} \left(\frac{P}{RT_{g}}\right)^{2} = \frac{(28,000)(737)}{4} \left(\frac{1}{1.316}\right)^{2} \frac{(1-f)^{2}}{T_{g}^{2}}$$
$$C_{0} = 2,982,000 \left(\frac{1-f}{T_{g}}\right)^{2} (T_{g} \text{ must be expressed in } ^{\circ} \text{ K.})$$

 $C_1 = 426,200 \left(\frac{1-0}{633}\right)^2 = 1.046$ $C_0 = 2,982,000 \left(\frac{1-0}{633}\right)^2 = 7.45$

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Figure 6. Solution for Temperatures in Cross Section of Slab-Shaped Catalyst Bed for Negative Values of $(C_1 - h)/k$

 $n = C_0 + ht_g = 7.45 + (2.440)(10) = 31.85$ $p = C_1 - h = -1.376$ $t_R + \frac{n}{p} = 10 + \frac{31.85}{-1.376} = -13.16$

For precision it is advisable to use following alternate computation:

$$\left(t_{R} + \frac{n}{p}\right) = t_{R} + \frac{C_{0} + ht_{g}}{C_{1} - h} = t_{R} - t_{g} + \frac{C_{0} + C_{1}t_{g}}{C_{1} - h}$$
$$= 10 - 10 + \frac{7.45 + (1.064)(10)}{-1.376} = -13.14$$

$$R \sqrt{\frac{p}{k}} = \left(\frac{1.5 \text{ in.}}{12 \text{ in./ft.}}\right) \sqrt{\frac{-1.314 \frac{\text{C. h. u.}}{(\text{sec.})(\text{cu. ft.})(^{\circ} \text{ C.})}}{0.001 \frac{\text{C. h. u.}}{(\text{ft.})(\text{sec.})(^{\circ} \text{ C.})}}} = 4.63 i \text{ (dimensionless)}}$$

Since p is negative (hence $R\sqrt{p/k}$ is imaginary), use Figure 3 (dotted line) for mean temperature group:

$$\frac{t_m - t_R}{t_R + \frac{n}{p}} = -0.61$$

$$t_{m} - t_{R} = (-13.14)(-6.17) = 8.12$$

 $t_{m} = 18.12^{\circ} \text{ S}.$

Continue the calculations by taking an increment $\Delta f = 0.01$. From computational step VII,

$$\Delta t_{\sigma} = \frac{(\Delta f)(t_m - t_{\sigma})(T_{\sigma})^2_{\mathrm{av}}}{(1 - f_{\mathrm{av}})^2(k'_{\mathrm{av}})} \left[\left(\frac{n_i^2 R^3}{a A P^2} \right) \left(\frac{h}{C_p G} \right) \right]$$

Since $n_i = 2a$ and $G = n_i M_2/A$, if P is constant at 1 atmosphere,

$$\Delta t_{g} = \frac{(\Delta f)(t_{m} - t_{g})(T_{g})^{2} \mathbf{a}_{v}}{(1 - f_{av})^{2}(k'_{av})} \left[\frac{2h(359)^{2}}{C_{p}M_{2}(273)^{2}}\right]$$

The latter bracket is constant throughout the bed length and may be precomputed.

Since k'_{av} varies rapidly with temperature, it is necessary to estimate the value of T_m (absolute value of t_m) for the next cross section (at $f_2 = f_1 + \Delta f$). Estimate $t_m = 27.5^{\circ}$ S. and $t_q = 19.0^{\circ}$ S.; then $t_{max} = 22.8^{\circ}$ S. and $t_{max} = 14.7^{\circ}$ S. or 637.7° K. From the plot of Equation 2, $k'_{av} = 3050$. Thus,

$$\Delta t_{\varphi} = \frac{(0.01)(18.12 - 10.00)(637.7)^2}{\left(1.00 - \frac{.01}{2}\right)^2 (3050)} \left[\frac{(2)(2.440)(359)^2}{(0.33)(30)(273)^2}\right]$$

Therefore t_q at $f = 0.01 = 10.00 + 9.40 = 19.40^{\circ}$ S., and the assumption of t_q checks.

In computations of the above type special care must be taken to use small values of the computational interval Δf when the curvature of t vs. f is sharp (large second derivative).

Now, at f = 0.01, $C_0 = 7.09$, $C_1 = 1.012$, and p = -1.428,

$$t_{R} + \frac{n}{p} = 10 - 19.40 + \frac{7.09 + (1.012)(19.40)}{-1.428} = 28.09$$
$$R \sqrt{\frac{p}{k}} = \frac{1.5}{12} \sqrt{\frac{-1.428}{0.001}} = 4.73$$

From Figure 3,

$$\frac{k_m - t_R}{k_R + \frac{n}{p}} = -0.622; \quad t_m = 27.46$$



Figure 7. Solution for Temperature in Cylindrical Catalyst-Bed Cross Section on Rectangular Coordinates for Positive and Negative Values of $(C_1 - h)/k$, with r/R as Parameter

The assumption of t_m checks. If it had not, a recalculation of Δt_{σ} from f = 0.00 to f = 0.01 would have had to be made as well as the recalculation of the conditions in the cross section at f = 0.01.

Repeat the above procedures, letting $\Delta f = 0.02$. Assume t_m and t_o for f = 0.03 and proceed. A summary of the results of the calculation of this and subsequent steps is given in Table I.

CALCULATION OF l as a Function of f. From Equation 51:

$$\frac{df}{Adl} = \frac{k'a(1-f)^2}{n_l^2} \frac{P^2}{R_1 T_{\bullet}}$$

Since $n_t = 2a$, $R_1 = 359/273$, and P = 1 atmosphere,

$$\frac{df}{Adl} = \frac{k'(1-f)^2(273)^2}{4aT_g^2(359)^2}$$

$$Al = \int_0^f \frac{4aT_g^2(359)^2 df}{k'(1-f)^2(273)^2}$$

All data are now known except l. Integrate graphically by plotting $4aT_0^2$. $(359)^2/k'(1 - f)^2(273)^2$ against f, take cumulative areas under the curve from 0 to several values of f, and thus obtain Al. Plot these values of l against f, pass a smooth curve, and thus obtain l for any value of f. Now all computed results may be referred to the length position in the bed instead of the f position.

Heat Released through Periphery of Catalyst Bed. The method of computation is described in computational steps II, IV, V, and VI. At f = 0.00, the rate of heat release per volume per second is:

 $C_0 + C_1 t_m = 7.45 + (1.064)(18.12) =$ 26.7 $\frac{\text{C. h. u.}}{(\text{sec.})(\text{cu. ft.})}$

TABLE	I.	SUMMARY	OF	A	Complete	CALCULATION
-------	----	---------	----	---	----------	-------------

								$t_m - t_R$						
ſ	• ^{<i>T_g</i>, K.}	C ₀	C_1	° S.a	p = h $C_1 - h$	$l_R + \frac{n}{p}$	$R\sqrt{\frac{p}{k}}$	$\iota_R + \frac{n}{p}$	$t_m - t_R$	° S.a	tmax. S.a	Δt_g	Length l. Ft.	Radial Heat Flowb
0.00 0.01 0.03	633.0 642.3 657.3	7.45 7.09 6.49	1.064 1.012 0.928	$10 \\ 19.40 \\ 34.30$	1.376 1.428 1.512	$\begin{array}{r} 13.14 \\ 28.09 \\ 49.62 \end{array}$	4.63 4.73 4.86	0.617 0.622 0.632	$8.12 \\ 17.46 \\ 31.37$	18.12 27.46 41.37	22.47 36.70 57.45	9.40 15.00 10.90	0 0.070 0.150	1,560 3,420 6,220
0.05 0.07 0.10	668.2 675.8 683.3	$\begin{array}{r} 6.04 \\ 5.65 \\ 5.18 \end{array}$	0.862 0.807 0.739	45.20 52.80 60.26	1.578 1.633 1.701	63.70 72.35 79.48	$ \begin{array}{r} 4.97 \\ 5.06 \\ 5.16 \end{array} $	$0.639 \\ 0.645 \\ 0.651$	$40.70 \\ 46.63 \\ 51.68$	$50.70 \\ 56.63 \\ 61.68$	71.35 79.85 87.00	7.60 7.46 1.86	$0.215 \\ 0.280 \\ 0.370$	8,170 9,450 10,650
$\begin{array}{c} 0.12 \\ 0.13 \\ 0.14 \end{array}$	685.1 685.2 685.1	4.92 4.81 4.70	0.703 0.687 0.671	$\begin{array}{c} 62.12 \\ 62.21 \\ 62.06 \end{array}$	$1.737 \\ 1.753 \\ 1.769$	80.04 79.31 78.29	$5.22 \\ 5.24 \\ 5.26$	$\begin{array}{c} 0.653 \\ 0.655 \\ 0.657 \end{array}$	$52.25 \\ 52.00 \\ 51.50$	$62.25 \\ 62.00 \\ 61.50$	87.70 87.00 86.10	$ \begin{array}{r} 0.09 \\ - 0.15 \\ - 0.41 \end{array} $	0.435 0.470 0.500	10,870 10,800 10,640
0.15 0.17 0.20	684.7 683.2 678.9	4.60 4.41 4.14	$0.657 \\ 0.630 \\ 0.591$	$ \begin{array}{r} 61.65 \\ 60.19 \\ 55.89 \end{array} $	$1.783 \\ 1.810 \\ 1.849$	$\begin{array}{r} 76.93 \\ 73.57 \\ 66.02 \end{array}$	5.28 5.32 5.38	$\begin{array}{c} 0.659 \\ 0.660 \\ 0.662 \end{array}$	$50.70 \\ 48.55 \\ 43.70$	60.70 58.55 53.70	84.85 81.60 64.30	-1.46 -4.30 -12.98	$0.530 \\ 0.600 \\ 0.730$	10,520 10,180 9,260
0.25 0.30 0.35	665.9 653.8 647.9	3.79 3.42 3.01	$0.541 \\ 0.489 \\ 0.429$	$\begin{array}{r} {\bf 42.91} \\ {\bf 30.78} \\ {\bf 24.91} \end{array}$	1.899 1.951 2.011	$\begin{array}{r} \textbf{47.12} \\ \textbf{30.26} \\ \textbf{21.72} \end{array}$	$5.45 \\ 5.52 \\ 5.61$	0.668 0.672 0.677	$31.47 \\ 20.28 \\ 14.71$	41.47 30.28 24.71	55.90 39.50 31.25	-12.13 - 5.87 - 3.01	1.00 1.405 1.945	6,630 4,380 3,170
0.40 0.45	644.9 633.4	$\begin{array}{c} 2.58 \\ 2.21 \end{array}$	$\begin{array}{c} 0.369 \\ 0.315 \end{array}$	$\begin{array}{r} 21.90 \\ 16.39 \end{array}$	$2.071 \\ 2.125$	17.05 9.68	$5.69 \\ 5.77$	$\begin{array}{c} 0.681 \\ 0.686 \end{array}$	$\begin{array}{r} 11.61 \\ 6.64 \end{array}$	$\begin{array}{r} 21.61 \\ 16.64 \end{array}$	26.68 19.48	- 5.51	2.650 3.575	2,530
° 0° S.	= 350° C). b C. 1	h. u./(hr.)((sq. ft.).										





The rate of heat transfer from solid to the gas is:

$$h(t_m - t_g) = 2.44 (18.12 - 10) = 19.8 \frac{\text{C. h. u.}}{(\text{sec.})(\text{sq. ft.})}$$

The rate of heat loss by radial conduction is:

$$26.7 - 19.8 = 6.9 \frac{C_* h_* u_*}{(sec_*)(cu_* ft_*)}$$

The rate of heat transfer through the catalyst wall is:

$$\frac{C_0 + C_1 t_m - h(t_m - t_0)]\Delta V}{2\pi R \Delta l} = \frac{C_0 + C_1 t_m - h(t_m - t_0)R}{2} = \frac{(6.9)(1.5)}{(2)(12)} = 0.431 \frac{\text{C. h. u.}}{(\text{sec.})(\text{sq. ft.})} = 1550 \frac{\text{C. h. u.}}{(\text{hr.})(\text{sq. ft.})}$$

The major variables computed in the sample calculation are presented in Figure 9. The maxima curves obtained conform to the expected type of temperature distribution in a catalyst bed.

The sample calculation provides a rough check upon the validity of the third assumption in the thermal derivations; i. e., heat conduction is in a radial rather than lengthwise direction. In the region of the maximum temperature the radial temperature gradient is approximately ten times that along the bed, and the assumption is therefore justified as a first approximation.

The results of the sample computations in this paper have been compared with those obtained by Damkoehler's approximate equation (citation 1, paragraph 66γ , Equation C19). For a maximum temperature rise of 78° C., Damkoehler's equation leads to an estimated catalyst tube diameter of 1.5 inches. The design method in this paper would predict a diameter of 3.0 inches for the same temperature rise and same auxiliary operating and design assumptions.

NOMENCLATURE

Dimensional Units

Length = LMass = MQuantity of heat = HTime = Θ Temperature = d

- = moles of reactant A entering bed per unit of time, (M/Θ)
- = cross-section area of catalyst bed, (L^2) = lateral distance from center of thin-slab catalyst bed to act at distance from center of thin-slab catalyst bed to any point, (L)= ${}^{1}/{\epsilon}$ width of thin-slab catalyst bed, (L)= concentration of gas components, (M/L^{3}) = intercept of straight-line variation of q/V_{cat} with t, $(H/\Theta L^{3})$

- $C_{e}, C_{e} =$ concentration of gas components A and C at any point in the bed, (M/L^{3}) $C_{1} =$ slope of straight line variation of q/V_{eat} with $t, (H/\Theta L^{3}a)$ $C_{p} =$ heat capacity of gases at bed conditions, (H/Md)
- C_p = heat capacity of gases at bed conditions, (u, v, u, v) C.h.u. = centigrade heat unit, heat required to raise temp. of 1 lb water 1° C.

 - water 1° C. = basis of natural logarithms = 2.718 = energy of activation, (H/M)= fraction conversion of reactant A at any cross section = mass velocity of gas, $(M/\Theta L^2)$ = volumetric film heat transfer coefficient, $(H/\Theta L^3d)$ = surface film heat transfer coefficient $(H/\Theta L^3d)$

Figure 8. Solution for Temperatures in Cylindrical Catalyst-Bed Cross Section for Positive and <u>Negative</u> Values of $(C_1 - h)/k$, with $R \sqrt{(C_1 - h)/k}$ as Parameter

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Figure 9. Computed Variations of Mean and Maximum Catalyst Temperatures, Mean Gas Temperature, Radial Heat Flow Rate, and Fraction Conversion at Different Length Positions in a 3-Inch Diameter Catalyst Bed

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 R_1

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- $I_0(x)$ = Bessel function, first kind, zero order, imaginary argument
- = Bessel function, first kind, first order, imaginary argu- $I_1(x)$ ment
- $I_2(x)$ = Bessel function, first kind, second order, imaginary argument
- $J_0(x) \\ J_1(x) \\ J_2(x)$
- Bessel function, first kind, zero order
 Bessel function, first kind, first order
 Bessel function, first kind, second order
- = thermal conductivity of catalyst under bed conditions
- $(H/\Theta Ld)$ k' = reaction rate coefficient, dependent on temperature.
 - Dimensions depend upon order of reaction; for second order $(L^3/M\Theta)$
 - = reaction rate constant independent of temperature. Dimensions depend upon order of reaction; for second order $(L^3/M\Theta)$
 - = length along catalyst bed in direction of gas flow, (L)
- 1T = total length of catalyst bed, (L)m
- = slope of straight-line variation of k' with t, $(L^3/M\Theta d$ for second-order reaction) = integration constant
- M_1 Mz = molecular weight
- n n_a, n_c -
- $C_0 + ht_o$ moles A and C passing any point per unit time, (M/Θ) total moles gas passing any point per unit time, (M/Θ) = $\frac{n_t}{N}$ = integration constant • h
- C. $p \\ P$
- = absolute pressure of gas at any point, (M/L^{2})

- = rate of heat release, (H/Θ) = heat of reaction, (H/M)
- = radial distance to any point in cylindrical catalyst cross section, (L)= outer radius of cylindrical catalyst bed, (L)= gas law constant, appropriate units, (L/d)

- SV
- space velocity, $(1/\Theta)$ 350° C., an arbitrary temperature scale for computa-tional purposes 0° S. =
 - = wall temperature of thin-slab catalyst bed, (d)
 - = temperature of solid catalyst at center of bed, (d)= temperature of solid catalyst, (d)
 - - = temperature of cylindrical catalyst bed at wall, (d)
 - mean temperature of solid catalyst at any cross section of bed, (d)
 - = temperature of gas stream at any cross section in catalyst bed, (d)
- absolute temperature of gas at any cross section in catalyst bed, (d)
 volume of catalyst, (L³)
 total volume of gas flowing per unit time at any point in catalyst bed, (L³/Θ) T.
- V_{cat}. V_t

$$= R \sqrt{\frac{C_1 - h}{k}}$$
$$= r/R$$
$$= \frac{t - t_R}{t_R + \frac{C_0 + ht_g}{C_1 - h}}$$

For a cylinder (dimensionless, use consistent units)

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$$= B \sqrt{\frac{C_1 - h}{k}}$$

= b/B
= $\frac{t - t_B}{t_B + \frac{C_0 + ht_g}{C_1 - h}}$ For a slab (dimensionless, use consistent units)

- $Y_{0}(x)$ = Bessel function, second kind, zero order $Y_{1}(x)$ = Bessel function, second kind, first order β = height of thin slab catalyst bed, (L)

 - = intercept of straight-line variation of k' with t, $(L^{1}/M\Theta)$ for second-order reaction)
- A time, (Θ)

= 3.1416

σ

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- $= t t_g$ = viscosity, $(M/L\Theta)$

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Vapor-Phase Esterification Rates

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THE esterification reaction between organic acids and alcohols has been studied quantitatively in the liquid phase from the standpoint of equilibria and of reaction rates. The reaction in the vapor phase has not been investigated so thoroughly, however. The equilibrium constants for the vapor-phase reaction have been accurately determined (2), and various catalysts have been employed; silica gel apparently has been the most successful (1, 2, 5, 6). No data are available to correlate the effect of mass velocity of the gases and the effect of temperature on the reaction rate. In this investigation the esterification reaction between ethyl alcohol and acetic acid in the vapor phase was studied in a flow system, operated at atmospheric pressure, and employing a silica gel catalyst.

ESTERIFICATION UNIT

The apparatus consisted, in general, of a calibrated delivery system for the reactants, a proportioning pump, vaporizers,

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> The esterification rate of acetic acid with ethyl alcohol in the vapor phase was investigated in a flow system using a silica gel catalyst. The mass velocity of the vapor did not affect the constants in the rate equations representing conditions at specific locations in the bed. It appears then that mass transfer in the vapor phase was not significant.

> Furthermore, with temperature increase, these constants were augmented linearly, which indicated that the surface reaction

reaction chamber, Dowtherm heating system, condenser, and control panel (Figure 1). The calibrated delivery system for acetic acid and for ethyl alcohol was constructed of glass. All the other units in the reaction system were constructed of KA2SMo stainless steel.

The reactants were pumped separately from the calibrated glass burets by the proportioning pump in order to adjust the pump to the desired flow rate. After the rate was set, the reactants were pumped from storage carboys to avoid repeated refill-ing of the flasks which supplied the burets. Calcium chloride tubes were connected to all air inlets of the feed system so that only dry air came in contact with the hygroscopic reactants.

only dry air came in contact with the hygroscopic reactants. A separate vaporizer was built for each reactant from a $1^{1}/_{e^{-1}}$ inch stainless steel nipple, 18 inches long. These nipples were capped on the ends, and were cast in parallel into two aluminum blocks which were heated separately by chromel resistances. The purpose of these heated aluminum blocks was to vaporize the liquids at an initial, controlled, constant temperature. In addition, a second similarly controlled region was provided at the discharge end of each vaporizer to control the degree of superaddition, a second similarly controlled region was provided at the discharge end of each vaporizer to control the degree of super-heat. The aluminum blocks acted as constant-temperature reservoirs of heat, preventing slow vaporization of the reactants and consequent collection of liquid in pools in the vaporizers. The superheating section was necessary to obtain close control of the temperature of the reactants entering the mean themper the temperature of the reactants entering the reaction chamber.

rate was not a controlling factor. The experimental evidence shows that the rate of vapor-phase esterification is controlled by the rate of mass transfer or diffusion through a condensed phase present in the capillaries of the silica gel. The temperature effect is in agreement with this observation, as is the magnitude of the activation energy. The second-order reaction rate ordinarily encountered in liquidphase esterification was negligible in the catalyzed reaction.



Figure 1. Vapor-Phase Esterification Unit

In addition, an electrically heated box was placed over the tubes which carried the reactants from the superheater to the reaction chamber, and the degree of superheat was finally controlled by adjusting the temperature in this box. The temperatures of all units in the vaporizing and superheating section were controlled by thermostats consisting of silica rods set in holes drilled in the aluminum blocks or, in the case of the box, set in a brass tube closed at one end. The difference in coefficients of expansion produced a shift in the relative positions of the terminal points of the silica and of the metal tube or block with change in temperature. This motion actuated a microswitch which, in turn, moved a mercury swing relay that carried the electric current to the heating elements.

A stainless steel pipe, 2 inches in diameter and 6 feet in length, was the reaction chamber. Flanges were used to seal the ends, and the catalyst was supported in the tube by a perforated plate resting on the lower flange. To maintain a constant temperature over the entire length of the reaction chamber, a jacket was built around the stainless steel pipe. Dowtherm was circulated upward through this jacket and through a system containing an immersion heater and a silica rod thermostat. By this means it was possible to maintain the temperature of the entire catalyst bed constant within 1° C. from top to bottom. Thermocouples for temperature readings were placed at the top and bottom of the catalyst bed and on the outside wall of the jacket equidistant from the ends.

The vapors from the reaction chamber were condensed and cooled rapidly in a condenser filled with ice and water, so that no further reaction would take place. The liquid product was collected continuously in a large flask, and samples were withdrawn for analysis by means of a side arm above the flask. To calculate the reaction rate and the equilibrium constant

To calculate the reaction rate and the equilibrium constant for the four-component system acetic acid-ethyl alcohol-ethyl acetate-water, the following information was necessary: composition of reactants introduced into reaction chamber, rate of introduction of reactants into reaction chamber, composition of product leaving the system. The composition of the reactants was determined by density measurements with a calibrated 100-cc. pycnometer. All reactants used were over 99.50 per cent pure, the impurity being water. The composition of the product was determined by titrating samples of the liquid product at 0° C. for the free acid with standard sodium hydroxide containing barium hydroxide. A 1-cc. pipet was used to withdraw an exact portion of the sample for titration, and also to withdraw identical portions which were weighed in a glass-stoppered weighing bottle. Care was taken to bring the pipet to 0° C. before withdrawing these portions.

The unit was operated continuously for each run until periodic sampling of the product gave the same titration for at least three consecutive samples. After completion of a run the reaction chamber was flushed with nitrogen and a positive pressure of nitrogen was maintained in the reaction chamber until the unit had cooled to room temperature. This was done to prevent air from entering the system and oxidizing any alcohol which might have remained on the catalyst.

To determine whether the wall of the stainless steel catalyst chamber had any catalytic effect on the reaction, a run was made with no catalyst in the chamber. The product showed no measurable conversion of the reactants beyond experimental error.

Since no data on equilibrium were available at temperatures above 200° C., equilibrium runs were also made at 230° and 270° C. These were carried out by starting with a mixture of one mole of acetic acid to one mole of ethyl alcohol. The pumping system was first flushed with the mixture. Using only one feed line, the mixture was then pumped through the reaction chamber at a rate as slow as possible. Careful analyses of the product were made, and when no changes in analysis were noted, collection of the product was begun. After all the initial mixture had passed through the reaction chamber, the product was sent back through the system and the process repeated. The recycling of the product was noted. The cata

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RESULTS WITH VARIOUS CATALYSTS

The catalyst was the standard silica gel manufactured by the Davison Chemical Company; four lots were prepared from it. The first was a mixed catalyst in which the particle sizes ranged from No. 3 to No. 8 Tyler Standard Screen (2.4 to 6.7 mm.). The total volume occupied by this catalyst was 3520 cc., of which 51 per cent was void space. The other three catalysts were carefully screened to definite Tyler Standard Screen mesh sizes: (a) through No. 3, held on No. 4 (4.7 to 6.7 mm. in diameter), (b) through No. 4, held on No. 6 (3.3 to 4.7 mm.), and (c) through No. 6, held on No. 8 (2.36 to 3.3 mm.).

With the mixed catalyst, four sets of runs were made respectively at 150°, 190°, 230°, and 270° C. using in each case a constant mole ratio of reactants of 1:1, but with varying mass velocities. The results of these tests are shown in Figure 2. It was not possible to investigate temperatures higher than 270° C. because pyrolysis of the alcohol is known to begin at 300°. The first series of runs was made at 150°, and the results obtained are shown as curve A. The catalyst for this series had not been used previously, and the data for curve A therefore represent the initial activity of the catalyst. Using the same catalyst, similar series of runs were made at successively higher temperatures. After completion of the runs at 270° C., it was desirable to make sure that the catalyst activity had remained constant, and a check run was made at 150° C. (run 38). The results obtained lay below line A and indicated that the activity of the catalyst had decreased. An attempt was then made to reactivate the gel by heating it to 300° C. for 15 hours while air was passed through. After this treatment, a second identical check run at 150° C. was made (run 39); the results duplicated those of run 38 and showed that the decrease in activity of the gel was permanent. Following this a run was made at 190° C. (run 40) to determine whether the data previously obtained at this temperature could be reproduced. The results coincided with the data originally obtained at 190° C. It was concluded, therefore, that the catalyst had reached constant activity at some time after the first series of runs at 150° C. The data for 150° C. were then re-established by making two further runs at that temperature, which with the check runs previ-

ously mentioned, constitute the data for curve B. The data on B were used in all of the correlations cited. Complete data for the mixed catalyst are shown in Table I.

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The runs with the screened catalyst were conducted in each case at 230° C. with a 1:1 mole ratio of reactants. For each set of runs, 2500 grams of catalyst were used and the volume occupied was 3380 cc. for each of the screened catalysts. The data are presented in Table II.

CORRELATION OF DATA

Since the conversion of ethyl alcohol and acetic acid to ethyl acetate and water does not proceed to completion, it was necessary to know the equilibrium constants for this reaction at all temperatures investigated, in order to make an analysis of the data on reaction rates. The equilibrium constant based on fugacities or activities can be expressed as follows:

$$I_a = \frac{k_1}{k_2} = \frac{f_{\text{ElA}e} \times f_{\text{H}_2\text{O}}}{f_{\text{H}Ae} \times f_{\text{ElOH}}}$$
(1)

here
$$K_{\star} = \text{equilibrium constant}$$

$$k_1 =$$
 velocity constant of forward reaction

 $k_{a} =$ velocity constant of reverse reaction

= fugacity of any specified component of system

It has been shown (2) that the partial pressures of the ester, water, and alcohol can be considered equal to their fugacities at pressures less than one atmosphere. But for acetic acid vapor such simplification is not tenable, because even at 300° C. the association of the acid is significant and must be considered. Furthermore, since the equilibrium constants were determined at one atmosphere total pressure, the mole fractions of the components other than acetic acid may be substituted for their respective partial pressures in the equation. Thus Equation 1 becomes:

$$K_{a} = \frac{N_{\text{EtAe}} \times N_{\text{H} \otimes 0}}{f_{\text{HAe}} \times N_{\text{EtOH}}}$$
(2)

where N = mole fraction of any individual component

Charts were developed from data taken from the International Critical Tables to show the relation of the partial pressure of acetic acid to its fugacity at various temperatures. These charts were used in all calculations.

Essex and Clark (2) determined values for K_a experimentally up to 200° C., and their values were used at 150° and 190° C. The data of runs 55 and 56 obtained as outlined previously were used to calculate the equilibrium constants at 230° and 270° C. The values of K_a and the corresponding values of the equilibrium degree of conversion using a 1:1 mole ratio of reactants follow:

Temp., ° C.	K_a	of Conversion
150	33.62 caled. (2)	0.846
190	18.37 caled. (2)	0.807
230	15.60 exptl.	0.796
270	11.20 exptl.	0.768



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Figure 3. Coefficient of Mass Transfer vs. Mass Velocity

The esterification reaction in the liquid phase is a classical example of a second-order reversible reaction, and there is no evidence to indicate that the vapor-phase catalytic reaction proceeds in any different fashion. If the rate-controlling step in the heterogeneous vapor-phase reaction is the actual rate of reaction, the experimental data should fit the second-order reversible reaction equation developed for a flow process, and a constant for the reaction rate should be obtained which is unaffected by changes in space velocity. Equation 3 is the differential form of the equation for a second-order reversible reaction:

$$- dA/dt = k_1 AB - k_2 CD \tag{3}$$

where ABCD= fugacity of acetic acid = fugacity of ethyl alcohol

- = fugacity of water fugacity of ethyl acetate
- = time

This equation was expanded for application to a flow process and integrated graphically, using the data obtained at 230° C. with the mixed catalyst. A value for k_1 was found which varied significantly with mass velocity and indicated that the rate-controlling step in the esterification was not the actual rate of reaction. Supporting evidence for this conclusion is found in the observations that the catalyst activity after its initial small decrease remained unchanged throughout the investigation, and that during experimental runs as much as 12 hours of operation were required to reach constant conversion. These phenomena point toward mass transfer as the controlling factor in the rate of reaction rather than limitation by chemical rate of combination.

If the velocity of reaction at the catalytic surface is large enough, the rate of formation of the product may be controlled principally by the rate of diffusion of the reactants from the gas stream to the catalyst surface or the rate of diffusion of the

products from the catalyst surface to the gas stream. Where the van der Waals type of condensation on a catalyst surface is possible, it can logically be concluded not only that a gas film resistance exists, but also that a condensed phase may be present in the capillaries of the gel and that diffusion through it may control the formation of product.

Maxwell and Stefan (8) derived an expression for the diffusion of two components of a binary gas mixture where the net movement of the mixture is zero. This may be applied to a catalytic reaction, such as the esterification reaction, since no change in volume occurs and the moles of reactants diffusing to the catalytic surface are equal to the moles of product diffusing from the surface into the gas stream. Since four components were actually present, the equation is not rigorously applicable to the esterification reaction, but is a sufficiently good approximation and was used because of the complexity of an exact equation for the system:

$$dN_a/dA = (D_m/B_f) (y_{ai} - y_{ai}) P$$
(4)

- where N_a moles of component a diffusing past any point in film per unit time = A
 - area of cross section for diffusion process measured at right angles to direction of diffusion

$$B_{\rm m} = \text{film thickness}$$

mole fractions of component a at terminal points of Yais Yas = film P = total pressure

The equation is valid for both reactants and products if due consideration is given to the sign of dN_a . In engineering calculations this equation is usually expressed in terms of a net transfer coefficient, grouping both terms D_m and B_f into a single term K, called the "coefficient of mass transfer".

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		TABL	EI. D	ATA FOR M	IXED CATA	LYST		
Run No. 4 ⁶ 7 ⁶ 9 ⁶ 10 ⁶ 11 ⁶ 12 ⁶ 13 ⁶ 38 39 52	Tem- perature, ° C. 150 150 150 150 150 150 150 150 150 150	Reaet Moles HAc 0.885 4.080 5.77 10.62 2.455 0.854 3.362 1.377 1.061 5.81 5.81 5.82 1.665 11.86	ants, /Hr. EtOH 0.938 4.048 5.70 10.49 2.42 0.844 3.34 1.390 1.100 5.71 5.76 1.650 11 98	$\begin{array}{c} H_1 O \text{ in } \\ Reactants, \\ Moles/H, \\ 0.034 \\ 0.048 \\ 0.021 \\ 0.007 \\ 0.028 \\ 0.020 \\ 0.015 \\ 0.048 \\ 0.048 \\ 0.048 \\ 0.048 \\ 0.018 \\ 0.132 \end{array}$	HAc in Product, Molee/Hr. 0.242 2.820 4.53 9.36 1.423 0.216 2.235 0.321 4.75 0.855 10.83	EtAc Product, Moles/Hr. 0.643 1.160 1.24 1.26 1.03 0.683 1.13 0.865 0.740 1.06 1.07 0.800	K Gram moles Hr., liter, atm.	
17 19 20 21 22 23 40	190 190 190 190 190 190 190	13.20 3.92 16.70 2.52 1.722 7.40 5.79	13.00 3.95 16.92 2.47 1.70 7.33 5.70	$\begin{array}{c} 0.168\\ 0.056\\ 0.241\\ 0.037\\ 0.025\\ 0.106\\ 0.048 \end{array}$	9.79 1.477 13.20 7.04 0.369 4.485 3.04	3.410 2.443 3.50 1.817 1.353 2.92 2.75	3.46 3.92 3.48 3.78 4.30 3.38 3.46	
25 26 27 28 29 30 31	230 230 230 230 230 230 230 230	$\begin{array}{r} 7.34 \\ 10.02 \\ 14.57 \\ 18.84 \\ 5.38 \\ 3.525 \\ 2.455 \end{array}$	7.24 10.05 14.80 18.78 5.43 3.52 2.465	$\begin{array}{c} 0.065\\ 0.094\\ 0.137\\ 0.176\\ 0.051\\ 0.033\\ 0.023\\ \end{array}$	3.05 5.20 9.30 13.25 1.798 0.892 0.543	4.29 4.82 5.27 5.59 3.59 2.63 1.91	$\begin{array}{c} 6.00 \\ 5.81 \\ 5.63 \\ 5.49 \\ 6.09 \\ 6.15 \\ 6.09 \end{array}$	
34 35 36	270 270 270	9.95 14.58 17.60	9.85 14.58 17.70	0.093 0.137 0.165	4.25 8.09 10.72	5.70 6.49 6.88	8.25 7.65 7.61	
55 b 56 b a b	230 270 Made before Equilibrium	25.10 94.11 the cataly runs.	24.93 94.04 rat had re	0.264 1.00 ached final a	5.23 21.95 etivity.	19.87 72.15		

If the film is considered to have a definite thickness, and a sharp change in concentration occurs at the film and the main gas stream interface, y_{ai} is equal to the concentration of component *a* in the main gas stream. Also, in the case of a catalytic reaction where such reaction takes place at the catalyst surface, and the reaction reaches an equilibrium, y_{ai} approaches the concentration of component *a* at equilibrium. At one atmosphere total pressure, the pressure term equals unity. Rewriting,

$$dN_a/dA = K (y_{ag} - y_{as}) \tag{5}$$

6)

where y_{ac} = mole fraction of component *a* in gas stream y_{ac} = mole fraction of *a* at equilibrium

In the application of the experimental data to Equation 5, all calculations were based on acetic acid as the diffusing component, and fugacities were used in place of mole fractions. Hence dN_a/dA equals the moles of acetic acid diffusing to the catalyst per unit time per unit area of transfer surface. This

quantity is numerically equal to the moles of ethyl acetate diffusing from the catalyst surface to the gas stream, which is equal to the moles of ethyl acetate produced per unit time per unit area. The area of transfer may be taken as the area of the catalyst surface, which for any given catalyst is proportional to the volume of the catalyst. Integration of Equation 5 over the volume of the catalyst gives:

$$\frac{N_{P_1}}{N_{P_1}} \int \frac{dN_P}{y_{ag} - y_{as}} = K V_R \tag{6}$$

where N_P = moles of product formed per hour

 V_B = volume of reaction chamber Subscripts 1 and 2 refer to terminal points of reaction chamber Because of the cumbersome nature of the graphical integrations of Equation 6, a solution of the equation based on terminal conditions in the chamber was attempted. An average driving force was calculated for the entire chamber using the logarithmic mean averages for $(y_{ag} - y_{ae})$ determined from the end conditions. Expressed mathematically,

$$\frac{N_p}{(y_{ag} - y_{as})_{lm}} = K V_R \tag{7}$$

Very close agreement was obtained by Equation 7 with several values of K calculated by graphical integration, and Equation 7 was therefore used to correlate the entire experimental data. Figure 3 shows the relation of the mass transfer coefficient to mass velocity for the mixed catalyst at various temperatures, and for a constant temperature of 230° C. with catalysts of different sizes.

MASS TRANSFER COEFFICIENT

At 150° C. with the mixed catalyst, a value of K was found which was unaffected by changes in mass velocity. At higher temperatures K decreased slightly with increase in mass velocity but reached a The reached a

constant value at the higher rates of flow. The values obtained for K with the catalyst of different sizes showed the same tendency to reach a constant value.

The fact that the mass transfer coefficient is not influenced by mass velocity at high rates of flow is significant. If the controlling resistance to diffusion were a gas film on the outside of the gel particles, the transfer coefficient would increase markedly with increase in mass velocity. The absence of any such effect shows that the rate of diffusion through such a gas film is not the controlling factor in the apparent reaction rate, but rather that the major resistance to diffusion is in either a gas phase or a condensed phase present in the capillaries of the catalyst. Because the temperatures of the investigation were below the pseudo critical temperatures of mixtures of the reaction system, and because of the highly porous structure of the catalyst, the assumption that the van der Waals type of condensation occurs is reasonable (7). The magnitude of this adsorption of reactants and products by silica gel is indicated by the fact that, after operation at

	TABLE I	I. DATA	FOR CA	TALYSTS OF	DIFFEREN	TT SIZE AT 2	230° C.
Run No. 59 60 61 62	Catalyst Mesh Size ^a 2	React Moles HAc 5.77 7.73 10.11 13.80	ants, s/Hr. 5.79 7.73 10.11 13.69	H:O in Reactants, Moles/Hr 0.074 0.100 0.130 0.18	HAc in Product, Moles/Hr. 2.19 3.68 5.72 8.98	EtAe Product, Moles/Hr. 3.58 4.05 4.39 4.82 5.22	<i>K</i> Gram moles Hr., liter, atm 5.77 5.40 5.18 5.18 5.18
63 65 66 67 68 69	1	18.62 5.79 7.77 10.25 13.77 18.81	18.55 5.96 7.83 10.39 13.76 18.95	0.24 0.10 0.13 0.16 0.21 0.30	13.29 1.99 3.18 5.09 8.06 12.50	3.80 4.59 5.16 5.71 6.31	6.78 6.92 6.75 6.60 6.75
74 75 76 77 78 4	3 Figure 3.	6.18 7.65 10.05 14.00 18.39	$\begin{array}{r} 6.18 \\ 7.68 \\ 10.05 \\ 14.10 \\ 18.53 \end{array}$	0.08 0.10 0.14 0.19 0.25	3.07 4.33 6.54 10.37 14.60	3.11 3.32 3.51 3.63 3.79	4.03 3.94 3.82 3.61 3.61

150° C., 161 cc. of condensed vapors were desorbed by 2500 grams of catalyst by continued heating of the catalyst at 300° C. in a stream of nitrogen.



Coefficient of Mass Transfer vs. Figure 4. Temperature

Since the thickness of a layer present in the capillaries would be independent of mass velocity, only the value of the diffusivity would affect the magnitude of the transfer coefficient. At higher mass velocities the value of the transfer coefficient tended to become constant as the mass velocity was increased. The value of diffusivity would be expected to show the same tendency. The diffusion equation used to correlate the experimental data was developed for point conditions in the catalyst bed, assuming a constant value of diffusivity. However, the Stokes-Einstein equation for diffusivity of liquids (4) predicts that the diffusivity is inversely proportional to the viscosity. At low mass velocities, high percentage conversion is achieved and the relative masses of the components of the system vary widely from top to bottom of the catalyst bed. Consequently, the viscosity and the diffusivity also vary. At higher rates of flow, the percentage conversion decreases and the diffusivity approaches constancy over the length of the bed, giving constant values for the mass transfer coefficient. The diffusivity of gases is independent of concentration as reported by Gilliland (3), and the assumption of a gas phase in the capillaries thus does not explain the deviations of the mass transfer coefficient with mass velocity.

Variation of transfer coefficient K at low mass velocities may also be augmented by experimental errors. At low mass velocities, where equilibrium conversion is approached at the lower end of the catalyst bed, the driving force for diffusion between the catalyst surface and the main gas stream is decreased, and any experimental error or error in the value of the degree of conversion at equilibrium destroys the accuracy of the logarithmic mean value of the driving force.

The relation between values of mass transfer coefficient Kand the temperature further supports the belief that the ratecontrolling step in the apparent rate of reaction is the rate of diffusion through a condensed phase. When mass transfer coefficient K, calculated from data at high mass velocities (after K had reached a constant value), was plotted against absolute temperature, a linear function was found to exist (Figure 4). Gilliland reports that variation of gas diffusivity with temperature is proportional to the 3/2 power of absolute temperature (3). If the actual reaction rate were the controlling factor, a much greater variation with temperature would be expected. However, the Stokes-Einstein equation predicts that, except for changes in viscosity of the system with temperature, a linear proportionality does exist between the diffusivity of liquids and the absolute temperature.

At the suggestion of Henry Eyring of Princeton University, the observed activation energy for diffusion was determined from the equation,

$$D_m = A \ e^{-B/RT} \tag{8}$$

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where $D_m = \text{diffusivity}$

= a constant A E = observed activation energy

gas constant R

== absolute temperature

Since transfer coefficient K is proportional to the diffusivity, values of ln K were plotted against 1/T, and values of Ewere obtained from the slope of the line at various operating temperatures (Figure 5). E was found to vary significantly with temperature:



Figure 5. Calculation of Observed Energy of Activation for Diffusion

The values obtained were of the correct order of magnitude for diffusion through liquids. The fact that E does vary with temperature also supports a diffusion hypothesis, since the activation energy of a chemical process is essentially independent of temperature over small temperature ranges.

ACKNOWLEDGMENT

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Catalysis in the Oxidation of LUBRICATING OIL

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The catalytic effect of iron, copper, and lead in the bulk and dissolved form on three oils broadly representative of those obtainable from Pennsylvania, Mid-continent, and California crudes has been studied in detail. It is concluded that the variations in catalytic susceptibilities of the oils, as well as the variations of catalytic activities of the metals with concentration, are so great that no specified catalyst can be used in labora-

THE "stability" of a lubricating oil may be classified, with other nebulous characteristics such as "oiliness", as a generally desired property the true meaning or requirements of which are but vaguely defined. It must be conceded, however, that a "stable" oil is one which does not break down in an engine to form sludge, corrode bearings, stick rings, or permit excessive wear. To define stability we must understand the underlying principles of all these phenomena.

The theory has been presented that, since almost all engine deposits contain relatively large amounts of oxygen and since bearings are corroded by acids produced by oxidation, stability of an oil toward oxygen is an essential requirement of a good engine lubricant. The authors believe this to be true; in an earlier report (14) they showed that oxidation stability of a lubricant is not achieved by removal of "unstable aromatics", but rather that it is a result of the presence of natural antioxidants which stabilize the relatively reactive hydrocarbons constituting the bulk of the oil. These findings are confirmed by many experimenters, among the most recent being Fenske and co-workers (11) and von Fuchs and Diamond (12). Before they are applied to refinery practice, it is well to appreciate the importance of factors external to the oil itself which may alter or modify the quantitative aspects of oil stability. Thus, while there can be no question that natural or synthetic antioxidants are needed to produce satisfactory lubricants, the actual amount or type required may be modified by the environment in which the oil is to be used. The effect of an engine on the oil must therefore be studied.

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The most important environmental factors affecting the oxidation stability of an oil in an engine are temperature and catalysis. The extreme range of temperatures encountered has led many investigators (2) to the conclusion that no laboratory test can satisfactorily measure the performance of an oil in an engine. This view is unduly pessimistic since,

tory oxidation tests unless correspondence with engines is first well established.

In addition, the catalytic effect of engines on oils was investigated. It was found that the oil insolubles (called "crankcase catalysts") which accumulate in engine lubricants are extremely active catalysts. This catalytic activity resides in the metallic components, particularly the halides of iron.

fortunately, the variation of chemical reactivity with temperature is subject to precise mathematical definition; many recent experimenters, such as Dornte and co-workers (6, 7, 8), have shown that mineral oils behave normally in this respect. Thus, fundamentally the effect of temperature on oxidation stability is understood. The effect of temperature on eracking, polymerization, condensation, and volatilization of lubricants or their oxidation products is, however, not well understood and requires further study.

When it first became desirable to have a laboratory test for oxidation stability, the only accelerating factor employed was temperature. Such widely accepted tests as the Indiana, Sligh, and British Air Ministry tests oxidize oils at high temperatures but are devoid of other accelerating factors. Within the past decade there has been a growing tendency to recognize that various metallic catalysts must also be used. Thus, practically all of the tests recently described employ catalysts in some form. The Indiana test has been modified by the addition of a coil of iron wire and then referred to as the Continental oxidation test (17), or by the use of copper. iron, and lead in a test described by Burk and co-workers (3). A further modification described as the stirring Indiana test uses iron and copper (13). In the work of Davis and coworkers (5) a modified Sligh apparatus is used in conjunction with various catalysts, particularly soluble iron salts. The McCoull test measures stability as well as corrosivity in the presence of iron and copper and copper-lead (15) bearings. The Underwood test employs soluble lead or iron catalysts. The possibility of using copper or iron alone is discussed by Evans (10). Many of these experimenters leave the test conditions sufficiently flexible so that several "engine" metals may be added if desired.

It is evident that a great many tests may be used to evaluate oxidation stability, each varying in the amount or type of catalyst used, the oxidation temperature employed, or in the method of contacting the oil with air or oxygen.

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Automatic Oxidation Apparatus

Many investigators have already made a study of the catalysis of oil oxidation by metals and soluble metal salts. Matthijsen (16) refers to approximately forty papers, a large number of which deal with the effect of catalysts; Downing and co-workers (9) give thirty references to such studies. Dornte, Fenske, Davis, and co-workers have reported extensive laboratory studies of the subject. The present paper is believed to be more comprehensive than those already published, since it includes a wider variety of oils, covers a greater range of catalyst concentration, and introduces new concepts of catalysis which may be of importance in laboratory evaluation of oxidation stability of lubricants.

OXIDATION APPARATUS

The oxidation apparatus and general technique were described in the earlier paper (14). The automatic oxidation apparatus was particularly useful for this study since rate variations were considerable and would have required an unusual amount of attention. In all the experiments the catalyst was added directly to the charged oxidation cell, stirring being employed when necessary to ensure homogeneity. The oxidation cell was then placed in the oil bath, connected to the system, and evacuated to prevent oxidation during the heating period. When temperature equilibrium had been reached, the system was refilled with oxygen. The process of evacuation and refilling was repeated three times, circulation started, and the test begun. The oxidation temperature of 150° C. made it possible

The oxidation temperature of 150° C. made it possible to obtain sufficiently accurate data on unstable oils and still permit the study of uncatalyzed oils. This temperature is not much higher than the crankcase of the Chevrolet 36-hour heavy-duty test (1). Oils are subjected to higher temperatures on piston and cylinder surfaces, but in these regions only iron and aluminum are generally present. The reproducibility of results obtained with this apparatus

The reproducibility of results obtained what the preference and these test conditions is in the order of ± 5 per cent, although unexplained large deviations occasionally occur. Consequently, in the experiments reported here, check runs were made only if the data failed to form a smooth curve when stability was plotted as a function of concentration of metal, or when maxima or minima occurred.

The oils chosen for the study are broadly representative of those obtainable from Pennsylvania, Mid-continent, and California crudes. The latter two had been solventextracted. The properties are listed in Table I.

In all experiments, oxidation was continued until 1800 ml. of oxygen had been absorbed per 100 grams of oil. The time in hours necessary to accomplish this is arbitrarily defined as the stability of the oil. This degree of oxidation is sufficient to produce a saponification number of about 16 mg. potassium hydroxide per gram, a neutralization number of about 4, and an asphaltene content of about 1 per cent, depending upon the type of oil. It was chosen as representing the maximum deterioration found in service.

CATALYSIS BY BULK METALS

In agreement with other experimenters it is believed that, of the metals present in an engine, those most likely to be effective as catalysts (due either to the amount present or to activity) are iron, copper, and lead. Other substances, particularly aluminum, cadmium, silver, chromium, magnesium, phosphorus, and tin, may also be present but are not considered in this study. The amount of iron so far exceeds the amount of other metals that iron has frequently been regarded as the only metal of importance from a catalytic viewpoint. Downing and co-workers (9) studied the problem of catalysis in an engine by successively eliminating selected metal parts by means of lacquers; they concluded that the total catalytic effect of iron is greater than that of copperlead, silver-cadmium, or Babbitt present as connecting rod bearings. Of the bearing alloys, the copper-lead combination is most active, with Babbitt and silver-cadmium following in that order.

TABLE I. PROPERTY	ies of O	ILS	
Oil	Penna.	Mid-cont.	Calif.
Sp. gravity	0.8835	0.8780	0.8979
d20	0.8818	0.8764	0.8963
Refractive index n ²⁰ _D	1.4903	1.4838	1.4903
Specific dispersion (F and C lines) Viscosity Saybolt Universal sec.	117 (?)	108	104
100° F. 210° F.	$423.4 \\ 60.2$	450.8 60.66	530.4 57.4
Viscosity index	102	96	51
Color (Natl. Petroleum Assoc.) Sulfur, % Waterman analysis % C atoms in:	6 0.23	0.09	11/3 0.27
Aromatic rings Naphthenic rings	7	5 27	6 41
Paraffin side chains Mol. weight	72 485	68 492	53 439

In spite of the considerable activity of iron, however, the catalytic effects of other metals may become serious and require study. Also, it is possible that lacquered metal surfaces have little catalytic activity, and consequently only those surfaces freed of such surface films by rubbing are of catalytic importance.

In the experiments involving catalysis by iron surface, analytical grade iron wire was used as a catalyst, since it W W

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Figure 1. Effect of Bulk and Dissolved Metals on Oxidation Stability of Extracted Mid-continent Oil at 150° C.

Metal content shown in parts per million or sq. cm. per gram of oil.

gave more reproducible results than other forms of iron. However, recently fabricated wire of this type was found to be much less active than the older wire (produced in 1937-38). Considerable study has failed to give a satisfactory explanation of this difference. The physical appearance of each wire is much the same; spectrographic and x-ray investigations could not distinguish between them. But there were differences in the chemical behavior of the two wires. The older wire was more readily attacked by reagents such as sulfuric acid and cupric nitrate. The catalytic effect of the new, less active wire can be increased by exposure to the vapors of hydrogen chloride but is changed little by reduction with hydrogen. These results indicate that the type of metallic surface is of extreme importance. It is possible that the iron surfaces of an engine may be less active than the iron surfaces used in these experiments. The wire (No. 36 Washburn and Moen gage, of which 0.043 gram or 13.82 cm. is required to give 1 sq. cm. of surface) was added to the oxidation cell in the form of a loose coil which had been wound on a 1/4-inch mandrel. Before being added to the oxidation cell, the coil was washed with acetone and then dried under vacuum.

In the experiments with copper, electrolytic wire (No. 30 Washburn and Moen gage, of which 0.075 gram or 8.94 cm. is required to give 1 sq. cm. of surface) was wound into coils as described above. The most reproducible surface was obtained by soaking the coils for an hour in 6 N ammonium hydroxide, washing with distilled water and acetone, and drying as in the case of iron. Pickling in acid decreased the activity and produced a nonreproducible catalyst.

Lead was used in the form of c. p. analytical grade foil (at least 99.5 per cent pure) since a lead wire free from antimony could not be found. The foil (weighing 0.075 gram per sq. cm. total surface) was cut into ribbons, pickled with dilute acid (or base), washed in hot water and acetone, and dried.

A large number of curves have been obtained showing the effect of these three engine metals upon the stability of the three representative oils. Typical are the curves in Figure 1 for the Mid-continent oil. One curve for each metal is replotted in Figure 2 on a more extended time scale to show differences in the behavior of the three catalysts. Iron promotes a rapid initial rate of absorption of oxygen by the oil which subsequently decreases; this metal is probably functioning through a mechanism of heterogeneous catalysis, a conclusion reached by Dornte (7) with respect to catalysis by copper. This view is further sup-ported by the data in Table II which show that the amount of metal dissolved in the oil during oxidation is not sufficient to account for the catalytic effect on the basis of homogeneous catalysis. The curve for oxidation with lead shows an induction period confirming the work of Fenske (11) who reported that lead shows a pronounced induction period in its catalysis of oxidation. The existence of an induction period and the fact that large amounts of lead were dissolved (Table II) would indicate that catalysis by lead metal is at least partly homogeneous. Copper appears to be in an intermediate position. The decrease in oxidation rate shown by Figure 1 is probably due to a decrease in the activity of the metal surfaces as a result of the passivating

effects of the oxidation products.

The complete data on the catalysis of the three oils by bulk metals are summarized in Figure 3. The relative activities of the various catalysts are shown by the distance from the line for the uncatalyzed stability of the oils (as defined above) to the corresponding points on the curve for the catalyzed reaction. Catalytic susceptibility of the oil is difficult to define since it varies with the amount of metal.



Figure 2. Effect of Bulk and Dissolved Metals on Oxidation Stability of Extracted Mid-continent Oil at 150°C.

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Figure 3. Effect of Extent of Metal Surface on Oxidation Stability at 150° C.

Figure 4. Effect of Dissolved Metals on Oxidation Stability at 150° C.

In general, we prefer to emphasize the catalytic effects at the low ratios of metal surface to oil volume, in which cases the susceptibility is most readily determined by taking the ratios of the differences between the uncatalyzed and catalyzed oxidation for the various oils at the same metal surface oil-volume ratios. If the points fell on a straight line, the slope of the line could be taken as a measure of catalytic susceptibility.

The curves of Figure 3 lead to the following conclusions:

1. The oils are susceptible to catalysis by all three metals. For example, they are reduced in stability to less than 50 per cent of the original value by only 0.01 sq. cm. of copper per gram of oil. The ratio of copper surface to oil weight in a Chevrolet engine is about 0.04 sq. cm. per gram, and of iron about 5.0, depending upon the use of copper oil lines and copper alloy bearings (3). If the metals in the engine are active catalytically (i. e., have not become passivated or coated with lacquer), it is evident that there is a sufficient quantity to activate the oil greatly.

2. Copper is the most active catalyst at low ratios of surface to oil volume, but at high ratios lead and iron approach or surpass copper in activity. The relative activities of iron and lead vary, depending upon the oil as discussed in the next paragraph. The pronounced catalytic activity of copper has been noted by others, although some disagreement exists. Donnte (7) reported that with copper the catalytic activity passed through a maximum, but this was not observed in the present investigation over the range studied. Matthijsen (16) reported that, at high temperatures (230° C.) all nonferrous metals were inactive or even anticatalysts, although he also found copper to be active at low temperatures. Since such high temperatures exist only in the power section of an engine where copper is largely absent, the significance of high-temperature experiments with copper may be questioned, although such experiments with ferrous metals and alloys may be of great importance.

3. Catalytic susceptibility of the oils varies from catalyst to catalyst. Thus, although the California oil is more susceptible to iron than the Mid-continent oil, the reverse is true for lead. The reasons for this behavior are not clear although in the case of lead, formation of a lacquer film on the metal surface by the California oil is undoubtedly a factor. The Pennsylvania oil is particularly resistant to catalysis by lead.

4. Judging from Table II and Figure 3, there is little direct relation between the amount of metal dissolved and the reactivity of the oil, especially in the case of iron.

Iron and copper did not significantly alter the amount or type of oxidation products except that a reduction in the formation of asphaltenes was noted with greatly reduced oxidation time. Since asphaltene formation is a secondary reaction, which may be little affected by the rate of the primary reaction, a decrease in asphaltenes with decreased time of oxidation might be expected. Oils oxidized in the presence of lead formed fewer insoluble oxidation products, presumably owing to the formation of detergent lead salts.

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CATALYSIS BY DISSOLVED METALS

In the experiments with the dissolved metals, the metals were added in the form of their naphthenic acid salts. As was the case with oxidation by bulk metals, the curves given in Figure 1 for the Mid-continent oil are representative of a large number obtained with all three oils. The close similarity in type to the curves obtained with bulk

TABLE II.	Metal Content Buly	of Oils Oxi k Metals	DIZED IN P	RESENCE OF
Metal	Sq. Cm. Metal/Gram Oil	Metal Penna.	Content P. Mid-cont.	P. M. Calif.
Copper	$\begin{array}{c} 0.0085\\ 0.034\\ 0.068\\ 0.102\\ 0.170\\ 0.238\\ 0.341\\ 0.682\\ 1.705\\ 5.115\\ 10.23\end{array}$	2.5 3.6 2.9 10.3 11.2 17.2 	2.5 3.9 3.0, 6.3 3.9 11.3 17.8	3.9 2.5 2.5 10.2 30.9 12.5
Iron	$\begin{array}{c} 0.044\\ 0.11\\ 0.22\\ 0.43\\ 0.88\\ 1.76\\ 3.5\\ 7.0\\ 14.1 \end{array}$	 	0.(5) 0.(3) 0.(5) 1 1 1 1	$\begin{array}{c} 0.(6) \\ 1 \\ 0.(2) \\ 0.(4) \\ 0.(4) \\ 1.(2) \\ 1.(8) \\ 0.(8) \end{array}$
Lead	0.1 0.3 1.0 3.0 5.0 10.0	12,700 19,500 22,500	4,600 3,500 12,000 12,500 16,180	9,350 19,900 22,250

metals is striking. The constantly decreasing effectiveness of the catalyst with time is probably a function of the ability of the oil either to remove it from solution by precipitation or to render it inactive by the formation of inert metal complexes. Complete data for the three oils are summarized in Figure 4. The following conclusions are readily apparent:

1. All oils are quite susceptible to catalysis by very low concentrations of soluble copper and iron. In most cases the initial superior stability of the Mid-continent oil is not preserved in the presence of catalysts; for example, in the case of iron naphthenate all three oils have nearly the same stability at about 6 p. p. m. of catalyst. The Mid-continent oil is considerably more susceptible to catalysis by soluble lead than are the other



Figure 5. Effect of Dissolved Copper on Oxidation Stability at 150° C.



Chronograph for Automatically Recording Volume of Oxygen Absorbed as a Function of Time

two, possibly because of the greater tendency of the other oils to precipitate the lead as a catalytically inactive sludge.

2. The oils show a great tolerance for lead naphthenate which must be overcome by the use of large amounts of catalyst before the oil becomes unstable. Once the tolerance is exceeded, however, the activity of lead naphthenate is as great as that of the other catalysts. This concept of tolerance toward catalysts was used by Davis (5) in evaluating oil additives.

3. At low concentrations (below 5 p. p. m.) copper is more active than iron; above this concentration iron is the more active. In the case of the Mid-continent oil, at very high concentrations the stability is nearly the same for all three catalysts.

4. The naphthenate salts generally show a maximum in catalytic activity which is particularly pronounced in the case of lead and copper.

From the above discussion of the catalytic effects of bulk and dissolved metals on oil stability and from comparison of Figures 3 and 4, it is evident that by proper choice of catalyst and concentration any one of the oils can be the most stable or the least stable of the three. To illustrate this point, the curves obtained with copper naphthenate for all three oils are reproduced in Figure 5. The curves cross and recross a number of times; as the concentration of this catalyst is increased, the stability of each oil relative to the other two changes. Table III shows that all of the six possible orders in which three oils can be rated on the basis of stability are obtainable with this catalyst merely by

varying the concentration. The concentrations listed are not the only ones in which the given ratings occur.

Although these variations with dissolved copper are greater than with the other catalysts, it is evident that arbitrary amounts or kinds of either dissolved or bulk catalysts will accelerate oxidation in rather an unpredictable manner; hence laboratory tests in which the catalyst is arbitrarily chosen cannot be expected to give any more reliable measure of the stability to be expected of oils in service than tests employing no catalyst unless the catalysts chosen correspond to those with which the oil comes in contact in the engine. This correspondence cannot be assumed from correspondence in volume ratios of metal to oil alone, since a large extent of the metal surfaces in a well-used engine have undoubtedly become coated with lacquer or otherwise rendered catalytically inactive or less active than fresh metal surfaces.

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EFFECT OF ENGINES ON OIL REACTIVITY

give an estimate of their catalytic activity, other possible engine catalysts remain. These substances may be oxidized oils or fuels, residues resulting from the fuels or from chemical attack of engine surfaces, or contaminants such as dust carried into the oil from the outside. To learn something of these effects, a study was made of the stability of oils after use in engines. The rate of oil deterioration was not determined in the engine itself since there is no suitable method available, and interpretation of such data would be difficult. Instead, oil samples were periodically removed from the engine crankcase by a stopcock installed in the oil pressure line, and their stability was studied in glass without the addition of catalysts. The procedure followed was to flush the engine by draining the old oil, operate for 200 miles on the experimental oil, drain again, and refill with the experimental oil for the test, which was run largely under conditions of city driving. Several hundred milliliters of oil were withdrawn through the pressure line while the engine was running before each sample was taken.

While engine metals or the soluble salts of these metals are active catalysts for oil oxidation, and the foregoing results

Several types of oil were studied. The results obtained with a California oil used in two different engines are shown in Figure 6. Both engines were used in passenger car service as described above. Engine 1 was in good mechanical condition; about half the fuel used was of the leaded variety. Engine 2 was in poor mechanical condition as shown by an oil consumption of 7 quarts during the 1000-mile test; leaded gasoline was used as fuel. In both engines the fresh stable oil became reactive as soon as it had been thoroughly mixed (10 minutes with engine idle) with the oil remaining after draining. The course of the decrease in stability with use is seen in Figure 6. The oil became very reactive after a few hundred miles of use and reached a stability as low as one per cent of the initial value within 1000 miles. The greater activity of the oil used in the engine in poor condition is striking. In this case catalytic "saturation" was apparently reached, for addition of 4 quarts of fresh oil (total crankcase capacity, 7 quarts) increased stability only slightly.

TABLE III. ORDER OF STABILITY RATINGS OF THREE OILS OXIDIZED AT 150° C. IN PRESENCE OF DISSOLVED COPPER CATALYST

Copper Content, P. P. M.	Order of	f Stability (Decre	asing →)
0 1 100 1000 2700 3000	Mid-cont. Mid-cont. Penna. Calif. Penna. Calif. Mid-cont.	Calif. Penna. Mid-cont. Penna. Calif. Mid-cont. Calif.	Penna. Calif. Calif. Mid-cont. Mid-cont. Penna. Penna.



Figure 7. Oxidation Stability of a Treated Crankcase Oil

Stability is the time required to absorb 1800 ml. oxygen per 100 grams oil at 150° C.; neutralization and saponification numbers were determined potentiometrically. Insolubles represent per cent insoluble in isopentane-diluted oil.

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The observation that fresh stable oils become very unstable after a short period in an engine is considered highly significant since there can be no question here as to the activity or inactivity of metal surfaces. In addition, the catalyst has been picked up by the oil and is carried to every engine part. This, then, is a form of engine catalysis which is real and, apparently, dependent upon some engine operating factor.

The possible causes of catalysis of this type have already been indicated. In order to discover which factor is most important, the final drainings from engine 2 were studied in detail (Figure 7). Removal of the oil-insoluble portion by filtration greatly increased stability; therefore this material is the most active catalyst. The accelerating effect of these oil-insoluble contaminants upon oil deterioration in the engine was previously noticed by Davis (4). The amount of iron and copper dissolved in the oil (2.7 and 1.0 p. p. m., respectively) is sufficient to account for the slight catalysis of the filtered oil. The fuel ends were removed by steam distillation with little effect on stability. Washing with dilute hydrochloric acid to remove all the metals, and percolation through clay restored the oil nearly to its original stability.

The solid oil-insoluble material is highly oxidized as indicated by a saponification number of 283 mg. potassium hydroxide per gram and is very high in ash, which contains principally lead. The metals were removed from this material by extraction with constant-boiling hydrochloric acid. The resulting residue was low in ash (still principally lead), and still contained the highly oxidized material. While the metal-containing oil insolubles were a strong catalyst, giving an oxidation stability in the fresh oil of only 2.3 hours, the same quantity of the extracted material actually had a slight inhibiting action, increasing stability to 220 hours. This latter effect was confirmed by oxidizing the same oil in glass apparatus, removing the oil-insoluble sludge (saponification number 240). and adding it to the fresh oil, a stability of 247 hours being obtained.

TABLE IV.	ANALYSES	AND ACT	TIVITY OF C	RANKCASE	CATALYST
Analysis, %	950 Miles, LaSalle Engine	1000 Dodg No lead) Miles, e Engine Leaded fuel	25-Gal. Composite	30-Gal. Composite
Ash Lead Iron Copper Sulfur	35.8 19.8 4.5 0.12	$22.4 \\ 2.9 \\ 10.66 \\ 0.08 \\ 4.5$	48.1 24.2 10.69 0.17 3.5	47.2 27.4 5.4 0.34	$\begin{array}{r} 46.0\\ 36.45\\ 5.82\\ 0.07\\ \end{array}$
Total halogen Bromine Chlorine Carbon Hydrogen	a	0 	10.1 6.2 1.7	7.44.51.330.612.57	$10.9 \\ 6.74 \\ 1.85 \\ 22.1 \\ \cdots$
Activity b, hr.	2.3	25.0	3.0	4.5	2.8,3.0
⁴ Calculated	as bromine.				

• Time to absorb 1800 ml. oxygen per 100 grams oil when 0.5% is added to a California oil (uncatalyzed stability, 213 hours).

The evidence at hand thus indicates that the insoluble, although extremely finely dispersed, metal salts or free metals (here designated "crankcase catalysts") occurring in the crankcase lubricant are largely responsible for the catalyzed activity of such oils. This view was confirmed by studying the effect of an efficient filter on the stability of two oils when used in a 1941 Mercury engine. The data recorded in Figure 8 show that after 1000 miles without a filter, one oil had a stability of only 4 hours, while the stability was about 153 hours when the same oil was used in the same car equipped with a filter, and the oil was clear and free from



Figure 8. Effect of Removal of Crankcase Solids on Stability

visible solids. The second oil was used for a long period. Soluble catalysts gradually accumulated in the filtered oil, so that after 5000 miles of use it was quite unstable. No inspections were made to observe the effect of decreased stability on the engine.

CATALYTIC ACTIVITY OF CRANKCASE CATALYSTS

Several samples of crankcase catalyst were obtained from a number of different engines. The analyses as well as activity of these samples are listed in Table IV. The 25- and 30-gallon composite samples were obtained several months apart from service station drainings, and are thus representative of perhaps fifty cars operating under the usual variations in fuels and lubricants. The catalyst from the 25- and 30-gallon samples was removed efficiently by centrifuging the heated (approximately 100° C.) undiluted oil in a Sharples supercentrifuge at about 20,000 times gravity. The residue was washed several times with naphtha and then air-dried, which left a gray-black heavy powder.

In order to obtain comparable particle sizes in the tests for the activity of the crankcase solids, the samples of the powder were ground fine enough to pass through a 325mesh screen. This appeared sufficient to give a dispersion in unused oil nearly equivalent to that naturally occurring in used oils, since in all cases tried the stability of the unused oil was thus reduced to a value roughly equal to that of a corresponding used oil containing an equivalent amount of solids.

The crankcase catalyst from the 25-gallon composite was added to a California oil in varying concentration, with the results plotted in Figure 9, where the catalytic activity is compared with that for the various soluble metal catalysts. This comparison is not quite valid since the crankcase catalyst is essentially an oil-insoluble material; it is given, however. to show the maximum catalytic effect which a given component of the crankcase catalyst might exert. Thus when crankcase catalyst is plotted on the basis of its lead content, it is more effective than lead naphthenate; therefore some material other than lead must be the active catalyst. On the basis of iron content it is somewhat less effective than iron naphthenate, while on the basis of copper content it is comparable to copper naphthenate at low concentrations. At higher concentrations, however, the activity is greater than the copper content would allow. These results do not lead to definite conclusions regarding the cause for reactivity of crankcase catalyst, but they do indicate that a seemingly small content of some material cannot be ignored.

To shed additional light on this subject, a number of inorganic compounds which may be present in the crankcase catalyst were studied. The results are listed in Table V. By far the most active of these compounds are the iron and copper halides, which are almost as active as the corresponding naphthenates. All of the sulfates are inactive while ferrous sulfide is moderately active. The only lead compounds showing appreciable activity are the oxide and bromide. The oxides and nitrate of iron are moderately active. Considerable work has been done in actually separating the crankcase catalyst into its components. Although this work is not reported in detail at this time, it may be stated that the halides of iron were found to be present and to show considerable activity. The sulfates were also separated and found to be without activity. The possibility that free metals contribute to the catalysis is not excluded although the only one likely to be present in the free state is iron which may have been abraded from engine parts. Reduced iron powder or piston ring filings, added in the same weight concentration (on the basis of iron content) as the crankcase catalyst, shows much lower catalytic activity. It is believed that the iron halides contribute most to the reactivity of the catalyst. This view is given support by the data of Table IV; it is evident that the crankcase catalyst from the Dodge car using nonleaded fuel is much less active than the one obtained when leaded gasoline was used. These tests were run consecutively so little opportunity existed for other factors to alter the oil-insoluble material.

TABLE V. CATALYTIC ACTIVITY OF INORGANIC MATERIALS IN CALIFORNIA OIL AT 150° C.

1800 Ml. O ₂
213
4.5
150 62.7 20.5
200 38.5
212 198 203
28.0
173 1.50 2.55 11.2 71.5 115

STANDARD CATALYSTS FOR OXIDATION TESTS

The results show that the arbitrary use of soluble metal salts or a specified set of bulk metals in laboratory tests will usually serve to accelerate oil oxidation; but owing to variations in catalytic susceptibilities, variations of catalytic activity with concentrations and the like may not be wholly adequate to distinguish between oils of good stability. Although the authors do not wish at this time to urge the general use of crankcase catalyst, it is believed to have certain advantages which warrant consideration. Since accumulation of oil-soluble catalyst is generally slow and engine metals may not be active, these oil insolubles are probably the most active catalyst in the engine. It should thus be possible to obtain the same catalytic effects in glass as in engines by the addition of this catalyst. There is the disadvantage, however, that used oil analyses may be hard to interpret since the crankcase catalyst contains oxidized and insoluble materials; but a proper "blank" on the oil may largely overcome this difficulty. Another possible disadvantage



Figure 9. Effect of Dissolved Metals and Crankcase Catalyst on Oxidation Stability of Extracted California Oil at 150° C.

Effect of dissolved meta is designated by broken lines.

is that not all oils may form the same amount of catalyst on use; this point requires further study although the tendency to reach catalytic saturation in the engine in a short time may minimize this difficulty. Since crankcase catalyst is so complex in nature, its use would eliminate the objections to specific catalysts which are responsive to specific anticatalysts. The latter may not be required in an engine although they make it possible for the oil to pass laboratory tests with flying colors.

The concept of crankcase catalyst is described at this time, not because it is a recommended standard or a completely defined substance, but rather because it appears to be useful to an understanding of the catalysis of lubricating oils, and as such may be of interest.

ACKNOWLEDGMENT

The authors are indebted to G. M. Whitney whose work on the separation of crankcase catalyst was briefly mentioned, and to L. M. Smithbauer who performed the laboratory work in connection with the oxygen absorption experiments.

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Adsorption of Riboflavin by Lactose

Influence of Concentration

In crystallizing from whey concentrates, lactose adsorbs riboflavin selectively. The relation between de-

gree of adsorption and initial riboflavin concentration under conditions of complete crystallization is linear. A minimum concentration of riboflavin exists below which no adsorption occurs. Under conditions of incomplete crystallization the value of the riboflavin concentration below which no adsorption occurs is displaced toward lower and lower values as the degree of supersaturation with respect to lactose is lowered, and reaches a final minimum value of 2.5 micrograms per ml. It has been found practical to pre-

In THE crystallization of lactose from concentrated whey, a portion of the coloring matter of whey is adsorbed. This property of lactose is undesirable in certain respects since it necessitates additional processing in the manufacture of lactose; but when properly understood and utilized, it becomes of practical significance.

The importance of the adsorption of riboflavin by lactose as a basis for the preparation of riboflavin adsorbates has passed unnoticed, notwithstanding the fact that the general subject of adsorption on crystals during their growth has been amply investigated. The phenomenon relating to the adsorption by lactose was extensively investigated, and as a result the preparation of potent and pure adsorbates has been placed upon a practical basis.

A large number of factors influence the degree and rate of adsorption. Of these, variations in riboflavin concentration and in the degree of supersaturation with respect to lactose are most significant. These variables will be considered here to the exclusion of others, such as temperature, nature of solvent, nature of adsorbent, hydrogen-ion concentration, and stirring, which require further study.

PREPARATION OF STOCK SOLUTIONS AND ADSORBATES

Experiments were conducted largely on whey concentrates of known riboflavin and lactose concentration. These concentrates were obtained from spray-processed Cheddar cheese whey powder (2). Briefly, 1 part of powder was treated with 17.5 parts of 70 per cent ethyl alcohol by weight. After several minutes the undissolved proteins were removed by filtration, and after 24 hours lactose which had crystallized was recovered from the acidified filtrate. Following neutralization of the mother liquor, the alcohol was recovered and the residual liquor concentrated to contain approximately 40 per cent solids. Decolorizing carbon was added, and the mixture was agitated one week at 2° to 5° C. and then filtered. This riboflavin-free filtrate, the stock solution

ABRAHAM LEVITON

Bureau of Dairy Industry, U. S. Department of Agriculture, Washington, D. C. pare lactose containing as high as 300 micrograms riboflavin per gram. Much higher concentrations may

be realized, but the rate of crystallization under the conditions required for the preparation of the more concentrated adsorbates becomes exceedingly slow. Concomitantly, the lactose crystals change from a characteristic tomahawk to a thin platy form. Riboflavin exerts a definite retarding action on the rate of crystallization of lactose, an effect which becomes more and more pronounced as the riboflavin concentration is increased, and as the degree of supersaturation with respect to lactose is decreased.

in these experiments, had a pH of 4.5 and a solids concentration of 30.5 per cent, and contained lactose in slight excess of the quantity (17.4 grams per 100 ml. water) required to effect saturation at 5° C.

ration at 5° C. Adsorbates containing natural riboflavin were prepared along approximately the same lines as indicated above. Following the recovery of alcohol, however, and the concentration of the mother liquor, the addition of carbon was omitted. The concentrate, after storage at 2-5° C. for one day, was filtered and stirred at 7° for a week. The adsorbate which crystallized to the extent of 12 grams per 100 grams of concentrate was washed with 70 per cent alcohol. Analysis showed 170 micrograms riboflavin per gram, representing approximately 85 per cent recovery of riboflavin. In one experiment in which 5 parts of the concentrate were diluted with 1 part by weight of water, the adsorbate which was recovered contained 230 micrograms riboflavin per gram, representing a yield of 75 per cent.

which was recovered contained 250 interograms ribonavin per gram, representing a yield of 75 per cent. The method outlined was applied on a small pilot plant scale to the preparation of adsorbates. The concentrated liquor from which the adsorbate crystallizes is obtained as a by-product in an extraction process developed in this laboratory for the preparation of soluble proteins and lactose. Directions for the recovery of this concentrated liquor have been published (2). METHODS. Experiments were conducted on measured por-

METHODS. Experiments were conducted on measured portions of the stock solution fortified with measured quantities of synthetic riboflavin and lactose. These fortified solutions were seeded with 0.05 per cent milk sugar. Sealed 22×175 mm. test tubes containing the solutions of varying riboflavin and sugar content were rotated in a thermostat maintained at $5.0 \pm 0.1^{\circ}$ C. Tubes were removed periodically, their contents filtered rapidly (within 15 seconds), and the lactose residues washed well, but without elution, with 70 per cent alcohol saturated with lactose.

Riboflavin determinations were conducted fluorimetrically and colorimetrically. Preliminary experiments had established the good agreement between results obtained with colorimetric, microbiological, and fluorimetric methods. It was found sufficiently accurate in all colorimetric and fluorimetric methods to consider riboflavin as the only pigment associated with lactose. Absorption curves were obtained by means of a sensitive photoelectric spectrophotometer employing a Hilger monochromator with 0.0025-inch slits.

RELATIVE ABSORPTION OF ADSORBATE SOLUTIONS

Figure 1 is a plot of the relative absorption of solutions of two adsorbates, one containing natural and the other synthetic riboflavin. The relative absorption of the concentrate from which the natural riboflavin adsorbate was derived is also plotted over a limited range of wave length. The ordinates are expressed in terms of absorption of natural riboflavin adsorbate; the absorption at 445 millimicrons is taken as 100 per cent.

Solutions of the adsorbates were prepared to contain approximately 8 micrograms riboflavin per ml. simply by dissolving the required quantities of the adsorbates.

Figure 1 shows that the location of the maxima at 370 and 445 millimicrons and the shape of the curves representing the absorption of the adsorbates are in agreement with each other and in agreement (not illustrated) with corresponding features of the absorption curves of crystalline riboflavin. The highly selective nature of the adsorption is demonstrated by the decrease in relative absorption of the concentrate with increases in wave length in the region 400–425 millimicrons compared with corresponding increases in the absorption of the adsorbates. This selectivity is also shown by the good agreement between results of microbiological and of colorimetric and fluorimetric methods in which no attempt was made to exclude absorption of radiation by any interfering pigments which might have been present.

RELATION BETWEEN ADSORPTION AND INITIAL RIBOFLAVIN CONCENTRATION

Figure 2 shows the relation between the degree of adsorption and the initial concentration of riboflavin. The concentration of riboflavin is expressed in micrograms per ml. of the original concentrate. Criticism may be directed against the use of initial rather than equilibrium concentrations as abscissa, and against the use of solutions instead of pure solvents as standards of reference; but inasmuch as the data are plotted to emphasize the practical rather than any theoretical aspect of the problem, the treatment is suitable.

In these experiments crystallization was allowed to proceed to completion.



Whey Is Concentrated as in the Commercial Process for the Manufacture of Milk Sugar; Slightly Modified, This Process Permits Recovery of Riboflavin Adsorbate without Using Solvents



Figure 1. Relative Absorption of Solutions Containing Natural Riboflavin Adsorbate, Synthetic Riboflavin Adsorbate, and Whey Solids from Which the Natural Riboflavin Adsorbate Was Derived

The relation between degree of adsorption (micrograms riboflavin adsorbed per gram lactose) and initial concentration of riboflavin is linear. The lines corresponding to various levels of supersaturation with respect to lactose converge at a point representing a concentration of 2.5 micrograms ribo-

> flavin per ml. This concentration, then, is the minimum concentration below which no adsorption occurs. In all experiments but one, lactose crystallization reached completion under the conditions of agitation employed within 3 to 5 weeks. Crystallization, however, from the concentrate containing 42 micrograms of riboflavin and 0.084 gram of added lactose per ml. had hardly begun even after 5 weeks. Riboflavin exerts a definite retarding action on the rate of crystallization of lactose, an effect which becomes more and more pronounced as the riboflavin concentration is increased and as the degree of supersaturation with respect to lactose is decreased. This retarding action occurs concomitantly with a change in habit of the crystals from their characteristic tomahawk to a thin platy form (Figure 3).

> The linear relation and the existence of a minimum concentration below which adsorption does not occur are not features peculiar to the system under study. Analogous

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relations in the crystallization of inorganic salts from solutions of dyestuffs were reported by Rigterink and France (4).

Table I gives additional data on the variation of percentage adsorption with variations in the quantity of sugar recovered under conditions of complete crystallization. The data in the fourth column indicate that, for practical purposes. the percentage adsorption may be considered independent of the quantity of sugar recovered under conditions of complete crystallization although small systematic variations are present which point to the existence of a maximum adsorption value. The percentage adsorption is proportional to the difference between the initial riboflavin concentration and the minimum concentration below which adsorption does not occur; consequently, it increases with increasing riboflavin concentration. The value of the minimum calculated from the difference between the initial concentration of riboflavin and the quantity

adsorbed per ml. of concentrate agrees with the value obtained by the extrapolation of the curves of Figure 1. The table and graphs show that the degree of adsorption, a, is equal to the difference between the initial and minimum riboflavin concentration, c-2.5, divided by the quantity of lactose, s, separating per ml. of concentrate. This empirical formula,

 $a = \frac{c - 2.5}{s} \tag{1}$



Figure 2. Relation between the Degree of Adsorption and Initial Riboflavin Concentration

Relation is valid under conditions of complete lactose crystallization for concentrates containing 0.084-0.268 gram excess lactose per ml. at 5° C.



Adsorbate, Consisting of Riboflavin and Milk Sugar, Is Recovered by a Chemical Centrifuge

is well adapted for practical purposes and establishes a basis for the controlled preparation of adsorbates from whey. It should be borne in mind, however, that this formula applies only under conditions in which lactose crystallization is complete.

RELATION BETWEEN ADSORPTION AND CRYSTALLIZATION

When crystallization is incomplete (Figure 4), the quantity of riboflavin adsorbed is influenced by variations in the percentage of lactose which has separated. These curves were obtained at 5° C. for five series of solutions, the initial riboflavin concentrations of which ranged from 5.25 to 42.0 micrograms per ml.

At low riboflavin levels (but exceeding 2.5 micrograms per ml., the lowest level below which adsorption does not occur), no significant adsorption took place until an appreciable percentage of sugar had crystallized. The slopes of the curves, excepting the slope representing crystallization from the most potent concentrate, indicate that the degree of adsorption increases at first with increase in the percentage crystallization, reaches a maximum, and then decreases. From a study of these curves and of the data already discussed, it is clear that, as the degree of supersaturation with respect to lactose is decreased, the value of the riboflavin concentration below which no adsorption occurs during the early stages of crystallization is displaced toward lower and lower values and reaches a final minimum value of 2.5 micrograms per ml.

From a practical standpoint these curves indicate the extent to which and the manner in which crystallization should be carried out to obtain potent adsorbates consistent with good yields.

APPLICATION TO RIBOFLAVIN RECOVERY

Applying the data to the preparation of adsorbates from whey, lactose can be produced containing between 200 and 300 micrograms riboflavin per gram, representing 75-80 per cent recovery of riboflavin. Greater concentrations may be realized, but the rate of crystallization of lactose under the conditions required for the preparation of more concentrated products becomes exceedingly slow.

The data are capable of application not only to those con-

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Figure 3. Photomicrographs of Lactose Crystals (×150)

Above. Shortened tomahawk form crystallizing at 5° C. from concentrate containing 46 micrograms riboflavin and 0.21 gram excess lactose per gram concentrate.

Below. Shortened tomahawk form derived from concentrate containing 16.0 micrograms riboflavin and 0.145 gram excess lactose per gram concentrate.

centrates which form the subject of this paper but also to any number of related concentrates. These embrace concentrates obtained from whey in the commericial production of milk sugar and in the production of fermented products (alcohol and lactic acid, for example). They may be used either separately or to supplement one another, or they may be combined with concentrates derived from sources other than milk. Obviously, certain details of processing must be worked out in order to establish optimum conditions, and in this respect each particular concentrate presents its own problem.

LIMITATIONS OF METHOD. Empirical formula 1 defines the conditions which must be met in order to obtain potent adsorbates consistent with good yields. In the application of this equation to whey, a material containing both riboflavin and lactose, it may readily be seen that the potency of Above. Thin platy form derived from a concentrate containing 46 micrograms of riboflavin and 0.15 gram of excess lactose per gram.

Below. Thin platy form derived from a concentrate containing 16.0 micrograms of riboflavin and 0.095 gram of excess lactose per gram.

the adsorbate is limited by the pre-existing concentrations of riboflavin and lactose in whey. The yield, Y, is given by the following formula derived from formula 1:

$$Y = \frac{c - 2.5}{c}$$

To obtain a satisfactory yield, it is necessary to concentrate the whey to a considerable degree. A liquor containing lactose in a high degree of supersaturation is subsequently obtained which, if crystallization were permitted to proceed to completion, would result in the recovery of weak adsorbates albeit in good yields.

The graphical relations in Figure 4 indicate how to recover concentrated adsorbates consistent with good yields. At each riboflavin level corresponding to a definite degree of

CRYSTALLIZATION										
Riboflavin Concn. c, Microgram/ Ml.	Lactose Recovered s, Gram/Ml.	Riboflavin Adsorbed, Micrograms/ Gram Lactose	Riboflavin Recovery, Per Cent	Residual Riboflavin co, Micrograms/ Ml.						
2.10	$\begin{array}{c} 0.084 \\ 0.191 \\ 0.249 \\ 0.268 \end{array}$	0.5 0.2 0.2 0.2	0.20 0.20 0.25 0.25	2.1 2.1 2.1 2.1						
5.25	0.084 0.191 0.249 0.268	36.2 16.0 11.0 9.7	58.0 58.2 52.2 49.5	2.2 2.2 2.5 2.6						
10.5	$\begin{array}{c} 0.084 \\ 0.191 \\ 0.249 \\ 0.268 \end{array}$	94.0 43.0 33.0 30.0	75.2 78.2 78.2 76.6	2.6 2.3 2.3 2.5						
21.0	0.084 0.191 0.249 0.268	218.0 97.0 75.0 67.5	87.3 88.2 88.9 86.2	2.6 2.5 2.3 2.9						
31.5	0.084 0.191 0.249 0.268	338.0 151.0 117.0 105.0	90.2 91.6 92.4 89.3	3.0 2.6 2.4 3.3						
42.0	0.084 0.191 0.249 0.268	204.0 160.0 146.0	92.8 95.0 93.1	3.0 2.2 2.8						
		Av. co derived	Av I from Figure	2.49 ± 0.25 1 2.50						

TABLE I. RELATION BETWEEN RIBOFLAVIN RECOVERY AND

LACTOSE RECOVERED UNDER CONDITIONS OF COMPLETE

supersaturation, adsorption on the growing crystals is insignificant at the onset of crystallization and increases sharply only after the degree of supersaturation has reached sufficiently low levels. The values of these low levels are indicated for concentrates containing 5.25 and 10.5 micrograms riboflavin per ml., but unfortunately data are lacking for their evaluation at higher concentrations. The qualitative application of these data to the preparation of adsorbates indicates the desirability of conducting the crystallization operation in two steps; in the first only insignificant quantities and in the second the greater portion of riboflavin would be adsorbed. In the crystallization of lactose from ethyl and methyl alcohols, a considerable percentage of milk sugar can be recovered in the first stage, and consequently satisfactory conditions exist for the recovery of concentrated adsorbates in good yields in the second stage (3).

A difficulty encountered in the preparation of concentrates exceeding 200 micrograms per gram is the diminished rate of crystallization under the conditions required for their preparation. To overcome this difficulty it is essential to increase simultaneously the rate of diffusion of lactose and riboflavin or to provide increased adsorbing surface. Encouraging possibilities are the use of increased stirring rates and copious seeding material. A factor of some significance is pH. Preliminary experiments indicate that maximum adsorption is attained at a pH of 6.7, corresponding to 75 per cent crystallization. This may mean that adsorption is more rapid at pH 6.7, but it does not necessarily mean that both adsorption and crystallization are more rapid.

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Concerning the change in habit of the lactose crystal from its characteristic tomahawk to a thin platy form, experiments show that there is no definite relation between the degree of adsorption and crystal habit. Although adsorbates containing in excess of 300 micrograms riboflavin per gram tend to crystallize as plates, there is overlapping; and tomahawk-shaped crystals containing more than 300 micrograms per gram and platy crystals containing less are recoverable. Figure 3 emphasizes the wide variety of conditions under which the platy form is obtained. This form was described by Herrington (1), who observed it as a transitional form in

CONCLUSION

A word may be said about the practical significance of the product. At present there is a shortage of riboflavin in a form suitable for human consumption. Because of this shortage public hearings before the Federal Security Administrator on the subject of mandatory riboflavin requirements in the definitions and standards for enriched flour and allied products have been postponed although all other provisions of the definitions and standards of identity are already effective. This shortage will probably be met, in part at least, by the expanded production of both the synthetic vitamin and various types of concentrates. To what extent the adsorbate described in this paper can compete with these products depends largely on the utilization of the other ingredients of whey, either in their natural or in converted form. The cost of production incidental to the manufacture of the adsorbate would then constitute but a small proportion of the total cost of production.



Concerning the purity of the product, the adsorption curves indicate that the adsorbate is interchangeable with admixtures of milk sugar and crystalline synthetic riboflavin of like potency. Pharmaceutical preparations of riboflavin in tablet form usually consist of synthetic riboflavin admixed with the vehicle or diluent milk sugar; consequently the product derived from whey may be u'ilized directly, or if lacking in potency it may be supplemented with the synthetic vitamin to meet pharmaceutical requirements.

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S. E. BECK, Holabird Ordnance Depot, Baltimore, Md.

Two series of lusterless olive drab enamels were prepared; the extender or extender combination was varied in one series, and the pigment volume percentage of total solids in the other. Steel panels coated with the paints were exposed out of doors for one

USTERLESS olive drab enamels used by the Army for painting equipment have much higher pigment contents than ordinary paints intended for outdoor use. The pigmentation consists largely of extenders. A typical material contains 43 per cent pigment by weight, corresponding to 47 per cent pigment by volume on total solids bases. The pigment contains 80 per cent extenders by volume.

In enamels where the extender content is so high, extender performance assumes unusual importance. The total pigment content is also an important factor. In general, the highest possible pigment volumes are used in lusterless enamels to obtain freedom from gloss and to achieve the economy necessary in a highly competitive market.

A project was undertaken to determine, for lusterless olive drab finishes, the durability of various extenders and year. Results indicate that all extenders studied are satisfactory and that pigment volumes exceeding 60 per cent of the total solids volume cause failure by fading and chalking. All work was done on an alkyd resin vehicle.

the relation between pigment volume and durability. The investigation was confined to alkyd resin base enamels.

Spray-outs of the enamels were made on 4×12 inch, 20gage primed steel panels. The same primer was used throughout. Dry film thickness of the lusterless enamel coats ranged from 1.2 to 1.8 mils. Duplicate panels were exposed in Baltimore at 45° to the south for one year. The panels were returned to the racks following inspection, and further observations will be reported at the end of the second year.

EFFECT OF EXTENDER

A master lusterless drab enamel formula was used; and extenders of various types were incorporated on an equal pigment volume basis. Total solids was fixed at 60 per cent by weight. The formula is shown in Table I. Fixed resin and color pigments were used in all materials to

Photo by courtesy of U.S. Army Signal Corps.

TABLE I.	Formul	A FOR EXTENDER	STUDY	
Pigmentation-	% by vol. of total pigment	Forn	nulation % by wt. of total paint	% by vol. of total solids
Hydrated yellow oxide Lamp black Chrome yellow me- dium, c. p.	$13.6 \\ 3.3 \\ 3.5$	Solids Alkyd resin (35% phthalic anhydride)	60	53.3
Extender	79.6 100.0	Total pigment Volatile (mineral spirits)	40	100.0

no change on exposure; 35 to 48 per cent showed slight fading, and 50 to 70 per cent gave moderate to extensive fading, increasing directly with pigment volume. However, only panels from 60 to 70 per cent, inclusive, showed bad enough fading or chalking to be considered failures.

Adhesion was satisfactory up to 60 per cent pigment volume; other factors, such as abrasion resistance, might affect the suitability of such a high pigment volume. Above 60 per cent, films were powdery, dry, and easily removed with the thumbnail. However, even the 70 per cent pigment volume material adhered to the primer and showed no noticeable erosion or wearing through.

PANEI Extender No.	EXPOSURE OBSERVATION	Extender	No.	EXPOSURE OBSERVATION
sbestine 1, 2	Slight chalking	Diatomaceous silica 50%,	1, 2	Slight chalking
sbestine 50%, CaCO3 50% 1,2 sbestine 50%, barytes 50% 1,2	No change Very slight darkening	Diatomaceous silica 50%,	1,2	Moderate chalking
sbestine 50%, diatoma- 1,2 ceous silica 50%	Very slight chalking	Silica	1	Marked chalking and fading Moderate chalking
sbestine 50%, silica 50% 1, 2 sbestine 50%, slate flour 1	Moderate chalking Slight chalking	Slate flour	1	Slight chalking
50% 2 sbestine 50%, water- 1,2	Moderate chalking Very slight chalking	Water-ground mica	1	Very slight chalking Slight chalking
ground mica 50% sbestine 50%, china clay 1,2	Slight chalking	China clay	1	Moderate chalking Very slight chalking
50% CaCO ₃ 1, 2	No change	ceous silica 33 ¹ / ₃ %, CaCO ₃	2	No change
Barytes 1, 2	Slight darkening and chalk- ing	Asbestine 33 ¹ / ₃ %, diatoma-	1	Moderate chalking and fad-
Diatomaceous silica 1, 2 Diatomaceous silica 50%, 1, 2	Slight chalking No change	clay $33^{1/3}\%$	2	Very slight chalking Very slight chalking
CaCO ₃ 50% Diatomaceous silica 50%, 1	Slight chalking	ceous silica 40%, barytes	2	No change
barytes 50% 2	Slight darkening, very slight chalking	Slate flour 50%, china clay	1	Moderate chalking Slight chalking
Diatomaceous silica 50%, 1 silica 50%	Moderate fading and chalk- ing	Slate flour 50%, CaCO ₂ 50%	1,2	No change Moderate fading
2	Slight darkening and chalk- ing	ceous silica 30%, CaCO,	2	Very slight chalking
Diatomaceous silica 50%, 1 slate flour 50% 2	Moderate chalking Slight chalking, darkening	Diatomaceous silica 60%, as- bestine 30%, CaCO ₃ 10%	1 2	Slight chalking Slight darkening, chalking

TABLE II. EFFECT OF EXTENDER ON COLOR RETENTION AND CHALKING RESISTANCE

obtain uniformity. Enamels were ground on a ball mill. Drier content (in per cent of resin solids) follows: 0.03 cobalt, 0.01 manganese, and 0.20 lead.

Evaluations of duplicate panels are reported in Table II for each extender. Appraisals were made by the same operator and were based on visual appearance only.

The results indicate that none of the extenders studied is so poor that it is necessary to omit it from formulations for lusterless olive drab enamel. Calcium carbonate appears to be the most desirable from the point of view of color retention and chalking resistance.

EFFECT OF VOLUME OF PIGMENT

Materials used, conditions of grind, driers, etc., were the same as in the extender study. Pigment volumes are expressed on a total solids basis. A range from 20 to 70 per cent pigment volume was used, increasing in steps of 5 per cent between 20 and 40 and between 60 and 70, and of 2 per cent between 42 and 60. The general formula is shown in Table III.

Inspections were based both on visual appearance and mechanical film properties. No panel-by-panel description is necessary because of the uniform manner in which fading and chalking increased directly with pigment volume. With a pigment volume of 20 to 30 per cent there was practically TABLE III. FORMULA FOR PIGMENT VOLUME

		Formu	lation	
Pigmentation-	% by wt. of total pigment	,P (I MU	% by wt. of total paint	% by vol. of total solids
Hydrated yellow oxide Lamp black Chrome yellow medium, C. P.	18 2 7	Solids Total pigment Alkyl resin (35% phthalic anhydride)	60	x 100-x
Asbestine	33 26	Volatile (mineral	40	100
Diatomaceous sinca	14	spirits)	100	
Barytes	14		100	
	100			

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THIS report is based on laboratory findings and is presented only for its technical interest. It is not to be considered in the light of an official Government pronouncement, nor is adoption of any of these recommendations or formulas required of manufacturers dealing with the Government, directly or indirectly.

Present Status of PLANT HORMONES

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Phenoxy and benzoic acids substituted in the nucleus with halogen, methyl, and nitro groups have opened a new line of attack on plant hormone problems. Phenoxyacetic acid is slightly active for cell elongation but does not induce formative effects of growing plants. When substituted in the ortho and para positions, the resulting dichlorophenoxyacetic acid is effective, causing cell elongation, adventitious roots, parthenocarpy, and formative effects. p-Chlorophenoxyacetic is less active than the dichloro, and the ortho compound is less active than the para. Bromo-substituted compounds are slightly less active than the chloro. 2,4,6-Tribromophenoxyacetic acid is inactive, but 2,3,5-triiodobenzoic acid is very active. The higher homologs, such as chlorophenoxy- α -propionic and chlorophenoxy- α -butyric acids, are active for cell elongation and adventitious roots but not very

THE purpose of this paper is to list the most important physiologically active substances discovered to date and to discuss some of their practical applications which have been reported from or verified at the Boyce Thompson Institute laboratories. No references will be made to other workers in this field.

Owing to the fact that hormonelike substances induce many varied responses when applied to plants, unwarranted claims have been made, especially for the purpose of exploitation. Vitamin B_1 has fallen by the way as a cure-all for plants, although recently attempts were made to revive it for horticultural practice. The vitamin stories printed in the trade journals and advertisements were fantastic but popular, and it took scientists a long time to convince gardeners that they were wasting their time and money when they added B_1 to fertilizers or sprayed it on their lawns.

Although growth substances of the auxin groups have some practical value, they are not cure-alls and must not be considered as fertilizers. They are commonly referred to as plant hormones although the ones in practical use (with the possible exception of the indoles) have never been isolated and chemically identified from green tissue. This, however, should not be taken to mean that these substances do not exist in nature. A variety of physiologically active substances has been extracted from fungi, pollen, seeds, bark, and growing parts of plants. These crude extracts, when applied to growing plants, bring about responses similar to those induced with synthetic compounds. In some cases these substances may be by-products of metabolism, acting like hormones only when applied in relatively high concentrations.

For practical purposes the synthetic substances are applied as acids, esters, amides, or salts. Wherever a given acid is active for formative effects. Benzoic acid is physiologically inactive until substituted with halogen or nitro groups. 2-Chloro-5-nitrobenzoic acid is inactive for cell elongation but is active for modifying the pattern of leaves. 2-Bromo-3-nitrobenzoic acid is active for both factors.

Considering the increased activity of substituted phenoxy and benzoic acids over phenoxy and benzoic acids, the activity of many other substances in the hormone field might be increased by this method. The principal uses for growth substances are to propagate plants from cuttings, prevent preharvest drop of apples, induce seedless fruit (especially tomatoes), and inhibit buds (especially buds of potato tubers). Flowering of plants can be regulated to some extent with the most active compounds. Treatment of seeds with growth substances to increase the crop has not been effective.

active, its derivatives (salts, esters, and amides) have approximately equal activity. Owing, however, to their differences in volatility, solubility, availability, or ease of application, one may be preferred over the other for a particular use. When applied as a vapor, the methyl or ethyl esters are preferred because they are more volatile than the acids; when used as a lanolin preparation, the acid may be preferred; and when used as a water solution, the salts or acids are preferred. The amides and esters are nearly insoluble in water but can be used for certain purposes in water solutions because only small amounts of the growth substances are required to induce responses in plants.

EFFECT OF VARIOUS GROUPS

The various groups of compounds have different practical uses although there is considerable overlapping. For convenience and brevity the groups are considered separately.

Naphthalene Compounds. When properly applied, α -naphthaleneacetic acid and its derivatives inhibit buds, induce roots on cuttings, and prevent abscission layers from forming. It is frequently important to prevent buds of tubers, bulbs, corms, cuttings, and trees from growing. For this purpose naphthalene compounds are very effective. After treatment with α -naphthaleneacetic acid, potatoes can be stored indefinitely without much shrinkage, and fruit trees can be prevented from flowering (although methods have not been fully perfected) until the danger of frost has passed. The same treatment may be important to delay flowering of trees and thus to spread the fruit crops over a longer period for harvest. This would apply particularly to tropical species such as mango and avocado. Also, the flowering period for ornamental shrubs can be regulated to some extent. Wherever inhibition is desired, the α -naphthalene compounds appear to be most effective. The beta isomers as well as the higher homologs of α -naphthaleneacetic acid are inactive. An important recent use of α -naphthaleneacetic acid spray solution is for prevention of preharvest drop of apples. There is considerable variation in effectiveness of naphthaleneacetic acid for different varieties of fruit, but on the whole the reports from both scientists and practical

growers are favorable.

Indole Compounds. Indolebutyric acid appears to be of most practical importance in this group. Its main use is for propagation of plants by cuttings (Figure 1). It was one of the first found to be generally effective when applied to cuttings of many species of plants. Recent tests with mixtures of indolebutyric acid, naphthaleneacetic acid, and chlorophenoxy compounds indicate that they will be an improvement over a single substance.

When a lanolin preparation of indolebutyric acid is applied to the stigma of an open flower, it induces parthenocarpy and fruit set without pollination. The result is a seedless tomato with a delicious and slightly sweeter than normal flavor.

Naphthoxy Compounds. The following naphthoxy compounds synthesized in this laboratory are active: β naphthoxyacetic acid, melting at 155° C.; β -naphthoxy- α -propionic acid, 106° C.;

 β -naphthoxy- α -propionic acid, 106° C.; β -naphthoxy- α -butyric acid, 125° C. The corresponding 1-naphthyl isomers and β -naphthoxy- β -propionic acid are inactive.

 β -Naphthoxyacetic acid and its active higher homologs induce adventitious roots, cause plants to grow with modified organs, and induce seedless fruit. They are not so favorable for propagating plants from cuttings as indolebutyric acid, but for some species they can be used effectively. For inducing parthenocarpy and seedless tomatoes β -naphthoxyacetic acid is twenty to thirty times as effective as indolebutyric acid but not so active as dichlorophenoxyacetic acid. From a scientific point of view, the naphthoxy compounds are interesting because they induce formative effects when applied to growing plants. Growth which develops after treatment frequently shows leaves, stems, flowers, and fruit modified in size, shape, venation, and pattern.

To induce seedless tomatoes, the flower clusters are sprayed with a water solution of 50 to 150 mg. per liter of β -naphthoxyacetic acid or β -naphthoxypropionic acid or a mixture of the two. Vapors of the esters of β -naphthoxyacetic acid may be used to set fruit in an entire greenhouse at one time. For this purpose methyl- or ethyl- β -naphthoxyacetate is volatilized over a hot plate, and the air is stirred with an electric fan. Twenty-five milligrams are sufficient for a greenhouse with a volume of 2500 cubic feet. The house is kept closed for several hours after the treatment is started.

Substituted Phenoxy Compounds. Substituted phenoxy compounds have received very little attention, but they are now proving to be, perhaps, the most effective of all growth substances. The following are some of the physiologically active substituted phenoxy compounds synthesized in this laboratory: 2-chlorophenoxyacetic acid, melting point 148° to 149° C.; 4-chlorophenoxyacetic acid, 159° to 160°; 2,4dichlorophenoxyacetic acid, 140° to 141°; 2,4-dibromo-

phenoxyacetic acid, 153° ; 2,4-dichlorophenoxy- α -propionic acid, 117° to 118°; 2,4-dichlorophenoxy- α -butyric acid, 83° to 84°; 2,4,5-trichlorophenoxyacetic acid, 157° to 158°; 2,4,5trichlorophenoxy- α -propionic acid, 177° to 178°; 2,4-dichlorophenoxyacetamide, 155° to 156°; 2,4-dichlorophenoxy- α -propionic amide 85° to 86°; and 2,4-dichlorophenoxy- α -butyric amide, 110° to 111° C. Other substitutions are shown in Table I. (Substances are said to be active if they



Figure 1. Showing Roots of *Celastrus* Cuttings Induced with Growth Substances

Left to right: controls without treatment; basal end treated with 2-chlorophenoxyacetic acid; basal ends treated with 2,4-dichlorophenoxyacetic acid; basal ends treated with indolebutyric acid.

> cause unusual cell elongation within an hour or two after local application to the epidermis of stems or leaves. Some substances have a formative influence on new organs which grow after the plant is treated; this response is referred to as modification of organs. A substance may be active for both or either one of these responses.) Bromo-substituted phenoxy compounds showed approximately the same activity as the corresponding chloro-substituted compounds.

Phenoxyacetic acid as such is practically inactive, but halogen-substituted phenoxy compounds are activated according to the position and the number of substituted groups in the nucleus of the molecule. For example, o-chlorophenoxyacetic acid is slightly active. The substitution of the chloro group in the para position increases the activity ten to twenty fold. However, a substitution of the chloro groups in both the ortho and para positions increases the activity still further. A substitution of chlorine in the 2,4,5 positions also brings about a very active compound, approximately equal in activity to 2,4-dichlorophenoxyacetic acid. Tetrachlorophenoxyethyl chloride with chloro groups in the 2,3,4,6 positions was synthesized and found inactive. The higher homologs of substituted phenoxyacetic acid are also very active. 2,4-Dichlorophenoxy- α -propionic acid is active. Nitro substitutions did not act the same as halogen groups. 2,4-Dinitrophenoxyacetic acid was inactive. m-Nitrophenoxyacetic acid was active. m-Aminophenoxyacetic acid was also active. Methyl groups substituted in the 3,5 positions were inactive for cell elongation but induced modifications showing a formative influence on the plants. Many other groupings have been used, bringing about varying degrees of activity in the compounds. However, the most active substituted phenoxy compounds for cell elongation were the 2,4dichlorophenoxyacetic acid and the 2,4,5-trichlorophenoxy-

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		Activity Invol	ving Induced:		A	ctivity ^a Involv	ing Induced:
Phenoxy Phen	or Substituted oxy Acid	Cell elongation and curvature	Modification of organs	Phenoxy Phenory CH-COOH	or Substituted loxy Acid	elongation I and curvature	Modification of organs
	Phenoxyacetic	Active	Inactive		4-Chlorophenoxy- acetic	Active	Active
CH₄CHCOOH 0				CH1CH1CHCOOH			
Ŏ	Phenoxy- α-propionic	Active	Active	Ó	4-Chlorophenoxy- α-butyric	Active	Inactive
CH2CH2CHCOOH O				Čl CH₂COOH			
CH-COOH	Phenoxy- α-butyric	Active	Active	CI	2,4-Dichlorophenoxy- acetic	Active	Active
0				ČI CU CUCOOU			
CI	2-Chlorophenoxy- acetic	Active	Active				
CH₃CHCOOH │ O					2,4-Dichlorophenoxy- α-propionic	Active	Inactive
CI	2-Chloropheno xy- α-propionic	Active	Inactive	CH₅CH₂CHCOOH │ O	•		
Сн₁Сн₂СнСООН				Cl	2,4-Dichlorophenoxy- α-butyric	Active	Inactive
CI	2-Chlorophenoxy- α-butyric	Active	Inactive	CI CH2COOH			
CH ₂ COOE				CI	2,4,5-Trichlorophenoxy acetic	v- Active	
С	3-Chlorophenoxy- acetic	Active		CI CH4CHCOOH			
CH₃CHCOOH 							
Oci	3-Chlorophenoxy- α-propionic	Active	Inactive	CI	2,4,5-Trichlorophenox α-propionic	y- Active	Inactive
CH3CH3CHCOOH				CH ₁ CH ₂ CHCOOH			
- Oci	3-Chlorophenoxy- α-butyric	Active	Inactive	cl	2,4,5-Trichlorophenox α-butyric	y- Active	Inactive
CH ₃ CHCOOH				CH2COOH			
o O	4-Chlorophenoxy- α-propionic	Active	Inactive	CI	2,4,6-Trichlorophenox	y- Inactive	

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Figure 2. Modified Leaves, Flowering Habit, and Correlation Phenomena of Tomato Shoots Induced with 2,3,5-Triiodobenzoic Acid

Control untreated shoot in upper left. Others from plants treated on soil of 4-inch pot with 5 mg, of chemical in 50 ec. of water. Note terminal shoots ending in flower clusters and auxillary buds growing flower clusters instead of leafy shoots.

acetic acid. It is possible that with other combinations still greater activity could be obtained with substituted phenoxy compounds.

Though not fully tested, it is evident at this time that substituted phenoxy compounds will be important for propagating plants, for preventing preharvest fruit drop, for inhibiting buds, and for inducing seedless fruit. For the latter response, dichlorophenoxyacetic acid is far more effective than any other compound yet discovered. For example, 10 mg. per liter of water as a spray is approximately optimum for inducing parthenocarpy and seedless fruit of tomatoes. This is in contrast with 3000 mg. per liter for indolebutyric acid and 100 mg. per liter for naphthoxyacetic acid. One application of the spray to a cluster with two or more open flowers causes development of the ovaries without pollination of all but the smallest buds. When used as a vapor in a greenhouse with a volume of 2500 cubic feet, 5 mg. of methyl dichlorophenoxyacetate were sufficient to induce fruit set throughout the house.

For propagation of plants, halogen-substituted phenoxy compounds were effective when used alone (Figure 1) or in a mixture of other well-known substances. 2,4-Dichlorophenoxyacetic acid and 2,4-dichlorophenoxy- α -butyric acid were particularly effective when mixed with indolebutyric acid and naphthaleneacetic acid. It appears possible that a mixture can be made to include several of the active substances and thus extend the effectiveness of a preparation to include more species of susceptible plants. So far, no one substance used alone has been found effective on all species.

Not all of the substituted chlorophenoxy compounds have the same formative influence on plants. Phenoxyacetic acid is inactive for modifying organs, whereas both phenoxy-apropionic and phenoxy- α -butyric are active for this type of response. Dichlorophenoxyacetic acid is active for both cell elongation and organ modification. Dichlorophenoxy-apropionic and -a-butyric acids, although active for cell elongation and induction of roots, are inactive for modification of organs. It has not yet been possible to determine what part of the molecule is responsible for a given response. Table I shows graphic formulas of a number of substances which have the capacity to induce both formative effects and cell elongation. The table also shows formulas of substances which lack the capacity for inducing one or the other of the two responses.

Substituted Benzoic Acids. This group has not been investigated so thoroughly as the substituted phenoxy compounds, but enough has been done to show that, when various combinations of halogen and nitro groups are substituted in the nucleus, the molecule is activated. Benzoic acid is physiologically inactive, but 2,3,5-triiodobenzoic acid has a pronounced formative influence on plants. 2-Bromo-3nitrobenzoic acid is mildly active for cell elongation but very active for modification of organs. 2-Chloro-5-nitrobenzoic acid is inactive for cell elongation but modifies organs. Triiodobenzoic acid has a pronounced effect on the flowering habit and correlation phenomena. For example, treated tomato plants produce flower clusters at the end of the main branches (Figure 2) instead of or in addition to those along the stem.



Axillary shoots are modified in form and produce abnormally long internodes (Figure 2).

The possible practical applications for substances of the substituted benzoic group have not been thoroughly investigated. It would seem, however, that any substance as active as the substituted benzoic group for regulating the growth of plants is certain to be found useful. As a matter of fact, the morphogenetic effects which can be induced by this group make these substances appear more like hormones than the well-known auxins which are effective for causing quick responses through cell elongation. The animal biologists are not concerned with cell elongation but rather with morphogenetic effects in their work with animal hormones in relation to growth.

ACTIVITY AND METHODS OF APPLICATION

The activity of growth substances is usually detected by curvatures resulting from induced cell elongation or by formative effects on later growth (Figure 3). The former response occurs within a comparatively short period of time, considered in terms of minutes or hours. Morphogenetic (formative) effects appear within days or weeks after the plant has had time to grow and produce new organs. The first evidence of INDUSTRIAL AND ENGINEERING CHEMISTRY

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Figure 3. Response of Tomato Plants to Tests

Above: Control (left) and three plants responding to local treatment with lanolin preparation of methyl indolepropionate 0.05, 0.025, and 0.01 per cent. Below: Control (left) and plant which grew in a glass cage previously used with vapors of ethyl dichlorophenoxyacetate.

formative effects appears on the new leaves which are modified in size, shape, pattern, and texture, differing considerably from the normal organs of the species. Later the effects appear on flowers, fruit, growth habit, and correlation phenomena of organs (Figure 2). If a chemical compound does not induce curvatures, cell elongation, or formative effects, it is considered inactive. By way of definition, the active ones are called growth regulators, growth substances, auxins, etc. They are incorrectly called "plant hormones" since the synthetic substances, with the exception of cinnamic acid, ethylene, and indoleacetic acid, are not known to be identical with naturally occurring hormones.

Methods of treating plants with hormones are varied. To detect activity of unknown substances on green tissue test objects, lanolin preparations are convenient (Figures 3 and 4). To induce roots on cuttings to propagate plants, the basal ends are dipped into powder preparations or solutions of the substance. The concentration requirements vary with the species, and for general use more than one strength is necessary. To prevent preharvest apple drop, a water solution containing 10 to 50 mg. of naphthaleneacetic acid per liter is sprayed on the entire tree at the time apples begin to fall prematurely. To inhibit growth of buds on tubers, bulbs, corms, rhizomes, trees, shrubs, etc., the plants or plant parts are exposed to vapors, dipped into solutions, sprayed with solutions, dusted with powder preparations, or otherwise treated with naphthaleneacetic acid or its derivatives. For inhibition by vapor treatments, methyl and ethyl naphthaleneacetate are particularly effective. The esters of the halogenomato riants to rests Above: Control (left) and plant which grew after 5 mg. of triiodoben-zoic acid had been applied to the soil. Below: Control (left), plant sprayed with o-chlorophenoxyacetic acid 300 mg./liter (middle), and plant sprayed with trichlorophenoxyethyl chloride approximately 500 mg./liter (right).

substituted phenoxy compounds are very volatile and can be used effectively for inhibiting growth by way of vapor treatments. The same substances which accelerate growth with low concentrations will inhibit growth when the concentration is great enough.

Several methods are used for inducing seedless tomatoes and eggplants. The two most commonly used are treatment of the excised stile of open flowers with a lanolin preparation or spraying the open flowers with water solutions or emulsions. According to Howlett, 0.3 per cent lanolin preparation with indolebutyric acid is near the optimum. In water solution the most effective concentrations for five chemicals are as follows: indolebutyric acid, 3000 mg. per liter; β naphthoxyacetic acid, 100; β -naphthoxypropionic acid, 50 to 100; p-chlorophenoxyacetic acid, 50 to 100 (Figure 5); dichlorophenoxyacetic acid, 10. Approximately 100 per cent fruit set without pollination is assured when open flowers are treated with these recommended concentrations. One treatment of a tomato cluster with dichlorophenoxyacetic acid when two or more flowers are open causes set of fruit on buds as well as open flowers. To apply vapors in a greenhouse, the esters are warmed over a hot plate and an electric fan circulates the air. For vapor treatments the esters of β naphthoxyacetic, β -naphthoxypropionic, p-chlorophenoxyacetic, dichlorophenoxyacetic, and trichlorophenoxyacetic acids are most effective. The milligrams per 1000 cubic feet required vary with the condition of a greenhouse, the amount of heat applied to the chemical, etc. One to ten milligrams of the dichlorophenoxyacetic acid ester or 25 to 50 mg. of the Figure 4. Modified Growth Habit and Correlation Phenomena of Kalanchoe Plants Induced with 4-Chlorophenoxyacetic Acid

Normal plant at upper left. Other plants were treated around the stem with a preparation containing 5 mg. of chemical per gram of lanolin. The modification occurred approximately 6 inches above the treated part.

 β -naphthoxyacetic acid ester should be sufficient. Indolebutyric esters are only slightly volatile and cannot be used successfully as vapors. Seedless fruit have been induced by spraying the entire plant with substituted phenoxy compounds or by adding the chemical to the soil, but the methods have not been perfected to the point where they can be safely recommended.

To date it has been possible to produce successfully seedless tomatoes, peppers, eggplant, cucumbers, and squash. Seedless watermelons have not been produced for practical purposes by any method although the idea is popular.

UNPROVED CLAIMS

Above we have discussed only the responses which can be readily duplicated by scientists and growers. It is necessary to mention a few claims which do not find good scientific backing.

Cut flowers have not lasted longer after treatment with plant hormones. However, some flowers last longer when treated and remain attached to the plant.

Treatment of seeds of grass and crop plants in this laboratory with a number of the most effective substances has not improved the crop. However, reports on the effect of seed treatment with growth substances are conflicting. Some extravagant claims in favor of this method have been made. Based on personal experience and the scientific reports of others, recommendation of seed treatments with growth substances for agricultural use would be premature and unwarranted. The seedlings can be readily inhibited or otherwise affected by this method, but there is not yet any convincing evidence of stimulation that improves or increases the harvest.

Since growth substances induce adventitious roots, it would seem that treatment of the root system at transplanting time should be favorable for re-establishing the plants. Favorable reports along this line have been made, but no convincing evidence has been presented to show that trees or other plants have benefited by treatment of the root system with vitamins or hormones during transplanting. We now have under observation 13,000 tree seedlings growing on the institute grounds; they have been treated in a variety of ways with the best known growth substances, but so far no favorable results are in evidence. It is well known, however, that roots as well as stems respond to treatment with growth substances, and it would be premature to rule



The practice of adding vitamins and plant hormones to fertilizers has more sales than practical value. If any substances to be discovered in the future should stimulate growth of the entire plant, there may be something in favor of applying it with fertilizers. There are many substituted phenoxy and benzoic compounds which have not been fully tested, and among them may be some which can be used profitably with fertilizers. At present, however, this method should be used only for experimental purposes.

CONCLUSION

The plant hormone field is still new and holds much for the future. Much more has been accomplished than could have been predicted even five years ago. The new method of substituting halogen and other groups in the nucleus to activate the molecule makes possible many new substances for research, and some of them are certain to be of considerable

practical importance for horticultural and agricultural purposes.

PRESENTED before the Division of Fertilizer Chemistry at the 104th Meeting of the American CHEMICAL SOCIETY, Buffalo, N. Y.

out future possibilities along this line. It would be premature also to recommend the treatment of transplants for horticultural practice. The subject may still serve as the basis of an extensive field project.



Figure 5. Cross Sections of Seedless Fruit Induced on Tomato Plants in a Garden by Treating a Flower Cluster with a Spray Containing 100 Mg. of 4-Chlorophenoxyacetic Acid per Liter of Water

Thermodynamic Properties of Propane

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Sun Oil Company, Marcus Hook, Penna.

THE use of propane as a refrigerant has increased substantially within the last few years, and thermodynamic data for this refrigerant have not been compiled for the whole region normally employed in refrigeration. While Dana *et al.* (2) published tables for the saturated liquid and vapor, no satisfactory compilation has been made for the superheated vapor region.

This paper represents a close correlation of the published experimental data of a number of authors on certain phases of the thermodynamic properties of propane. While Sage, Schaafsma, and Lacey (10) and Burgoyne (1) published thermodynamic charts, the data used in calculating these

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charts did not show the agreement between the experimental data pointed out in this paper. By correlating the actual experimental data of the authors cited, we have been able to show close agreement between the results of these authors. This agreement may be best understood if the following processes are examined. If, for example, we take the saturated liquid at -40° F., evaporate this liquid to the saturated vapor, heat the resulting vapor at constant pressure to 160° F., and compress it isothermally until the saturated vapor is reached, the actual heat content of the resulting vapor will then agree within about 0.2 B. t. u. with the heat content of the vapor which would be obtained by heating the saturated liquid to 160° F. and then evaporating the liquid to form a saturated vapor. Such agreement is possible







Figure 2. Entropy-Temperature Chart for Propane

only if all these various thermodynamic factors are correct or if two or more of these factors will produce compensating errors over the complete range. The latter probability is somewhat remote, in view of the complexity of the functions involved. This paper presents the first correlation of the thermodynamic properties of propane based on purely experimental data while these experimental data are not so complete as would be desired, the over-all picture is in close agreement.

PROPERTIES INVESTIGATED

The vapor pressure values employed in these correlations are calculated from the formula:

$$\log P = A/T + B \log T + C$$

where A = -1018.502

= -0.16646В

C P+6.67979=

- = absolute pressure, cm. Hg = absolute temperature, °K.

These values agree well with those of Kemp and Egan (6)above -80° F., with the low-temperature values of Dana et al., and with the values of Deschner and Brown (S) to about +195° F. From +195° F. up to and including the critical point, the values of Deschner and Brown are utilized. For temperatures below -43.7° F. the specific heats of the liquid of Kemp and Egan (6) are employed. From -43.7° to +155° F., the values represent a smooth curve through the data of Dana et al. and of Sage and Lacey. The values of Sage and Lacey (9) are apparently a revision of the earlier data of Sage, Schaafsma, and Lacey (10). Above +155° F. the values are drawn as a smooth curve roughly following the values of Sage, Schaafsma, and Lacey at the lower end and to the observed values of these authors at the higher end corrected for their deviation from the apparent true critical temperature.

The heats of fusion are taken from the observations of Kemp and Egan.

The values for latent heat were taken from a smooth curve drawn through the experimental values of Kemp and Egan (6), Dana et al. (2), and of Sage, Evans, and Lacey (8).

The specific volume and density of the liquid are taken from a smooth curve through the values of Dana (2), Sage, Schaafsma, and Lacey (10), and Deschner and Brown (3). The data for the compressed liquid are taken from Deschner and Brown.

The specific volumes of the saturated vapor show good agreement between the experimental values of Dana et al. and of Deschner and Brown. The tabulated calculated data of Dana are not in agreement and show increasing divergence with increasing temperature.

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Table I. Temperature Data for Saturated Propane

Description Description <thdescription< th=""> <thdescription< th=""></thdescription<></thdescription<>						Dei	nsity	Hant C	ontont	Tatont	Entr	ODV.
UIL 1: 2: J JP Lange J Lange J <thlange j<="" th=""> Lange J <thlange <="" j<="" th=""><th>Tempera-</th><th>Pressure, Ll Absolute,</th><th>b./Sq. In. Gage,</th><th>Volume, Cu</th><th>. Ft./Lb.</th><th>Liquid $(1/v)$,</th><th>Vapor $(1/V)$,</th><th>B. T. U</th><th>J./Lb. Vapor H</th><th>Heat L, B. T. U./Lb.</th><th>B. T. U./ Liquid s</th><th>Lb./° F. Vapor S</th></thlange></thlange>	Tempera-	Pressure, Ll Absolute,	b./Sq. In. Gage,	Volume, Cu	. Ft./Lb.	Liquid $(1/v)$,	Vapor $(1/V)$,	B. T. U	J./Lb. Vapor H	Heat L , B. T. U./Lb.	B. T. U./ Liquid s	Lb./° F. Vapor S
1 1		P 5.65 5.87 6.00 6.32 6.35 6.71 6.86 7.18 7.35	<i>gp</i> 18 in. ^{<i>a</i>} 17 in. 16 in. 15 in.	Liquid v 0.0265 0.0265 0.0266 0.0266 0.0266 0.0267 0.0267 0.0267 0.0268	Vapor V 16.2 15.6 15.3 14.6 14.6 13.8 13.5 13.0 12.7	1D./gal. 5.052 5.043 5.041 5.030 5.030 5.020 5.019 5.009 5.009	$\begin{array}{c} 0 & 062 \\ 0 & 064 \\ 0 & 065 \\ 0 & 068 \\ 0 & 068 \\ 0 & 068 \\ 0 & 072 \\ 0 & 074 \\ 0 & 076 \\ 0 & 079 \end{array}$	$\begin{array}{c} 162.6\\ 163.2\\ 163.6\\ 164.6\\ 164.6\\ 165.6\\ 166.0\\ 166.6\\ 166.2\end{array}$	$\begin{array}{c} 354.0\\ 354.4\\ 354.6\\ 355.2\\ 355.2\\ 355.8\\ 356.0\\ 356.4\\ 356.5\\ \end{array}$	$191.4 \\ 191.2 \\ 191.0 \\ 190.6 \\ 190.6 \\ 190.2 \\ 190.0 \\ 189.8 \\ 189.5 \\ 189.5 \\ 180.$	$\begin{array}{c} 0.8794\\ 0.8812\\ 0.8821\\ 0.8847\\ 0.8850\\ 0.8874\\ 0.8884\\ 0.8900\\ 0.8918\\ \end{array}$	$\begin{array}{c} 1.3832\\ 1.3826\\ 1.3822\\ 1.3812\\ 1.3811\\ 1.3801\\ 1.3797\\ 1.3791\\ 1.3785 \end{array}$
	$\begin{array}{r} -70 \\ -68.4 \\ -68 \\ -66.1 \\ -66 \\ -64 \\ -63.9 \\ -62 \\ -61.9 \end{array}$	7.48 7.84 7.91 8.32 8.33 8.80 8.81 9.28 9.30	14 in. 13 in. 12 in. 11 in.	$\begin{array}{c} 0.0268\\ 0.0268\\ 0.0268\\ 0.0268\\ 0.0269\\ 0.0269\\ 0.0269\\ 0.0269\\ 0.0269\\ 0.0270\\ 0.0270\\ \end{array}$	12.5 12.0 11.9 11.3 11.3 10.8 10.8 10.3 10.3	4.998 4.990 4.988 4.978 4.978 4.968 4.968 4.968 4.957 4.957	$\begin{array}{c} 0.080\\ 0.083\\ 0.084\\ 0.088\\ 0.088\\ 0.093\\ 0.093\\ 0.097\\ 0.097\\ \end{array}$	$\begin{array}{c} 167.6\\ 168.4\\ 168.6\\ 169.8\\ 169.7\\ 170.7\\ 170.8\\ 171.7\\ 171.8\\ \end{array}$	357.0 357.5 358.1 358.2 358.8 358.8 358.9 359.4 359.5	$189.4 \\ 189.1 \\ 189.0 \\ 188.5 \\ 188.5 \\ 188.1 \\ 188.1 \\ 188.1 \\ 187.7 \\ 187.$	$\begin{array}{c} 0.8927\\ 0.8949\\ 0.8954\\ 0.8978\\ 0.8978\\ 0.9907\\ 0.9008\\ 0.9003\\ 0.9033\\ 0.9034 \end{array}$	$1.3781 \\ 1.3775 \\ 1.3773 \\ 1.3766 \\ 1.3766 \\ 1.3756 \\ 1.3756 \\ 1.3756 \\ 1.3748 \\ 1$
$ \begin{array}{c} -\frac{90}{-46} & -\frac{12}{6} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & $	$\begin{array}{r} -60 \\ -58.1 \\ -58 \\ -56.2 \\ -54.4 \\ -54.4 \\ -52.6 \\ -52 \\ -51 \end{array}$	$9.78 \\ 10.28 \\ 10.29 \\ 10.77 \\ 10.80 \\ 11.26 \\ 11.36 \\ 11.75 \\ 11.95 \\ 12.24$	10 in. 9 in. 8 in. 7 in. 6 in. 5 in.	$\begin{array}{c} 0 & 02703 \\ 0 & 02709 \\ 0 & 02719 \\ 0 & 02714 \\ 0 & 02715 \\ 0 & 02721 \\ 0 & 02721 \\ 0 & 02725 \\ 0 & 02725 \\ 0 & 02727 \\ 0 & 02730 \end{array}$	9.77 9.35 9.33 8.96 8.59 8.59 8.51 8.24 8.12 7.93	4.946 4.936 4.926 4.925 4.917 4.915 4.907 4.907 4.904 4.898	$\begin{array}{c} 0.102\\ 0.107\\ 0.107\\ 0.112\\ 0.112\\ 0.116\\ 0.117\\ 0.120\\ 0.122\\ 0.125\\ \end{array}$	$\begin{array}{c} 172.7\\ 173.6\\ 173.7\\ 174.6\\ 174.7\\ 175.6\\ 175.8\\ 176.5\\ 176.8\\ 177.3 \end{array}$	$\begin{array}{c} 360.0\\ 360.5\\ 360.6\\ 361.1\\ 361.1\\ 361.4\\ 361.7\\ 362.1\\ 362.3\\ 362.6\\ \end{array}$	$187.3 \\ 186.9 \\ 186.5 \\ 186.4 \\ 185.8 \\ 185.9 \\ 185.9 \\ 185.5 \\ 185.5 \\ 185.3 \\ 185.$	$\begin{array}{c} 0.9060\\ 0.9085\\ 0.9086\\ 0.9108\\ 0.9111\\ 0.9132\\ 0.9137\\ 0.9154\\ 0.9162\\ 0.9175\\ \end{array}$	$\begin{array}{c} 1.3740\\ 1.3732\\ 1.3732\\ 1.3726\\ 1.3725\\ 1.3719\\ 1.3717\\ 1.3717\\ 1.3712\\ 1.3710\\ 1.3706\\ \end{array}$
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{r} -50 \\ -49.6 \\ -48 \\ -47.9 \\ -46.5 \\ -46 \\ -44.9 \\ -43.71 \\ -42 \end{array}$	$12.60 \\ 12.73 \\ 13.20 \\ 13.22 \\ 13.71 \\ 13.85 \\ 14.2 \\ 14.52 \\ 14.70 \\ 15.28$	4 in. 3 in. 2 in. 1 in. 0	$\begin{array}{c} 0.02733\\ 0.02734\\ 0.02739\\ 0.02739\\ 0.02743\\ 0.02743\\ 0.02745\\ 0.02748\\ 0.02751\\ 0.02752\\ 0.02757\\ \end{array}$	$\begin{array}{c} 7.73\\ 7.72\\ 7.50\\ 7.44\\ 7.17\\ 7.06\\ 6.90\\ 6.74\\ 6.66\\ 6.42 \end{array}$	$\begin{array}{r} 4.893\\ 4.891\\ 4.882\\ 4.883\\ 4.875\\ 4.875\\ 4.872\\ 4.866\\ 4.861\\ 4.860\\ 4.850\end{array}$	$\begin{array}{c} 0.129\\ 0.130\\ 0.133\\ 0.134\\ 0.139\\ 0.142\\ 0.145\\ 0.148\\ 0.150\\ 0.156\\ \end{array}$	177.8 178.0 178.8 178.9 179.7 179.9 180.4 180.9 181.36 181.9	362.8 362.9 363.4 363.5 363.8 364.0 364.3 364.6 364.76 365.2	$185.0 \\ 184.9 \\ 184.6 \\ 184.6 \\ 184.1 \\ 184.1 \\ 183.9 \\ 183.8 \\ 183.5 \\ 183.3 \\ 183.$	$\begin{array}{c} 0.9188\\ 0.9193\\ 0.9213\\ 0.9214\\ 0.9232\\ 0.9238\\ 0.9252\\ 0.9264\\ 0.9266\\ 0.9289 \end{array}$	$1.3702 \\ 1.3701 \\ 1.3696 \\ 1.3696 \\ 1.3691 \\ 1.3689 \\ 1.3689 \\ 1.3683 \\ 1.3682 \\ 1.3682 \\ 1.3676$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	- 40 - 38 - 36 - 34 - 32	16.0016.7917.5618.4019.30	$1.30 \\ 2.09 \\ 2.86 \\ 3.70 \\ 4.60$	$\begin{array}{c} 0.02763\\ 0.02769\\ 0.02775\\ 0.02775\\ 0.02782\\ 0.02788\\ \end{array}$	$ \begin{array}{r} 6.16 \\ 5.92 \\ 5.66 \\ 5.44 \\ 5.22 \\ \end{array} $	4.839 4.828 4.818 4.807 4.797	$\begin{array}{c} 0.162 \\ 0.169 \\ 0.177 \\ 0.184 \\ 0.192 \end{array}$	183.0 184.0 185.1 186.2 187.3	365.7 366.3 366.9 367.5 368.0	182.7 182.3 181.8 181.3 180.7	$\begin{array}{c} 0.9315 \\ 0.9340 \\ 0.9365 \\ 0.9391 \\ 0.9416 \end{array}$	$\begin{array}{c} 1.3670\\ 1.3664\\ 1.3658\\ 1.3652\\ 1.3652\\ 1.3646\end{array}$
$\begin{array}{c} = 20 \\ = 20 \\ = 16 \\ = 7.30 \\ = 16 \\ = 7.30 \\ = 12 \\ = 12 \\ = 29.70 \\ = 114 \\ = 29.70 \\ = 13.80 \\ = 0.02838 \\ = 3.76 \\ = 4.708 \\ = 0.266 \\ = 196.0 \\ = 0.277 \\ = 197.1 \\ = 197.2 \\ = 177.7 \\ = 0.558 \\ = 1.3600 \\ = 13.80 \\ = 0.02848 \\ = 3.76 \\ = 4.708 \\ = 0.277 \\ = 197.1 \\ = 197.2 \\ = 10 \\ = 32.92 \\ = 177.5 \\ = 10 \\ = 0.02848 \\ = 3.76 \\ = 14.4 \\ = 29.70 \\ = 16.22 \\ = 13.80 \\ = 0.02848 \\ = 3.76 \\ = 4.666 \\ = 0.286 \\ = 196.0 \\ = 0.277 \\ = 197.1 \\ = 377.2 \\ = 177.5 \\ = 0.9646 \\ = 1.3888 \\ = 198.2 \\ = 377.5 \\ = 177.5 \\ = 0.9646 \\ = 1.3888 \\ = 10 \\ = 0.2886 \\ = 3.23 \\ = 10 \\ = 0.2886 \\ = 3.23 \\ = 10 \\ = 0.2886 \\ = 3.23 \\ = 10 \\ = 0.2886 \\ = 3.20 \\ = 1.3686 \\ = 3.20 \\ = 10.27 \\ = 10 \\ = 0.2286 \\ = 3.20 \\ = 10.27 \\ = 10$	-30 -28 -26 -24 -22	$\begin{array}{c} 20.18\\ 21.05\\ 22.01\\ 22.98\\ 23.98\end{array}$	5.48 6.35 7.31 8.28 9.28	$\begin{array}{c} 0.02794 \\ 0.02800 \\ 0.02807 \\ 0.02813 \\ 0.02820 \end{array}$	5.02 4.82 4.63 4.44 4.25	4.786 4.775 4.764 4.752 4.741	0.199 0.207 0.216 0.225 0.235	188.4189.4190.5191.6192.7	368.6 369.2 369.8 370.3 370.9	180.2 179.7 179.3 178.7 178.2	$\begin{array}{c} 0.9441 \\ 0.9467 \\ 0.9492 \\ 0.9517 \\ 0.9543 \end{array}$	$1.3640 \\ 1.3634 \\ 1.3628 \\ 1.3622 \\ 1.3616$
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	-20 -18 -16 -14 -12	$\begin{array}{c} 25.05 \\ 26.15 \\ 27.30 \\ 28.50 \\ 29.70 \end{array}$	$10.35 \\ 11.45 \\ 12.60 \\ 13.80 \\ 15.00$	0.02826 0.02833 0.02839 0.02846 0.02852	$\begin{array}{c} 4.06\\ 3.90\\ 3.76\\ 3.61\\ 3.47\end{array}$	$\begin{array}{r} 4.730 \\ 4.719 \\ 4.708 \\ 4.697 \\ 4.686 \end{array}$	$\begin{array}{c} 0.246 \\ 0.256 \\ 0.266 \\ 0.277 \\ 0.288 \end{array}$	193.8 194.9 196.0 197.1 198.2	371.5 372.1 372.7 373.2 373.8	177.7 177.2 176.6 176.1 175.6	$\begin{array}{c} 0.9568 \\ 0.9592 \\ 0.9617 \\ 0.9641 \\ 0.9666 \end{array}$	$\begin{array}{r} 1.3610 \\ 1.3604 \\ 1.3599 \\ 1.3593 \\ 1.3588 \end{array}$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{r} -10 \\ -8 \\ -6 \\ -4 \\ -2 \end{array} $	$\begin{array}{c} 30.95\\ 32.23\\ 33.55\\ 35.00\\ 36.40 \end{array}$	$16.25 \\ 17.53 \\ 18.85 \\ 20.30 \\ 21.70$	0.02859 0.02866 0.02873 0.02879 0.02886	3,33 3,20 3,08 2,98 2,86	$\begin{array}{r} 4.675 \\ 4.664 \\ 4.652 \\ 4.641 \\ 4.629 \end{array}$	$\begin{array}{c} 0.300 \\ 0.313 \\ 0.325 \\ 0.336 \\ 0.350 \end{array}$	$199.4 \\ 200.5 \\ 201.6 \\ 202.7 \\ 203.8 \\$	374.4 375.0 375.5 376.1 376.7	175.0 174.5 173.9 173.4 172.8	0.9690 0.9714 0.9739 0.9763 0.9788	$\begin{array}{c} 1.3582\\ 1.3577\\ 1.3571\\ 1.3566\\ 1.3560\end{array}$
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	- 0 + 2 + 4 + 6 = 8	$\begin{array}{r} 37.81 \\ 39.30 \\ 40.85 \\ 42.50 \\ 44.13 \end{array}$	$\begin{array}{r} 23.11\\ 24.60\\ 26.15\\ 27.80\\ 29.43\end{array}$	$\begin{array}{c} 0.02893\\ 0.02900\\ 0.02908\\ 0.02915\\ 0.02923 \end{array}$	$2.74 \\ 2.66 \\ 2.56 \\ 2.47 \\ 2.38$	$\begin{array}{r} 4.618 \\ 4.607 \\ 4.596 \\ 4.584 \\ 4.573 \end{array}$	$\begin{array}{c} 0.365 \\ 0.376 \\ 0.391 \\ 0.405 \\ 0.420 \end{array}$	205.0206.1207.2208.4209.6	377.2 377.8 378.3 378.9 379.5	172.2 171.6 171.1 170.5 169.9	0.9812 0.9836 0.9860 0.9884 0.9908	$1.3555 \\ 1.3550 \\ 1.3545 \\ 1.3541 \\ 1.3536 \\ 1$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	10 12 14 16 18	$\begin{array}{r} 45.85\\ 47.55\\ 49.35\\ 51.20\\ 53.10\end{array}$	31.15 32.85 34.65 36.50 38.40	0.02930 0.02938 0.02946 0.02954 0.02962	2.30 2.22 2.14 2.08 2.00	$\begin{array}{r} 4.562 \\ 4.550 \\ 4.538 \\ 4.526 \\ 4.514 \end{array}$	$\begin{array}{c} 0.435 \\ 0.450 \\ 0.467 \\ 0.481 \\ 0.500 \end{array}$	$210.7 \\ 211.9 \\ 213.1 \\ 214.2 \\ 215.4$	380.0 380.6 381.1 381.6 382.1	169.3 168.7 168.0 167.4 166.7	0.9932 0.9956 0.9979 1.0003 1.0026	$1.3531 \\ 1.3527 \\ 1.3523 \\ 1.3518 \\ 1.3514$
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	20 22 24 26 28	55.00 57.05 59.10 61.25 63.45	$\begin{array}{r} 40.30\\ 42.35\\ 44.40\\ 46.55\\ 48.75\end{array}$	0.02970 0.02978 0.02986 0.02995 0.03003	1.93 1.86 1.79 1.73 1.67	$\begin{array}{r} 4.502 \\ 4.590 \\ 4.477 \\ 4.465 \\ 4.452 \end{array}$	$\begin{array}{c} 0.518 \\ 0.538 \\ 0.559 \\ 0.578 \\ 0.598 \end{array}$	$216.6 \\ 217.7 \\ 218.8 \\ 220.0 \\ 221.2$	382.6 383.1 383.6 384.1 384.6	166.0 165.4 164.8 164.2 163.5	1.0050 1.0073 1.0097 1.0120 1.0144	${}^{1.3510}_{1.3506}_{1.3502}_{1.3499}_{1.3495}$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	30 32 34 36 38	65.70 67.95 70.33 72.75 75.20	51.00 53.25 55.63 58.05 60.50	$\begin{array}{c} 0.03011\\ 0.03020\\ 0.03029\\ 0.03037\\ 0.03046 \end{array}$	$1.60\\1.54\\1.48\\1.43\\1.39$	$\begin{array}{r} 4.440 \\ 4.427 \\ 4.414 \\ 4.401 \\ 4.388 \end{array}$	$0.625 \\ 0.649 \\ 0.676 \\ 0.699 \\ 0.719$	$\begin{array}{r} 222.3\\ 223.4\\ 224.5\\ 225.6\\ 226.8\end{array}$	385.1 385.6 386.1 386.6 387.1	162.8 162.2 161.5 160.8 160.2	$1.0167 \\ 1.0190 \\ 1.0213 \\ 1.0237 \\ 1.0260$	$1.3491 \\ 1.3487 \\ 1.3484 \\ 1.3480 \\ 1.3477$
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	40 42 44 46 48	77.80 80.40 83.05 85.83 88.65	$\begin{array}{c} 63.10 \\ 65.70 \\ 68.35 \\ 71.13 \\ 73.95 \end{array}$	$\begin{array}{c} 0.03055\\ 0.03064\\ 0.03073\\ 0.03083\\ 0.03092 \end{array}$	1.33 1.28 1.25 1.21 1.17	$\begin{array}{r} 4.375 \\ 4.362 \\ 4.348 \\ 4.335 \\ 4.321 \end{array}$	0.752 0.781 0.800 0.826 0.855	$\begin{array}{r} 227.9 \\ 229.1 \\ 230.2 \\ 231.4 \\ 232.6 \end{array}$	387.5 388.0 388.5 389.0 389.5	159.6158.9158.2157.5156.8	1.0283 1.0306 1.0329 1.0352 1.0352	$1.3473 \\ 1.3470 \\ 1.3466 \\ 1.3463 \\ 1.3459$
	50 52 54 56 58	91.50 94.50 97.5 100.6 103.7	76.80 79.80 82.80 85.9 89.0	$\begin{array}{c} 0.03101\\ 0.03111\\ 0.03121\\ 0.03130\\ 0.03140 \end{array}$	1.14 1.10 1.07 1.04 1.01	$\begin{array}{r} 4.308 \\ 4.294 \\ 4.281 \\ 4.267 \\ 4.254 \end{array}$	0.877 0.909 0.935 0.962 0.990	$233.8 \\ 234.9 \\ 236.1 \\ 237.3 \\ 238.5$	389.9 390.4 390.8 391.3 391.7	156.1 155.4 154.7 154.0 153.3	1.03981.04211.04431.04661.0488	1.34561.34531.34501.34471.3444

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	Deserves Th	- /9 - T-			Dens	Vapor	Heat Co	ontent,	Latent	Entro	py, b/• F
mpera-	Absolute,	Gage,	Volume, Cu.	Ft./Lb. Vapor V	(1/s). lb./gal.	(1/V), lb./cu. ft.	B. T. U Liquid h	Vapor H	Heat L , B. T. U./Lb.	Liquid 8	Vapor S
60 62 64 66	106.9 110.2 113.6 117.1	92.2ª 95.5 98.9 102.4 105.9	$\begin{array}{c} 0.03150\\ 0.03162\\ 0.03174\\ 0.03185\\ 0.03197\end{array}$	0.984 0.958 0.932 0.906 0.880	4.240 4.226 4.213 4.199 4.186	$1.016 \\ 1.044 \\ 1.073 \\ 1.104 \\ 1.136$	239.6 240.8 242.0 243.2 244.4	392.2 392.7 393.1 393.5 394.0	152.6 151.8 151.1 150.3 149.5	$1.0511 \\ 1.0534 \\ 1.0556 \\ 1.0579 \\ 1.0601$	1.34411.34381.34351.34331.34331.3430
70 72 74 76 78	124.3 127.9 131.7 135.6 139.6	109.6 113.2 117.0 120.9 124.9	$\begin{array}{c} 0.03209\\ 0.03221\\ 0.03233\\ 0.03245\\ 0.03257\end{array}$	$\begin{array}{c} 0.854 \\ 0.832 \\ 0.810 \\ 0.788 \\ 0.766 \end{array}$	4.172 4.158 4.144 4.131 4.117	$1.171 \\ 1.202 \\ 1.235 \\ 1.269 \\ 1.305$	245.7246.9248.1249.4250.2	394.4 394.8 395.2 395.6 396.0	$148.7 \\ 147.8 \\ 147.0 \\ 146.2 \\ 145.4$	$\begin{array}{c} 1.0624 \\ 1.0647 \\ 1.0669 \\ 1.0692 \\ 1.0714 \end{array}$	$1.3427 \\ 1.3424 \\ 1.3421 \\ 1.3419 \\ 1.3416$
80 82 84 86	143.6 147.7 151.8 156.2 160.6	$128.9 \\ 133.0 \\ 137.1 \\ 141.5 \\ 145.9 $	$\begin{array}{c} 0.03269\\ 0.03281\\ 0.03293\\ 0.03305\\ 0.03317\end{array}$	$\begin{array}{c} 0.745 \\ 0.725 \\ 0.704 \\ 0.684 \\ 0.663 \end{array}$	4.103 4.088 4.074 4.059 4.045	$1.342 \\ 1.379 \\ 1.420 \\ 1.462 \\ 1.508$	$251.9 \\ 253.1 \\ 254.4 \\ 255.6 \\ 256.9 \\$	396.4 396.8 397.2 397.6 398.0	144.5 143.7 142.8 141.9 141.0	1.0737 1.0760 1.0782 1.0805 1.0827	$1.3413 \\ 1.3410 \\ 1.3408 \\ 1.3405 \\ 1.3403$
90 92 94 96	165.0 169.6 174.2 178.9 183.7	150.3 154.9 159.5 164.2 169.0	$\begin{array}{c} 0.03329\\ 0.03341\\ 0.03353\\ 0.03366\\ 0.03378\end{array}$	$\begin{array}{c} 0.643 \\ 0.626 \\ 0.609 \\ 0.592 \\ 0.575 \end{array}$	4.030 4.015 4.001 3.986 3.972	1.555 1.597 1.642 1.689 1.739	258.2 259.5 260.8 262.1 263.3	398.3 398.7 399.1 399.5 399.9	140.1 139.2 138.3 137.4 136.5	1.0850 1.0873 1.0895 1.0918 1.0940	$1.3400 \\ 1.3398 \\ 1.3395 \\ 1.3393 \\ 1.3393 \\ 1.3390$
100 102 104 106	188.7 193.8 198.9 204.1	174.0 179.1 184.2 189.4	$\begin{array}{c} 0.03390\\ 0.03402\\ 0.03415\\ 0.03427\\ 0.03427\\ 0.03439 \end{array}$	0.558 0.544 0.530 0.516 0.502	3.957 3.941 3.925 3.910 3.894	1.792 1.838 1.887 1.938 1.992	264.6 265.9 267.2 268.5 269.8	400.2 400.5 400.9 401.2 401.6	135.6 134.6 133.7 132.7 131.8	1.0963 1.0986 1.1010 1.1033 1.1057	1,3388 1,3386 1,3384 1,3382 1,3382 1,3380
108 110 112 114 116	209.3 214.8 220.4 226.0 231.6 231.6	200.1 205.7 211.3 216.9	0.03452 0.03468 0.03484 0.03500 0.03516	$\begin{array}{c} 0.487 \\ 0.475 \\ 0.463 \\ 0.451 \\ 0.439 \end{array}$	3.878 3.862 3.846 3.830 3.814	$2.053 \\ 2.105 \\ 2.160 \\ 2.217 \\ 2.278$	$271.1 \\ 272.5 \\ 273.9 \\ 275.2 \\ 276.6$	401.9 402.3 402.7 403.0 403.4	130.8 129.8 128.8 127.8 126.8	$1.1080 \\ 1.1103 \\ 1.1126 \\ 1.1149 \\ 1.1172$	$1.3378 \\ 1.3376 \\ 1.3374 \\ 1.3372 \\ 1.3370 $
118 120 122 124 126	237.3 243.4 249.7 255.7 261.7 261.7	222.0 228.7 235.0 241.0 247.0	0.03532 0.03548 0.03564 0.03580 0.03580	$\begin{array}{c} 0.426\\ 0.415\\ 0.404\\ 0.393\\ 0.382\end{array}$	3.798 3.780 3.763 3.745 3.728	2.347 2.410 2.475 2.544 2.618	278.0 279.4 280.9 282.3 283.8	$\begin{array}{r} 403.8\\ 404.1\\ 404.5\\ 404.8\\ 405.2 \end{array}$	$125.8 \\ 124.7 \\ 123.6 \\ 122.5 \\ 121.4$	$\begin{array}{c} 1.1195\\ 1.1218\\ 1.1241\\ 1.1264\\ 1.1287\end{array}$	1.3368 1.3366 1.3363 1.3361 1.3358
128 130 132 134 136	267.9 274.5 281.1 287.9 294.7	259.8 266.4 273.2 280.0	0.03612 0.03630 0.03648 0.03666 0.03684	$0.370 \\ 0.360 \\ 0.350 \\ 0.340 \\ 0.330$	3.710 3.692 3.674 3.657 3.639	2.703 2.778 2.857 2.941 3.030	285.2 286.7 288.2 289.7 291.2	405.4 405.7 406.1 406.4 406.7	120.2 119.0 117.9 116.7 115.5	$1.1310 \\ 1.1334 \\ 1.1358 \\ 1.1358 \\ 1.1382 \\ 1.1406$	$\begin{array}{r}1.3356\\1.3353\\1.3350\\1.3348\\1.3348\\1.3345\end{array}$
138 140 142 144 146	308.4 315.5 322.8 330.2	293.7 300.8 308.1 315.5	0.03702 0.03725 0.03748 0.03771 0.03794	$\begin{array}{c} 0.320 \\ 0.312 \\ 0.303 \\ 0.295 \\ 0.286 \end{array}$	3.621 3.600 3.578 3.557 3.535	3,125 3,205 3,300 3,390 3,496	292.7 294.2 295.7 297.2 298.6	407.0 407.3 407.6 407.8 408.0	$114.3 \\ 113.1 \\ 111.9 \\ 110.6 \\ 109.4$	$1.1430 \\ 1.1454 \\ 1.1479 \\ 1.1503 \\ 1.1528$	$ \begin{array}{r} 1.3347\\ 1.3339\\ 1.3336\\ 1.3332\\ 1.3329 \end{array} $
148 150 152 154 156	337.6 345.4 352.9 360.8 368.6	330.7 338.2 346.1 353.9	0.03817 0.03846 0.03875 0.03904 0.03903	$\begin{array}{c} 0.278 \\ 0.270 \\ 0.263 \\ 0.255 \\ 0.248 \end{array}$	3.514 3.487 3.460 3.434 3.407	3.597 3.704 3.802 3.922 4.032	300.2 301.8 303.4 305.1 306.8	408.2 408.4 408.6 408.7 408.8	$108.0 \\ 106.6 \\ 105.2 \\ 103.6 \\ 102.0$	$\begin{array}{c} 1.1552 \\ 1.1578 \\ 1.1603 \\ 1.1629 \\ 1.1654 \end{array}$	$\begin{array}{r} 1.3326 \\ 1.3321 \\ 1.3317 \\ 1.3312 \\ 1.3308 \end{array}$
158 160 162 164 166	376.6 385.0 392.9 401.0 409.3	370.3 378.2 386.3 394.6	0.03962 0.03962 0.03996 0.04030 0.04064	0.240 0.234 0.227 0.221 0.214	3.380 3.351 3.322 3.292 3.263	4.167 4.273 4.405 4.525 4.673	308.4 310.2 312.0 313.9 315.7	408.8 408.8 408.9 408.9 408.8	100.4 98.6 96.9 95.0 93.1	$1.1680 \\ 1.1707 \\ 1.1734 \\ 1.1762 \\ 1.1789$	1.3303 1.3297 1.3291 1.3284 1.3278
168 170 172 174 176	417.8 426.0 436.4 445.9 455.2	403.1 411.3 421.7 431.2 440.5	0.04132 0.04179 0.04226 0.04273	0.208 0.202 0.197 0.191 0.186	3.234 3.201 3.168 3.136 3.103	4.808 4.950 5.076 5.236 5.376	317.5 319.5 321.5 323.5 325.5	408.6 408.6 408.6 408.4 408.2	91.1 89.1 87.1 84.9 82.7	$\begin{array}{c} 1.1816 \\ 1.1847 \\ 1.1878 \\ 1.1908 \\ 1.1909 \end{array}$	$\begin{array}{c} 1.3272\\ 1.3262\\ 1.3252\\ 1.3243\\ 1.3233\end{array}$
178 180 182 184 186 188	464.1 473.2 483.0 492.9 503.1 512.8 523.4	449.4 458.5 468.3 478.2 488.4 498.1 508.7	$\begin{array}{c} 0.04320\\ 0.04367\\ 0.04436\\ 0.04505\\ 0.04574\\ 0.04643\\ 0.04712\end{array}$	0.180 0.180 0.174 0.168 0.161 0.155 0.149	3.07 3.03 2.99 2.95 2.91 2.87	5.556 5.747 5.952 6.211 6.452 6.711 8.850	327.5 329.8 332.2 334.5 336.9 339.4 339.4 353.5	407.6 407.4 407.1 406.6 406.6 405.9 404.0 398.3	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{c} 1.1970\\ 1.2004\\ 1.2038\\ 1.2072\\ 1.2106\\ 1.2140\\ 1.2360\end{array}$	$\begin{array}{c} 1.3223\\ 1.3210\\ 1.3190\\ 1.3183\\ 1.316\\ 1.315\\ 1.304\end{array}$

3.03 2.99 2.95 2.91 2.87 2.59

 $\begin{array}{c} 0.180\\ 0.174\\ 0.168\\ 0.161\\ 0.155\\ 0.149\\ 0.113\\ \end{array}$

Table I. Temperature Data for Saturated Propane (Concluded)

" Inches of mercury vacuum.

503.1 512.8 523.4 575.0

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Specific volumes of superheated vapor were calculated from compressibility factors as based on Deschner and Brown.

 $\begin{array}{c} 0.04301\\ 0.04436\\ 0.04505\\ 0.04574\\ 0.04643\\ 0.04712\\ 0.0521 \end{array}$

These values were plotted and extrapolated on a largescale chart. A few of them deviate from the smooth curve by amounts which indicate a strong possibility that the tabulated values were either misread from the original chart or that a typographical error had been made.

These values were smoothed as indicated; in addition, the deviation of the saturated specific volumes from those calculated from the simple gas law were plotted as unique or limiting values for the compressibility factors at any given temperature. The compressibility factors were then interpolated and extrapolated for the vapor to cover the whole range above -70° F.

 $1.3196 \\ 1.3183 \\ 1.3169 \\ 1.3156 \\ 1.3040$

Except in the case of the saturated liquid, the data substantially below 86° F. may be considered purely imaginative, without experimental basis. Actually, the curves drawn are merely similar to those in the known experimental regions, and the accuracy of these values must be judged in the light of their agreement or disagreement with other experimental data.

From the compressibility factors as plotted above, the corresponding isobars were plotted and their slopes accurately evaluated; the corresponding values for $(\partial Z/\partial T)_P$ were plotted against pressure.

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From the smoothed values the isothermal change of enthalpy with pressure was calculated at constant temperature by the well-known formula:

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$$\begin{bmatrix} \frac{\partial H}{\partial P} \end{bmatrix}_T = \frac{-NRT^2}{P} \begin{bmatrix} \frac{\partial Z}{\partial T} \end{bmatrix}_T$$

The values of the function -H at constant temperature are obtained by graphical integration of the values for the change in enthalpy with pressure at constant temperature when plotted against absolute pressure.

The agreement between our values for 190° F. and those of Deschner and Brown for 194° F. is striking. The disagreement between our 160° values and those of Deschner and Brown at 158° F. is substantial; but since errors occur in their tabulated figures for this range, the results of the correlation weigh strongly in favor of our 160° figures.

In the field of specific heat of propane vapor, the values in the literature have no satisfactory agreement.

The values of Edmister (5) are based on a correlation and have no independent value unless confirmed by experimental data. This is particularly true in the case of propane, which deviates substantially in most correlations.

The values of Kistiakowsky and Rice (7) for propane have no confirmation from other sources. Their experimental values for other gases obtained with the same equipment have had substantial confirmation, however, and this correlation also checks their data. When used as a basis for calculation of the absolute enthalpy values, their values give extremely good agreement with heat content data for the saturated

liquid over the whole range of experimental work.

The values of Dobratz (4) are based on assumptions concerning certain potential barriers producing hindered rotation of the methyl groups in this compound; he gives different data for different assumed values of this potential barrier. On this basis we have assumed that the data of Kistiakowsky and Rice (7) are correct. As a matter of fact, no other values will produce a satisfactory correlation, and the correlation indicates that they are probably accurate to about one in the third decimal place.

	1	able II	. Proper	ties* of S	uperhe	ated Propa	ne Vapor		
mn.	$P = 15 {\rm In}$	Hg, $t =$	-70.6° F.	P = 10 I	n. Hg, $t =$	$= -60^{\circ} F.$	P = 5 In	n. Hg, $t =$	~51° F.
F.	V 12.72	H 356.5	S 1.3785	V 9.80	H 360.0	S 1.3740	V 7.90	H 362.75	8 1.3718
-70 -60 -50	12.78 13.11 13.45 12.70	357.0 360.3 363.5 366	1.3791 1.3869 1.3946 1.4023	10.042 10.30	$363.2 \\ 366.5$	1.3816 1.3893	7.978 8.182	362.8 366.2	1.3720 1.3796
- 30 - 20 - 10	$13.79 \\ 14.13 \\ 14.47 \\ 14.81$	370.1 373.4 376.8	1.4025 1.4100 1.4177 1.4253	10.55 10.81 11.06	369.8 373.1 376.6	$1.3970 \\ 1.4045 \\ 1.4121$	$8.387 \\ 8.591 \\ 8.796$	369.6 373.0 376.4	$1.3872 \\ 1.3948 \\ 1.4024$
0 10 20 30 40 50	$15.14 \\ 15.48 \\ 15.82 \\ 16.16 \\ 16.50 \\ 16.83 $	380.2 383.8 387.4 391.1 394.8 398.6	1.4329 1.4405 1.4481 1.4557 1.4633 1.4709	$11.321 \\ 11.57 \\ 11.83 \\ 12.08 \\ 12.34 \\ 12.59$	380.0 383.6 387.2 390.9 394.6 398.4	$\begin{array}{c} 1.4197 \\ 1.4273 \\ 1.4349 \\ 1.4349 \\ 1.4425 \\ 1.4501 \\ 1.4577 \end{array}$	9.000 9.204 9.409 9.613 9.818 10.02	379.9 383.4 387.0 390.7 394.4 398.2	1.4100 1.4176 1.4252 1.4328 1.4404 1.4404
60 70 80 90 100	17.1717.5117.8518.1918.52	$\begin{array}{r} 402.4\\ 406.3\\ 410.2\\ 414.3\\ 418.4 \end{array}$	$1.4785 \\ 1.4861 \\ 1.4937 \\ 1.5013 \\ 1.5088$	$12.85 \\ 13.10 \\ 13.36 \\ 13.61 \\ 13.87$	$\begin{array}{r} 402.2 \\ 406.1 \\ 410.0 \\ 414.1 \\ 418.2 \end{array}$	$1.4652 \\ 1.4727 \\ 1.4802 \\ 1.4877 \\ 1.4952$	$10.23 \\ 10.43 \\ 10.64 \\ 10.84 \\ 11.050$	402.0 406.0 410.0 414.0 418.1	$1.4556 \\ 1.4630 \\ 1.4706 \\ 1.4780 \\ 1.4854$
110 120 130 140 150 160 170 180 190 200	$18.86 \\ 19.20 \\ 19.54 \\ 19.88 \\ 20.21 \\ 20.55 \\ 20.89 \\ 21.23 \\ 21.57 \\ 21.90 \\$	$\begin{array}{r} 422.5\\ 426.6\\ 430.8\\ 435.2\\ 439.6\\ 444.1\\ 448.6\\ 453.1\\ 457.9\\ 462.5\end{array}$	$\begin{array}{c} 1.5162 \\ 1.5235 \\ 1.5308 \\ 1.5380 \\ 1.5452 \\ 1.5524 \\ 1.5596 \\ 1.5668 \\ 1.5740 \\ 1.5812 \end{array}$	$14.12 \\ 14.38 \\ 14.63 \\ 15.14 \\ 15.65 \\ 15.91 \\ 16.16 \\ 16.42 $	$\begin{array}{r} 422.3\\ 426.4\\ 430.6\\ 435.0\\ 439.4\\ 443.9\\ 448.9\\ 448.4\\ 452.9\\ 457.7\\ 462.4\end{array}$	$\begin{array}{c} 1.5026\\ 1.5101\\ 1.5174\\ 1.5245\\ 1.5317\\ 1.5389\\ 1.5461\\ 1.5533\\ 1.5605\\ 1.5677\end{array}$	$11.25 \\ 11.45 \\ 11.66 \\ 12.07 \\ 12.27 \\ 12.47 \\ 12.68 \\ 12.88 \\ 13.09 \\ 13.09 \\ 11.25 \\ 12.2$	$\begin{array}{c} 422.1\\ 426.2\\ 430.6\\ 435.9\\ 439.3\\ 443.8\\ 448.4\\ 452.9\\ 457.6\\ 462.4 \end{array}$	$\begin{array}{c} 1.4928\\ 1.5002\\ 1.5075\\ 1.5148\\ 1.5221\\ 1.5293\\ 1.5365\\ 1.5437\\ 1.5509\\ 1.5581\end{array}$
	P = 14.	696 Lb. A 43.708° I	bs., $t = F$.	P = 16 Lb	Abs., $t =$	-40.01° F.	P = 20 Lb	Abs., $t =$	— 30.30° F.
td.	6.66	364.6	1.3681	6.195	365.5	1.3670	5.050	368.4	1.3640
- 40 - 30 - 20 - 10 0	6.775 6.949 7.123 7.297 7.471	365.8 369.3 372.8 376.3 379.8	$1.3788 \\ 1.3866 \\ 1.3943 \\ 1.4020$	$ \begin{array}{r} 6.212 \\ 6.371 \\ 6.530 \\ 6.659 \\ 6.848 \\ \end{array} $	369.2 372.6 376.1 379.6	$1.3784 \\ 1.3825 \\ 1.3902 \\ 1.3979$	$5.060 \\ 5.186 \\ 5.313 \\ 5.439$	368.6 372.2 375.8 739.3	$1.3642 \\ 1.3719 \\ 1.3796 \\ 1.3873$
10 20 30 40 50 60 70 80 90 100	$\begin{array}{c} 7.644\\ 7.816\\ 7.988\\ 8.160\\ 8.332\\ 8.503\\ 8.674\\ 8.844\\ 9.016\\ 9.187\end{array}$	$\begin{array}{c} 383.3\\ 386.8\\ 390.6\\ 394.3\\ 398.1\\ 401.9\\ 405.8\\ 409.8\\ 413.9\\ 418.0\\ \end{array}$	$1.4096 \\ 1.4772 \\ 1.4248 \\ 1.4324 \\ 1.4399 \\ 1.4474 \\ 1.4549 \\ 1.4623 \\ 1.4698 \\ 1.4698 \\ 1.4772$	$\begin{array}{c} 7.007\\ 7.166\\ 7.324\\ 7.482\\ 7.640\\ 7.798\\ 7.955\\ 8.112\\ 8.269\\ 8.426\end{array}$	383.2 386.8 390.4 394.2 398.0 401.8 405.8 409.8 413.8 417.9	$1.4056 \\ 1.4132 \\ 1.4208 \\ 1.4284 \\ 1.4359 \\ 1.4434 \\ 1.4508 \\ 1.4582 \\ 1.4656 \\ 1.4730 \\ 1$	$\begin{array}{c} 5.567\\ 5.695\\ 5.823\\ 5.951\\ 6.079\\ 6.207\\ 6.334\\ 6.461\\ 6.588\\ 6.716\end{array}$	$\begin{array}{c} 382.9\\ 386.5\\ 390.2\\ 393.9\\ 397.7\\ 401.6\\ 405.5\\ 409.4\\ 413.5\\ 417.6\end{array}$	$\begin{array}{c} 1.3949\\ 1.4025\\ 1.4101\\ 1.4177\\ 1.4252\\ 1.4327\\ 1.4402\\ 1.4477\\ 1.44551\\ 1.4625\\ \end{array}$
110 120 130 140 150 160 170 180 190 200	$\begin{array}{r} 9.358\\ 9.528\\ 9.699\\ 9.869\\ 10.040\\ 10.21\\ 10.38\\ 10.51\\ 10.72\\ 10.84\end{array}$	$\begin{array}{r} 422.1\\ 426.2\\ 430.4\\ 434.8\\ 439.2\\ 443.7\\ 448.3\\ 452.9\\ 457.5\\ 462.4\\ \end{array}$	$1.4845 \\ 1.4918 \\ 1.4991 \\ 1.5064 \\ 1.5137 \\ 1.5210 \\ 1.5283 \\ 1.5256 \\ 1.5428 \\ 1.5500 \\ 1$		$\begin{array}{r} 421.9\\ 426.1\\ 430.4\\ 434.8\\ 439.2\\ 443.7\\ 448.2\\ 452.8\\ 457.4\\ 462.2 \end{array}$	$1.4804 \\ 1.4878 \\ 1.4952 \\ 1.5026 \\ 1.5099 \\ 1.5172 \\ 1.5245 \\ 1.5317 \\ 1.5389 \\ 1.5460 \\ 1.5560 \\ 1$	$\begin{array}{c} 6.843\\ 6.969\\ 7.095\\ 7.221\\ 7.347\\ 7.473\\ 7.599\\ 7.725\\ 7.851\\ 7.977\end{array}$	$\begin{array}{r} 421.7\\ 425.9\\ 430.2\\ 434.6\\ 439.0\\ 443.5\\ 448.0\\ 452.6\\ 457.3\\ 461.9\end{array}$	$1.4698 \\ 1.4771 \\ 1.4844 \\ 1.4917 \\ 1.4990 \\ 1.5063 \\ 1.5136 \\ 1.5209 \\ 1.5282 \\ 1.5355 \\ 1$
	P = 24 Lb.	Abs., $t =$	-21.97° F.	$P = 30 {\rm Lb.}$	Abs., $t =$		P = 40 Lb	Abs., $t =$	+2.90° F.
td.	4.25	370.9	1.3615	3.30	374.00	1.3588	2.61	378.2	1.3548
-10	4.390 4.499	375.3 378.9	1.3032 1.3712 1.3790	3.47 3.559	$\begin{array}{r} 374.6\\ 378.3\end{array}$	1.3597 1.3678			
10 20 30 40 50 60 70 80 90 100	$\begin{array}{r} 4.608\\ 4.716\\ 4.824\\ 4.932\\ 5.040\\ 5.147\\ 5.254\\ 5.361\\ 5.467\\ 5.573\end{array}$	382.5 386.2 389.9 393.6 397.4 401.3 405.2 409.2 413.3 417.4	$1.3806 \\ 1.3942 \\ 1.4018 \\ 1.4094 \\ 1.4170 \\ 1.4245 \\ 1.4320 \\ 1.4394 \\ 1.4468 \\ 1.4542$	$\begin{array}{c} 3.647\\ 3.735\\ 3.823\\ 3.911\\ 3.999\\ 4.087\\ 4.174\\ 4.261\\ 4.347\\ 4.432\end{array}$	$\begin{array}{r} 382.0\\ 385.7\\ 389.4\\ 393.1\\ 396.9\\ 400.8\\ 404.7\\ 408.7\\ 412.8\\ 417.0\\ \end{array}$	$1.3754 \\ 1.3830 \\ 1.3905 \\ 1.3980 \\ 1.4055 \\ 1.4130 \\ 1.4205 \\ 1.4280 \\ 1.4354 \\ 1.4354 \\ 1.4428$	$\begin{array}{c} 2.684\\ 2.753\\ 2.821\\ 2.889\\ 2.957\\ 3.025\\ 3.092\\ 3.159\\ 3.224\\ 3.289\end{array}$	$\begin{array}{c} 380.9\\ 384.7\\ 388.5\\ 392.2\\ 396.1\\ 400.0\\ 404.0\\ 408.0\\ 412.1\\ 416.2 \end{array}$	$\begin{array}{c} 1.3603\\ 1.3684\\ 1.3761\\ 1.3838\\ 1.3914\\ 1.3990\\ 1.4065\\ 1.4140\\ 1.4215\\ 1.4290\\ \end{array}$
110 120 130 140 150 160 170 180 190 200	5.679 5.785 5.891 5.997 6.103 6.209 6.315 6.420 6.525 6.630	$\begin{array}{r} 421.5\\ 425.6\\ 429.8\\ 434.3\\ 438.8\\ 443.3\\ 447.9\\ 452.5\\ 457.1\\ 462.0\end{array}$	$1.4616 \\ 1.4690 \\ 1.4764 \\ 1.4837 \\ 1.4910 \\ 1.4983 \\ 1.5056 \\ 1.5128 \\ 1.5200 \\ 1.5272 $	$\begin{array}{r} 4.517\\ 4.602\\ 4.687\\ 4.772\\ 4.857\\ 4.942\\ 5.027\\ 5.112\\ 5.197\\ 5.282\end{array}$	$\begin{array}{c} 421.2\\ 425.4\\ 429.6\\ 434.0\\ 438.4\\ 443.0\\ 447.6\\ 452.2\\ 456.9\\ 461.8\end{array}$	$\begin{array}{c} 1.4502\\ 1.4576\\ 1.4650\\ 1.4724\\ 1.4898\\ 1.4872\\ 1.4946\\ 1.5020\\ 1.5094\\ 1.5168\end{array}$	$\begin{array}{r} 3.354\\ 3.419\\ 3.484\\ 3.549\\ 3.614\\ 3.679\\ 3.744\\ 3.809\\ 3.874\\ 3.939\end{array}$	$\begin{array}{r} 420.4\\ 424.6\\ 429.0\\ 433.4\\ 437.9\\ 442.5\\ 447.1\\ 451.8\\ 456.5\\ 461.3\end{array}$	1.43651.44401.45141.45881.46621.47361.48101.48841.49571.5030

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	Table II	Prop	erties* of	Superhea	ted Pro	pane Vap	or (Conclu	ıded)	
	P - 50 Lb	Abs t =	= 14.7° F.	$P = 60 {\rm Lb}.$	Abs., $t =$	24.80° F.	P = 80 Lb.	Abs., $t =$	41.69° F
emp. • F.	V V	H	8	V	• H	S	V	H	S
	9 115	201 0	1 3591	1 76	383.8	1.3501	1.32	387.8	1.3470
20	2.115	383.5	1.3562	1.10	000.0				
30	2.217	387.4	1.3647	1.814	386.1	1.3547			
40	2.275	391.3	1,3726	1,803	390.1	1.3710	1.36	391.9	1.3540
60	2.386	399.1	1.3881	1.959	398.2	1.3789	1.424	396.1	1.3624 1.3707
70	2.441	403.1	1.3957	2.006	402.2	1.3808	1.500	400.5	1.3785
80	2.495	407.1	1.4109	2,099	410.5	1.4025	1.537	408.9	1.3863
100	2.602	415.4	1.4185	2.145	414.8	1.4102	1.573	413.2	1.3940
110	0 656	410.6	1 4261	2 190	419.0	1.4179	1.609	417.5	1.4017
120	2.709	423.9	1.4337	2.235	423.4	1.4254	1.644	421.8	1.4094
130	2.762	428.3	1.4412	2.280	427.8	1.4330 1.4404	1.079	420.5	1,4248
140	2.815	432.8	1.4487	2.370	436.8	1.4479	1.749	435.6	1.4325
160	2.921	441.9	1.4637	2.415	441.4	1.4554	1.784	440.3	1.4402
170	2.975	446.6	1.4711	2.460	446.1	1,4629	1.852	449.8	1.4554
180	3.027	451.5	1.4859	2.549	455.6	1.4777	1.886	454.7	1.4629
200	3.131	460.9	1.4933	2.593	460.5	1.4851	1.920	459.7	1.4704
	P = 100 Lb	Abs., t	$= 55.62^{\circ} F.$	P = 130 L	b. Abs., t =	⇒ 73.20° F.	$P = 160 {\rm Lb}$	Abs., $t =$	= 87.71° F.
Satd.	1.06	391.2	1.3448	0.8165	395.0	1.3424	0.6685	397.9	1.3404
60	1.094	393.5	1,3488						
70	1.131	402.6	1.3656	0.8456	398.8	1.3486	0.0005	200.2	1 2423
90	1.196	406.9	1.3735	0.8762	403.6	1.3571	0.6095	404.7	1,3521
100	1.227	411.4	1.3810	0.9045	100.0	1.0000	0.7000	400 6	1 2610
110	1.258	415.7	1.3893	0.9315	412.9	1.3740	0.7222	409.6	1.3698
120	1.289	420.3	1.3962	0.9566	420.7	1.3903	0.7691	419.7	1.3784
130	1.347	429.6	1.4130	1.006	425.7	1.3987	0.7908	424.8	1.3807
150	1.375	434.4	1.4209	1.029	430.7	1 4150	0.8319	434.9	1,4031
160	1,400	439.1	1.4362	1.076	440.7	1.4230	0.8520	440.0	1,4113
180	1,460	448.8	1.4440	1.098	445.3	1.4310	0.8712	440.1	1,4195
190	1.488	453.8	1.4518	1.120	450.9 456.1	1,4468	0,9093	456.1	1,4357
200	1.510	400.0	1.1000	D 000 T k	Aba t	- 191 1 85° F	P = 250 Lt	Abs.t =	122.12° F
	$\underline{P = 190 \text{ Lb}}$	Abs., t =	$= 100.50^{\circ} F$	P = 220 Lt	402.5	1.3375	0.4130	404.2	1.3355
Satd.	0.5540	400.4	1.3485						
120	0.5995	410.4	1.3580	0.4911	407.7	1,3460	0 4283	419.7	1.3450
130	0.6208	415.9	1.3670	0.53121	419.2	1.3650	0.4473	425.9	1.3550
140	0.6607	426.4	1.3844	0.5498	424.5	1.3739	0.4649	431.4	1.3640
160	0.6792	431.5	1.3930	0.5673	429.7	1.3827	0.4972	442.6	1.3819
170	0.6971 0.7144	437.0	1 4013	0.5998	440.6	1.3999	0.5121	448.0	1.3908
190	0.7311	447.5	1.4176	0.6149	445.9	1.4080	0.5200	458.9	1.4074
200	0.7472	452.7	1.4255	0.6302	451.2	1.4101	0.0100	100.0	
	$P = 300 {\rm Lm}$	b. Abs., t	$= 137.55^{\circ} F$	-					
Satd.	0.3332	406.6	1.3345	* 1	Pressures 1	below atmos	pheric are exp	ressed in i	inches of H
140	0.3392	408.7	1.3480	vacui	im pressu	res; above	atmospheric,	in pounds	s per squar
160	0.3745	422.0	1.3580	inch	absolute.				
170	0.3896	427.8	1.3674						
180	0.4037	439.2	1.3855						
200	0.4303	444.9	1.3944						

CORRELATION OF RESULTS

ABSOLUTE ENTHALPY. Figure 1 gives the first correlation of data. The reference value for the heat content of the saturated liquid at atmospheric pressure was obtained by graphical integration of the specific heat values of Kemp and Egan between absolute zero and the boiling point at atmospheric pressure. Therefore, these data give the enthalpy of propane above the solid at absolute zero and are based on the assumption that the entropy at this point is zero.

From this reference value for the liquid and from the specific heats, specific volumes, and latent heats previously discussed, the saturated liquid and saturated vapor curve was calculated. From a reference point at -40° F. on the saturated vapor line, H_0 was calculated at -40° F. and infinite dilution from our $-\Delta H$ data. From this point the absolute values were calculated for the heat content at infinite dilution at various temperatures between -70° and $+200^{\circ}$ F. from the data of Kistiakowsky and Rice as extrapolated. From these reference values and the $-\Delta H$ data previously calculated, the absolute heat contents at various temperatures and pressures were obtained. Then the extension of the lines showing the change in enthalpy with pressure at constant temperature, as expressed in absolute values, agrees with chart and plotted against the temperature coordinate and the pressure parameters. The enthalpy parameters were read from the heat content chart and plotted in the same manner.

All data are reported on the B. t. u.-° F.-pound system, except as noted. The actual molecular weights employed by each author were used in calculating data from the molal basis, and in each case the author's value for the absolute temperature was used in calculating the Fahrenheit temperature. The data of Deschner and Brown were corrected for ethane content of their sample. H signifies the absolute enthalpy referred to the solid at absolute zero. S refers to absolute entropy on the same basis, V is in cubic feet per pound units, and J is taken as 0.18511.

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the values on the saturated vapor curve within 0.2 B. t. u. in most cases.

Over the range from -40° to $+200^{\circ}$ F., independent of the interpolations and extrapolations on the compressibility chart, the values of Kistiakowsky and Rice are in good agreement, since $-\Delta H$ at -40° F. is relatively small. However, the values obtained from the compressibility chart correlate well with the other data.

Specific heats of the vapor at constant pressure for 0 pound absolute were taken from Kistiakowsky and Rice; and for the higher pressures, they were read from the heat content chart.

ENTROPY-TEMPERATURE. Figure 2 gives a second correlation of data. The reference value for the entropy of the liquid at its boiling point was taken from the experimental values of Kemp and Egan. The saturated liquid and saturated vapor curves were then calculated in the conventional manner. The lines of constant quality, expressed as per cent vapor, were calculated directly from these values. The lines of constant pressure in the superheat region were calculated from our values for the specific heat of the vapor at constant pressure. The lines of constant volume were calculated from the compressibility

Barium and Strontium Sulfate Decomposition in Aqueous Solution

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The decomposition of barium and strontium sulfates by the action of strong solutions of calcium chloride results in the formation of the soluble modification of anhydrite (CaSO₄). Dilution of the reaction mass at this point with water results in immediate reversion to the initially reacting materials, due to the reactivity of the soluble modification of the anhydrite. The soluble anhydrite is converted to the much less reactive insoluble modification

THE production of inorganic salts is often carried out by ordinary double decompositions. Usually such reactions, involving the formation of insoluble salts, are considered essentially quantitative in one direction. A few double decomposition reactions involving insoluble salts reverse their equilibrium position as the solution is changed from dilute to concentrated. Among them are barium sulfate and calcium nitrate in equilibrium with barium nitrate and calcium sulfate (δ , 11), barium sulfate and calcium chloride in equilibrium with barium chloride and calcium sulfate (δ), strontium sulfate and calcium nitrate in equilibrium with strontium nitrate and calcium sulfate (10), and barium sulfate and an alkali carbonate in equilibrium with barium carbonate and an alkali sulfate (12).

The change in equilibrium position as the solution medium is changed from dilute to concentrated has been studied in the Purdue Chemical Engineering Laboratories especially in the cases of barium and strontium sulfates decomposed by calcium chloride and calcium nitrate. As the solution is made more concentrated, the reaction proceeds farther in the direction of obtaining the soluble strontium and barium salts. Efforts to produce soluble strontium and barium compounds were reviewed in previous publications (4, 6, 7). In this work only enough water was used to make the ionic reaction possible. The consistency of the reaction mass was that of a thick mush.

The experiments of Shreve and Toner (8) and Shreve and Watkins (9) indicated a possible mechanism for these equilibrium reactions. They and others observed that the solubility of calcium sulfate decreases with a rise in tempera-

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by heating the reaction products at elevated temperatures. This procedure makes practical the use of aqueous methanol as an extraction solvent for the recovery of the barium chloride made. Under these circumstances even water alone will extract most of the barium chloride initially formed before the insoluble anhydrite has had time to react. The effect of aqueous extractions on decompositions carried out by fusing the reactants also gives similar results². Var. 1943

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ture, the solubilities of strontium and barium sulfates increase with a rise in temperature, calcium chloride lowers the solubility of calcium sulfate, and barium and strontium chlorides are virtually insoluble in concentrated calcium chloride solutions. Under the conditions in which these experiments were carried out, highly concentrated solutions of calcium chloride were employed; since this double decomposition was carried out in the presence of only a small amount of water, the problem of separating the reaction products without causing reversion (the opposite of conversion) had to be solved.

A number of methods might be possible for the separation of two inorganic salts which have been produced by evaporation of an aqueous solution media or by fusion. Extractions with water would be the first obvious choice. However, if the properties of the salts are such that the reversion reaction takes place (for example, the reaction products of barium and strontium sulfates with calcium chloride), water alone may not be satisfactory. In this case an organic solvent has been used successfully. Previous work on the decomposition of barium and strontium sulfates with calcium chloride and nitrate (6-10) describes the use of organic solvents for extracting the reaction products. As the salts are essentially un-ionized in the organic solvents, no reversion takes place. The chlorides are soluble and are separated from the insoluble sulfates by filtration. If certain modifications could be made so that aqueous methanol or even water could be substituted for the organic solvent under special conditions without obtaining too much reversion, the process would be more economical. A large part of the experimental work described here is a study of these possibilities on the double decomposition products of barium and strontium sulfates with calcium chloride.

² After this work had been completed, a paper appeared on "Thermodynamic Properties of Gypsum and Its Dehydration Products" [Kelley, Southard, and Anderson, U. S. Bur, Mines, *Tech. Paper* 625 (1941)].



Figure 1. Effect of Extraction Solvent Composition on Aqueous Reaction Product of Barium Sulfate and 10 Per Cent Molar Excess of Calcium Chloride

When the reaction was carried out by fusing the reactants, aqueous methanol gave a satisfactory extraction. When a similar procedure was tried on the ball mill reaction mass (in stirred saturated solution as described in a following paragraph), Shreve and Toner (β) found that almost complete reversion took place at once. These results indicated that there was a difference between the two types of reaction products which was responsible for the change in behavior. On the basis of synthetic reaction mixtures representing different reaction products, it was pointed out (β) that the difference in reversion tendencies between the fusion and ball mill products was a result of a difference in the properties of calcium sulfate formed.

CALCIUM SULFATE AND ITS HYDRATES

There are four modifications of calcium sulfate: gypsum (CaSO₄.2H₂O), plaster of Paris (CaSO₄. $\frac{1}{2}$ H₂O), soluble anhydrite, and insoluble anhydrite (2). Newman and Wells (3) observed the conditions of heating necessary to change the x-ray pattern from the soluble anhydrite to the insoluble

anhydrite form. Under conditions of sustained elevated temperatures the pattern changed; although the ultimate stable phase above 42° C. is insoluble anhydrite, the metastable soluble anhydrite forms at temperatures from just below the boiling point to approximately 150° C. (4).

Since the reaction was carried out in the aqueous phase and at atmospheric pressure, the molecular form of the calcium sulfate was that of soluble anhydrite. This is a reactive form of calcium sulfate readily reacting in aqueous solutions of strontium and barium salts.

The form in which calcium sulfate exists after fusion is the insoluble anhydrite (8), and the fusion products may be extracted with water but with some reversion because of the low reactivity of this insolubilized calcium sulfate. The transformation of gypsum to insoluble anhydrite by heating suggested subjecting the products of these aqueous reactions to elevated temperatures. In the experimental work this method of changing calcium sulfate from a reactive form to the less reactive insoluble anhydrite form was used.

AQUEOUS DECOMPOSITION OF BARIUM AND STRONTIUM SULFATES

A heated ball mill to carry out inorganic reactions when one or more reactants are insoluble has been used frequently in this laboratory (8). For mixing purposes, steel balls of







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Figure 3. Effect of Time on Extraction with Water of Aqueous Reaction Product of Barium Sulfate and Calcium Chloride

Above, 10 per cent molar excess CaCl₂; *below*, 25 per cent excess CaCl₂. The volume of water refers to that used for extractions.

assorted sizes are placed inside with the reacting substances. As the ball mill rotates, these balls keep the materials ground and well intermixed.

The reaction conditions were as follows: The finely ground reactants were placed in the ball mill, and sufficient water was added to give a thin creamy mass. Heat was gradually applied to the rotating mill, and 24-36 hours were allowed for the water to be driven off. The heat input was such that the equilibrium temperature finally reached was a little over 200° C. The product was removed, ground in a mortar, and stored in a bottle from which the samples were taken.

BARIUM SULFATE. The reaction,

 $BaSO_4 + CaCl_2 = BaCl_2 + CaSO_4$

was carried out in a ball mill for two different molar ratios of reactants, one with 10 per cent and the other with 25 per cent molar excess of calcium chloride. Three moles of barium sulfate were used in each experiment. The reaction product consisted of a mixture of four salts: calcium chloride, barium chloride, barium sulfate, and calcium sulfate. The reaction products were separated for analysis by extraction with a mixed solvent of ethylene glycol and methanol in 1:3 ratio. The methanol was added to give the solvent satisfactory fluidity properties, but it was not used alone because of its limited solubility for barium chloride. The extraction resulted in a separation of the soluble chlorides from the insoluble sulfates. The analysis was based on the amount of barium present in the extract compared to the total amount of barium present in a duplicate unextracted sample. The barium in the latter was determined by adding water to the sample; reversion to barium sulfate resulted. The method of analysis of the filtrate was similar to that described by Shreve and Toner (8) which is a modification of the standard analysis for alkaline earths. Barium was determined as barium chromate. A 95 per cent conversion was obtained using 10 per cent excess calcium chloride, and a 97 per cent conversion using 25 per cent excess calcium chloride.

Aqueous methanol extractions were carried out on the heated reaction product (thereby insolubilizing the calcium sulfate by changing it to the insoluble anhydrite form) which had been furnaced for periods of 1 to 24 hours at temperatures from 300° to 700° C. Aqueous extractions were carried out on samples after heating at 700° C. for 12 hours; various amounts of water were used for different time periods.

The apparatus for heating the samples consisted of a small vertical cylindrical furnace calibrated for temperature against current. Two-gram samples were weighed out and transferred to flat-bottomed crucibles. At the end of the heating periods the crucibles were removed from the furnace; their contents were ground in a mortar and transferred to 100-ml. tincture bottles for extraction. The bottles were mounted on a rotary shaker and rotated for the timed extraction period. At the end of this interval the bottles were removed and their contents allowed to settle for 10 minutes previous to their filtration through Gooch crucibles. The results for the 500° and the 700° C. furnace temperatures are plotted for the aqueous methanol extractions in Figures 1 and 2; 100 ml. of extraction solvent were used in each case. An example of the data follows for Figure 1 (at 500° C.). The extraction time was one hour with the exception of the runs marked^a in which case it was 10 minutes. A settling time of 10 minutes was allowed before filtration. The volume of extraction solvent was 100 ml. The sample weight was 2 grams:

% Methanol in Extn. Solvent	Heating Time, Hr.	% BaCl ₂ Yield	% Methanol in Extn. Solvent	Heating Time, Hr.	% BaClz Yield
0 40 60 80	1 1 1 1	0 12 24 51	0 20 60 80	12 12 12 12 12	0 22 68 73
0 40 60 80	3 3 3 3	0 23 48 72	0 40 60 80	24 24 24 24 24	2 56 75 89
0 60 80	6 6 6	0 56 80	0 a 60 a 80 a	1 1 1	0 49 58

^a Ten-minute extraction.

The curves show increased yield as the temperature was increased and the heating time was extended. The 10minute extraction for a sample heated 1 hour at 500 ° C. gave a better yield than a duplicate sample extracted for an hour. The corresponding comparison at the 700 ° C. furnace temperature showed a smaller yield for the 10-minute extraction. This behavior seems to indicate that, although the hour extraction was more complete than the 10-minute one, with the product heated at the lower temperature the reversion was the more important factor; with the product heated at the higher temperature, the greater insolubilizing of the calcium sulfate lessened the reversion and made the completeness of extraction relatively more important. Increasing the excess of calcium chloride in the initial reaction mass (25 as compared to 10 per cent excess) made considerable

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Figure 4. Effect of Extraction Solvent Composition on Aqueous Reaction Product of Strontium Sulfate and 10 Per Cent Molar Excess of Calcium Chloride

difference at the higher furnace temperatures when the extraction solvent contained larger quantities of water. At lower furnace temperatures or at the higher furnace temperatures when the solvent was high in methanol, the effect of increasing the calcium chloride content of the reaction mass resulted in only a slight increase in yield.

The results for the aqueous extractions of samples heated at 700° C. for 12 hours using 10 to 200 ml. of water for extraction are plotted in Figure 3. For the reaction mass containing 10 per cent excess calcium chloride, the maximum volume of water used for extraction was 200 ml.; for the mass containing 25 per cent excess, it was 100 ml. The extraction times ranged from 10 minutes to 2 hours. The low yields in the 10-ml. extractions were probably caused by mechanical difficulties. When enough solvent was used for good mechanical contact, a further increase in volume did not have much effect. In all cases the yield dropped as the extraction time was increased. There was an optimum value for the volume of extraction solvent, as indicated by the fact that the 50-ml. and the 200-ml. extractions of the upper graph gave yields less than those obtained with 100 ml. of water. The balance between completeness of extraction and extent of reversion would vary empirically with the equipment; but extraction was favored by the use of sufficient



Figure 5. Effect of Extraction Solvent Composition on Aqueous Reaction Product of Strontium Sulfate and 25 Per Cent Molar Excess of Calcium Chloride

solvent and a short extraction period. Increasing the calcium chloride content (from 10 to 25 per cent in excess of that theoretically required) of the initial reaction mass made a marked difference in yield for the shorter extraction periods. As the extraction time was lengthened, the effect of the increased calcium chloride content became progressively less significant.

STRONTIUM SULFATE. The reaction,

$$SrSO_4 + CaCl_2 = SrCl_2 + CaSO_4$$

was carried out in the same manner as that for barium chloride, with 10 and 25 per cent molar excesses of calcium chloride for the two molar ratios of reactants. Three moles of strontium sulfate were used in each experiment. The reaction product consisted of a mixture of four salts: calcium chloride, strontium chloride, strontium sulfate, and calcium sulfate. Separation for analysis was by extraction with methanol, in which strontium and calcium chloride are both soluble; the result was separation of the soluble chlorides from the insoluble sulfates. Analysis was based on the amount of strontium present in the extract compared with the total amount of strontium present in a duplicate unextracted sample. The strontium in the latter was determined by adding water and causing a reversion to strontium sulfate. The method of analyzing the filtrate was that of Shreve and Watkins (9). The strontium and calcium chlorides were precipitated as carbonates, the carbonates were converted to nitrates, and the nitrates were extracted with acetone in which the strontium nitrate is virtually insoluble and the calcium nitrate soluble. A 92 per cent conversion was

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obtained with 10 per cent excess calcium chloride, and a 97 per cent conversion with 25 per cent excess calcium chloride.

Aqueous methanol extractions were carried out on the reaction product, which had been heated for 1 to 24 hours at 300° to 650° C. Aqueous extractions were carried out on samples, which had been heated at 650° C. for 12 hours, with various volumes of water for different extraction times. The furnace was the same as that used for the barium salts.

The results for the 500° and the 650° C. furnace temperatures are plotted in Figures 4 and 5; 100 ml. of solvent were used in these extractions which were all for one hour. The curves show an increased yield as the temperature was increased and the heating time extended. Increasing the excess calcium chloride in the initial reaction mass (25 as compared to 10 per cent excess) did not increase the yield notably as in the reaction with the barium salts. The explanation is that the furnace temperature was higher for the barium salts, and it has already been mentioned that at the lower heating temperatures the effect of increasing the calcium chloride content was only slight.

The results for the aqueous extractions of samples heated at 650° C. for 12 hours are plotted in Figure 6, using 10 to 200 ml. of water for extraction for periods of 10 minutes to 2 hours. The lowest yields again were with the 10-ml. extractions, probably because of lack of thorough contact of the water with the salts. An optimum value for extraction is indicated by the fact that both the 50- and 200-ml. volumes of water for extraction gave values less than those obtained for the 100-ml. volume. A few exceptionally low values resulted from some of the solid salts adhering to the sides of the tincture bottle and thus not being thoroughly extracted.

FUSION REACTIONS WITH BARIUM AND STRONTIUM SULFATES

The fusions of barium sulfate with calcium chloride and of strontium sulfate with calcium chloride were made in wideform No. 60 porcelain crucibles. The furnace was brought to 900° C., which was 175–225° C. above the fusion temperature of either of the mixtures. Five minutes after the contents had completely melted, the crucibles were removed and cooled, and the solidified contents ground in a mortar.

The fusion reaction,

$BaSO_4 + CaCl_2 = CaSO_4 + BaCl_2$

was investigated in detail by Shreve and Toner (8). The reaction has been shown to be one of equilibrium, and the effects of time, temperature, and ratios of reactants were determined. The fusion here was carried out with a 25 per cent molar excess of calcium chloride in a charge containing 0.2 mole of barium sulfate. The conversion of the fusion was 98 per cent. Extractions of 2-gram samples of the fusion product were made with various volumes of water for different extraction times. The results are plotted in the upper graph of Figure 7.

The fusion reaction,

$SrSO_4 + CaCl_2 = CaSO_4 + SrCl_2$

was investigated by Shreve and Watkins (9). This results in more decomposition than does the fusion of barium sulfate with calcium chloride. It was carried out for a 25 per cent molar excess of calcium chloride in a charge containing 0.2 mole of strontium sulfate. The conversion was 91 per cent. Extractions were carried out in the same manner as for the fusion with barium sulfate. The results are also plotted in Figure 7.

In the fusions of both the strontium and the barium salts, the mechanical limitations favored the larger volumes of





water for complete extraction. A short extraction time gave less chance for reversion to take place and thus favored a higher yield. The over-all yield of barium chloride was higher than for strontium chloride, but this was due probably to the higher yield in the initial fusion, in which barium chloride is less volatile than strontium chloride, and not to the amount of reversion.

CONCLUSIONS

Extractions of samples from the furnace were made with both water and aqueous methanol. Higher yields were obtained with aqueous methanol than with water alone. In the aqueous decomposition of barium sulfate, the effect of increased molar ratio of calcium chloride in the reaction mass did not give a pronounced increase in yield when a solvent of high methanol concentration was used. In the extractions with water or with solvents of low methanol concentration, the product containing the higher molar ratio of calcium chloride gave a yield as much as 25 per cent greater. The aqueous extractions of the fused product resulted in yields up to 88 per cent if a short extraction time of 10 minutes and sufficient water were used. A short time was desired such May, 1943



Figure 7. Effect of Time on Extraction with Water of Fusion Product of Barium Sulfate (above) and of Strontium Sulfate (below) with 25 Per Cent Molar Excess of Calcium Chloride

that the soluble chlorides could be dissolved and yet not have opportunity to begin a reversion reaction. A large volume of water aids in dissolving the chlorides readily, and the reversion tendencies are apparently not much affected. The 88 per cent yield is somewhat higher than the 81.52-83.7 per cent yield reported by Averko-Antonovich (1). With the extraction solvent of 80 per cent methanol, little reversion was observed for the ball mill product heated at 700° C. for 3 or more hours. Aqueous extractions of 73 per cent yield were possible.

In the aqueous decomposition of strontium sulfate the effect of increased molar ratio of calcium chloride was not so pronounced. Theoretical recovery is possible without heating the reaction product when extracting with pure methanol, in which the strontium chloride is soluble, and the calcium sulfate insoluble. When extracting with aqueous methanol, heating the reaction product was necessary to get good yields. Heating is necessary to convert the calcium sulfate from the soluble to the insoluble anhydrite form. Heating for 12 hours or more at 650° C. gave a yield of 88 per cent or better for the aqueous solvent containing 80 per cent methanol. Aqueous extractions of the heated ball mill product gave results somewhat higher than those observed in the barium chloride production. With a rapid 10-minute extraction using 100 ml. of water on a 2-gram sample of the fused product, a reversion of only 7 per cent to give an over-all yield of 84 per cent was observed.

A comparison of the fusion method with the aqueous decomposition method in the barium chloride production shows that, under the most favorable conditions, the 88 per cent yield on the aqueous extraction of the fusion product was 15 per cent greater than any obtained from the other method. Organic extractions were not carried out on the fusion products, but the 95 per cent yield for the aqueous decomposition method using 80 per cent aqueous methanol extraction solvent was higher than any direct aqueous extraction of the fused product.

In the strontium chloride production by the fusion method, yields in the aqueous extractions of 84 per cent were 6 per cent higher than those possible with the aqueous decomposition method; but again the organic extractions with the solvent as 80 per cent methanol made possible the higher yield of 88 per cent and, with pure methanol, the theoretical (same as initial conversion) yield of 91 per cent. The latter did not require that the products be heated after conversion, as the insolubilized form of calcium sulfate is not necessary for the pure methanol extraction.

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PRESENTED before the Division of Industrial and Engineering Chemistry at the 102nd Meeting of the AMERICAN CHEMICAL SOCIETY. Based upon a thesis submitted by Heroert F. Wiegandt to the faculty of Purdue University in partial fulfillment of the requirements for the degree of doctor of philosophy

Tar Elimination in Pyroligneous Acid (Correction)

An error in Figure 9 on page 294 of this article in the March, 1943, issue of INDUSTRIAL AND ENGINEERING CHEMISTRY has been called to our attention. The arrows pointing to the respective scales are drawn incorrectly. Curve I should have the arrows pointing to the left and down, indicating the pH of acetic solution plotted against added amounts of sulfuric acid. The arrows of curve II should point upward and to the right, indicating the pH of acetic acid solutions (free of sulfuric acid) plotted against per of acetic acid solutions (free of sulfuric acid) plotted against per cent acetic acid in such solutions.

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Composition of Vapors from BOILING BINARY SOLUTIONS

The composition of vapors resulting from boiling solutions of binary liquids or, as usually expressed, vapor-liquid equilibrium data, can be readily and accurately determined by a method presented earlier. The method has been standardized and used in laboratories throughout the world, under pressure conditions ranging from high vacua to several hundred pounds per square inch and in apparatus modified to suit various requirements. Detailed dimension drawings are presented of a simple unit for the purpose which may be constructed by any glass blower, since slight deviations have sometimes resulted in difficulties and inaccuracies in operation. Various factors are discussed with relation to the technique of utilization; and the vapor-liquid data of twenty-six different binary systems are reported.

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The method was devised to give data for the design of distillation equipment. With minor modifications it is probably possible to determine data by this method as precisely as by any other; and even with only moderate care, data may be obtained which will satisfy most engineering requirements. However, the wide variety of its applications and the fact that

scores of different glass blowers have been called upon to build the apparatus have resulted in minor changes and, sometimes, operating difficulties. A drawing is therefore included which gives dimensions and details of a standard unit. Data obtained in these laboratories throughout the past few years are also presented.

Usually determinations are made in a pressure range from slightly above atmospheric to high vacuum. The pressure may be maintained constant if desired by barostats (3, 4, 7). A constant operating pressure is desirable throughout a series

Lower Part of a Thirty-Plate Distillation Unit for Research and Development Work on a Wide Variety of Distillation Problems, at the Chemical Engineering Laboratories of Polytechnic Institute of Brooklyn

Courtesy, Vulcan Copper & Supply Company



of determinations; but variations of a few millimeters usually make no appreciable difference since the variation of vapor composition with a slight change of pressure is small.

There are special requirements for work above atmospheric pressure; and several units have been built for determining equilibrium data for distillation processes at pressures up to several hundred pounds per square inch.

Normally the chemical engineer works at a fixed pressure. However, some physical chemical data are reported at constant temperature because thermostats are convenient to use. The apparatus is more adaptable to constant-pressure work but may also be used in a thermostat. In either case, determinations are made of P-T-X data; and if data are obtained at two different constant temperatures, they may be used to define the systems throughout the entire pressure and temperature range (6).

Other *P-T-X* data which are useful in engineering design work are the vapor pressures for solid-liquid solutions such as aqueous salt solutions. Equilibrium data obtained with the apparatus and methods discussed may be used to indicate elevations of boiling point. Solutions of three or more volatile liquids have also been studied by various investigators with this method; and systems having two phases (either the boiling liquid or the condensate liquid or both) have been investigated, with stirrers in both the flask and the condensate reservoir.

REQUIREMENTS FOR VAPOR COMPOSITION DETERMINATIONS

The purpose is to obtain a sample of vapor (condensed to a liquid) which is in exact equilibrium with a sample of the liquid itself. These samples are analyzed by means suitable to the particular liquid. Numerous errors tend to make a vapor sample either more or less rich in the more volatile component than a true equilibrium sample. These errors may or may not tend to balance one another; however, they do not retain their relative effectiveness in different parts of the equilibrium curve. Thus, an accumulation of errors which might balance one another in one range might give highly erroneous results in another.

GENERAL REQUIREMENTS. The apparatus should be a compact and simple unit, easily constructed for any laboratory in a more or less standard pattern, and reproducible in form and results. It should be one which can be set up and started easily and yet be immediately demountable for storage. Thus, it can be readily used, particularly in industrial laboratories where the need for data on a single system may arise occasionally.

The unit should be constructed of a material unaffected by the usual liquid or vapor. In general, this means all-glass construction (except where superatmospheric pressures are to be studied). Steel or iron is objectionable where water or acid is encountered; and even copper is unsatisfactory for esters (1) and for alcohols, which it slowly reduces to aldehydes (9).

and even copper is unsatisfactory for esters (1) and for alcohols, which it slowly reduces to aldehydes (9). Units for atmospheric pressures have been constructed of metals and other materials (as many as ten different materials in a single apparatus), but the cheapness and general utility of Pyrex makes its use desirable.

EQUILIBRIUM REQUIREMENTS. There should be no change in the composition of the boiling solution (and hence in the vapor sample also) as the vapors richer in the more volatile component are evolved. This has been taken care of by the return of the condensate to the boiling liquid until there is no appreciable change in either vapor or liquid composition. Carveth (\mathcal{Z}) used his apparatus for analyses of samples and encountered several major errors; Sameshima (10) designed and operated his apparatum for detorminations at constant temperature.

The vapor should be disengaged evenly from a uniformly mixed boiling liquid. In the ordinary boiling operation, and in other operations where gas or vapors have been bubbled through the liquid, it has been assumed that the vapors which form at some (but not every) zone of the boiling liquid either (a) are in equilibrium at formation with an average sample of the liquid or (b) obtain such equilibrium while rising to the surface. The correctness of these assumptions has never been investigated. In the recycling apparatus it is necessary to return the condensate cold and in such a manner that it may be promptly and intimately



Figure 1. Vapor-Liquid Equilibrium Apparatus for External Heater

(Exactly one fourth size; dimensions in inches)

mixed with the boiling liquid because of its different composition. If the condensate inlet is placed well beneath the surface and at some distance from the sample outlet, normal ebullition probably gives adequate mixing.

ably gives adequate mixing. There should be no spray of liquid in the vapor. The "quality" of the vapor should thus be 100 per cent because any droplets of spray carried over will give a vapor low in the more volatile components.

There should be no superheated surface in contact with thin films or droplets of liquid. Either droplets or thin films of liquid on such heated surfaces will evaporate almost completely to give a total rather than an equilibrium vaporization and the same error that would be caused by entrainment.

that would be caused by entrainment. Mechanical agitation (1, 4) has been used both in glass and metal units to give a uniform liquid for the normal boiling action and to stir up condensate which is recycling. Agitation, however, tends to throw up droplets or films on the hot surface of the boiling chamber directly above the liquid and thus to cause the total vaporization of small amounts of liquid; but this effect may be largely eliminated by proper design. Less violent agitation has been secured by thermal action in the electrically heated unit previously described (8); and another thermocirculating system will be described later. It is probably unnecessary to use any mechanical stirrer unless there are two liquid phases in the boiler or in the condensate receiver.

A total condenser should be so located that there will be no return of liquid through the vapor passageway back to the boiling liquid—e.g., due to condensation caused by radiation. Such reflux of condensate would cause a fractionating action on the vapors passing to the condenser. Only a negligible amount of condensation results if the vapor

Only a negligible amount of condensation results if the vapor neck is jacketed with the same vapors; this is the simplest precaution, although insulation and electrical heating have also been used outside the vapor jacket itself when high-boiling liquids were being distilled. Heated oil was circulated around this vapor neck by Langdon and Keyes (4). Any additional heating may cause superheating of the vapors, and the vapor temperatures will then be undependable. A droplet of liquid on the thermometer bulb indicates there is no superheating.

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SAMPLING REQUIREMENTS. The amount of boiling liquid should be large in comparison to the size of the vapor sample obtained and to the boiling rate. If the recycling system is omitted, considerable liquid must be used in relation to the condensate obtained; otherwise there is a large difference in the composition during the run (theoretically, only an infinitesimally



Figure 2. Apparatus with Internal Electrical Heater (Cross section, front to back of Figure 1, taken to right of center line, looking left)

small vapor sample should be taken). The condensate is the average sample during the run while the liquid sample has the final composition. Thus considerable discrepancy may result. The recycling system prevents this; but even with its use a large ratio of boiling liquid to condensed liquid makes possible a much

shorter time for the system to come to the steady state where samples can be taken. Furthermore, this large ratio of boiling liquid to condensate, especially a high ratio of liquid volume to liquid distilled per unit time, will minimize the possible error of the condensate return being flashed due to its higher concentration of more volatile compound.

After a satisfactory vapor sample has been distilled off, the liquid sample should be so taken that there will be no change in composition of the liquid during the sampling period due to evaporation of the more volatile component.

The time of obtaining the samples should be a minimum.

In the operation of a recycling system, there should be no liquid distilled and no condensate returned to the still while sampling.

The heat reservoir of the equipment, particularly the parts adjacent to the boiling liquid, should be minimized so that vaporization may be substantially stopped almost instantaneously when samples are to be taken. In the use of massive metal apparatus with jackets for heating by circulating hot oil, the large amount of heat stored in the systems causes distillation to proceed (with consequent loss of more volatile material) during the

causes distillation to proceed (with consequent loss of more volatile material) during the sampling period. With the light glass apparatus, this source of error is eliminated.

Multiple samples and analyses should not be required for any one composition. Extrapolations of plots of analyzed values back to the time of starting (i. e. the total amount of liquid before sampling starts) should not be required. In some cases such extrapolations have allowed considerable latitude in the selection of the liquid composition.

OPERATION OF APPARATUS

The apparatus is substantially that of the previous article (\mathcal{S}) , and the purpose of Figure 1 is to give an exact reproduc-

tion of the unit with dimensions carefully measured. Changes in relative sizes or positions of the several parts have caused differences and difficulties in operation.

Usually, a micro gas burner with a fine blue cone flame is used at the bottom. This minimizes bumping (small porous porcelain chips help further) and eliminates the superheating of the flask wall just above the liquid surface due to hot gases from a larger luminous flame. Boiling may often be started advantageously from the ground surface of the cock which seals the liquid sampling tube by playing the flame on this tube just above the cock; a stream of fine bubbles then arises from this point.

Not only the electrical heater of the previous unit, which gave an efficient thermosiphon agitation, but several other forms of special electrical heaters have been used. The arrangement for two of them is indicated in Figures 2 and 3. Figure 2 is a cross section, front to back, of Figure 1 taken from a point just to the right of the center line of the flask. Two tapered tubulatures, approximately 1/2 inch in size, lead in the terminals of an internal-resistance coil constructed of any suitable wire and supplied with electrical current through an adjustable transformer or rheostat. The heavier leads are simply drawn through holes pierced in rubber or cork stoppers and attached to the lighter-gage resistance wire. Where neither rubber nor cork may be used because of the nature of the liquids, the lead wires may be sealed through the bottom of a hollow stopper of the standard size to fit the tapered opening; they may be connected externally, either mechanically or through a pool of mercury in the hollow stoppers, into which the power wires are dipped through openings in their tops. Brass plugs with binding posts top and bottom have been ground for these openings and used where it was known that brass was not objectionable. This unit gives many of the advantages of the less readily constructed internal heater previously used.



Figure 3. Apparatus for External Electric Heater Wound on One Leg of a U-Shaped Projection (Dimensions in Inches)

The side openings with standard ground plugs have other uses either with or without the electrical heater. They are not shown in Figure 1, since they are directly in front and back, but may well be included in any unit for general work. They allow (a) an inlet for a liquid thermometer, (b) an inlet for a fine nozzle for bubbling in gas, (c) an inlet for a stirrer, (d) an inlet for liquid additions, and (e) an opening for the pipet for withdrawing liquid sample. In the last case the sample cock need not be used. One of several special designs of external electrical heaters which have given satisfaction

- 1.	Acetami	ide	2.] C	Ethylene hloride		3. Xylene	e	4. Iso Ace	amyl tate		5. Toluen	ie		6. Aceto	ne
X	Y	T, ° C.	X	Y	X	Y	T, ° C.	X	Y	X	Y	<i>T</i> , ° C.	X	r	1, 0
0 3 5 10 20 30 40 50 60 70 80 90 100	0 38.7 47.2 61.5 79.2 88.0 92.5 95.4 97.2 98.2 98.2 98.8 99.4 100.0	$\begin{array}{c} 222.0\\ 212.8\\ 208.9\\ 199.1\\ 183.0\\ 168.9\\ 157.8\\ 148.9\\ 140.1\\ 132.7\\ 126.4\\ 121.2\\ 118.1 \end{array}$	0 5 10 20 30 40 50 60 70 80 90 100	0 13.: 27 49. 64. 74. 82. 87. 91. 94. 97. 100.	$\begin{array}{c} & 0 \\ 3 & 3 \\ 5 \\ 7 & 10 \\ 5 & 20 \\ 2 & 30 \\ 0 & 40 \\ 4 & 50 \\ 2 & 80 \\ 5 & 70 \\ 2 & 80 \\ 0 & 5 \\ 0 & 95 \\ 90 \\ 95 \\ 100 \end{array}$	$\begin{array}{c} 0\\ 21.5\\ 30.6\\ 42.1\\ 50.5\\ 66.4\\ 70.1\\ 73.2\\ 76.4\\ 80.7\\ 83.2\\ 86.5\\ 91.6\\ 100.0 \end{array}$	$\begin{array}{c} 138.8\\ 135.0\\ 132.8\\ 128.5\\ 128.5\\ 128.5\\ 120.1\\ 118.3\\ 117.0\\ 116.3\\ 115.6\\ 115.2\\ 115.3\\ 115.4\\ 116.2\\ 118.1 \end{array}$	$\begin{array}{c} 0\\ 5\\ 10\\ 20\\ 30\\ 40\\ 50\\ 60\\ 70\\ 80\\ 90\\ 100 \end{array}$	$\begin{array}{c} 0 \\ 7.7 \\ 15.9 \\ 30.9 \\ 43.5 \\ 55.2 \\ 65.8 \\ 74.4 \\ 81.7 \\ 88.2 \\ 94.2 \\ 100.0 \end{array}$	$\begin{array}{c} 0\\ 5\\ 10\\ 20\\ 30\\ 60\\ 70\\ 80\\ 85\\ 95\\ 100\\ \end{array}$	$\begin{array}{c} 0\\ 15.5\\ 25.5\\ 37.2\\ 46.0\\ 54.1\\ 57.0\\ 61.5\\ 66.6\\ 71.8\\ 75.8\\ 81.0\\ 88.5\\ 100.0\\ \end{array}$	$\begin{array}{c} 118.1\\ 111.3\\ 108.9\\ 105.6\\ 103.3\\ 101.7\\ 100.8\\ 100.6\\ 100.6\\ 100.9\\ 101.4\\ 102.6\\ 104.9\\ 110.8 \end{array}$	$\begin{array}{c} 0\\ 5\\ 10\\ 20\\ 30\\ 40\\ 50\\ 60\\ 70\\ 80\\ 90\\ 100 \end{array}$	$\begin{array}{c} 0\\ 16.2\\ 30.6\\ 55.7\\ 72.5\\ 84.0\\ 91.2\\ 94.7\\ 96.9\\ 98.4\\ 99.3\\ 100.0 \end{array}$	$118.1 \\ 110.0 \\ 103.8 \\ 93.1 \\ 85.8 \\ 79.7 \\ 74.6 \\ 70.2 \\ 66.1 \\ 62.6 \\ 59.2 \\ 56.1 \\ $
7. Cy	vclohexyl	Acetate		<u></u>	8. Diacety Y	$T, \circ C.$	$\frac{9.B}{X}$	utyl Aceta Y	ite	X	10. Fench Y	one T, ° C.	<u>11.</u>	Diisobut X	yl Ketone Y
A 0 2 5 10 20 30 40 50 60 70 80 90 100	0 36.5 47.0 55.9 65.5 73.1 79.6 85.3 90.0 93.7 96.4 98.3 100.0	177.0 177.0 166.0 157.5 149.1 142.1 137.0 132.5 128.2 125.0 122.3 120.1 118.1		0 2 3 5 10 20 30 40 50 60 70 80 90 100	$\begin{array}{c} 0\\ 3.0\\ 5.3\\ 9.2\\ 19.6\\ 38.5\\ 52.7\\ 60.3\\ 71.2\\ 78.6\\ 84.7\\ 89.8\\ 94.7\\ 100.0 \end{array}$	$\begin{array}{c} 118.1\\ 116.8\\ 116.0\\ 114.5\\ 111.0\\ 104.0\\ 101.1\\ 99.0\\ 97.1\\ 95.4\\ 93.9\\ 92.5\\ 91.2\\ 88.0 \end{array}$	0 5 10 20 30 40 56 60 77 8 90 10	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3 4 7 6 0 8 8 3 0 1 5 0	$\begin{array}{c} 0\\ 2\\ 5\\ 10\\ 20\\ 30\\ 40\\ 50\\ 60\\ 70\\ 80\\ 90\\ 100\\ \end{array}$	$\begin{array}{c} 0\\ 22.5\\ 46.1\\ 66.8\\ 81.7\\ 88.8\\ 93.5\\ 96.4\\ 98.0\\ 98.9\\ 99.3\\ 99.6\\ 100.0 \end{array}$	$\begin{array}{c} 193.0\\ 181.0\\ 175.2\\ 165.0\\ 152.0\\ 143.0\\ 136.0\\ 131.0\\ 127.0\\ 124.0\\ 121.5\\ 119.5\\ 118.1 \end{array}$		0 2 5 10 20 30 40 50 60 70 80 90 100	0 16.0 29.4 44.6 62.1 74.6 83.0 87.8 91.0 93.3 96.3 98.5 100.0
12	. Methyle hexanor	cyclo- ne T ° C.		13. Fu	rfural Y	$\frac{14. \text{ Me}}{X}$	thyl Isobut	yl Ketone T, °C.		15. Met <u>n-Amyl K</u> X	hyl etone Y	16. M Isoamy X	Acetate Y	x	A cetate Y
0 5 10 20 30 40 50 60 70 80 90 100	0 18.9 33.1 53.5 67.2 77.7 84.9 89.7 93.4 96.3 98.5 100.0	$\begin{array}{c} 165.0\\ 162.0\\ 158.9\\ 152.0\\ 145.0\\ 139.0\\ 134.0\\ 129.5\\ 126.0\\ 122.8\\ 119.5\\ 118.1 \end{array}$		0 5 10 20 30 40 50 60 70 80 90 100	$\begin{array}{c} 0\\ 13.6\\ 27.0\\ 46.5\\ 60.2\\ 70.4\\ 78.3\\ 84.5\\ 89.4\\ 93.5\\ 97.2\\ 100.0 \end{array}$	$\begin{array}{c} 0\\ 5\\ 10\\ 20\\ 30\\ 40\\ 50\\ 60\\ 70\\ 80\\ 90\\ 100\\ \end{array}$	$\begin{array}{c} 0\\ 5.01\\ 10.02\\ 20.03\\ 30.05\\ 41.00\\ 51.20\\ 61.70\\ 72.20\\ 82.40\\ 91.60\\ 100.00\\ \end{array}$	$\begin{array}{c} 118.1\\ 118.06\\ 118.02\\ 117.94\\ 117.84\\ 117.73\\ 117.65\\ 117.52\\ 117.32\\ 116.96\\ 116.38\\ 115.80\\ \end{array}$		0 5 10 20 30 40 60 70 80 90 90 100 1	0 12.7 22.8 44.0 58.2 67.3 74.5 81.0 86.9 91.8 96.1 00.0	$\begin{array}{c} 0\\ 5\\ 10\\ 20\\ 30\\ 40\\ 50\\ 60\\ 70\\ 80\\ 90\\ 100\\ \end{array}$	$\begin{array}{c} 0\\ 14.1\\ 24.5\\ 41.0\\ 53.7\\ 63.3\\ 71.3\\ 78.4\\ 84.9\\ 90.4\\ 95.4\\ 100.0 \end{array}$	0 5 10 20 30 40 50 60 70 80 90 100	$\begin{array}{c} 0 \\ 7.6 \\ 15.1 \\ 29.3 \\ 41.3 \\ 51.0 \\ 0 \\ 59.6 \\ 67.5 \\ 83.8 \\ 9 \\ 100.6 \end{array}$

TABLE I. MOLE PER CENT LOW BOILER IN LIQUID (X) AND IN VAPOR (Y) FOR SYSTEMS CONTAINING ACETIC ACID AS ONE COMPONENT

even under vacua, where bumping presents a problem, is shown in Figure 3. This is simply a U-arrangement at the bottom, with the smaller leg wound first with a single layer of asbestos paper, then with turns of Nichrome resistance wire, and finally with several layers of asbestos paper. The removable internal heater of Figure 2 is, however, simpler.

The small insealed nozzle of the condensate return inlet permits delivery into the body of the liquid rather than along the superheated bottom and, in case of bumping, constricts the surging of liquid back through this tube. On some units, a cock has been placed in this line at the bottom of the trap to prevent flow or diffusion of condensate liquid into the boiling liquid after the heating has stopped and while sampling. A three-way cock with drain has been suggested (4) to allow drainage of that held up on the flask side. It might also serve for taking the liquid sample after this purging; if so used, the other liquid sampling cock could be eliminated.

Other units for special purposes (e. g., where a two-phase condensate results) have had a three-way cock at this point with one branch connecting to the bottom of the reservoir. Thus, the reservoir may be periodically or continuously draining from the bottom back to the flask as well as from the top. This is not usually desirable.

In some cases an auxiliary condenser attached on the vent has been used. Obviously, no vapors should leave the primary condenser, and the condensate should be cold. Such a condenser has been attached sometimes as an integral part of of the unit (11) and alongside the main condenser. In other cases it has been a standard condenser attached if and when needed as an auxiliary, particularly for determinations under vacuum.

In vacuum work it is usually possible to operate satisfactorily without automatic control. Two 12-liter flasks (or a single 22-liter one) are installed in series with the vent and evacuated; boiling is started; and the exhauster, usually a water-jet aspirator, is closed off after the desired pressure is adjusted. If the connections are tight, the boiling for recycling may be continued without continuous operation of the exhauster; and even minor changes in the rate of boiling will not change appreciably the pressure on the manometer con-

TABLE II. MOLE P	ER CENT LOW BOILER IN LIQUID (X) AND	2
VADOR (V) FOR SY	STEMS CONTAINING ACETALDEHYDE AS UNI	G
IN VAPOR (1) FOR OI	Composition	

X	$\frac{1. \text{ Toluene}}{Y T, \circ C.}$		<u>2.</u> Be	$\frac{2. \text{ Benzene}}{Y T, \circ C.}$		$\frac{3. \text{ Furfural}}{Y T, \circ C.}$	
0 2 3 5 10 20 30 40 50 60 70 80 90 100	$\begin{array}{c} 0\\ 40.5\\ 48.5\\ 57.3\\ 68.8\\ 78.3\\ 83.7\\ 88.2\\ 92.1\\ 95.5\\ 98.5\\ 99.5\\ 99.9\\ 100.0\\ \end{array}$	$\begin{array}{c} 110.8\\ 109.0\\ 108.0\\ 106.0\\ 102.0\\ 88.0\\ 77.0\\ 67.5\\ 58.0\\ 49.8\\ 42.0\\ 34.0\\ 26.0\\ 20.8 \end{array}$	$\begin{array}{c} 0\\ 9.0\\ 31\ 3\\ 52.2\\ 69.4\\ 76.7\\ 81.6\\ 85.4\\ 88.7\\ 91.6\\ 94.4\\ 96.8\\ 100.0\\ \end{array}$	$\begin{array}{c} 80.1\\ 76.4\\ 71.0\\ 63.0\\ 54.2\\ 49.4\\ 46.2\\ 44.0\\ 42.0\\ 39.8\\ 37.7\\ 36.0\\ 20.8\\ \end{array}$	0 13.2 24.0 42.9 61.6 78.8 90.2 94.7 97.3 98.7 99.5 103.0	161.7 149.5 140.0 124.0 110.0 96.0 82.0 70.0 58.0 48.0 36.0 20.8	

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Figure 4. Vapor-Liquid Equilibrium Curves for Systems in Which Acetic Acid Is One Component

nected to the system. The accompanying compensations in the amount of air pushed in and out of the condenser, to allow more or less of the condensing area to be effective as the condensing load changes, are insignificant compared to the total volume in the evacuated system. It is necessary that the cocks and plugs be carefully ground if a vacuum-tight unit is desired.

As noted above, the maximum ratio of boiling liquid to condensed liquid is desirable to minimize the number of changes of liquid in the condensate reservoir necessary before a steady state is reached. (This ratio must be greater with a greater difference in composition between vapor and liquid, usually in the lower part of the curve.) The rate of boiling then determines the time required to distill over the amount necessary to fill the reservoir from five to twenty-five times to ensure equilibrium samples. It will be desirable, with a given size flask, to make the condensate reservoir as small as possible to give a sample of the requisite size. This size depends on the method of analysis to be used.

The size of reservoir shown in Figure 1 gives a good average size sample for many methods of analysis. The size sample required for chemical analysis will, for example, vary with the composition and hence the position on the curve. In order to minimize the unnecessarily large holdup of a unit with a general-purpose reservoir, glass beads have often been added to the reservoir (through the vent) to reduce the space available for the liquid, and then only the void space, plus the volume above the beads, is available for the sample. If only a small sample for analysis is required for all systems to be investigated and all compositions (e. g. if an Abbe type refractometer is to be used for analyzing the samples), the reservoir may be made much smaller. For example, the over-all length may be reduced from $3^3/_8$ to 2 inches and the diameter from 1 to 3/4 inch; this gives a unit requiring only a relatively short time to obtain an equilibrium sample.

The top opening is ground for a standard glass plug; and if the temperature of the vapors is not to be taken, this is used to close it. Usually a cork or rubber stopper supports a



Figure 5. Vapor-Liquid Equilibrium Curves for Acetaldehyde Systems

thermometer, however, with the bulb in the internal vapor tube. When neither cork nor rubber may be used in contact with the vapors, either a thermometer formed integrally with a glass plug, ground the size of the opening, may be used; or a short thermometer may be suspended on a glass hook on the underside of the glass stopper.

DATA TAKEN

Considerable data have been taken on the apparatus over a period of years. In general, only a degree of precision has

Г	ABLE	III.	MOLE PER	CENT .	Low Bo	ILER IN J	LIQUID (. ZSTEMS	A) AND
IN VAPOR (I) 1. Acetone- Monochlorobenzene			3. Water- Propionic Acid			5. Butanol- Butyl Butyrate		
	0 2 5 10 20 30 40 50 60 70 80 85 90 95 100	0 19.1 38.2 56.5 72.9 81.2 85.6 88.7 91.0 92.6 94.2 95.1 96.2 97.8 100.0	$\begin{array}{c} 1, \ 0.1\\ 131.6\\ 125.5\\ 108.0\\ 93.5\\ 84.1\\ 77.5\\ 72.0\\ 68.2\\ 65.5\\ 62.8\\ 62.0\\ 61.0\\ 58.1\\ 56.1 \end{array}$	0 2 5 10 20 30 40 50 60 70 80 90 95 80 90 95 8100	$\begin{array}{c} 0\\ 10.0\\ 22.0\\ 37.0\\ 54.5\\ 66.0\\ 74.9\\ 80.5\\ 84.4\\ 87.5\\ 90.3\\ 93.2\\ 94.8\\ 97.3\\ 100.0\\ \end{array}$	$\begin{array}{c} 141.4\\ 138.0\\ 117.2\\ 109.0\\ 104.2\\ 102.2\\ 101.1\\ 100.4\\ 100.0\\ 99.7\\ 99.1\\ 99.6\\ 99.8\\ 99.9\\ 100.0\\ \end{array}$	0 2 5 10 20 30 40 50 60 70 80 90 100	0 11.7 27.5 53.4 67.9 74.7 79.7 83.8 87.6 90.7 93.8 97.1 100.0
2. Methyl Ethyl Ketone-Propionic Acid			4. Acetone-Benzene X Y T , ° C.			6. Water- Butyric Acid X Y		
		0 5 10 20 30 40 50 60 70 80 90 100	0 15.6 29.2 51.8 68.3 80.6 87.9 92.6 95.5 97.5 98.9 100.0	0 2 5 10 200 300 40 50 600 700 80 90 100	$\begin{array}{c} 0 \\ 6.3 \\ 14.0 \\ 24.3 \\ 40.0 \\ 51.2 \\ 59.4 \\ 66.5 \\ 73.0 \\ 79.5 \\ 86.3 \\ 93.2 \\ 100.0 \end{array}$	$\begin{array}{c} 80.1\\ 79.5\\ 78.3\\ 72.8\\ 69.6\\ 66.7\\ 64.3\\ 62.4\\ 60.7\\ 59.6\\ 58.8\\ 56.1 \end{array}$	$\begin{array}{c} 0\\ 2\\ 5\\ 10\\ 20\\ 30\\ 40\\ 50\\ 60\\ 70\\ 80\\ 80\\ 85\\ 90\\ 95\\ 98\\ 100\\ \end{array}$	0 16.0 39.5 57.7 76.2 83.4 87.8 90.0 90.8 91.4 91.6 92.1 92.9 94.8 97.1 100.0



Figure 6. Vapor-Liquid Equilibrium Curves for Miscellaneous Systems

been used commensurate with the design of distillation equipment where plate efficiencies are not known with a high degree of accuracy. There are, however, cases (particularly where the upper or lower parts of the x-y curve are involved in careful determination of plate efficiencies) when somewhat more precise determinations might be desirable. No attempt has been made here to determine the data for any system as precisely as, say, 0.05 mole per cent.

Usually commercially pure samples were used for the experiments because they were to be encountered in the distillation processes involved. No attempt was made to purify further except to distill the commercial sample and take closecut fractions.

The vapor jacket was always vented at the top, after boiling started and until vapors drove out the air and started to issue from the tube and condense on it. The vent was closed and boiling continued until a steady state was reached in the apparatus. This usually required from 15 to 30 minutes. After distillation had filled and flushed out the reservoir, a steady

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state was assumed when the vapor thermometer remained at a given point for a time, during which condensate flow was an additional amount of two or three times the volume of the reservoir. Heating was then stopped, and the liquid sample was taken as follows: After a small amount of the liquid was run to waste to wash out the line, a test tube surrounded by an ice-water mixture was held up and around a two-hole stopper fixed on the drain outlet, as liquid sample was drawn; the test tube was promptly stoppered. The condensate sample cock was purged, and a sample of the condensate was drawn immediately into another chilled test tube which was also promptly stoppered.

Tables I, II, and III and Figures 4, 5, and 6 give the data. The graphs show the experimental points. For ease in using the data, these points and the best curves through them were carefully plotted on a large scale; values for the vapor compositions are tabulated for even mole per cent compositions of the liquid. Unless otherwise noted, the pressure was within a few millimeters of the normal barometer and was substantially constant throughout the time necessary to obtain the samples.

ACKNOWLEDGMENT

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PRESENTED before the Division of Industrial and Engineering Chemistry at the 104th Meeting of the AMERICAN CHEMICAL SOCIETY, Buffalo, N. Y.

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Vol. 35, No. 5



Since Pearl Harbor the rate of acceleration has reached a peak. Andas in the past-Powell Engineering has been meeting every challenge.* Let us help you with any valve problem you may have-Powell has the valve you need-or we'll design one for you.

*For the contribution we are making toward winning this War, we have been honored with the Army-Navy "E", the Maritime "M" and the Victory Fleet Flag.

The Wm. Powell Company

Dependable Valves Since 1846 Cincinnati, Ohio

Fig. 1453

Fig. 1453—All Iron "Model Star" Gate Valve for 125 pounds W. P. Flanged ends, outside screw rising stem, bolted flanged yoke, taper wedge double disc. Also available with solid disc-Fig. 1816.

Fig. 171—All Iron "Irenew" Globe Valve for 150 pounds W. P. Screwed ends, union bonnet and regrindable, renewable iron plug type seat and disc. Steel stem.



Safer leather clothing for America's airmen

PRIMALS

NOT long ago gasoline and oil absorbed into flyers' leather clothing presented a serious hazard. But not today.

Now shearlings for flying suits are resistant to these materials because they are finished with PRIMAL.

The PRIMALS are a series of resin finishes developed in the Rohm & Haas Leather Laboratory, produced in a Rohm & Haas plant. Before the war they found wide use in leather clothing, upholstery and many other products where flexibility and water resistance were needed.

Today the PRIMALS help clothe America's flyers... help produce the shearling garments that are safer and that remain flexible under extreme conditions.

- * DIMETHYLAMINE The synthetic form of nature's own accelerator of the liming process.
- * OROPON The original synthetic bate.

Also and

the fair

able in

- * LEUKANOL The tanning material responsible for the popular acceptance of white leather.
- * TAMOL NNO The dye assist which made pastel colors possible.
- * PRIMAL Resin finish offering outstanding flexibility in finished leather.
- * ORTHOCHROM The finish which produces washable leather.

DIMETHYLAMINE, OROPON, ORTHOCHROM, TAMOL NNO, PRIMAL and LEUKANOL are trade-marks, Reg. U.S. Pat. Off.



ROHM & HAAS COMPANY WASHINGTON SQUARE, PHILADELPHIA, PA.



Manufacturers of Chemicals including Plastics . . . Synthetic Insecticides . . . Fungicides . . . Enzymes . . . Chemicals for the Leather, Textile and other Industries

INDUSTRIAL AND ENGINEERING CHEMISTRY

MAGNETROL



ID-5

H-5000 LIQUID LEVEL CONTROL

The problem of a liquid level control to stand up under extremely high pressure, non-shock service is answered with the H-5000 MAGNETROL. It is especially recommended for hydraulics, carbon dioxide, ethane, propane, etc. In the chemical field, it is often used in high pressure experimental pilot plants.

Post Yourself on the

Liquid Level Control

PRESS

that Handles

This control features the simple and highly dependable MAGNETROL magnetic operating principle. Such troublemaking parts as bellows, packing boxes, diaphragms or electrodes are completely eliminated, making possible virtually fool-proof, maintenance-free operation.

The H-5000 will handle pressures up to 5,000 lbs. It can be designed for special applications and to handle considerably greater pressures. A companion control, the H-2500, is available for maximum pressures up to 2,500 lbs.

SPECIFICATIONS OF MODEL H-5000 - Maximum Pressure: other Features: Furnished with lens ring or screwed connections. Available with or without explosion-proof head.



WRITE TODAY FOR COMPLETE ENGINEERING DATA

FRED H. SCHAUB ENGINEERING CO., INC. 671 N. Orleans Street, Chicago, Illinois

NDABL



* The Lubrication of Piercers, Tools and Dies in Metal-Forming Operations

Lubricants containing "**dag**" colloidal graphite. used for various forging, punching, extruding, stamping and drawing operations, etc., provide the following advantages:

- 1. Finer surface finish.
- 2. Closer dimensions.
- 3. Fewer subsequent machining operations.
- 4. Scale minimized.
- 5. Increased die life.
- 6. Man hours saved on replacements and redressings.
- 7. Lubricants can be sprayed—eliminates manual swabbing.

"dag" colloidal graphite is not affected by the heat at operating temperatures and is not washed

> Write for free leaflet entitled "The Treatment of Piercers, Tools and Dies Used in Metal-Forming Operations".

> > ACHESON COLLOIDS

CORPORATION PORT HURON • MICHIGAN

*A TYPICAL APPLICATION



Completely blended petroleum lubricants containing "**dag**" colloidal graphite may be secured from major oil companies. For those operations where water-soluble lubricants containing "**dag**" colloidal graphite are preferred, they likewise are available, in a completely blended, readyto-use form.



families will be eligible). (2) All entries must be legible. (3) All entries must state the publication in which the advertisement was seen. (4) Entries must be postmarked not later than July 15, 1943. (5) In case of ties, duplicate awards will be made. (6) Entries become the property of the Acheson Colloids Corp. (7) The verdict of the judges will be final.

INDUSTRIAL AND ENGINEERING CHEMISTRY



"Test airplanes on the ground under conditions encountered at 45,000 feet." That was quite an assignment—temperatures of -67° F. They couldn't stand for any moisture in the air when it got that cold.

A Lectrodryer was selected for this warplane testing laboratory; it dries air DRY. There's no trouble caused by moisture precipitating at those extremely low temperatures.

Lectrodryers, charged with Activated Aluminas as their drying agent, are doing this same efficient drying job in many spots throughout industry. They are drying liquids, air and gases to dew points below -110°F., at atmospheric pressures and up to 3,000 pounds per square inch.

Manufacturers of materials for war are speeding their production because air dried by Lectrodryers has enabled them to standardize their processes. Other Lectrodryers have boosted product quality. If you have a wartime problem on which DRYing will assist, get in touch with PITTSBURGH LECTRODRYER CORPORATION, 305 32nd Street, Pittsburgh, Penna.



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ALCOA ALUMINUM

Of course, you are driving your aluminum alloy equipment to the limit. We need every gallon, every pound, every foot, every piece of the products that can possibly be produced to help win the war. But, bear in mind that you must make your equipment last a long time.

You can lengthen the life of hard-working, irreplaceable aluminum alloy equipment. Here are some ways of doing it; each must be engineered to suit the problem.

Cathodic protection has proved effective where the chemicals or cooling water employed are corrosive. Simply add zinc strips in the right places, and the corrosive attack is stopped or slowed down considerably. Alcoa engineers, with years of research on such problems, can advise you on how and where to place those zincs.

Protective coatings offer another means of making aluminum alloy parts last longer. Corrosion-resisting, pure aluminum coatings can be applied by spraying. Oxide finishes are produced by chemical and electrolytic treatment. Baked resin coatings are very effective, where aluminum is subjected to severe attack.

Metallizing—building up worn, corroded, or damaged aluminum parts with new metal—will give these parts a new lease on life.

Inhibitors may be the key to longer life of aluminum alloy processing equipment. Only a few parts of inhibitor per million of liquid are needed to deprive corrosive materials of their kick. Here again, the research of Alcoa engineers will guide you.

Alcoa engineers stand ready to help you get every possible hour of service out of your aluminum alloy equipment. Write and tell us your problems. ALUMINUM COMPANY OF AMERICA, 2154 Gulf Building, Pittsburgh, Pa.

HOW "VINYLITE" PLASTICS

HELP TO MEET TODAY'S CRITICAL NEEDS

They are immediately adaptable to established fabricating methods and offer an unusual combination of useful properties

ONE OF THE MANY reasons why VINYLITE Plastics have attained front-rank importance in vital production is the variety of ways by which they can be fabricated—frequently without major changes in existing equipment and manufacturing methods built around other materials. Of equal importance is the fact that these versatile plastics offer industry an unusual combination of properties unobtainable with other materials.

For example, one VINYLITE Resin Compound can be *extruded* into flexible, non-oxidizing, abrasion- and flameresistant insulation for electrical wire and cable. Another VINYLITE Elastic Plastic can be *injection molded* into flexible, rubber-like shapes and forms, such as grommets and terminal insulators. Other types can be applied to cloth by *knife*- or *calender-coating* to provide waterproof clothing and paulins that will remain flexible even at -50 deg. F. Rigid VINYLITE Plastic Sheets can be *punched* and *printed* to form accurate *calculating* instruments that are noted for their exceptional dimensional stability. VINYLITE Resins, in solution, can be *sprayed* into cans, containers, drums, and tanks to provide non-toxic, chemical-resistant linings.

The opposite page presents information on the properties, forms, fabricating methods, and applications of VINYLITE Plastics and Resins. For more detailed information, write for technical literature, or call upon our Engineering Staff and Development Laboratories for assistance in solving your essential production problems.

Plastics Division CARBIDE AND CARBON CHEMICALS CORPORATION Unit of Union Carbide and Carbon Corporation

30 East 42nd Street, New York, N. Y.

"VINYLITE" ELASTIC PLASTICS

These are a relatively new group of VINYLITE Plastics with rubber-like or elastometic properties. They are produced in a variety of forms, ranging from soft to semirigid. They possess great toughness, and good resistance to continued flexing, and to severe wear and abrasion. Tensile strength is higher than that of most rubber compounds. Their electrical insulating properties are excellent. They are not subject to oxidation. By correct choice of plasticizer, they can be made non-flammable and highly resistant to water, oils, and corrosive chemicals. They are available in a wide range of colors, either translucent or opaque, or can be supplied in their natural, colorless, transparent state. Since all of the VINYLITE Elastic Plastics are thermoplastic, no curing or vulcanizing is required. They are more affected by temperature changes than is rubber, but their operating range is wide, some types remaining flexible at -50 deg. F., yet tack-free at 200 deg. F.

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VINYLITE Elastic Plastics are supplied as sheeting and as compounds for calendering onto cloth, as molding and extrusion compounds, or as powdered resins for those industries that, like the rubber industry, possess adequate compounding equipment.

Applications of VINYLITE Elastic Plastics include many products formerly made of rubber, as well as many others that take advantage of their unique properties. Some of these are: non-flammable insulation extruded around wires and cables; flexible, waterproof cloth coatings for rainwear, upholstery. inflatable equipment, and paulins; extruded, transparent or opaque, chemical-resistant tubing; molded grommets, and wire terminal insulators.

"VINYLITE" RIGID PLASTICS

Produced from unplasticized vinyl resins, VINYLITE Rigid Plastics possess a combination of properties found in no other thermoplastic material. Because of their extremely low water absorption, these plastics remain dimensionally stable under widely varying atmospheric conditions. They are outstanding in their resistance to alcohols, oils, and corrosive chemicals. They have high impact strength and tensile strength. They are odorless, tasteless, and non-toxic. They do not support combustion. They are available in a wide range of colors, translucent or opaque, and also in colorless, transparent forms. They are supplied as rigid sheets or as molding and extrusion compounds. Rigid sheets can be fabricated by forming, drawing, blowing, spinning or swaging, and can be punched, sheared, sawed, and machined on standard metalworking tools. Molding compounds are suitable for both compression and injection molding. Extrusion compounds give highly finished continuous rigid rods, tubes, and shapes directly from the die.

Applications of VINYLITE Rigid Sheets include precise calculating and navigating instruments of high dimensional stability; shatterproof gauge glasses and dials for radios, clocks, and instruments; name plates, transparent aircraft enclosures; storage battery separators. Compression-molded applications include transcription records and printing plates; injection-molded uses include

Corporation.

safety-goggle frames, combs, pen and pencil barrels. Rigid extrusion compounds are produced as continuous rods, tubes. and shapes by screw extrusion. They are readily fabricated with standard woodworking or metalworking equipment.

"VINYLITE" RESINS FOR SURFACE COATINGS

Correctly formulated and applied, VINYLITE Resins yield finishes of unusual toughness, gloss, adhesion, and chemical resistance. They can be applied by spraying, knife-coating or dipping to a wide variety of surfaces, such as metal, cloth, paper, and concrete. Prepared by dissolving resins in organic solvents, these finishes can be modified with a wide variety of pigments, dyes, and plasticizers. These resins are generally not employed with other filmforming bases, therefore, coatings formulated from them exhibit the desirable features of VINYLITE Resins alone. Drying is solely by evaporation of solvent, and finishes can be either air-drying or baking types.

Applications of vinyl chloride-acetate resins for coatings include container linings, stop-off lacquers for electroplating, corrosionresistant linings for processing equipment, wall-tile finishes, heatsealing paper coatings, cement finishes, and waterproof cloth coatings. Coatings based on vinyl butyral resins are also used for waterproof cloth coatings, as on rainwear, hospital sheeting, paulins, and inflatable equipment. Coatings based on these latter resins can be made heat-curing through proper modification.

"VINYLITE" RESINS FOR ADHESIVES

Unusual toughness, resiliency. and impact resistance are characteristic of adhesives made of VINYLITE Resins. These resin adhesives are widely used as bonding agents for such materials as cellophane, cloth, paper, cardboard, porcelain, metal, mica, stone, leather, wood, and plastic sheets and film. They are available as powders for the compounding of adhesives, or as solutions sold under the trade-mark "VINYLSEAL." The latter are especially recommended for bonding impervious materials, such as metals, and the urea and phenolic plastics. Their bonding strength is comparable to that obtained with soft solder. An oustanding example of their use is the lamination of cores of small electric motors. By the addition of plasticizers, adhesives based on VINYLITE Resins can give almost any degree of flexibility desired.

ELASTIC PLASTICS · RIGID PLASTICS RESINS FOR ADHESIVES RESINS FOR SURFACE COATINGS



X-RAY INSPECTION: As additional guarantee of soundness, every inch of main welds is explored with powerful X-Ray equipment. This examination definitely locates ANY defect, shows it clearly, and provides a permanent record of each welded job.

Each of these three steps plays a major role in the efficient manufacturing technique that B&W engineers have developed to save time and steel—important factors in the March to Victory. Ask The Babcock & Wilcox Co. to help meet your need for modern process equipment.

The Marilime Victory flag and "M" burges new flaat proudly alongside the Navy "E" at the Barberton Works, Each is an award for "outstanding achievement" and is "an honar nat lichtly bestawed"



THE BABCOCK & WILCOX CO., 85 LIBERTY ST., NEW YORK, N.Y.

Monster elbow connection and header produced by the exclusive B&W forging method. Drum is 66 inches in diameter, tapering to 17-inch opening. The forged elbow tapers from 30 inches in diameter on one end, to 25 inches on the other. Steel plate, four inches thick is used throughout.

S-36T

May, 1943

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opening 30 inches 25 inches our inches

GS

Science Hids

MANUFACTURING METHODS on Process Equipment

Three modern and scientifically sound operations help build dependability with speed into Babcock & Wilcox high-temperature, high-pressure process equipment.

WELDING: All longitudinal and circumferential joints are welded by automatic welding machines, other connections are welded manually to drums and shells.

> STRESS-RELIEVING: After the welded joints have been tested by the X-Ray, and all parts welded to the drum, the drum is stress-relieved by the B&W heat-treating process. The structure is brought up to the specific temperature slowly, at a rate dependent on the wall thickness and the form of the vessel. This entire operation conforms to the A.S.M.E. Boiler Code.

TWO SUPER REFRACTORIES THAT OPERATE SAFELY AT 3200° and 4000° F

TAM Zircon (Zirconium Silicate) refractories operate safely at temperatures over 3200° F. while TAM Zirconium Oxide refractories are used in applications over 4000° F.

These two TAM super refractories resist acids and oxidizing atmospheres. They are being successfully used in the manufacture of phosphates, fused silica, aluminum melting and platinum smelting. They are also widely used as crucible backing and for various high temperature applications. VUL. UU,

An experienced staff of field engineers located in various parts of the country are available for consultations without obligation. Write:

TAM PRODUCTS INCLUDE Jircon bricks, special shapes and crucibles...Zircon insulating refractories...Zircon ramming mixes, cements and grag...Zircon milled and granular...Electrically Fused Zirconium Oxide Refractories...Electrically Fused Zirconium Oxide cements and ramming mixes...Electrically frically Fused Zirconium Oxide in various mesh sizes

TITANIUM

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Representatives for Europe . . . UNION OXIDE & CHEMICAL CO., Ltd., Plantation House, Fenchurch St., London, E. C., Eng.

Where Gasoline GETS ITS "WINGS".

... HYPER-RESET is making history in stabilized process operation!

In aviation gasoline production . . . where gasoline is given "wings" to power fighting planes . . . Foxboro HYPER-RESET has set new precedents for precision process control!

At critical control-points in the majority of today's aviation gasoline plants, Stabilog Controllers with this exclusive new control function are furnishing stability never even approached before! And this performance is consistently confirmed by results in synthetic rubber plants and other wartime chemical operations.

One of the many installations of HYPER-RESET Stabilog Controllers now giving closer control in aviation gasoline plants.

Here's why. By accurately measuring the rate of change of every process disturbance at the very start, HYPER-RESET anticipates the maximum . . . then, instantly applies hyper-corrective action to suit. It produces smoother recovery from any disturbance . . . in as little as ¹/₄ the usual time . . . with as much as 50% reduction in the size of upset!

Write for Bulletin A-330 containing detailed discussion of HYPER-RESET Stabilog Controllers. The Foxboro Company, 40 Neponset Ave., Foxboro, Mass., U.S.A. Branches in principal cities of U.S. and Canada.



VCI. 35, NO. 3



• Predetermine, in laboratory, effects of sun, laundering, and weathering.

 Reduce years of actual use to just a few days testing.

 Recognized by manufacturers and consumers as the standard accelerated test equipment for more than a quarter-century.

• Used in 36 countries . . . all over the world.

ATLAS FADE-OMETER

The accepted standard for determining the fastness to light of dyestuff and dyed fabrics—originated and made solely by Atlas, and now used all over the world. Atlas enclosed Violet Carbon Arc represents closest approach to natural sunlight. Temperature automatically controlled.

ATLAS WEATHER-OMETER

Reproduces faithfully the destructive action of sun, rain, thermal shock with all the attendant phenomena of expansion and contraction. Shows natural weathering effect from any given conditions at any time, any location. Latest model has twin arcs, full automatic with temperature control.



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Standard laboratory washing machine of A.A.T.C.C. Tests washing action, textile shrinking, staining, and color fastness to dry cleaning solvents, soaps and detergents. All factors, including washing action, carefully controlled—can be reproduced identically at any time.



361 West Superior Street, Chicago, Illinois



DRACCO Engineers have shown many how to reduce handling costs to the **MINIMUM.** Millions of tons of chemicals are moved each year with DRACCO Pneumatic Conveyors on the basis that the **DRACCO** way does the job CHEAPER and **BETTER. DRACCO Pneumatic Conveyors** always reduce labor cost, because in most installations, ONE man with a DRACCO Pneumatic Conveyor can do the work formerly done by SEVERAL men. Another important point is that the maintenance cost is very low. The use of DRACCO **Pneumatic Conveyors is conducive to** better working conditions because they control dust of powdered material. There is no loss of material in handling, and in many installations this means a big saving.

• For Further Information Write •

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116th St. Cleveland, Ohio
New York Office, 130 W. 42nd St. ●

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PNEUMATIC CONVEYORS • DUST COLLECTORS

Dependable Data Assured With DESPATCH LABORATORY OVENS

Control accuracy $\pm 1^{\circ}$ C. with constant uniformity in the work chamber assures maximum dependability for years of service in chemical and analytical testing. Gives accurate data technicians need.



CHEMICAL AND ANALYTICAL TESTING

Rapid airflow and close temperature control, plus rugged oven construction and efficient heating system, assure maximum production of test-finish baking. Ideal for all paints, lacquers.



BAKING & DRYING PAINTS, LACQUERS

Faster heat penetration of every piece in the oven and uniformity of temperature guarantee most satisfactory service for preheating many kinds of plastic pre-forms and powders.



PRE-HEATING VARIOUS PLASTICS

OVEN COMPANY MINNEAPOLIS

Widely used in research and production control tests, drying, sterilizing, dehydrating. WRITE for Bulletin 105.

105. STANDARD SIZES V-5 13' x 13' x 13' V-13 19' x 19' x 19' V-21 37' x 19' x 25' V-27 37' x 25' x 37' PROMPT DELIVERY on roled orders When you want a good Unit



Use the 'SHELLFIN', standardized shell & finned tube heat exchanger!



You get the benefits of a premium quality heat exchanger built on a cost-saving, time-saving, production basis when you choose the SHELLFIN. For — expensive, time-consuming individual engineering is eliminated.

SHELLFIN units are varied only with minor changes in construction, such as baffle spacing and length combinations. Otherwise they conform to the standard design developed by Downingtown engineers . . . a design which meets fully the conditions common to a wide variety of uses for heat exchangers!

AN IDEAL UNIT FOR COOLING, HEATING, CONDENSING, EVAPORATING

Use SHELLFIN for any forms of heat exchange between two fluids in medium temperature ranges, where the heat transfer rate of one fluid is materially greater than that of the other. Use it for cooling oils, benzene, toluene and similar organic compounds, alcohols, chemical compounds generally . . . for cooling jacket water for diesel or gas engines, drain and condensate cooling . . . for air cooling in compression systems . . . for heating in any of the above or similar fluids . . . for condensing organic vapors, hydrocarbon oil vapors, refrigerants . . . for evaporating organic liquids, light hydrocarbons and refrigerants. It's an excellent performer in all of these services'

NEW FOLDER answers your questionsabout SHELLFIN. Write on your letterhead for copy.

DOWNINGTOWN IRON WORKS DOWNINGTOWN, PA. HEAT EXCHANGERS

Vol. 35, No. 5

Do you know about... *Vingen*^{*} Fiber Filter Fabrics?



Studies of many industrial applications of Vinyon fiber filter fabrics have given us much valuable performance data which can be of help to you in the solution of filtration problems arising out of the presence of strong mineral acid or alkali in filtering operations.

Subject always to certain heat limitations, the use of Vinyon fiber filter fabrics offers definite advantages in filtration processes involving strong mineral acid or alkali solutions because Vinyon fiber is a synthetic product highly resistant to mineral acids and alkalis.

If you have the problem of obtaining suitable filter fabrics for any of the following, please check and return to us with information regarding your particular filtration process.

Pigments and Dry Colors Dyes and Intermediates Metallurgical Processes Pharmaceuticals Mineral Acid Solutions Salt Solutions Bleach Liquors Electroplating Processes Ceramics

Please address inquiries to our New York Office.

WELLINGTON SEARS COMPANY 65 WORTH STREET NEW YORK CITY

* Reg. Trade Mark C. & C. C. C.



REMOVE THE PIPING FROM A PETROLEUM REFINERY and what have you left? From well to tank car an unfathomable maze of piping provides FLUID TRANSPORT.

Here, as in scores of other industries, the piping formula is made up of such components as: materials to be carried, heat, cold, expansion, contraction, pressure and corrosion. Grinnell provides the specialized engineering combined with the manufacture and fabrication of the many connecting links needed to convert a pile of pipe into a complete *piping system*. For war construction, or maintenance and repair of existing piping, call Grinnell Company, Inc. Executive offices, Providence, R. I. Plants and offices throughout United States and Canada.





INDUSTRIAL AND ENGINEERING CHEMISTRY

Vol. 35, No. 5



willing and ready to learn. But it's up to you and us to give them practical aids for doing a better job.

In hundreds of plants today, training of maintenance crews is being speeded by Crane "Piping Pointers." These bulletins, based on Crane's 88-year experience in the flow control field, are aimed at a single purpose: to keep pipe linesyour plant's lifelines-operating at peak efficiency.

"Piping Pointers" give practical aid to veterans as well as beginners. They're full of do's and don'ts and rights and wrongs of sound piping practice. They show

RANE VALVES

short-cuts-correct repair proceduressubstitutions to solve material shortages -and safety hints. Anyone can understand and use them.

SENT FREE TO ANY PLANT

For Victory's sake, faster training of workers for better maintenance of piping is a vital must. In "Piping Pointers," Crane Co. shares its basic information for that use, with all industry, and offers these bulletins free to any plant. Ask your Crane Representative or write direct for your supply. Crane Co., 836 South Michigan Avenue, Chicago, Ill.

TTER

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DUST.



— alike in the fact that Schneible Multi-Wash Equipment can liquidate the problem — different, of course, in the nature of the dust and fumes encountered, and possibly in the equipment and the working medium required. Schneible engineers have repeatedly demonstrated their ability to adapt standard equipment to the successful control of any contaminated air condition found in process plants. In a Mid-Westernvarnish plant, pigment dust from the handling and mixing operations created a health hazard and had a



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serious effect on the working efficiency of the personnel. This float dust was also damaging to the machinery, especially bearings. A 2,500 c.f.m. Schneible Multi-Wash Collector was installed, and pigment dust no longer contaminates the air of this plant.

Pictured is Schneible equipment which overcame comparable conditions in a large printing ink plant. Here a plant and community nuisance was eliminated, and valuable oils exhausted from the kettles were recovered.

Schneible Multi-Wash Dust Collectors are preferred throughout the chemical industry because they definitely overcome all dust and fume conditions, because they provide for product recovery and because they operate indefinitely with minimum attention and maintenance. Only water, or some other washing liquid, is used over and over again in the collector system. The collectors have no moving parts—nothing to break, burn, clog or rapidly wear.

Let us send you complete information.



CONTROL

FUME

EQUIPMENT

A 10-year-old installation of Twin G-Fin Sections...still operating with complete satisfaction. Today, more than 800 concerns are using these "Universal Heat Exchangers" on a greater variety of services than any other design of heat transfer apparatus on the market.

10 YEARS OF PERFORMANCE

When you buy a Twin G-Fin Section for any heat exchanger requirement, you can be SURE that its specified heat transfer rates will be obtained...that its operation will be thoroughly satisfactory...and that its construction will prove lastingly reliable. Every claim made for this pioneer finned-tube heat exchanger is backed by 10 years of successful performance and by the results obtained in more than 30,000 installed sections. BULLETIN ON REQUEST.

THE GRISCOM-RUSSELL CO. · 285 MADISON AVENUE, NEW YORK





AT RIGHT 30" Sperry Filter Press with Type EHC closure operated in a defense plant by one girl.

BELOW — Three men closing 24" Filter Press with capstan closure.

MORE POWER TO MARY JONES

Mary Jones is filling many important industrial jobs these days, and doing them well too, but she just wasn't strong enough to operate big, heavy filter presses until Sperry developed the type EHC electric closing device. It used to take the combined muscular energy of two husky men to close some presses, but Sperry's type EHC closing permits full control of even the largest press by easy hand adjustment at only two places. Check these important advantages:

- 1. Quicker opening and closing speeds the filter cycle.
- 2. Wear and tear on filter cloths is greatly reduced.
- 3. Operating bazards are minimized.
- 4. Press can be operated by girls, and workmen released for other duties.

The type EHC closing can be applied to your present filter presses without extensive alterations. For Sperry presses, only removal of the cross head is necessary.

Phone or wire for complete information on this timely equipment today.

D. R. SPERRY & COMPANY, Batavia, Ill. Filtration Engineers for Over 46 Years



Eastern Sales Representative Henry E. Jacoby, M. E., 204 E. 42nd St., New York City Telephone: Murray Hill 4-3581

Western Sales Representative B. M. Pilhashy, Merchant's Exchange Bldg., San Francisco, Calif.



EQUIPMENT FOR VICTORY

You want it that way and so do we. It has been our privilege to build hundreds of vessels and other special equipment for the war effort. Naturally, we still have many more to deliver and this fact may, in some cases, make it impossible to give the kind of prompt service we like to give to all our customers. However, we will serve you to the best of our ability and we welcome your inquiries.

J. P. DEVINE MANUFACTURING CO., INC.

CHEMICAL PROCESS EQUIPMENT

HOME OFFICE AND PLANT, Mt. Vernon, Illinois

Raschig Rings of Lapp Porcelain

Facilitate

eres to ow:

Gas Absorption Processes

WEAR Raschig Rings of Lapp Chemical Porcelain are standard tower packing in many American plants today because, at low cost, they offer long life and a high purity standard. These are properties of Lapp Chemical Porcelain as a material. A thoroughly vitrified ceramic, completely iron-free, it offers high mechanical strength. Its absolute nonporosity guards against contamination of subsequent batches, means exposure to corrosion is limited to the surface, avoids crumbling.

WATE TO Reasonable quantities of Lapp rings in most sizes are available for shipment from stock. Large orders can be accommodated on a delivery schedule satisfactory to you. For specifications and trial samples, write Lapp Insulator Co., Inc., Chemical Porcelain Division, LeRoy, N. Y.



• Pipe and valves of Lapp Chemical Porcelain are still available for industrial installation. For the handling of corrosive liquids they offer highest purity, mechanical ruggedness, and long life.

Chemical Porcelain

Values · Pipe · Raschig Rin

Vol. 35, No. 5

WILL HELP YOU KEEP EQUIPMENT OPERATING AT TOP EFEIGLENCY

ENGINEERING

T is vitally important today that Simpson Intensive Mixers keep operating at top efficiency. That is why the Simpson Service Manual has been developed and sent to the thousands of users of Simpson Mixers . . . and also why National Field Service Engineers are alert and on the job wherever needed, helping the chemical and process industries find the way to better, faster mixing at less cost.

86

The Service Manual contains all the important details describing installation, adjustment, operation, maintenance, lubrication, parts and use of auxiliary equipment. It is an aid in assuring peak operating efficiency of Simpson Mixers so they may continue to produce the highest quality-quantity output.

National Field Service Engineers assist in planning for and installing equipment, and in solving new problems stimulated by changes in production, product development or any problem involving better mixing to achieve improved quality of product, lower costs and time saving.

National Service has played an important part in bringing the advantages of better mixing to hundreds of plants handling dry, semi-dry or plastic materials. National Service is ready and available to work with you on your mixing problems. Write for a catalog or ask to see a National Engineer, SIMPSON Intensive MIXERS Mix dry, semi-dry and plastic Materials...Better...Faster... For Less.



May, 1943

INDUSTRIAL AND ENGINEERING CHEMISTRY

Busy Chemicals for the War and After

GUNS-on-wheels now; FUN-on-wheels later

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Caustic soda plays a dual role in the success of today's mobile artillery. It helps to refine high-

powered gasoline. It helps produce the rubber on which the guns roll. And it will perform the same services when post-victory cars become available for pleasure driving.

along with Bleaching Powder, is one of the two products originally manufactured by HOOKER. From this pair, the list of HOOKER Chemicals has grown to more than a hundred* today. As a result, the HOOKER organization now is able to serve more industries in more ways than ever before.

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HOOKER CAUSTIC SODA

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*For list of principal HOOKER products consult current Chemical Engineering Catalog, or write us.



STILL & STERILIZER CO.Inc

Vol. 35, No. 5

THE NEAREST THING YOU CAN GET TO

If water were only 2 parts hydrogen and 1 part oxygen, manufacturing chemists would have much less trouble with the quality control of many of their products. But unfortunately, the ordinary water supply is H_2O PLUS many types of impurities...nitrates, chlorine, free and albuminoid ammonia, carbon dioxide, volatile and inorganic solids... impurities that directly affect the total success of processes.

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The answer is to use Barnstead water stills for your process water supply. Then you'll have water that is free from impurities. You'll have water of the same degree of purity that chemists insist for laboratory work . . . BARNSTEAD purity.

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VOI. 33, NO. 3

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INDUSTRIAL AND ENGINEERING CHEMISTRY

VOI. 35, IND. J

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May, 1943

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INDUSTRIAL AND ENGINEERING CHEMISTRY

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Right: Special VW nested coil with double accumulators, used in a Blizzard quick-freezer.





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INDUSTRIAL AND ENGINEERING CHEMISTRI

VOI. 30, NO. 5



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INDUSIRIAL AND ENGINEERING CHEMISTRY

109

Permanent Piping

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TTS" 6" TAYLOR FORM

Vol. 35, No. 5

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SIZE AND THICKNESS MARKED ON EVERY FITTING

have everythin

6" STD. TAYLOR FORDE WEIDEN

NO GUESSWORK HERE-

THE welder's job is welding; not fussing around to find a fitting of the right size and weight —or waiting for the other fellow to do it. And yet that is just what he's up against when he works with fittings that are not clearly identified. When such things happen it isn't surprising that the welder may "take it out on the job"—particularly when he's working against time as most everyone is today.

110

Anything can happen when unmarked or poorly marked fittings are used. The wrong size may be delivered, and not discovered until too late. A helper may lug a heavy fitting a long way from the stockroom, only to do it all over again.

But there's little chance of this sort of thing when the fittings are WeldELLS* or other Taylor Forge Welding Fittings. Every Taylor Forge Fitting wears its size and weight on its back—permanently marked so that it can be read ten years from now as well as it can today!

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By eliminating the danger of using wrong thickness fittings, this feature ranks with the many features of WeldELLS that contribute to sound engineering design. And by simplifying and speeding up welding, it ranks with the many features that contribute to convenience and economy.

Yet it is just one of many reasons why WeldELLS are known as the fittings that have *everything*—everything *any* welding fitting has; some things that no other has.



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General Offices & Works: Chicago, P. O. Box 485

• WeldELLS are just one of many Taylor Forge Products that are vital to war and victory. An example is huge rolled steel rings—an important part of U. S. tanks now in action.

***WeldELLS** alone have all these features

In addition to the feature described, they include:

Seamless—greater strength and uniformity.

Tangents—keep weld away from zone of highest stress—simplify lining up.

▶ Precision quarter-marked ends simplify layout and help insure accuracy.

Selective reinforcement — provides uniform strength.

► Wall thickness never less than specification minimum—assures full strength and long life.

Machine tool beveled endsprovides best welding surface and accurate bevel and land.

► The most complete line of Welding Fittings and Forged Steel Flanges in the world — in sures complete service and undivided responsibility.

* * *

* WeldELLS and many other Taylor Forge Products are produced in Byers Genuine Wrought Iron. i finel Se mus to a intense i unpor intense intense i unpor intense in

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ONE OF A SERIES DESCRIBING PLASTICIZERS AND MODIFIERS—FOR USE WITH NATURAL AND SYNTHETIC ELASTOMERS—PRODUCED BY THE RESINOUS PRODUCTS & CHEMICAL COMPANY

Dibutyl Sebacate at 35,000 feet

WIDE commercial use has proved that Dibutyl Sebacate materially aids processors to adapt natural and synthetic elastomers to industrial applications. This plasticizer is especially valuable in compounding elastomers for applications where the finished product must have *low-temperature lexibility*.

A typical use is in equipment for high flying bombing and fighting planes where extreme cold is encountered.

As produced by The Resinous Products & Chemical Company, Dibutyl Sebacate, is eminently workable in the rubber factory. Its purity, water-white color and uniform high quality guarantee users unvarying results from one production run to the next.

PHYSICAL PROPERTIES OF DIBUTYL SEBACATE

Purity	Over 99%
Acid (as Sebacic)	Less than 0.4%
Color (A.P.H.A.)	Less than 25
Boiling point 344	-345° at 760 m.m.
Specific gravity, 25°	C ./15° C .
-r o ,,	0.936-0.942
Pounds per gallon	7.8
Refractive Index	1.4391 at 25° C.
Saponification numb	ber Approx. 362
Dielectric constant	3.6
Power factor (60 cy	vcles) 6
Flash point	353° F.
Fire point	411° F.
Freezing point	11° F.
Water solubility	
Loss than 1%	by weight at 25° C.

OTHER PLASTICIZERS AND SOFTENERS

Photo through the courtesy of Boeing Aircraft Compan

1. SOFTENERS FOR HIGH TEMPER-ATURE SERVICE. Resin R6-3, Duraplex C-50LV (100% solids), Dibenzyl Sebacate*. *Excellent high temperature stability for elasticator type softeners.

2. SOFTENERS FOR HIGH DUROM-ETER HARDNESS. Resin R6-3, Duraplex C-50LV (100% solids).

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DETERMINATION OF MAGNESIUM

REAGENT—Titan Yellow

METHOD — Spectrophotometric

REFERENCE — Ludwig and Johnson, Ind. Eng. Chem., Anal. Ed., 14, 895 (1942)

Magnesium hydroxide, when precipitated in the presence of titan yellow, forms a lake which is suitable for spectrophotometric measurement. Determination of magnesium by this means is rapid, requiring about twenty minutes, and compares favorably in accuracy with the official gravimetric procedure. It is less subject to uncertainties than the standard volumetric methods, and for most practical purposes the interferences likely to be encountered do not affect the results. The reagent is available as *Eastman P 4454 Titan Yellow (Pract.)*.

> Write for an abstract of the article in which the determination of magnesium with titan yellow is described. . . . Eastman Kodak Company, Chemical Sales Division, Rochester, N. Y.







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psi

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