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EDITORIALS

FRANCIS PATRICK GARVAN occupied a unique place in American history. He had gained distinction in his chosen profession, the law, long before the promotion of science became his principal interest.

The Chemical Foundation, Inc., was conceived and formed by Mr. Garvan for the sole purpose of administering patents, patent applications, trade-marks, and copyrights being effectively used as a weapon by Germany in the war. The Chemical Foundation, Inc., saw to it that this property, purchased from the Alien Property Custodian, was used in the public interest for the development of an organic chemical industry in the United States and for the furtherance of science. Forced into long litigation with the Government during the Harding administration, the Chemical Foundation, Inc., through Mr. Garvan, asserted that the President was being duped by German interests anxious to regain the patents. The Foundation was successful in all the courts, including the United States Supreme Court, the opinion of which virtually placed the Foundation in the position of a trustee for the American chemical industry. Mr. Garvan lived to see the synthetic organic chemical industry grow to fourth place among American industries.

Mr. Garvan, who was joined in his work of philanthropy and education by his devoted wife, did more than any other layman to familiarize the public with the proper place of chemistry in everyday life. Prize essay contests were made possible through the generosity of Mr. and Mrs. Garvan, and hundreds of thousands of books and pamphlets freely made available in connection with that enterprise. But there was no sphere of public activities which he left untouched. Dozens of young people were assisted in their chemical education, and scores of professors were aided in their researches through grants quickly made available when convincing evidence was presented as to the need and importance of the work. Educational institutions, hospitals, publications, all received help at his hand, and the National Farm Chemurgic Council is indebted almost wholly to him for its existence and maintenance. He substantially aided projects in the fields of physics, radiology, and many medical specialties.

As time went on Mr. Garvan became more and more convinced of the possibility of the economic independence of the United States through the application of science in the utilization of our natural resources and struck out boldly and persistently against any movement or any idea that ran counter to his clearly defined economic nationalism. He gave as generously of his time as he did of his money, was sincere, patient, kindly, and helpful. Many an industry, organization, and individual owes him an everlasting debt of gratitude. His fundamental creed was to make the United States the best possible living place for all the people.

Unprotected

THE number of deaths known to have been caused by the "elixir" of sulfanilamide distributed by the S. E. Massengill Company of Bristol, Va.-Tenn., now exceeds 70, and it is unlikely that anyone will ever know the complete record. How can the recurrence of such a tragedy be prevented?

A number of spectacular cures made with sulfanilamide in the hands of skilled physicians early called attention to the potentialities of a compound about which not too much was then or is now known. A specific for certain types of coccus infections was sure to have wide application, and a number of manufacturers began production of this compound, which was quickly made readily available in most drug stores.

In some cases the dry tablet was difficult to swallow, so when salesmen began to report that even better business could be done if the drug were in solution, the S. E. Massengill Company searched for a satisfactory solvent, and unfortunately decided on diethylene glycol. Notwithstanding the extensive literature on the glycols, including ethylene, diethylene, and propylene glycol, and, so far as we have been able to learn, without making any physiological tests with the mixture, the company began to put it on the market. Something more than 700 shipments had been made by the time appeals started to come in for antidotes, advice as to treatment of cases, and distress signals from various places. The American Medical Association did all within its power to assist, and the officials of the Food and Drug Administration earned hearty commendation for the swiftness with which they acted and the completeness of their search, which extended in the case of opened packages to the very medicine cabinets in private homes and hospitals.

Be it noted, however, that the Government had to make its seizures first because of mislabeling. The mixture was not an "elixir." It is like convicting a murderer on the charge of speeding or income tax evasion. Note, too, that most of the deaths were among patients of physicians who had prescribed the "elixir." Evidently some members of the pharmaceutical profession, whose chosen duty it is to protect the health of the public, failed tragically in that prescriptions were filled with a substance the composition of which they did not know. It is also well-nigh criminal that those responsible for making the "elixir" did not at least consult the literature or indeed the manufacturers of diethylene glycol, who have habitually discouraged and recommended against diethylene glycol for any internal use.

The public, notwithstanding all our efforts, remains unprotected to a sad degree. While pending legislation to broaden the powers of the Food and Drug Administration would be helpful in discouraging a recurrence, such laws in the very nature of things are punitive and have to do with locking the stable after the horse is many miles away. It is regrettable, but true, that, among the scores of thousands of physicians, there are so many who are incapable that we cannot depend on the medical profession alone for complete protection. The physician, in common with many of the public, somehow has the opinion that because a preparation for internal use is on the market it must have been approved by federal or state authorities. Nothing is further from the truth, since these products are not manufactured under license and at present only mislabeling, short weight, miscount, or very obvious detriment to the public health are causes for seizure.

And so we find ourselves at times unable to depend upon the protection which the literature, the drug manufacturer, the pharmacist, the physician, or federal authorities might be supposed to give us. What can be done about it?

Why license electricians and plumbers and allow any one who has the capital to engage, without let or hindrance, in the manufacture of our medicines? We suggest, notwithstanding our objection to extensive control, that some federal agency must be given the power to license those who would manufacture drugs, pharmaceuticals, and similar compounds, mixtures, or materials for internal use. Perhaps the U. S. Public Health Service should add this to its list of activities, with some reasonable fee for the license, thereby placing the whole transaction in the Treasury Department. Such licenses, which should be on an annual basis, would be granted only after competent authorities were convinced of the ability and intent of the manufacturer to take all possible steps to protect the public and that he was prepared to use the highest approved standards. A further safeguard might be the required disclosure on the label of the bottle or other package of the composition of the contents and some authoritative approval for intended use prior to distribution.

Whatever may be done in this direction the difficulty of assuring proper use is still to be overcome. Education must be regarded as a continuing process. Notice has already been broadcast, discouraging the promiscuous use of sulfanilamide, advising it only where the infection is by organisms susceptible to its action, urging the physician to individualize and make the diagnosis, to attempt to make the dosage compatible with each individual requirement, determine quantitatively the concentration of the drug in the blood and keep it below 15 mg. per cent, and watch the hemoglobin, the white blood cell count, and the daily excretion of the drug. Things known to be harmful in their cross action when given with sulfanilamide must be avoided.

Here is a compound of great potentialities and a creditable history. It must not be misused, nor should the reputation of diethylene glycol in its proper place suffer because of criminal carelessness born of greed in this case. Other compounds considered harmless might prove toxic if taken in equally massive doses. Out of it all it is to be hoped that some procedure will be evolved which will be a distinct gain for the public, even though it is won, as are so many advances, at such frightful cost.

Butyric Acid—Not Butter

IN AN editorial entitled "Tracers" in our October issue, we erred in interpreting the work of Rudolf Schoenheimer as reported at the Rochester meeting, and gave our readers reason to hope that they could help themselves to butter without adding to the deposit of fat in inconvenient places. The facts in the case are these:

> Animal experiments with fatty acids labeled with deuterium indicate that the higher acids, palmitic, stearic, and oleic, containing 16 and 18 carbon atoms to the molecule, are very slowly metabolized after ingestion, being largely deposited in the fat tissues prior to oxidation. On the other hand, the lowest naturally occurring members of the fatty acid series, butyric and caproic acids (containing 4 and 6 carbon atoms, respectively) are metabolized with surprising rapidity, and when labeled by deuterium cannot be detected in the fat depots.
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> The above observations bear on the metabolism of butter fat only to the extent to which butter contains these lower acids—namely, 5 to 6 per cent. Of the fate of the intermediate acids, caprylic (C_8), capric (C_{10}), lauric (C_{12}), and myristic (C_{14}), which constitute in all some 15 per cent of the acids of butter, nothing has as yet been ascertained by the deuterium technic. Statements in the daily press to the effect that butter fat is burned more rapidly than other fats may be correct, but are premature and lack experimental foundation. Only a systematic metabolic study of all the naturally occurring fatty acids can enable a decision to be reached. Such an investigation might explain why the newborn require a fat of such peculiar composition as that of milk.
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> The statement, given wide currency in the press, that butter, in contrast to other fats, is not fattening, is undoubtedly as incorrect as it is unjustified.

SYMPOSIUM ON
UNIT PROCESSES[1]

BECAUSE so many of the actual processes that are carried on in our factories depend upon chemical change, this symposium has been planned. The object of the symposium is to study, under the caption of unit processes, the chemical reactions taking place, the equipment in which these reactions function, and the conditions necessary to make such reactions pay dividends.

The invitation to participate in this symposium was sent to men both in industry and in universities. We very much appreciate their participation. We expect that this symposium is but the initial step in regular and periodic gatherings for the dissemination of research data that go to make up these unit processes. We anticipate that as a result of this work we shall be able to put a more quantitative background into unit processes.

R. NORRIS SHREVE,
Symposium Chairman

Classification of Unit Processes

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Too often unit processes have been presented in a purely descriptive manner. Although it is exceedingly difficult to obtain quantitative data and equations except for certain aspects of these unit processes, this paper presents a tentative system of classification which can be applied to each process. This classification involves such items as the generalized type of chemical reaction on which the unit process is based, the various factors influencing its chemical reaction, and treatment of the energy involved, with special emphasis upon the equipment necessary to make the unit process function economically. The items of the classification are tabulated and examples given to exemplify their application.

CERTAIN phases of chemical engineering are presented under the caption of "unit processes." Here the emphasis is upon the chemical changes, together with the conditions and the apparatus required to make these reactions take place in an economical manner. Unit processes are carried on in factories in wood, metal, or glass equipment. However, many of the essential and basic chemical changes involved can be more quickly studied on the laboratory scale and then applied industrially.

These unit processes have often, in a broader and older sense, been included in the term "chemical processes." Here many of the unit operations function as an integral part of the chemical change. The reverse is not always true since many unit operations function when no chemical change is occurring—for instance, in a salt-evaporating and -crystallizing plant.

Taking a lead from the splendid work that has been done in emphasizing and studying the quantitative phases of the physical or unit operations, it has been thought that a similar close study of chemical or unit processes would result in more order. Hence there would result greater ease in studying and applying unit processes and in using the equipment for carrying them on industrially.

This paper is an attempt to classify some of the unit features. It is realized that what chemical engineers wish is a series of equations, the solutions of which will convert chemical changes into dollars and cents. This is too idealistic; it is beyond hope. We may, however, reasonably expect that future research will put more quantitative data into many of the phases of unit processes, so that judgments of future process men will rest on a surer foundation than now. As the

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writer visions this problem, the first step involves the working out of the chemical and physical phases; the second, the apparatus required to commercialize these chemical changes economically.

The principal unit processes are as follows: nitration, esterification, sulfonation, amination by reduction, amination by ammonolysis, oxidation, hydrogenation, hydrogenolysis, alkylation, acetylation, halogenation, double composition, cracking, polymerization (depolymerization), resinification, diazotization and coupling, hydrolysis, hydration, and the Friedel and Crafts reaction.

Most of us have confined unit processes to organic technology, but there is no reason why this helpful system of classification should not include inorganic technology. The chamber process, the contact process, and the air oxidation of ammonia to nitric oxide would be subheads under the unit process of oxidation, with the better opportunity of emphasizing the analogous phases of such reactions—for example, the great amount of heat involved by such chemical changes together with the equipment necessary to handle it.

An excellent classification has been made for unit operations by Olive (*4*). Here the emphasis is on the physical changes. Although these physical aspects are always important in industry, there are many procedures where the central or controlling change is chemical. It would be helpful in these chemical changes to have as useful a classification as is given by Olive for physical changes. As a subject for discussion and elaboration, the author submits the following classification of unit processes which he has been using for several years to bring the fundamentals of order to unit processes:

- Types of reaction:
  - Addition
  - Oxidation
  - Reduction
  - Substitution
  - Pyrolysis
  - Polymerization
  - Condensation
- Factors affecting reaction:
  - Temperature
  - Speed of reaction
  - Solvents and solubility
  - Control—analysis
  - Phase—liquid, vapor, or solid:
    - If gaseous, effect of pressure
    - If solid, effect of particle size; equipment
    - If liquid, whether molten or in solution
    - If nonhomogeneous, effect of agitation
  - Effect of varying concentration and reactant ratios
  - Heat of reaction (see "Energy change" below)
  - Relative importance in aliphatic and aromatic fields
  - Influence of other substituents, orientation
  - Reversibility
  - pH
- Types of products:
  - Ease of recovery of product
  - Purity and analysis of product
- By-products or side reactions:
  - By-products
  - Prevention of by-products
- Energy change:
  - Exothermic or endothermic
  - Heat flow:
    - Rate
    - Medium—resistance
  - Power for mixing, etc.
  - Recovery
  - Heat balance
  - Energy balance
- Raw materials used for unit process:
  - Chemical properties:
    - Corrosion
  - Chemical grouping of agents used
  - Physical characteristics:
    - Liquid, solid, or gas
  - Concentration effects
- Catalysts:
  - Nature
  - Concentration
  - Recovery
  - Inhibitors
- Mechanism:
  - Free energy
  - Activation
- Material Balance
- Yields:
  - Factors affecting losses
  - Conversions
- Engineering flow sheet
- Equipment:
  - Materials of construction
  - Corrosion:
    - Special alloys
  - Erosion
  - Discontinuous and continuous operation
  - Types of equipment—design
  - Labor-saving devices
  - Time
  - Control
- Effect of unit process:
  - Nature of change in chemical properties
  - Nature of change in physical properties
  - Nature of change in physiological properties—e. g., toxicity
- Hazards and precautions:
  - Fire
  - Explosion
  - Toxicity
- Labor:
  - Direct or shift operations
  - Maintenance or repair
- Economics:
  - Statistics of industry
  - Avenues of sale
  - Sectional sources of raw materials
  - Sectional demand for products
  - Cost of product:
    - Small scale
    - Based on commercial tonnage
  - Plant site

This outline is mainly for instructional purposes, but the industrial viewpoint is always in mind. Chemical engineers are being trained to go out in industry; therefore it seems that, when we classify these unit processes, it would be far better to look at them from the manufacturing standpoint. The object of studying or operating unit processes is to make money from chemical reactions. The economic and the quantitative aspects are, therefore, the most important.

In unit processes, quantitative data are badly needed. If we glance over this field, we see that under some heads quantitative data can be obtained without too great trouble; in others it is very difficult. For a long time the right decisions will come as a result of mature experience developing into right judgment.

In the various headings listed, equipment is the most important; some men working in unit processes say that the design of equipment is the backbone of the process. The essence of the unit process is the economical application of a chemical reaction on a factory scale. Although design is of great importance, in a properly designed sulfonator, for instance, the exact conditions under which the equipment is operated will have a great deal to do with the chemical yields and hence with the costs. Therefore, the two most important phases seem to be the design of the apparatus and the conditions necessary to carry out this chemical reaction economically.

Purely chemical reactions have been ably treated for years in textbooks such as those by Lassar-Cohn (*3*) and Houben (*2*). These books are invaluable as the basis of much of the chemistry involved. On the other hand, when the chemical engineer looks at unit processes, the particular phase of chemical reaction that is paramount is to secure as high a yield as possible; consequently, he is not interested in the reactions which have little or no economical importance. So we have a great deal of investigational work to lay the requisite quantitative chemical foundation under our unit processes. We shall have to study the chemistry involved in all phases to raise yields to an economical level, or else eliminate the reaction in question.

Application of Unit Process Classification

For two years the writer has been applying this outline to the study of each of the unit processes presented. For example, the various factors involved in nitration were studied under all the heads listed in the outline; the same thing was done for the other unit processes. It is not to be expected that under each unit process will the facts support an equal treatment of every division of the outline. Quite the contrary is true, frequently because of the nature of the underlying chemical reaction or of the availability of more data for one process than for the same feature of another. The following of such an outline does bring order into the unit process and ties in very definitely the various factors making up the unit process.

It has always seemed best to study a given sequence from raw materials to the finished product. This is the exact procedure that would be carried out in the factory. Since a number of such procedures are sequences of one or more unit processes, it does not permit an exact scientific division into each and every unit process involved. Continuity of industrial movement from raw material to product is more important than any exact classification. Therefore, it has been the writer's practice to take up the most important of the unit processes involved and to classify the sequence in this process, mentioning the other processes but using the principal one as the example to fit into the outline.

Types of Reaction

One or more of the subheads under this caption will apply to any unit process. The reason for so classifying the reaction is to lay stress upon the chemical change taking place in the simplest possible terms. For instance, the cracking of petroleum is an example of pyrolysis. On the other hand, if we view resinification as a unit process, in most cases it would be an example of two types of reaction—namely, polymerization and condensation. Halogenation may be either a substitution or an addition or both.

Factors Affecting Reaction

If a reaction is to be carried out with high yields, and consequently with low cost, the various factors affecting the reaction must be studied in great detail. These pertain largely to the pure chemistry of the unit process; on the other hand, the chemical engineer is interested only in those chemical factors that give satisfactory yields. Fortunately the literature (*1*, *2*, *3*, *7*) contains many data pertaining to commercialized reactions, and therefore many of the subheads under this division have been investigated, such as the influence of temperature on reaction speed and yields, methods of analysis and control, and influence of other substitutions on the course of reaction.

The factors under this heading involve first the chemical aspects and can be more quickly determined on a laboratory scale. However, the chemical engineer should never be satisfied with the laboratory results but should apply the best conditions for the reaction to the semiworks scale first and, finally, to the factory. Here can be determined those factors which influence fundamentally the nature and design of the equipment, such as the effect of particle size on agitation in the nonhomogeneous phase.

Types of Products

The physical and chemical properties of the products are fundamental in influencing the design of the equipment in which the reaction is carried on or in which the products are handled following the chemical change. For instance, in amination by reduction, where nitrobenzene is changed to aniline by means of iron, the stirring and the erosive action of the resultant iron oxide require the use of a heavy replaceable stirrer, located on the bottom of the reducer. In the nitration of benzene to nitrobenzene, where all the products and by-products are liquid, the handling is much simplified. On the other hand, if the product is *m*-dinitrobenzene, the material is solid at ordinary temperature, and provision should be made for removing the nitration as a warm liquid.

Since these reactions are of interest only from the commercial viewpoint, the purity and method of analysis of the product are of the utmost importance. It is hard for one who has not been in industry to visualize the deciding weight in the sale of a product caused by a small amount of impurity. The controlling decision in the choice of a given reaction is often whether or not the resultant product is initially pure or can be readily purified.

By-Product or Side Reactions

Frequently men in chemical industry bemoan the fact that many reactions give more than one product; it is the very nature of things that many organic and inorganic reactions yield by-products. There is another way of looking at these by-products; they can be considered a challenge to the ingenuity of the chemical engineer to find a use for them. As we look at the past, we see certain materials that filled warehouses before avenues of utilization were discovered. Conditions may change markedly; at one time *o*-nitrotoluene was a drug on the market, and at another time, *p*-nitrotoluene; now firms making the nitration products of toluene are able to dispose of both isomers. By altering such conditions as temperature, for instance, the proportions of the by-products may be altered or greatly reduced in volume. This is true in the nitration of acetanilide as a step in the production of *p*-nitroacetanilide to be saponified into *p*-nitroaniline.

Energy Change

Energy change is important in any laboratory chemical reaction; it is frequently of paramount weight in a unit process. In industry this division of the unit process study should receive great emphasis, and wherever possible the figures should be worked out regarding the changes that take place. The study devoted to the unit operation of heat transfer enables this phase to be calculated with considerable sureness. It is frequently well to construct flow sheets for both the chemical change and the entire heat balance involved in the process. If such balances are before the chemical engineer, frequently a plan can be made for recovery of some of the energy expended; for example, in the pressure process for oxidation of ammonia by means of air, the compressed waste nitrogen is used to drive compressors to give a part of the air needed.

In nitration and oxidation a considerable amount of energy is released, and only by the proper removal of this exothermic heat of reaction can the process be kept under control and the necessary good yields be obtained. Much of the equipment design is for the proper handling of this heat transfer—for instance, in the Hough nitrator for nitrating benzene or other hydrocarbons, or for making glycerol trinitrate. A similar skillfully designed apparatus is the Downs reactor for the oxidation of naphthalene in the vapor phase to phthalic anhydride.

Raw Materials for Unit Processes

The physical and chemical properties of the raw materials govern not only any corrosion but also the means by which the materials can best be handled. New products are continually being put on the market, which can resist even corrosive materials—for example, rubber-lined steel for hydrochloric acid and stainless steel for nitric acid. Corrosion tests must always be made upon materials of the same purity that are expected to be used in the unit process, and not upon pure reagent chemicals. This rule seems self-evident, but it is surprising how frequently it is abused.

Concentration effects and their influence upon yield and purity should be emphasized. A good example is the use of many times the theoretical amount of ammonium hydroxide in the amination of organic halides by ammonolysis. For good yields it is necessary to handle this large amount in and out of the reaction equipment.

Catalysts

The utilization of a catalyst frequently spells success or failure of the commercial process, whether it be vanadium pentoxide in the manufacture of phthalic anhydride or in the oxidation of sulfur dioxide to sulfur trioxide. The life of the catalyst, or its cost of recovery, has a direct influence upon the economy of the operation.

Under inhibitors we may present anticorrosive agents to save equipment, and anticatalysts which have a negative influence upon the speed of the reaction.

Mechanism

Although an operator may run a plant without understanding the mechanism of the reactions involved in the process under his control, this state of affairs should certainly be remedied. It is to be hoped that physical chemists will devote more and more attention to the fundamental laws and data pertaining to the mechanism of reactions. When we have the fuller explanation of the cause of reactions, their handling on a large scale will be more easily directed. In each unit process we should discuss whatever is known regarding the specific mechanism.

Material Balance

As a preliminary to yield figures and cost calculations, a balance sheet should be drawn up for the materials entering and leaving a given unit process. This has long been done, and its value is well recognized.

Yields

Generally in unit processes the chemical yield is the most important factor in the cost of the product. Continued research should be carried out until it is demonstrated that the highest practical yield has been reached. In unit processes there are certain mechanical losses, such as spillage, and these should be considered in the material balance sheet. As a rule, they can be kept down to a small percentage.

A sharp differentiation should be made between conversion and yields, in accordance with industrial practice. If a reaction is put through a given equipment only once, the conversion would equal the yield; but frequently, before a cost calculation is made, a series is carried out that may extend over days or weeks. At the start of a given series the raw material may be put through the reaction and the products separated from the unused raw material. Then, in turn, this raw material would be used again. Consequently, although a conversion of only 15 or 25 per cent may result, at the end of the run the over-all yield may well be 90 or 95 per cent. Furthermore, at times it is found that, if the conversion per cycle is forced up, there is a greater destruction of the raw material with the consequent lowering of the yield at the end of the series. It is important to point out certain examples of this differentiation under the various unit processes.

Engineering Flow Sheet

No process is installed, nor should one ever be studied in detail, without drawing up at least a rough engineering flow sheet so that the chemical engineer, whether he be in the university or in industry, can see before him the movement of his material through the various pieces of equipment. A number of these flow sheets are generally made as a process is developed industrially. At first they may be rough block flow sheets, progressing to more complicated diagrammatic ones where sketches approximate the shape and size of the equipment as its design is evolved.

Equipment

The writer has already printed his ideas on how the equipment should be treated in typical unit processes (*5*). Frequently, though not always, the equipment is a distinguishing feature between a reaction carried on in a laboratory and in a factory. It is here that the skill and the imagination of the engineer is most usually shown.

In presenting any unit process, the materials from which the equipment can be constructed and their influence upon corrosion, erosion, and purity of product cannot be too greatly detailed (*5*). The man in the factory is particularly beholden to his fellow chemical engineers in the equipment concerns who have brought out the new stainless steels, special alloys, resins, etc.

Under equipment can best be presented the relative advantages and disadvantages of continuous operation for any given process. Here it can be emphasized that, although a continuous process is generally harder to start, when once it is in operation less labor and less capital per ton of product are required. On the other hand, the markets have to warrant a considerable tonnage before the continuous operation can be considered. It is under equipment that we need more quantitative data, but those working in unit operations of stirring, heat transfer, etc., have already put into the hands of the operating engineer many invaluable formulas. Yet it is here that many little devices or tricks of the trade have been evolved that either make or break a process—for instance, the use of the molten bath to carry away rapidly the great amount of heat involved in the catalytic oxidation of naphthalene to phthalic anhydride. If a glass stirrer breaks in a laboratory nitration, it is not usually very serious; but if a propeller drops off the bottom of the shaft in a nitrator making trinitrotoluene from toluene or nitrobenzene from benzene, it may be very serious unless the influx of the raw materials is immediately stopped. In the design of certain equipment, safety measures are used to take care of such contingencies.

Effect of Unit Processes

The object of unit processes is to change chemical properties and to make money by so doing. The chemical nature of these changes should be discussed in order to handle the process. This is likewise true of the changes in physical properties. Frequently the exact nature of the physical changes cannot be predicted from the laboratory but must be determined in a semiworks plant where conditions can be studied approaching those of the factory; for example, it can be discovered whether the products will be formed in a slimy or easily filterable condition.

Likewise in the factory scale the change in physiological properties has a decided bearing upon the design of the equipment to carry on a reaction safely. In the manufacture of the highly toxic dinitrobenzene, very efficient ventilation must be provided or else the equipment must be placed out of doors. An outstanding example of the safe handling of highly toxic material is in the manufacture of tetraethyllead.

Hazards and Precautions

With proper design, the careful handling of materials, and the efficient training of workmen and supervisors, explosive and toxicity hazards in the chemical industry can be brought to a very low figure. The student does not usually realize how safely the unit processes of nitration or esterification leading to the ordinary explosives such as picric acid, cellulose nitrate, or glycerol nitrate are carried out in the hands of experienced chemical engineers. In the chemical industry too great an emphasis cannot be placed on the avoidance of the fire hazard.

Labor

For some unit processes skillful design of equipment may save a considerable amount of labor, whether such operations are continuous or not. The distinction between operating and maintenance labor should also be made. From an instructional point of view the presentation of the amount of labor to carry out a unit process is difficult. It is necessary to cover this point well, since the young men have less comprehension of the facts here than under any other head.

Economics

Although the economics of an operation is generally the business of the manager, the operator or even the student should have clearly before him the main economic features involved in any process that he is operating or studying. The unit process is carried on in the factory with the idea of selling its products; therefore, such factors as statistics of production, channels of sale, and costs are the deciding ones in every unit process. In studying any process, much preliminary information can be obtained from small-scale operations and their cost. Suggestions as to how this can be presented have already been published by the author (*6*).

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Nitration

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The incentive for this study originated in an attempt to lower the cost of mixed acid used in nitrating monochlorobenzenes to *o*- and *p*-nitrobenzenes. Such favorable results were obtained that it was deemed advisable to extend the study to other nitrations. The method employed was the addition of the material to be nitrated to the mixed acid rather than vice versa. The materials nitrated were toluene, benzene, monochlorobenzene, naphthalene, and acetanilide.

The process has advantages when a product desired is the highest nitro compound readily formed. When the process is at all satisfactory, the results are so excellent that its application in other nitrations is recommended.

THE incentive for this study originated in an attempt to lower the cost of mixed acid used in nitrating monochlorobenzene to *o*- and *p*-nitrochlorobenzenes. A considerable number of nitrations were made, using highly concentrated nitric acid along with concentrated sulfuric acid and fuming sulfuric acid.

Monochlorobenzene Nitration

The nitration charge finally decided upon after an extended investigation of varying acid concentrations, acid ratios, temperatures, and times, with the customary addition of the acid to the chlorobenzene was as follows (in pounds):

Chlorobenzene	100	93.56% H_2SO_4	56.6
87.7% HNO_3	17.7	63% fuming H_2SO_4	34
77.2% HNO_3	64.1		

The percentage composition of this nitration charge was:

Chlorobenzene	37.1	H_2SO_4, calcd. 100%	34.0
HNO_3, calcd. 100%	23.4	Water	5.5

This acid mixture gave a satisfactory nitration, but a considerable period of time elapsed during the process and the cost of the mixed acid was somewhat high.

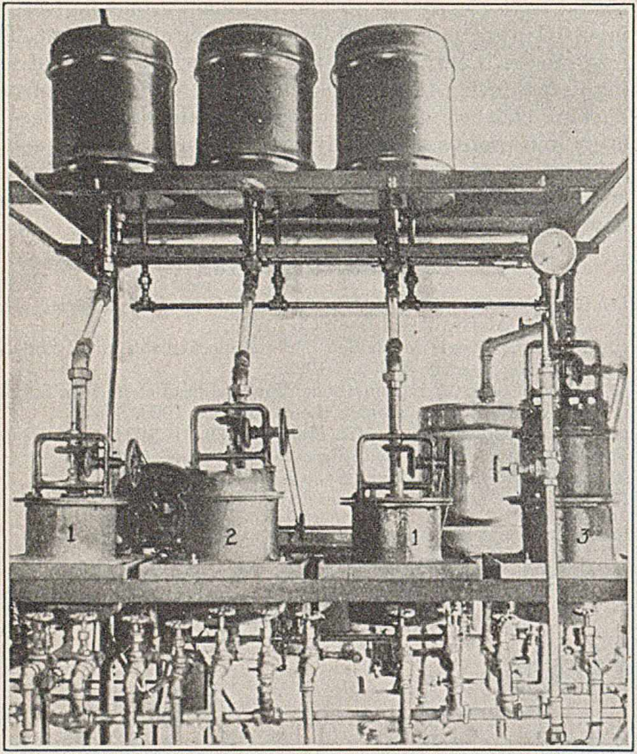
The nitrating conditions were then varied by adding chlorobenzene to the mixed acid. The final nitrating charge chosen for this procedure was as follows (in pounds):

Chlorobenzene	100
65.5% HNO_3	106.5
93.56% H_2SO_4	107.9

The nitrating charge, calculated on the percentage basis, was:

Chlorobenzene	31.7	H_2SO_4, calcd. 100%	32.0
HNO_3, calcd. 100%	30.5	Water	5.8

The products of nitration were the same in both cases, 66 per cent *p*-nitrochlorobenzene and 34 per cent *o*-nitrochlorobenzene, and the unnitrated chlorobenzene was found in both instances to be about 2 per cent.



Pilot-Scale Nitration Equipment

The cost of the mixed acid, using the first acid mixture, was $6.66 per 100 pounds of chlorobenzene nitrated. The cost of mixed acid in the second nitrating charge was $6.33. Thus, there is some advantage in cost of the second method. Further advantages are shown when the details of the two methods of nitration are compared.

In the first instance the chlorobenzene is cooled to −5° C.; the mixed acid is then added slowly, attempting to keep the temperature as low as possible by circulating cold water through the nitrator jacket. It was found best to conduct the nitration at a temperature not over 10° C., and at no time should it be permitted to rise above 30° C. This temperature control is secured by two operating conditions—water circulation through the jacket and the rate at which the mixed acid is added. To circulate as much water as possible through the jacket, about 4 hours were needed to complete the addition of the mixed acid.

The second method of nitration was conducted with the chlorobenzene hot; the temperature ranged between 80° and 95° C., and nitration was completed in 2.5 hours. In both instances about 7 per cent of the nitric acid used remained in the mixed acid at the end of nitration.

The customary practice in nitrations of this type is to strengthen the mixed acid and re-use it. This means a continued increase in the quantity of mixed acid available, and a time finally arrives when the residual nitric acid has to be separated from the sulfuric, and the sulfuric acid has to be concentrated.

An attempt to obviate this procedure was made by washing the spent mixed acid with chlorobenzene to determine whether all of the nitric acid could be removed in this way, leaving only a somewhat dilute sulfuric acid that could be easily concentrated and re-used.

One washing with approximately one-third of the chlorobenzene to be used in the final nitration mixture reduced the nitric acid concentration in the mixed acid to 0.73 per cent, and an additional washing with the same quantity of chlorobenzene removed all of the nitric acid from the mixed acid. Thus, two washings of this type recover all of the nitric acid, which is very desirable.

The equipment used in this pilot-scale nitration is shown in the photograph. (It includes other pieces than that used for this nitration.) Kettles 1 are used for reductions, kettle 2 for nitrations and sulfonations, and kettle 3 for steam distillation. The manifold pipe lines below the kettles are for steam condensate and cold water. The ample capacity of the reflux condensers is to provide desired space for the entire contents of the kettle should the reaction become too vigorous. This equipment was designed, fabricated, and erected by students in chemical engineering, as part of the senior project.

Benzene Nitration

The nitrations of chlorobenzene were followed with nitrations of benzene to *m*-dinitrobenzene. The customary procedure involves two steps, nitrating first to nitrobenzene, separating this from the mixed acid and then nitrating the nitrobenzene with stronger mixed acids to *m*-dinitrobenzene.

A considerable number of nitrations were conducted, and it was found that the most satisfactory acid mixture consisted of 617 grams of 59.4 per cent nitric acid and 836 grams of 20 per cent fuming sulfuric acid. The acid mixture was heated to 70° C., and then 69 grams of benzene were slowly added through a dropping funnel.

The heat of reaction would maintain the temperature at the desired point without any external heat. The time of the reaction was 2 hours. At the end of this period the temperature of the mixture was raised to 109° C. and maintained there for 2 hours. During this heating period it was necessary to stir vigorously because the nitrobenzene has a tendency to form an oily layer on top of the acid. At the conclusion of this heating period, the mixture was cooled to 80° C., drawn from the nitrator, and weighed. The results of such a nitration, together with all of the operating conditions, are as follows:

1.	Yield of dinitrobenzene, %	79.1
2.	HNO_3 used (sp. gr., 1.37):	
	% by weight	59.4
	Volume, cc.	450
	Weight, grams	617
3.	H_2SO_4 used (20% fuming):	
	Volume, cc.	450
	Weight, grams	836
4.	Benzene used:	
	Volume, cc.	80
	Weight, grams	69
5.	Total charge:	
	Volume, cc.	980
	Weight, grams	1522
6.	Total material after reaction, grams	1510
7.	Separated nitro- and dinitrobenzene, grams	37
8.	Separated mixed acids, grams	1473
9.	HNO_3 in mixed acids, grams	248
10.	H_2SO_4 in mixed acids, grams	930
11.	Water in mixed acids, grams	189
12.	Wash water used, grams	2000
13.	Product lost in wash water, gram	0.4
14.	Dinitrobenze recovered from wash water, gram	0.9
15.	Dinitrobenzene recovered from mixed oil	..
16.	Dinitrobenzene recovered from mixed acids (setting point 77.6° C., 85.6% dinitrobenzene, grams	84
17.	Total dinitrobenzene recovered, grams	81
18.	Oil separated from 15, grams	19
19.	Setting point of oil 18, ° C.	68.2

20. Dinitrobenzene in oil:	
% by weight	75
Weight, grams	14
21. Nitrobenzene in oil and product from acid, grams	17
21A. Dinitrobenzene left in acid, grams	22
22. Total dinitrobenzene formed, grams	117
23. Yield of dinitrobenzene, %	79.1
24. Yield of nitrobenzene (calcd. from remaining benzene), %	75.3
25. Benzene unaccounted for, grams	5.25
26. Period during addition of benzene:	
Time, hours	$1^5/_6$
Temperature, ° C.	70
27. Period during final heating:	
Time, hours	2
Temperature, ° C.	109
28. HNO_3 unaccounted for, grams	21.3

Other Nitrations

In a later series naphthalene was nitrated to α-nitronaphthalene; the details are as follows:

Naphthalene, grams	100
HNO_3 (sp. gr. 1.38, 61.3% HNO_3), grams	83
H_2SO_4 (sp. gr. 1.83, 91% H_2SO_4), grams	233
Average temperature, ° C.	25
Wash water used, liters	2
Product in wash water	Trace
Product, grams	115
Setting point of product, ° C.	58
Yield, % of theoretical	85
HNO_3 in spent acid, %	2.4

Following this, acetanilide was nitrated to *p*-nitroacetanilide. Results of a typical nitration are as follows:

Acetanilide, grams	200
H_2SO_4 to dissolve acetanilide, grams	810
H_2SO_4 (sp. gr. 1.83, 91% H_2SO_4), grams	152
HNO_3 (sp. gr. 1.38, 61.3% HNO_3), grams	156
Period of acetanilide addition, hours	5
Average temperature, ° C.	2
Maximum temperature, ° C.	6
Product, grams	223
Yield, % of theoretical	83.5

An attempt was also made to nitrate toluene to *p*-nitrotoluene by the process under investigation, but it was unsuccessful because a considerable amount of dinitrotoluene was formed. This result is in conformity with earlier results on the nitration of benzene, where it was also found impractical to attempt the nitration of benzene to the mononitro compound.

Conclusion

The rather meager data seem to show that the process of adding the material to be nitrated to the mixed acid is likely to be successful when the desired compound is the highest nitro derivative readily formed. When this is the case, the process has some operating advantages and can be conducted with a somewhat lower cost for nitrating acid.

In nearly every nitration it is possible to recover all of the nitric acid from the spent mixed acid by washing the latter with two or more portions of the material to be nitrated.

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Recent Progress in Chlorination[1]

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Some of the recent discoveries in the field of organic chlorinations are reviewed and discussed. Among these are the direct substitutive chlorination of olefins, the application of pressure to the chlorination of paraffins, the substantial absence of effect of catalysts upon the isomeric ratios obtained in the monochlorination of paraffins, the combined action of sulfur dioxide and chlorine upon hydrocarbons, and the extension of the conception of chain reactions to this field.

THE rather extensive literature of chlorinations has been recently reviewed (*3*, *5*) so that the present article will be confined to the developments of the past few years which seem to possess either theoretical interest, potential technical importance, or both. The steady development of research in this field during the past two or three decades has finally resulted in such a great demand for chlorine that the present plants are being taxed to capacity. Instead of being a troublesome by-product, chlorine is at present the most readily salable of the trio of substances produced in the electrolysis of brine. In spite of this, the patent literature gives the impression that research on new uses for chlorine and improvements of existing processes is continuing unabated.

Substitutive Chlorination of Olefins

Organic textbooks have for many decades pointed out that olefins differ essentially from paraffins and cycloparaffins in that the former add halogens rather than reacting substitutively. While this is, of course, perfectly true under the proper conditions, Kondakov showed many years ago that olefins which are capable of adding hydrogen chloride readily will yield substitution as well as addition products and that higher temperature increases the proportion of chlorine reacting substitutively. Deanesley (*2*) showed recently that the addition of chlorine to an olefin suffices (particularly in the absence of oxygen) to cause the substitutive chlorination of a copresent paraffin. Still more recently, Engs and Redmond

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[1] This paper, which contains material abstracted from the Ph.D. thesis of L. F. Hatch, is the sixth in a series on the subject of syntheses from natural gas hydrocarbons. The others appeared in IND. ENG. CHEM., 23, 352 (1931); 27, 1190 (1935); 28, 333, 339, 1178 (1936).

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(*4*) patented a process for the substitutive chlorination of olefins which consists essentially in preheating chlorine and olefin to a temperature of 200° to 500° C. and then mixing with extreme rapidity to cause the reaction. Thus, for example, allyl chloride may be produced directly from propylene. The hydrogen atoms of the methyl group, being removed by one carbon atom from the double bond, are in an "activated" position and therefore their substitution constitutes the predominant reaction. The low-temperature addition reaction is suppressed by preheating the reactants prior to mixing them.

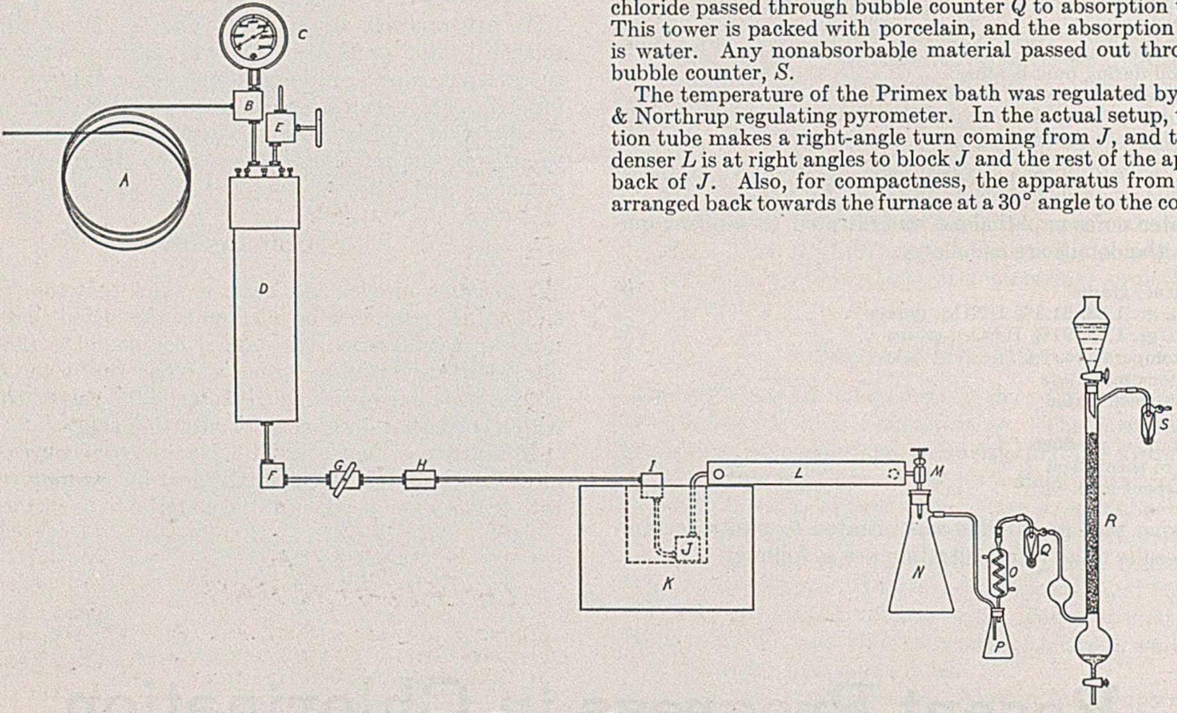


FIGURE 1. HIGH-PRESSURE CHLORINATION APPARATUS

Application of Pressure to Chlorination of Paraffins

The recent discovery (*6*) that liquid-phase chlorination of saturated hydrocarbons is capable of giving relative yields of primary substitution products which can be obtained in vapor phase only at much higher temperatures was the starting point for the investigation of liquid-phase chlorination at high temperatures and pressures.

A special apparatus had to be designed for chlorination work at high temperatures and pressures. There are several reasons for this. Even assuming that sealed glass tubes could withstand the high pressures which necessarily accompany the use of high temperatures, the contents might react before attaining the desired temperature.

Figure 1 shows a drawing of the apparatus used:

A charge was prepared by cooling the desired amount of *n*-heptane with a bath of alcohol and solid carbon dioxide to −70° C. Enough chlorine was dissolved in the heptane to give a mole ratio of 1 to 8. The mixture was immediately transferred to bomb *D*, and the head of the bomb was replaced. The $^{1}/_{4} \times ^{1}/_{16}$ inch tubing, *A*, was connected to the tee, *B*, and a pressure of 500 to 1000 pounds per square inch was passed to the bomb from a nitrogen tank. This pressure was indicated by hydraulic gage *C*. Valve *E* is also on the head of the bomb.

The bottom of the bomb is fitted with a $^{3}/_{16} \times ^{3}/_{16}$ inch Monel metal tube which goes to an angle block, *F*, and from there to valve *G*. At the start of the run, valve *M* was cracked; then valve *G* was opened, allowing the heptane-chlorine mixture to pass along to reducer *H* which is connected to the nickel reaction tube ($^{1}/_{4} \times ^{1}/_{16}$ inch). The mixture passed along the nickel tube to the right-angle nickel block, *I*, then into the Primex (hydrogenated vegetable oil) bath heated by furnace *K*. In this bath the tube makes a right-angle bend and enters another right-angle block *J* from which it emerges from the bath to pass through the copper water condenser, *L*.

Valve *M* released the pressure, and the chlorinated product was collected in flask *N*, along with the excess heptane. The hydrogen chloride formed by the reaction passed over to container *P* and through spiral condenser *O*. The condenser tends to take out and return to flask *P* any entrained liquid. From *O* the hydrogen chloride passed through bubble counter *Q* to absorption tower *R*. This tower is packed with porcelain, and the absorption medium is water. Any nonabsorbable material passed out through the bubble counter, *S*.

The temperature of the Primex bath was regulated by a Leeds & Northrup regulating pyrometer. In the actual setup, the reaction tube makes a right-angle turn coming from *J*, and thus condenser *L* is at right angles to block *J* and the rest of the apparatus back of *J*. Also, for compactness, the apparatus from *N* on is arranged back towards the furnace at a 30° angle to the condenser.

The apparatus, with the exception of the nickel reaction tube, was first made of stainless steel. This material proved unsatisfactory. The chlorine would chlorinate the iron of the stainless steel, resulting in the formation of ferric chloride. Ferric chloride is a catalyst for the splitting off of hydrogen chloride from chlorohydrocarbons. This reaction resulted in a high yield of polychlorides and a gum, probably a chloroölefin polymer.

All of the stainless steel parts which were in contact with the chlorine-hydrocarbon mixture were replaced by Monel metal which gave satisfactory service.

A typical charge and data table (Run 40) is as follows:

n-Heptane, ml.	400	Pressure, lb./sq. in.	900
Chlorine, mole	0.34	Elapsed time, min.	20
Mole ratio	8:1	Color of chlorides	Light orange
Temperature, ° C.	275		

The rate of flow should be so regulated that there will always be a small amount of free chlorine passing through the exit valve. As the valve was hard to regulate, this was not always accomplished. A two-way stopcock was inserted between flasks *N* and *P* which permitted the turning of the exit gas into a potassium iodide–starch solution to test for free chlorine.

The results obtained in the chlorination of pure *n*-heptane in this laboratory are summarized in Figure 2. From −65° C. to about +125° C. a logarithmic curve was obtained similar to those previously reported. From 125° to 300° C. the points are more irregular but are fairly well represented by a vertical straight line. It is believed that the place where these two parts of the curve intersect represents the temperature at which the pressure used was no longer capable of maintaining completely the liquid phase, and at the high temperatures the increased proportion of vapor-phase reaction was nearly balancing the opposite effect of the increased temperature.

A comparison of the two curves at 300° C., together with the fact that this is higher than the critical temperature of *n*-heptane, indicates clearly that the difference between the two curves is not essentially one of phase but of concentration. This deduction was tested by a series of chlorinations of propane at 300° C. and at various pressures. The results of these experiments are summarized in Figure 3 and in the generalization advanced tentatively as chlorination rule 11: In vapor-phase chlorination of saturated hydrocarbons, increased pressure causes increased relative rates of primary substitution.

The theoretical interpretation of this phenomenon is not yet entirely clear. The hypothesis of two competing mechanisms for the reaction—one relatively selective for secondary hydrogen atoms, the other relatively nonselective, the second of which involves an instable addition compound and hence is favored by higher concentrations—requires further proof. This can also be said of an alternative hypothesis based upon the chain mechanism for chlorination formulated by Pease and Walz (*8*) and by Yuster and Reyerson (*11*):

$$\mathrm{Cl_2 \rightarrow Cl + Cl} \qquad (1)$$

$$\mathrm{RH + Cl \rightarrow R + HCl} \qquad (2)$$

$$\mathrm{R + Cl_2 \rightarrow RCl + Cl} \qquad (3)$$

If we assume that reaction 2 is relatively nonselective but that before the free organic radical, R, reacts with Cl_2 it may rearrange to an isomeric radical R′—e. g.,

$$\mathrm{CH_3{-}CH_2{-}CH_2{-}} \rightarrow \mathrm{CH_3{-}\overset{|}{C}H{-}CH_3} \qquad (4)$$

the more rapid reaction with chlorine at the higher concentrations would tend to prevent reaction 4 and account for the lesser selectivity of the reaction under these conditions. If this mechanism is correct, the ratio of chlorine to hydrocarbon should change the isomeric ratios. Although this point has not been subjected to critical study, it seems quite unlikely.

In an earlier article of this series the theory was expressed that the function of light in chlorinations is to initiate reaction chains by decomposition of the chlorine molecule

$$\mathrm{Cl_2} + h\nu \rightarrow \mathrm{Cl + Cl} \qquad (5)$$

and that catalysts also function by starting reaction chains. If the same chain mechanism or mechanisms result whether catalysts are present or absent, the quantitative ratio of isomers would be the same in the presence or in the absence of catalysts, assuming that the resulting chlorides are substantially undecomposed by the catalysts. Although the observation had been formerly made (*6*) that neither light, moisture, nor carbon surfaces affect the isomeric ratios significantly, there were no data in the literature in regard to the effect of the other chlorine carriers on the chlorination of paraffins. Their powerful effect in the aromatic series of promoting ring substitution rather than reaction on the side chain is, of course, well known. The results of Table I indicate that at least those catalysts so far tested have no considerable effect upon the relative reaction rates of primary and secondary hydrogen atoms in paraffin molecules. This somewhat surprising result must be considered as substantial evidence for a chain mechanism.

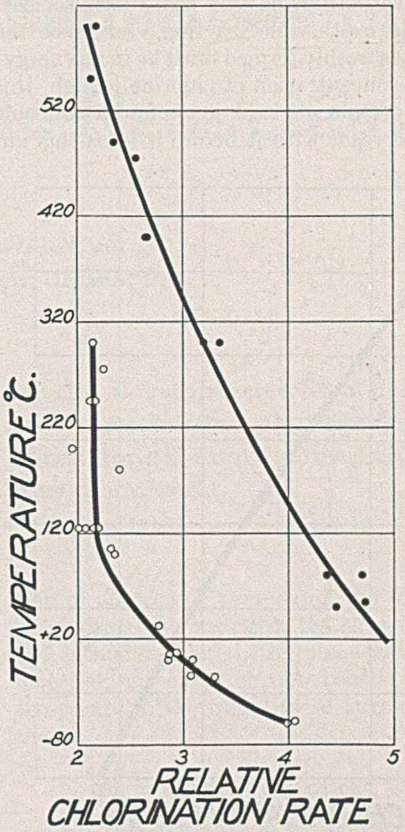


FIGURE 2. EFFECT OF TEMPERATURE UPON RELATIVE CHLORINATION RATE OF PRIMARY AND SECONDARY HYDROGEN ATOMS

○ Propane, vapor phase
● *n*-Heptane, liquid phase
(The significance of the term "relative chlorination rate" is given in a previous paper, *6*)

It was previously pointed out (*6*) that a simple equation of the type

$$X = KY$$

represents rather accurately the effect of excess hydrocarbon in suppressing the formation of polychlorides. In this equation X is the weight ratio of monochlorides over polychlorides, Y is the ratio of moles of hydrocarbon over moles of chlorine, and K is a constant peculiar to the hydrocarbon and the conditions. It has now been found (*7*) that the value of constant K can be altered significantly by changing the momentary concentration of chlorine during the reaction.

This is illustrated by two experiments involving the liquid-phase photochemical chlorination of 1-chloro-2-methylpropane. In experiment *a* the monochloride was added to a stirred, illuminated, three-neck flask maintained at a temperature of 7° C. by means of an ice bath. Chlorine was added continuously over a period of 4 hours at such a rate that only a very low concentration was present. The concentration of chlorine was followed roughly by observing the color of the reaction mixture; a comparatively small amount of chlorine appears as a distinct yellow. The product was rectified and found to contain 7.03 per cent of material boiling higher than dichlorides.

Experiment *b* was a duplicate of *a* except that the chlorine was added rapidly for a short time and then the addition stopped until the excess chlorine had reacted. This process was continued until the same amount of chlorine had been added as in the previous case. The product from this experiment was rectified and found to contain 14.4 per cent of overchlorinated product.

TABLE I. EFFECT OF CATALYSTS ON RELATIVE REACTION RATES OF PRIMARY AND SECONDARY HYDROGEN ATOMS

Run No.	Compound	Temp.	Polychlorides	Primary Monochlorides	Primary Monochlorides	Ratio Secondary: Primary	Average
		° C.	Ml.	Ml.	%		
1-C	I_2	11.5	3.2	3.2	17.63	2.80	2.80
2-C	S_8	3	5.2	5.2	17.86	2.76	2.76
3-C	$SbCl_3$	7	4.5	8.0	19.18	2.53	2.50
6-C	$SbCl_3$	7	4.4	8.0	19.56	2.47	
4-C	$SnCl_2$	6	4.5	7.7	18.47	2.65	2.62
11-C	$SnCl_2$	6	4.4	8.4	20.34	2.34	
16-C	$SnCl_2$	6	4.2	6.7	17.35	2.86	
5-C	$BiCl_3$	6	4.6	7.4	17.41	2.85	2.76
12-C	$BiCl_3$	7	4.5	7.6	18.27	2.68	
7-C	$AlCl_3$	6	4.4	7.7	18.82	2.59	2.62
13-C	$AlCl_3$	6	4.4	7.5	18.52	2.64	
8-C	$AsCl_3$	10	4.5	7.9	18.72	2.61	2.63
14-C	$AsCl_3$	7	4.5	7.7	18.48	2.65	
9-C	$TiCl_4$	6	4.2	7.8	19.79	2.43	2.44
15-C	$TiCl_4$	6	4.4	8.0	19.75	2.44	

The theoretical interpretation of this result seems clear. Chlorination is a highly exothermic reaction, and hence the monochloride molecule as freshly formed must be in an energy-rich condition. If the concentration of chlorine is high, this energy-rich or activated molecule is likely to find a molecule or atom of chlorine and react with it before it loses this unusual amount of energy. If, on the other hand, the concentration of chlorine is low, the chances are greater that this energy will be exhausted in intermolecular collisions before the free chlorine is reached. The effect of diluents in diminishing overchlorination noted by Boswell and McLaughlin (*1*) is susceptible of the same explanation.

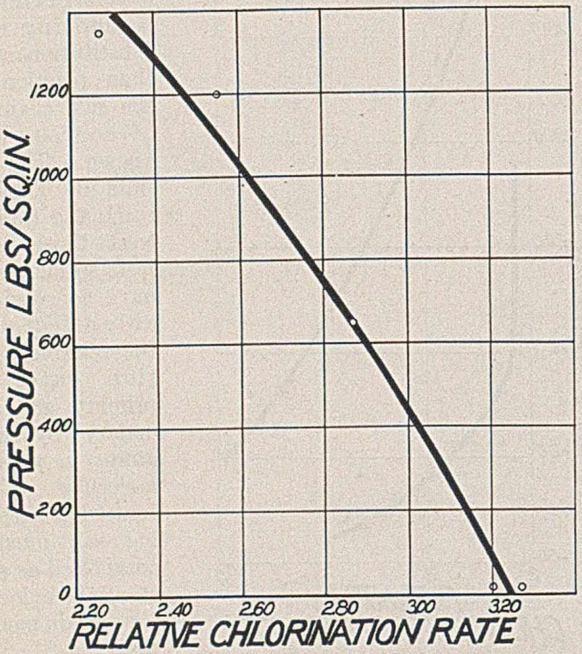


FIGURE 3. EFFECT OF PRESSURE UPON RELATIVE CHLORINATION RATE OF PRIMARY AND SECONDARY HYDROGEN ATOMS

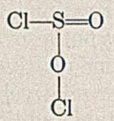
Propane, 300° C.

The potential importance of this means of diminishing overchlorination in vapor-phase reactions, where heretofore it has usually been customary to add at once all of the chlorine for a given pass through the reactor, is obvious in view of the low economic value of many of the overchlorinated materials such as the dichloropentanes. This matter is being actively investigated.

Combined Action of Sulfur Dioxide and Chlorine upon Hydrocarbons

One of the most interesting recent discoveries in the field of chlorination is reported in a patent by Reed (*9*) who studied the simultaneous action of chlorine and sulfur dioxide upon a number of hydrocarbons. It is not surprising that the presence of sulfur dioxide should initiate substitutive chlorination of copresent material; this much is in agreement with Deanesley's work (*2*) upon mixtures of olefins and paraffins and is in perfect harmony with the chain mechanism. Thus Rice observed (*10*) that, in general, any chain reaction which takes place readily is likely to start chains which involve the corresponding reaction upon some more sluggish material. The function of "carriers" such as antimony trichloride which are alternately chlorinated by free chlorine to a higher valence and reduced to a lower valence by the organic material undergoing chlorination is thus to be interpreted not upon the theory that all (or even necessarily a significant proportion) of the organic compound reacts with the catalyst directly but that ordinarily the chlorination of the catalyst starts reaction chains which continue without intervention of the catalyst.

Since the reaction of sulfur dioxide with chlorine to form sulfuryl chloride (SO_2Cl_2) is well known and since sulfuryl chloride is a mild chlorinating agent (*5*), it is not surprising that the presence of sulfur dioxide should induce reaction in a mixture of chlorine and hydrocarbon. The surprising feature of Reed's work is the formation of organic sulfur compounds. He interprets this as being due to an instable isomeric form of sulfuryl chloride having the structure



$$\mathrm{Cl{-}S({=}O){-}O{-}Cl}$$

which contains "positive" chlorine. Another possibility is that the free organic radicals believed to be formed during chlorination are capable of adding sulfur dioxide to form another type of free radical which subsequently reacts with chlorine molecules to continue the chain:

$$\dot{R}\text{—} + SO_2 \rightarrow RSO_2\text{—} \qquad (6)$$

$$RSO_2\text{—} + Cl_2 \rightarrow RSO_2Cl + Cl\text{—} \qquad (7)$$

It is premature at present to attempt a choice between these mechanisms; much careful work is needed here. If the second mechanism is correct, other reagents should also be capable of reacting with the free radicals. If chlorine does, in fact, convert a saturated hydrocarbon to the most reactive known type of organic compound, a free radical, this opens up a wholly new approach to the chemical utilization of paraffins.

Future Work

The conception of chlorinations, both of the substitutive and of the additive types, as chain reactions has so far been extremely fruitful. It has proved capable of offering a satisfactory interpretation of such diverse phenomena as the formation of pyrolytic products during thermal chlorination at temperatures at which both the hydrocarbons and their chloro derivatives are fairly stable (*6*) of the induction of substitutive chlorination by the additive chlorination of copresent olefins, of the absence of effect of catalysts upon the ratios of isomers obtained in the chlorination of paraffins, and of the effect of diluents and low momentary concentrations of chlorine upon the amount of overchlorination. The extension of this theory, accompanied by careful quantitative technic, to the chlorination of more complicated types of organic compounds comprises a field which holds much of interest both to the industrial and to the theoretical chemist.

Acknowledgment

Thanks are hereby extended to the Mathieson Alkali Company for defraying the expenses of L. F. Hatch's investigation as Purdue Research Foundation Fellowship No. 42.

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Industrial Possibilities of Electroörganic Reduction

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The more important advantages and disadvantages of the electrolytic method for reducing organic compounds are given. The factors that must be studied in the development of a process of electrolytic reduction, together with the conditions for controlling the process, are also discussed.

THE electrolytic method for reducing organic compounds should compare favorably with other methods of reduction. As has been pointed out in previous discussions, it has the distinct advantage over purely chemical methods that practically no metal is consumed in the reaction. This means that there is no contamination of the product by salts. On account of the more exact control of conditions than is possible with purely chemical reductions, the electrolytic method offers the hope of higher yields and a purer product. It has been found possible with better control to obtain higher yields by the electrolytic than by the catalytic method.

Regardless of these advantages, few electroörganic reductions are being carried out industrially. Glasstone and Hickling (*2*) state that the following compounds have been manufactured by electrolytic reduction: pinacol, piperidine, benzidine, tolidine, dianisidine, *p*-aminophenol, and glycolic acid. They further state that it is not known whether all of them are manufactured in this way at present.

In the United States the only successful electroörganic reduction, the details of which are published, is the Creighton process for the electrolytic reduction of glucose to mannitol and sorbitol (*6*).

A survey of United States patents uncovered only about fifty-four electroörganic reductions. Reasons for the lack of popularity of electrolytic methods in organic technology have been discussed many times in the literature. The main objections seem to be the relative slowness of the reaction and the consequent low capacity of the unit, the careful control of the process which is necessary, and in certain cases the cost of power.

The first objection is self-explanatory. In order to present the second objection more clearly, the important factors in the development and control of an electrolytic process of reduction will be discussed. Most of these factors are given in detail by Glasstone (*1A*) and by Glasstone and Hickling (*3*). Lowy (*9*) reviewed the controlling factors of electroorganic chemistry as a whole, with illustrations limited almost entirely to their effects on oxidation.

The electrolytic reduction of an organic compound is carried out by bringing it into contact with a cathode at which hydrogen is being evolved, because of the passage of current through a suitable electrolyte. The compound reacts with the hydrogen and is, therefore, a depolarizer. The cathode compartment is usually separated from the anode compartment by a porous diaphragm to prevent reoxidation of the product.

In the development of a process for the electrolytic reduction of an organic compound, the following conditions must be studied: the nature of the electrolyte, the composition of the cathode material, the physical structure of the cathode material, the effect of added salts, the current density, the temperature, the quantity of current, and power consumption.

Composition of Catholyte

That the composition of the catholyte will determine the type of product obtained from a given starting material is well known. The acidity or alkalinity of the solution will direct the formation of a certain product. A classical example is the reduction of nitrobenzene to aniline in acid solution and to partial reduction products in alkaline solution (*4*).

The concentration of the electrolyte may affect the yield of product. In the electrolytic reduction of methyl *n*-propyl ketone to *n*-pentane at a cadmium cathode (*12*), a minimum starting concentration of about 30 per cent sulfuric acid is necessary for the best results. On the other hand, the yield of pentane at a lead cathode is inversely proportional to the sulfuric acid concentration within limits (*17*).

Cathode Material

Whether the depolarizer will be reduced or not depends, practically speaking, on the cathode material. It was pointed out many years ago that, in general, a more complete reduction of an organic compound takes place at cathodes of high hydrogen overvoltage. There are examples in the literature, however, of the effectiveness of cathodes of low hydrogen overvoltage (*11*) so that the importance of the overvoltage is uncertain.

The best yields of pentane by the electrolytic reduction of methyl *n*-propyl ketone are obtained at cathodes of cadmium, zinc, lead, and mercury (*17*). The other common metals yield only very small amounts. On the other hand, satisfactory yields of amines from nitro compounds may be obtained at almost any cathode (*8*).

The activity of the cathodes in a given reduction may be varied by changing the electrolyte. When benzophenone is reduced to benzopinacol in aqueous sulfuric acid, appreciable yields are obtained only at cathodes of mercury (*16*) and aluminum (*13*). If the aqueous electrolyte is replaced by one of glacial acetic acid, all the common metals are active as cathodes; iron gives the best results (*14*). In this case benzopinacolone, the dehydration and rearrangement product of the pinacol, is the main product.

Alloys may also be used as cathodes. A 65 atomic per cent cadmium amalgam will give as good results as a pure cadmium cathode in the electrolytic reduction of methyl *n*-propyl ketone to *n*-pentane (*18*). On the other hand, a 99.9 per cent chemical lead will not be as active as a 99.99+ lead (*16A*). In trying to develop more efficient cathodes by alloying metals, a complete series from 100 atomic per cent of one metal to 100 atomic per cent of another should be studied.

Physical Structure of the Cathode

Many years ago it was shown that a roughened cathode surface gave better results than a smooth one (*19*). In this laboratory, it was recently found that the crystal structure of the cathode material influences the yield of product in an electrolytic reduction.

The yield of pentane from methyl *n*-propyl ketone was shown to vary with the composition of a cadmium-amalgam cathode (*18*). Slight changes in the chemical composition sometimes produce marked changes in the yield in the regions where the physical structure changes rapidly with the composition.

In the electrolytic reduction of methyl *n*-propyl ketone to pentane at a cadmium cathode, consistent results could not be obtained with commercial sticks, probably cast in a cold mold. The results became uniform when this cadmium was recast (*16A*). Evidence in part indicates that the yield changes with crystal size of the cathode and strain in it.

Added Compounds

In certain cases small amounts of compounds added to the catholyte markedly increase the yield of product. A small amount of arsenic doubles the yield of *N*,*N*-dimethylbenzylamine from *N*,*N*-dimethylbenzamide at a lead cathode (*5*). The action of added salts is not definitely known except in certain cases.

On the other hand, the iron contained in a new porous cup is enough to reduce the yield of benzopinacol from benzophenone at an aluminum cathode in sulfuric acid solution (*13*). In this connection it should be stated that care should be taken to prevent any extraneous substances from entering the cathode compartment, since they may poison the cathode. It is well known that small quantities of certain metals will poison the surface of a lead cathode (*19*). There is also the possibility of poisoning by other materials.

In the industrial electrolytic reduction of pyridine to piperidine, formerly carried out by the Rubber Service Laboratories, impurities in the cell poisoned the lead cathode so that the process had to be stopped and the lead reactivated (*1*). Careful supervision was therefore necessary.

Current Density

In many of the electrolytic reductions which have been investigated thoroughly, an optimum cathode current density has been found. This varies with the reduction and with the cathode material. In the electrolytic reduction of methyl *n*-propyl ketone to *n*-pentane at a cadmium cathode, the optimum current density is from 0.05 to about 0.15 ampere per sq. cm. (*12*).

On the other hand, the optimum current density for the reduction of benzophenone to benzohydrol in aqueous potassium acetate solution is 0.01 ampere per sq. cm. at a cadmium cathode (*16A*).

It is also possible to change the nature of the product by changing the current density. An example is the stepwise reduction of nitrobenzene. The cathode potential, which is controlled by the current density, determines the extent of reduction.

Temperature

The effect of temperature depends on the reduction studied and the cathode material. In the electrolytic reduction of methyl *n*-propyl ketone to pentane, slight increases in yield from 30° to 50° C. were noted at a cadmium cathode, whereas the yield at a lead cathode was doubled (*16A*).

It is obvious that the temperature control is relatively simple since the reactions take place in the presence of a liquid phase and at low temperatures.

Quantity of Current

The quantity of current necessary for the maximum yield of reduction product will vary with the rate of depolarization. In the reduction of methyl *n*-propyl ketone to *n*-pentane at a cadmium cathode (*12*), no better yield was obtained when more than theoretical current was used. In fact, 90 per cent theoretical current gave just the same yield as theoretical. However, in the case of a poorer depolarizer such as benzoic acid, the yield of benzyl alcohol may be increased markedly by passage of more current than is needed theoretically (*16A*).

Power Consumption

The power consumption will depend on the amount of current and on the resistance of the cell. Resistance exists at three places: the electrolytes, the diaphragm, and the electrodes. Electrolytes which are good conductors are therefore desirable. Agitation will help in eliminating the last factor. The other factors must be determined before a study of power consumption is made. Finally, losses from the cathode compartment into the anode compartment must be determined.

Conclusion

It is obvious, then, that a large number of factors must be studied and conditions must be controlled carefully to obtain optimum results in an electrolytic reduction.

The author has pointed out that a considerable number of electrolytic reductions of many types of organic compounds compare favorably in yield with other methods on a small scale (*15*). It should therefore be possible to commercialize some of these.

The usefulness of the electrolytic method is limited by the solubility of the depolarizer. Industrially it seems best suited to depolarizers which are soluble in dilute acids or alkalies. Concentrated solutions of poor electrolytes will cause loss of power due to low conductivity and consequent heating. It is true that a nonreducible blending agent such as alcohol may be employed, or even a nonaqueous electrolyte may be used. Both of these methods are open to the objection that they increase the power consumption due to poorer conductivity and will diffuse through the diaphragm into the anode compartment where they will be destroyed by anodic oxygen unless special pains are taken to remove them from the system.

The scope of electroörganic reduction has been extended greatly by the work of McKee et al. (*10*) who found that organic depolarizers will dissolve in appreciable amounts in concentrated solutions of alkali metal salts of aromatic sulfonic acids. When used as catholytes, reduction takes place under mildly alkaline conditions. Acidic reductions may be carried out by adding free acid. Excellent results have been obtained in the reduction of nitro compounds to azo and hydrazo compounds.

In answer to the objection to the low capacities of the cells, it may be possible to develop cathodes which, either by themselves or with the assistance of catalysts, will permit depolarization at high current densities.

The energy costs of electrolytic reduction compared to costs of chemical reducing agents appear to show a fair margin in favor of the former except for the very cheapest reducing materials, such as iron (*7*). An opportunity for reducing the cost of electrical energy is in the use of off-peak power.

With all the research that has been carried out in this field, the possibilities of the electrolytic method of reducing organic compounds are still undetermined, and more fundamental work is needed to overcome the uncertainties that exist.

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Esterification

Manufacture of Malonic Ester

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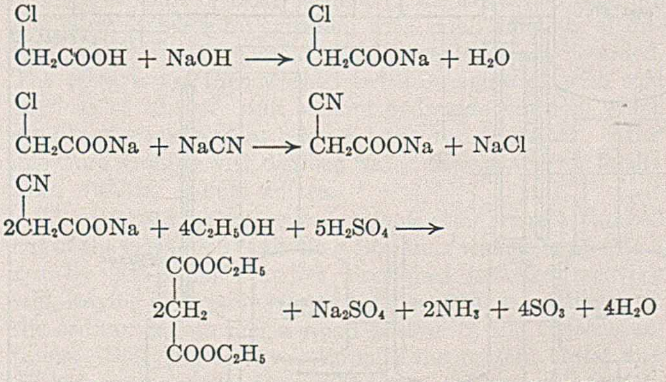
A brief outline is given of the chemistry of malonic ester (diethyl malonate) manufacture, emphasizing the quantitative application of the unit process, esterification, to industrial production. The chemical engineering principles involved in the straight-line production of this reagent are described; type and design of equipment, flow and transfer of materials, etc., are given.

THE classical malonic ester synthesis has, in recent years, received more than its share of consideration in the process industries. This has been due to the popularity of the barbiturates, a class of compounds for which malonic ester (diethyl malonate) is generally considered the starting material. The preparation of this chemical in the laboratory is a procedure well known to all organic chemists. Its manufacture on an industrial scale, however, presents many problems unknown to the laboratory technician, and this phase of the subject is to be discussed here.

The chemistry of this esterification process is generally so well known that it will be mentioned only briefly. The process depends upon the following reactions:



$$\overset{\text{Cl}}{\overset{|}{\text{CH}_2}}\text{COOH} + \text{NaOH} \longrightarrow \overset{\text{Cl}}{\overset{|}{\text{CH}_2}}\text{COONa} + \text{H}_2\text{O}$$

$$\overset{\text{Cl}}{\overset{|}{\text{CH}_2}}\text{COONa} + \text{NaCN} \longrightarrow \overset{\text{CN}}{\overset{|}{\text{CH}_2}}\text{COONa} + \text{NaCl}$$

$$2\overset{\text{CN}}{\overset{|}{\text{CH}_2}}\text{COONa} + 4\text{C}_2\text{H}_5\text{OH} + 5\text{H}_2\text{SO}_4 \longrightarrow 2\begin{array}{c}\text{COOC}_2\text{H}_5\\ |\\ \text{CH}_2\\ |\\ \text{COOC}_2\text{H}_5\end{array} + \text{Na}_2\text{SO}_4 + 2\text{NH}_3 + 4\text{SO}_3 + 4\text{H}_2\text{O}$$

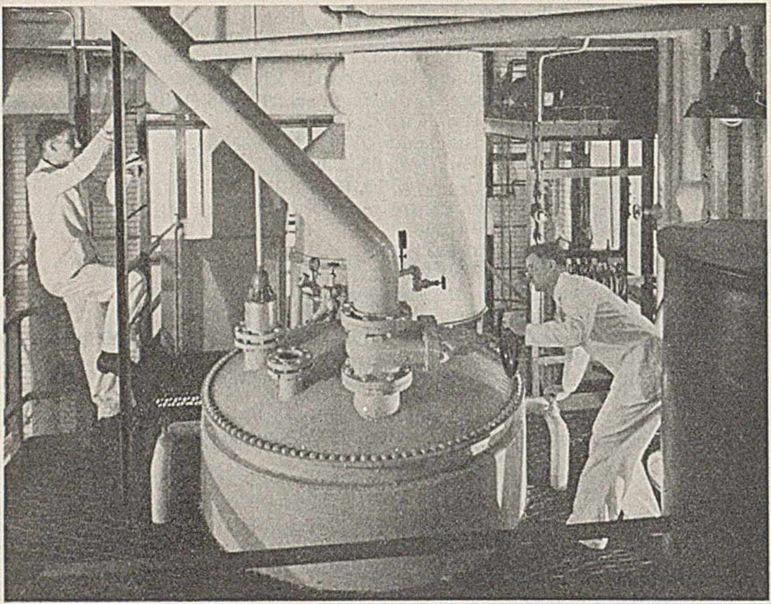
In the plant these reactions are accomplished in the following steps: (1) neutralization of the monochloroacetic acid with sodium hydroxide, (2) reaction of the formed sodium monochloroacetate with sodium cyanide, (3) concentration of the resulting mixture to a "cake," (4) hydrolysis of the cake by sulfuric acid and subsequent esterification of the "nascent" malonic acid by ethyl alcohol, (5) extraction of the malonic ester with benzene, (6) purification of the benzene extract, and (7) removal of the benzene by distillation.

Through various improvements in the method of manufacture over a period of years, this material is now produced in the plant by this process with an average yield of 70 per cent. When assayed by means of the saponification value, it contains not less than 90.0 per cent malonic ester, and the acidity in terms of malonic acid is less than 0.1 gram per 100 cc. The material thus obtained is not a colorless liquid as described in the literature but has a slight yellow or straw color. It can be rendered colorless by fractionation, but since it is used in malonic ester syntheses, it seems economically inadvisable to purify the material further.

A few years ago it became desirable to segregate this process from the manufacture of other chemicals because of the hazardous nature of one of the reagents used—namely, benzene. After careful study, therefore, the process was installed in an isolated building as a distinct unit process, where production was accomplished on a straight-line basis. The flow sheet evolved is shown in Figure 1.

Housing for the Process

This structure, made of red-faced reinforced brick, is 30 feet long, 18 feet wide, and 28 feet high, inside dimensions.



Sodium Cyanoacetate ("Cake") Still

Above and in the center of the roof is a Transite monitor, 12 feet long, 10 feet wide, and 7 feet high, in which is housed the exhaust fan for the ventilating system of the building and a three-stage Elliott steam ejector-condenser. The floor and ceiling of the building are concrete; the interior walls are white glazed brick. There are eight windows, three on each side and one on each end; each one practically fills an entire bay, except in the two bays where the doors are located. All of the sashes of these windows are operable so that there is good natural ventilation. Besides the ground floor, there are two mezzanines or working platforms at the 5- and 18-foot levels. Located just outside of the building is the storage space for the chemicals used in this process, such as sodium cyanide, monochloroacetic acid, sulfuric acid, etc.

Engineering Details

The manufacture of the ester begins in a 300-gallon stoneware jar located on the ground floor, in which are placed the monochloroacetic acid and an equal weight of ice. The acid is neutralized with a 50 per cent solution of sodium hydroxide which is run into the jar from a 300-gallon iron storage tank located on the upper mezzanine, where a week's supply has been previously prepared. The heat of neutralization of this reaction melts the ice, thereby yielding a cool solution of sodium monochloroacetate. Agitation of the acid and ice during this neutralization is accomplished by a Lightnin mixer.

This solution of sodium monochloroacetate is next drawn by vacuum into a 900-gallon jacketed iron still on the upper mezzanine where it is warmed to 60° C. (140° F.) with steam. After adjusting the pH of the solution to about 9.0, a hot concentrated solution of sodium cyanide is added. This cyanide solution has been previously prepared in an adjacent 150-gallon jacketed iron tank and is allowed to run slowly into the warmed solution of sodium monochloroacetate, resulting in a vigorous reaction, accompanied by a great amount of foaming and a rapid evolution of cyanide vapors which have to be exhausted from the still by an efficient ventilating fan.

When this reaction is complete, the mixture is concentrated under the vacuum of the jet condenser to about one-fourth of its original volume. This "cake," as it is termed in the plant, is a thick semisolid mass which flows readily when hot but immediately solidifies upon cooling. It is dumped through the bottom outlet by means of an iron chute into one of two 500-gallon Pfaudler glass-lined reaction kettles located on the lower mezzanine. This kettle contains warm, specially denatured alcohol which, incidentally, has been recovered from other malonic ester syntheses and is at least 99.5 per cent pure.

This esterification is a batch process which runs for about 36 hours. Thus, starting a new batch every morning, today's lot will have been processed up to the above point while yesterday's lot is being extracted from the reaction mixture. This is accomplished by using two reaction kettles; each one is charged on alternate days from one cake still.

The reaction kettles are equipped with anchor-type direct-driven agitators and 9-foot vertical brass reflux condensers, the vapor pipes of which lead into scrubbing towers where the evolved gases of the reaction are washed down the sewer with showering sprays of water. The kettles are also connected to a pipe line leading to a 185-gallon iron sulfuric acid charger. This latter is filled with a definite weight of commercial sulfuric acid from the glass carboys under 12 to 15 pounds per square inch of air pressure.

After the reaction kettle has been charged with the alcohol, which is pumped from 50-gallon drums, and with the cake, the acid is blown into the kettle from the acid charger under air pressure controlled by a Taylor temperature regulator. In this way the rate of addition of the acid is automatically controlled and depends upon the temperature and rate of reaction of the mixture within the kettle. When all the acid has been added, the entire mixture is gently refluxed overnight by heating with steam.

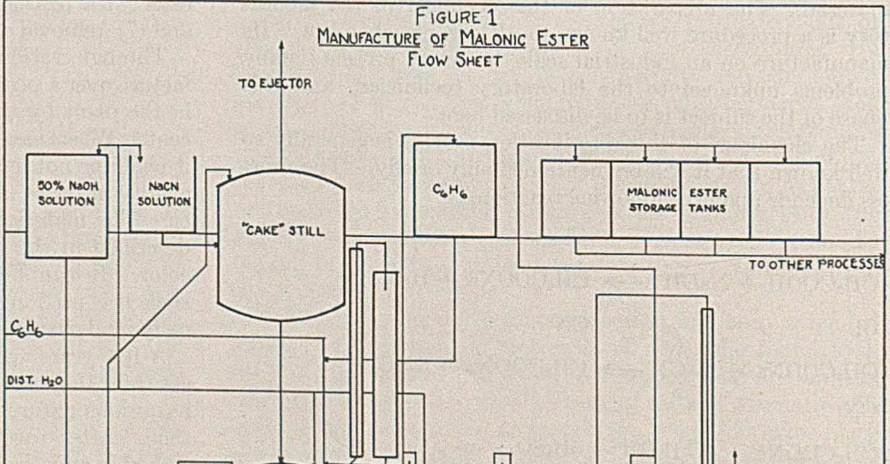
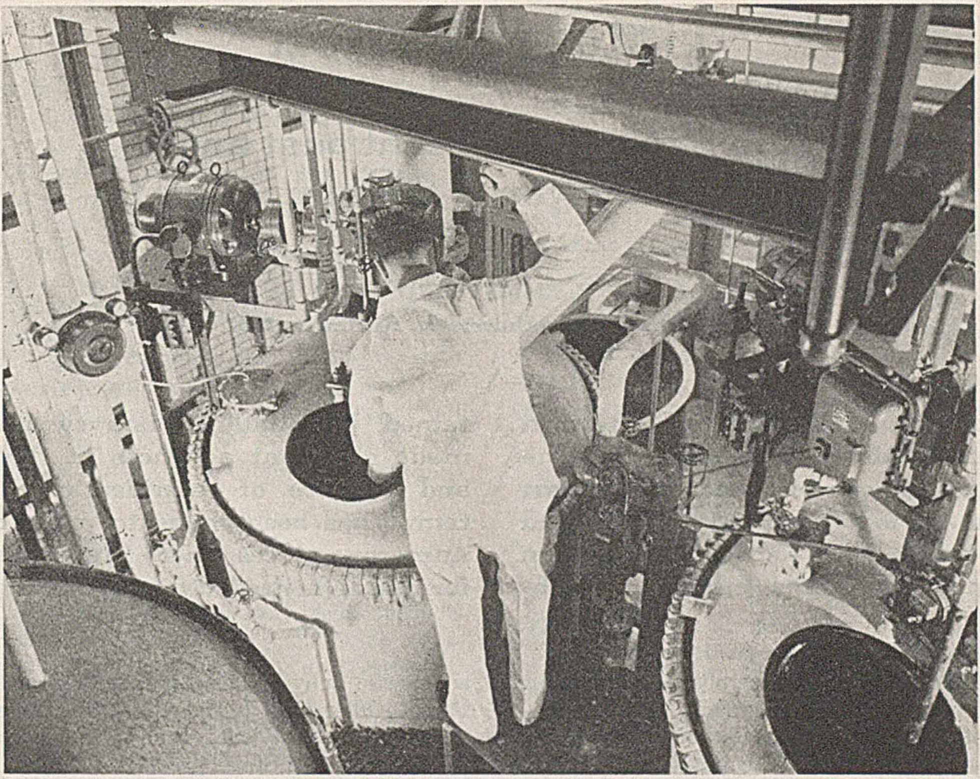


Figure 1
Manufacture of Malonic Ester
Flow Sheet



Malonic Ester Reaction Stills

The following morning there is added to the still an amount of distilled water equivalent to about one-fourth of the reaction mixture and an equal quantity of benzene, pumped from a 1000-gallon underground storage tank. This entire mixture is agitated and mixed intimately, and then allowed to settle and separate. The benzene, extracting out the malonic ester, rises as a top layer and is pumped off by a Duriron centrifugal pump into an adjacent 500-gallon Pfaudler glass-lined extraction tank, equipped with an anchor-type direct-driven agitator. Two additional extractions of the reaction mixture are made with benzene and added to the original extract in the extraction tank. Finally, three similar extractions of the reaction mixture are made with more benzene. However, these extracts are pumped by the Duriron pump into a 300-gallon stainless steel storage tank located on the upper mezzanine, where they are held until the next day to be used as the first three extractions for the next batch of ester and are returned at that time to the reaction kettle by gravity. The reaction mixture is then washed from the still directly down the sewer.

The combined benzene extracts in the extraction tank are now washed twice by agitation with small amounts of distilled water, which are removed as a lower layer and discarded. The extracts are then washed twice by agitation with cold portions of 12.5 per cent sodium hydroxide solution, which are likewise removed as a lower layer and discarded. After one more washing with distilled water, the extracts are finally dried with dry sodium sulfate.

The dry benzene extracts of malonic ester are now pumped out of the extraction tank by a Blackmer rotary pump into a near-by 300-gallon Pfaudler glass-lined jacketed recovery still, leaving as a residue in the bottom of the extraction tank the sodium sulfate and a small portion of the benzene extracts. Both are removed through the bottom outlet and filtered on a gravity filter. The extract thus recovered is added as tailings to the next batch when the benzene extracts are removed from the reaction still and transferred to the extraction tank.

The extract in the recovery still is next subjected to distillation under atmospheric conditions until 75 to 80 per cent of the benzene has been recovered by the aid of a condenser in an iron receiver. After the still has been cooled somewhat by circulating cold water through its jacket, a 15–20 inch vacuum, supplied by the jet condenser, is applied to the apparatus and the remainder of the benzene is distilled off into the receiver. This benzene distillate is then returned to the 1000-gallon underground storage tank to be re-used in future batches.

The residue remaining in the recovery still is malonic ester which is not less than 90 per cent pure. It is run out of the bottom of the still through a Y-pipe containing a strainer made of No. 20 mesh screen wire. This strainer, which can be readily emptied after each batch, serves as a filter to remove any last traces of sodium sulfate that may have been accidentally pumped into the recovery still from the extraction tank along with the benzene extracts. After passing through the strainer, the malonic ester is transferred by the Blackmer rotary pump to individual iron storage tanks, located on the upper mezzanine. These tanks are equipped with calibrated gage glasses so that the yield and percentage of yield of each batch can be easily determined.

These tanks are connected by individual bottom outlets and valves to a common header pipe which transfers the ester by gravity to the proper location in a neighboring building where it is used in subsequent malonic ester syntheses.

This paper discusses only the present working conditions of this esterification process. Naturally many problems had to be solved and much experimentation on a large scale had to be done before discovering the correct equipment, the right layout, and the proper manufacturing procedure to give the optimum results.

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Esterification

A review of the recent past and a look towards the future

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The present importance of esters in chemical industry is stressed. The literature has been searched for the past four-year period, and 460 articles and patents have been abstracted. From these and from some information obtained personally, a survey has been made of recent advances in the theory and practice of esterification. An attempt has been made to point out the numerous places where fundamental information is needed for further advances.

THE purpose of this paper is to emphasize the growing importance of esters, to note progress in their manufacture in the last four years, and particularly to point out lines in which further investigation is needed. Scientific scouts must go before the industrial army; in this as in so many other cases the army has caught up with the scouts.

The reaction of an alcohol and an organic acid to form an ester, a typical organic reaction, has interested organic chemists from the first. Ostwald, the great pioneer of physical chemistry, took up esterification as the best reaction with which to study the catalytic activity of acids. The ease and accuracy with which the velocities of esterification reactions can be measured have ever since made them favorites with physical chemists. Furthermore they are the best examples of reversible reactions. Biological chemists have had much to do with esters. Of late esters have become of great commercial importance, and making them is the chief concern of a number of industrial chemists. We start with an acid and an alcohol and get an equilibrium mixture of these with the ester and water. To complete the reaction, the water or the ester or both must be removed from the sphere of action. Water is volatile; so are the esters that are manufactured in largest quantity. The separation of these involves fractionation and has required the best efforts of the fractionation engineers. Now the making of esters is a problem of engineering.

Importance of Esters

Natural esters we have in enormous quantity and great variety; the tonnage is furnished by such esters as linseed and cottonseed oils, tallow, waxes, and the like, while essential oils supply the variety. Whole industries are engaged in the utilization of esters. But natural esters do not fill all of our requirements. Millions of pounds of esters are being manufactured; ethyl acetate and butyl acetate as solvents, triacetin and dibutyl phthalate as plasticizers, ester gum, glyptals, and cellulose nitrate for lacquers and paints, and cellulose acetate for textiles—to name a few individuals which may be taken as typical of classes. The most beautiful plastic so far made is an ester. The ester that is manufactured in the largest quantity never comes into commerce but is in the plant only as a transitory intermediate. That is cellulose xanthate. Another ester, ethylidene acetate, is of tremendous importance as an intermediate. The quest for cheap acetic acid and acetic anhydride engages many chemists and keeps the Patent Office busy. These are for making esters. When we get cheap acetylene, much of it will go into acetates of which the United States production for 1936 was 135,960,386 pounds. The largest use of phthalic anhydride is for making esters (over 10,000,000 pounds in 1936).

Government statistics show that the manufacture of synthetic nonaromatic organic chemicals increased 94 times in 15 years, passing the 2,000,000,000-pound mark in 1936. Esters have been large items in this increase. As the demand for esters has mounted from thousands of pounds to millions, small reductions in cost per pound become important; a cent a pound saving on 100,000,000 pounds is $1,000,000. Present-day efforts are aimed at reducing costs, a fraction of a cent per pound here, another fraction there. A 10,000-gallon still requires little more attention than a 100-gallon still; labor costs come down as the scale of operations is enlarged. Greater quantities of esters are being produced and prices are being lowered.

Theoretical

The theory of esterification and saponification continues to receive attention. Polanyi and Szabo (*187*) by the hydrolysis of amyl acetate in water containing O^{18} showed that the ester breaks thus Ac-OAm, the oxygen atom going with the alkyl. This accords with the conclusions from esterification velocities. Herold (*96*) found abnormalities in the ultraviolet absorption of carbonyl compounds in water and alcohol solution which indicate hydrate and hemiacetal formation and throw light on the mechanism of esterification. From observations of Kailan and co-workers (*119–123*) esterification goes 2,000 to 16,000 times as fast in formic acid as in acetic. There is no space to mention many articles on kinetics, salt effect, steric hindrance, and saponification (*2, 4, 19, 20, 25, 39, 44, 100, 101, 104, 105, 111, 130, 132, 142, 176, 179, 180, 185, 186, 190, 199, 201, 203, 207, 212, 229, 233, 253, 256, 262*).

Addition of Carbon Monoxide

There are many ways to make esters besides the action of acids on alcohols. These will be taken up first, beginning with the most novel, the addition of carbon monoxide to an ether or to an alcohol. With an ether we may represent it as simple addition:

$$ROR + CO \rightarrow RCOOR$$

With an alcohol we have the intermediate formation of the acid which is esterified by the excess alcohol. Naturally, high pressures are advantageous; 50 to 700 atmospheres are mentioned in the patents with temperatures from 400° down to 20° C. Activated charcoal, metal oxides, and acidic salts are favored as catalysts, although a sodium alcoholate may be used. There are already many patents. In two of these an olefin and an alcohol are used with the carbon monoxide; the result is that the alcohol is esterified by the acid formed by the addition of the carbon monoxide to the olefin (*22*, *55*, *57*, *78*, *177*, *184*, *241*, *255*).

This method, which is promising but does not seem to have been put into large-scale production as yet, will doubtless receive much attention in the near future, since it is direct and involves cheap materials. Obviously, improvements will come with better catalysts and a more thorough understanding of the process.

Ketene

Ketene still appears in the patents (*74*, *83*, *107*) but does not attract much attention. It reacts with acetic acid to give the anhydride and hence is useful in maintaining an effective concentration of the anhydride during an acetylation.

Aldehydes into Esters

The conversion of aldehydes into esters by aluminum alcoholates has been discussed by Kagan and Sabolev (*118*) and Batalin, Nikitina, Rivkin, and Sekretareva (*12*). The improvements relate to the preparation of the catalyst. This method, though of limited application on account of the poor supply of available aldehydes, is interesting in that one compound is almost quantitatively changed into another. There is one patent (*45*).

Esters from Amides

An amide, treated with an alcohol or phenol and boron fluoride, is converted into an ester (*170*). Formamide sulfate reacts with an alcohol to give a high yield of ester (*149*). Since esters are usually more available than amides, this method is of little practical interest but it should be useful for making esters from rare alcohols since the yields may be very high.

Addition of Olefins to Acids

A number of patents have appeared for the manufacture of esters by the addition of olefins to organic acids in the presence of various catalysts under different conditions of temperature and pressure (*21*, *23*, *36*, *43*, *54*, *64*, *75*, *82*, *109*, *113*, *124*, *141*, *173*, *202*, *206*, *225*). Two of these rely on boron fluoride as the catalyst. Syntheses of esters by means of boron fluoride are described by Dorris, Sowa, and Nieuwland (*49*, *216*). In other patents the monoalkyl sulfate is actually prepared and the organic acid or its salt reacted with this (*143*, *163*, *183*, *219*). This saves a step over making the alcohol from the monoalkyl sulfate, isolating it, and then esterifying it. There must be some difficulties not mentioned in the patents, or more esters would be manufactured in this way. More data are required on solubilities of the olefins in the mixtures used and on reaction rates.

Vinyl Esters

Two esters which are produced but never come on the market as such are vinyl acetate and ethylidene acetate. The conditions under which acetylene reacts with either one or two molecules of acetic acid are discussed by Morrison and Shaw (*164*). A few patents are concerned with additions to and modifications of the usual mercury catalyst (*108*, *164*, *182*, *189*, *251*). In view of the interest in polyvinyl alcohol, the vinyl acetate from which it is derived deserves more attention. Since millions of pounds of acetic anhydride are obtained from ethylidene acetate, this ester is of immense importance, and improvements in its manufacture are of great interest. In dealing with these two esters, which are not even mentioned in several of the widely used textbooks of organic chemistry, the industries are far ahead of the universities. More fundamental investigations on them are much needed. How can the reaction be controlled so that either one of these esters may be obtained in 100 per cent yield as desired? What can we do with vinyl acetate besides polymerizing it? What can we make out of ethylidene acetate besides acetanhydride?

Vapor-Phase Esterification

Esterification in the vapor phase (*254*) has been thoroughly treated by Essex and Clark (*66*), by thermodynamics as well as by experiment. Swietoslawski and Salcewicz (*198*, *230*) found the equilibrium K to be 40.8 at 75.9° C. Jatkar and Gajendragad (*115A*) obtained 75 per cent esterification at 260°. Turova et al. (*236*, *237*) used activated carbon with 25 per cent phosphoric acid as catalyst. Dolian and Briscoe (*48*) studied the effects of a large number of anhydrous salts.

Although the percentage of esterification at equilibrium is high, the reaction velocity is low and the space required to handle a ton of vapors is large. For these reasons vapor-phase esterification does not attract industrial attention.

Esters by Alcoholysis

The preparation of esters by alcoholysis continues to be of interest (*115*, *234*, *235*). Fehland and Adkins (*70*) determined the relative replacing power of different alcohols, and Patel and Watson (*181*) measured the velocity of alcoholysis by methanol and ethanol of esters of several dibasic acids. Oda published a series of articles on the "reësterification" of fats (*174*). These deal with replacements of the acids as well as of the glycerol of vegetable and animal oils. There are only a few patents (*37*, *110*, *246*); one of them claims the preparation of an ester by heating a vinyl ester with an alcohol or phenol in the presence of an acid catalyst. The vinyl alcohol is eliminated as acetaldehyde (*38*).

There is no published information as to the use of alcoholysis industrially though there are numerous places where it might be used and probably is. More numerous and more exact quantitative data are needed.

There is an interesting special case in which the desired esters can be obtained in no way except by alcoholysis. This has to do with the preparation of cyclic esters with 10 to 20 atoms in the ring, such as decamethylene carbonate. To make this ester, ethyl or butyl carbonate is alcoholized with decamethylene glycol which gives only the linearly polymeric ester. This, still containing the catalyst, is heated in a high vacuum. The cyclic ester distills out as it is formed, with the result that practically all of the linear polymer is transformed into the volatile cyclic ester (*28*, *61*, *99*, *214*, *217*).

Catalytic Conversion of Alcohol into Ester

The direct conversion of an alcohol into an ester by passing it over a dehydrogenation catalyst was of interest in this country some ten years ago. Recently Russian investigators have taken up this process (*1*, *14*, *26*, *46*, *114*, *131*, *133*). They claim (*47*) that the synthesis of esters at atmospheric pressure is new, although it was claimed in a German patent in 1935 (*33*). The writer remembers getting butyl butyrate as a by-product in making butyraldehyde about ten years ago; this and similar observations were doubtless made by many others.

In several patents the dehydrogenation is assisted by an oxidizing agent or chlorine (*69, 84, 165*). Conversely an ester can be obtained by the partial reduction of an acid (*16, 58, 81*).

That there is still some interest in this process outside of Russia is shown by several recent patents (*6, 60, 139, 165, 228, 240*). Making an ester directly from an alcohol simply by passing it over a catalyst is attractive. If the alcohol is much cheaper than the corresponding acid, and if catalysts and working conditions can be found which will give a high yield of ester and low yields of unwanted by-products, such a process will be interesting. The Russians have isolated and identified all of the products down to 0.1 per cent and can convert all of them into those that can be utilized (*46*).

Esters from Ethers, Salts, and Alkyl Halides

An acid may react with an ether in the presence of boron fluoride (*95*) or of strong acids as catalysts (*27, 41*).

When a halide, such as benzyl chloride, is more available than the corresponding alcohol, it may be reacted with a metal salt. Special cases and improvements of this old reaction are claimed (*7, 37, 80, 129, 138, 169, 188, 202, 223, 258, 261*).

Catalysts for Esterification

In the matter of catalysts several observations have been made which are interesting although their practical applications are not now evident. Flosdorf and Chambers (*71*) found that audible sound, 1,000 to 15,000 vibrations per second, speeds up the hydrolysis of esters. Forjaz (*72*) found that in "a forced-wave oscillatory circuit" esterification is accelerated. An alternating current is claimed (*218*). Langenbeck (*136, 137*) regards organic compounds containing the —$COCH_2OH$ group as analogous to esterase (*8, 9, 68, 158, 159, 244, 245*). The saponification of methyl butyrate was speeded up six times by 0.005 *M* phenacyl alcohol. Shemyakin (*208*) found silver hydroxide to be an esterification catalyst. Nieuwland and associates (*79, 216*) catalyzed esterifications with boron and silicon fluorides (*98*). Tertiary bases are used with acid chlorides or anhydrides (*91, 152, 156, 178, 224*).

It will be a long time before the use of sulfuric acid as a catalyst is discontinued. It is the cheapest known and is effective, but it has several disadvantages. It tends to discolor and even char some mixtures, and separates out in the water layer if one is formed. Aryl sulfonic acids have been used (*34, 168, 260*); alkyl sulfonic acids will be when they become cheap enough. Silica gel and various salts are advocated (*31, 191, 226, 243*). More consideration should be given to finding the most suitable catalyst and the proper amount of it to use for a given esterification.

Cellulose Esters

The interest in the esterification of cellulose is shown by the issuance of 155 patents in the past four years, 68 United States, 33 British, 23 German, 16 French, 11 Canadian, and 4 Swiss; three-fourths of them were issued in the first half of this period (*3, 5, 11, 13, 15, 16, 17, 22, 32, 35. 40, 45, 50, 51, 52, 53, 56, 59, 62, 65, 73, 77, 85–89, 92, 93, 94, 97, 102, 107, 116, 126, 127, 146, 147, 148, 150–155, 157, 160, 161, 162, 167, 171, 192, 193, 204, 205, 209, 210, 213, 215, 220, 221, 222, 227, 239, 249, 250, 257*. There are many more patents on applications of cellulose esters and mixtures containing them. The patent activity is in keeping with the volume of the products manufactured; the United States production of cellulose acetate was about 55,000,000 pounds in 1935 and about 70,000,000 in 1936, or over 200,000 pounds each working day. Nearly all of this is acetate although some propionate and other esters are said to be mixed with it. Obviously an analysis of these patents cannot be attempted here. There could hardly be 68 entirely new ways to esterify cellulose in addition to those that were known four years ago. The patents cover many modifications and improvements of previously used processes. Technology has far outrun pure science in this field; there are only 10 articles on the esterification of cellulose in the same period. One of these by Yarsley (*259*) is a review of patents and another by White (*252*) is a practical talk on "how to avoid difficulties in cellulose acetate production." There are four by Sakurada and associates (*194–197*) on the kinetics of acetylation. They measure the accelerating and degrading effects of catalysts and compare various pretreatments. A proper pretreatment may speed up the acetylation fifty to one hundred times. Krüger and Roman studied the catalytic action of various acids (*135*). Centola (*30*) experimented on the acetylation of alkali cellulose containing varying amounts of water. Ohl (*175*) acetylated cellulose swelled with water and found that 20 per cent of water gives the best mechanical properties.

As the price of acetic acid and its anhydride come down and as acetylation methods are improved, the price of cellulose acetate is being reduced. This makes it available for more and more uses. Its production, already a large industry, is destined to be far greater.

There is no doubt that excellent scientific work is being done on the acetylation of cellulose, but unfortunately little of it is published. Probably the same investigations are being carried on in a half-dozen industrial laboratories with the result that all spend about the same amount of money and obtain about the same information, which thus costs the industry as a whole about six times as much as if the work were done just once. Or putting it the other way, if coöperation could be secured, about six times as much information could be obtained for the money now spent.

Use of Azeotropes

As has been indicated, there are many ways of making esters, but to make an ester is not enough; it must be removed. Nearly all esterification processes give the ester mixed with other things from which it must be separated. The original, and still the most extensively used method of esterification, the reaction of an acid and an alcohol, with or without catalyst, is reversible reaction and comes to equilibrium long before it is complete. In this case if the ester or the water or both are removed, we can approach a yield of 100 per cent. Azeotropism is relied on for such removal. In the simplest case, in which the acid, alcohol, and ester are all nonvolatile, the water may be driven off by heating but even here some liquid as benzene is commonly put in to bring the water out at a lower temperature. In the more general case when reactants and products are volatile, azeotropes are all-important.

Wade in 1905 (*248*) made the epoch-making discovery of the ternary of ethyl acetate, alcohol, and water which comes off at 70.3° C. from any solution containing these three substances in any proportion whatsoever, and continues to come off as long as all three are present. This makes it possible to convert practically all of the acid of even a dilute acetic acid into ethyl acetate.

Lecat continued his studies of azeotropes (*140*). Sklyarenko and Baranaev (*211*) developed a general formula for binary azeotropes. Mund and Heim (*166*) restudied the ethyl alcohol-acetate system. Furnas and associates (*24, 76*) continued their important studies on ethyl alcohol–acetate and butyl alcohol–acetate systems. They find the azeotrope of the latter to contain 72.9 mole per cent of the alcohol and to boil at 116.5° C.; Lecat had found 56 per cent and a boiling point of 113.5° C. Kireev, Klinov, and Grigorovich (*128*) and

Longinov and Dzirkal (*144*) made measurements on the ethyl alcohol–acetate system and these with water. Hannotte (*90*) considered formic, acetic, and propionic esters of aliphatic alcohols. There are a few articles (*125, 145, 200, 231*) and numerous patents (*10, 18, 29, 42, 63, 67, 103, 106, 112, 117, 134, 172, 232, 238, 242, 247*).

One discrepancy has just been noted, others could be mentioned. The industry needs data that can be depended upon. In the ethyl acetate case, the ternary boils only a fraction of 1° C. from the water–ethyl acetate binary. The design of a column and the required reflux ratio depend on the differences of the boiling points of the materials to be separated. The cost of the fractionation depends on these and other factors. The amount of water required to wash the alcohol out of the ternary system depends on the percentage of alcohol present and on the amount that can be left in the finished ester. This wash water has to be distilled to recover the alcohol, and the cost of this operation depends on the amount of alcohol removed. The writer has heard privately of two companies that have recently spent considerable money on more accurate determinations on this ternary, and this of all ternaries is the best known.

Progress by Refinements

This is the day of refinements of manufacturing operations, of small savings per pound on large amounts of products.

Aside from the cost of acetic acid and alcohol, the cost of the steam for the necessary distillations is the big item in esterification. There is a negligible heat differential between alcohol plus acetic acid and ethyl acetate; the sulfuric acid required as catalyst is of trifling cost. Steam costs can be shaved by more accurate data and better column designs.

What has been said of ethyl acetate can be said with more force about the less well-known systems involving propyl and butyl acetates and other esters which are becoming large items.

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Quantitative Control of Sulfonation Processes

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Many conditions affect the results obtained in a sulfonation reaction. Control of these conditions affects not only the yield of the desired products but also the isomers formed and a considerable variety of by-products. A description is presented of the analytical steps necessary to determine the sulfones, relative amounts, of mono- and disulfonic acids from various ring systems. A number of practical sulfonations are also included, with the indicated analytical control.

A CONSIDERABLE number of conditions influence the results obtained in a sulfonation reaction. Control of these conditions affects not only the yield of the desired product but also the isomers formed and a considerable variety of by-products. Success or failure of the operation is often dependent upon the ability of the operator to follow quantitatively the progress of the reaction and determine the proper end point. When the numerous conditions which must be controlled have been determined, the sulfonation mass and products must be analyzed in order to find the optimum condition required to obtain the maximum yield of the desired product.

The complexity of the problem is evident from the following list of factors affecting the sulfonation reaction and yields:

Concentration of sulfuric acid or oleum. The strength may vary from less than 90 per cent sulfuric acid to 65 per cent oleum.

Temperature. The range for sulfonations is from room temperature to 250° C.

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Time of reaction. The time required for a sulfonation process may vary from a few hours to a few days.

Catalysts. In sulfonation processes catalysts usually take the form of an added metal salt and affect the orientation of the sulfonic acids produced.

Sulfonation aids. These aids take the form of a dehydrating agent and thus promote the sulfonation reaction.

Oxidation. Since sulfuric acid and especially oleum are oxidation agents under certain conditions, some oxidation usually accompanies every sulfonation process using these reactants.

Sulfone reactions. The tendency to form sulfones in a sulfonation process, instead of the desired sulfonic acid, must be minimized as much as possible by accurate control of all physical and chemical conditions involved.

The analytical control of the process is directed to the determination of the following:

Extent of sulfonation
By-products, such as sulfones, water, tars, and condensation products
Relative amount of mono-, di-, and trisulfonic acids
Identification of the various isomers
Final yield of product or products

Extent of Sulfonation

The progress of the sulfonation reaction may be followed most conveniently by a simple alkali reaction, since, for every sulfonic monovalent radical produced, one molecular weight of sulfuric acid or one molecular weight of sulfur trioxide must disappear. Although this method cannot be relied upon to produce exact results, it at least gives the experimenter an approximate measure of the extent of the reaction and thus enables him to save much time. For example, in the sulfonation of β-naphthol by 98 per cent sulfuric acid, the sulfonation time extends to 70-odd hours in order to introduce two sulfonic groups. The following data show the progress of this reaction. The acidity is calculated in terms of an arbitrary normality calculated from the number of gram or pound equivalents of sulfuric acid present and the total weight of the mixture; 144 grams of β-naphthol and 720 grams of 98 per cent sulfuric acid were used at 20–60° C.:

Time *Hr.*	Acidity	Progress[a] %
Start	16.66	0
2 (acid all in)	14.83	72.0
48	14.51	84.6
72	14.33	91.7

[a] For 100% disulfonation, acidity should fall to 14.12.

In certain cases the progress of the reaction can be followed by applying reactions peculiar to the compounds involved. In the sulfonation of β-naphthol-7-sulfonic acid to the 3,7-disulfonic acid, the color obtained by coupling the product with a diazo compound can be used to follow the progress of the reaction, since, for example, a bluish Bordeaux red with diazonaphthalene indicates small amounts of the monosulfonic acid. Again, in the case of naphthalene, it has been recommended to follow the degree and extent of sulfonation by oxidation with vanadic acid. The dry sulfonate salt mixture, free from sulfates, is oxidized to sulfophthalic acids with a solution of vanadic acid in 70 per cent sulfuric acid, and the vanadium is reoxidized by means of 0.1 N permanganate; the oxidation is quantitative for the mono- and disulfonic acids. Thus the extent of the sulfonation reaction is determined by measuring the hydrocarbon percentage in the sulfonate salt mixture.

When reactions peculiar to the compounds involved cannot be applied, it is necessary to analyze the calcium or barium sulfonate mixtures obtained from the sulfonation in order to determine the exact progress of a disulfonation reaction—i. e., analyze these salts for the percentage of mono- and disulfonic acids. From the analysis of the sulfonate salt mixture for exact calcium or barium content, it is possible to calculate the relative amounts of the sulfonic acids by applying the following simple algebraic relation:

$$l = S{\cdot}x{\cdot}n + S(100 - x)m$$

where l = known total metal content (determined by analysis)
x = monosulfonate, %
$100 - x$ = disulfonate, %
n = known metal in monoacid salt, %
m = known metal in disulfonic acid salt, %
S = known weight of sample

If carboxylic acid groups are present, they must be taken into consideration, since a correction must be made for the calcium or barium taken by the carboxyl group.

For the preparation of the barium sulfonate salt mixture a sample of the sulfonation mass is neutralized with barium carbonate and filtered from the barium sulfonate, and the barium sulfonate is recovered from the filtrate. Or the filtrate and washings from the barium sulfonate can be made up to a known volume and the barium content of an aliquot portion determined by the chromate method. This particular method is used in the disulfonation of benzene.

The calcium salt method can be carried out as follows: The sulfonation mass is limed after diluting with water, boiled, and filtered. The solution is then made slightly alkaline with lime, if it was not already so, and carbon dioxide gas is allowed to pass into the mixture until it is acid to litmus. Then it is boiled and filtered. The clear liquor is analyzed for solid content; a measured volume is treated with excess standard sodium carbonate solution, boiled, and filtered; and the precipitate is washed until the washings are neutral. The excess sodium carbonate is determined in the filtrate and washings. Then there is the familiar oxalate method for calcium.

As an example of the use of these sulfonate mixture analyses, naphthalene was sulfonated and the following results were obtained by analyzing the calcium salt mixture:

	1	2
Naphthalene, grams	500	500
98% sulfuric acid, grams	2000	2000
Hours at 160° C. after acid is all in	1.5	3
Disulfonate, %	74	81.4
Monosulfonate, %	26	18.6

UNSULFONATED MATERIAL. For unsulfonated volatile hydrocarbon in a sulfonation mass it is sufficient to steam-distill out of a diluted sample of the sulfonation mass the unreacted crude material. In the case of an amine, it is necessary to make the reaction mixture alkaline. Qualitative results can be obtained simply by diluting the mixtures, whereupon the crude material separates. For materials that cannot be vaporized readily, such as anthraquinone, the sulfonation must be diluted with water and the unreacted portion filtered off.

SULFONES. For sulfone determination in a sulfonation mass, it is recommended to neutralize a portion of the reaction mass, evaporate to dryness, and extract in a Soxhlet apparatus with petroleum ether.

WATER. For water determination, a sample is diluted with a known weight of water and neutralized with excess soda ash, and the total water is determined by passing in carbon dioxide gas, absorbing the water in calcium tubes, and finally heating to 180° C. in an oil bath.

Isomeric Sulfonic Acid Analysis

Investigation of isomeric acids formed in sulfonation reactions is a complicated procedure in many cases, involving the peculiar properties of the compounds in question. A few of these methods are as follows:

DYE METHOD. In the dye method of selective reaction, one sulfonic acid in the form of its salt forms a dye with a diazo compound but the other isomer does not. This method is illustrated in separating and determining 2-naphthol-6,8-disulfonic and 2-naphthol-3,6-disulfonic acids. The latter forms a dye with a diazo compound, and so a standard diazo-*m*-xylidine solution is prepared and used to titrate a solution prepared from the disulfonate. In this way the 3,6-isomer is determined. Then a diazo solution is made to react quantitatively with another sample, and soda ash is added. The color solution is boiled and salt is added to precipitate the dye, Ponceau 2 R. The latter is filtered, leaving in solution the 6,8-salt which is concentrated and salted out preferably after adding enough hydrochloric acid to form the acid salt.

SULFONYL CHLORIDE METHOD. Preparation and determination of the sulfonyl chloride derivatives of the sulfonic acids is the most common method of isomer analysis. The sulfonyl chlorides are generally prepared by reaction with phosphorus pentachloride, although phosphorus oxychloride and thionyl chloride can be used in some cases, the latter with some free sulfonic acids. Reactions are as follows:

$$R \cdot SO_2OH + PCl_5 \longrightarrow POCl_3 + HCl + R \cdot SO_2Cl$$
$$3R \cdot SO_2OH + POCl_3 \longrightarrow 3R \cdot SO_2Cl + PO(OH)_3$$
$$R \cdot SO_2OH + SOCl_2 \longrightarrow R \cdot SO_2Cl + SO_2 + HCl$$

By far the most convenient laboratory method is that using phosphorus pentachloride. The dry sulfonate salts are mixed cold with the proper amount of the pentachloride, and the mixture is then warmed in a flask. Reaction takes place readily, and, after warming to about 100° C., the mixture is poured on ice and water, whereupon the sulfonyl chlorides solidify after a short while. The mixture of sulfonyl chlorides is then taken up in a suitable solvent (carbon disulfide, for example) and recrystallized. Fractional crystallization can be used to separate the isomers which are then identified by melting point determination. For example, the sulfonyl chlorides of 1,6- and 1,7-disulfonic acids of naphthalene can be separated by benzene, the 1,6-acid being more easily soluble. When there are only two such sulfonyl chlorides, the melting point of mixtures of the two can be plotted, and the composition of any of these mixtures can be determined by taking the melting point of the particular mixture and locating the corresponding point on the curve. The sulfonamides may be used similarly. Eutectic mixtures are sometimes a possibility.

METALLIC SALT METHOD. Where possible, advantage is taken of different solubilities of a metal salt for the separation of isomers, as in the case of the calcium, magnesium, ferrous, zinc, manganese, cobalt, and nickel salts of α- and β-naphthalene sulfonic acids, lead salts for the separation of naphthalene-2,6- and -2,7-disulfonic acid, and potash salts in the α-sulfonation of anthraquinone. The difference in solubility of sodium and potassium salts of anthraquinone-2,6- and -2,7-disulfonates is another example; the 2,7-disulfonates are about ten times as soluble in water as the 2,6-disulfonates.

ARYLAMINE SALT METHOD. The arylamine salts have been proposed as a means of separating the constituents of a sulfonation. The amines used are β-naphthylamine, aniline, *p*-toluidine, and *m*-xylidine. A number of such salts of β-naphthol-1-, -6-mono-, -3,6-, and -6,8-disulfonic acids have been prepared and characterized.[2]

HALOGEN DERIVATIVE METHODS. Where possible, it is convenient to determine the orientation of isomers by bromine derivative formation. In this way metanilic acid can be distinguished from sulfanilic acid; the metanilic acid derivative forms a bromine addition product that is soluble, whereas the *o*- and *p*-aminobromine compounds are insoluble. Also β-naphtholsulfonic acids, other than those with a sulfonic group in position 8, are monobrominated quantitatively in 10 *N* sulfuric acid solution at ordinary temperature; therefore it is possible to determine the amounts of acids such as Schaeffer's acid or R acid in sulfonation melts containing croceic or G acid (Vaubel method).

For anthraquinone sulfonic acids, monochloro and dichloroanthraquinones are much used as a means of separation and identification. These are formed either through the sulfonyl chlorides by means of thionyl chloride or from the sulfonic acids by means of chlorate and hydrochloric acid. The composition of a mixture of isomeric sulfonic acids can be determined from the melting point of the chloroanthraquinones, as in the case of sulfonyl chlorides.

FUSION METHODS. Sometimes it is necessary to fuse the sulfonic acid isomers and then determine the proportions by analysis of the oxycompounds formed. Thus, the disulfonates derived from phenanthrene can be separated and identified through the diacetoxyphenanthrenes that are obtained by alkali fusion and acetylation.

Practical Sulfonations

For the purpose of illustrating practical sulfonation processes, a number of simple cases can be carried out in the laboratory. A suggested list follows:

Monosulfonation of benzene
Monosulfonation of naphthalene
Disulfonation of naphthalene
Monosulfonation of nitrobenzene
Preparation of sulfanilic acid
Monosulfonation of toluene
Disulfonation of benzene
Preparation of anthraquinone-1-sulfonic acid
Preparation of anthraquinone-2-sulfonic acid
Monosulfonation of β-naphthol
Disulfonation of β-naphthol

Reliable procedures are available for most of these. Following are the suggested procedures for naphthalene-2,6- and -2,7-disulfonic acids and for nitrobenzene monosulfonic acid.

DISULFONATION OF NAPHTHALENE. The disulfonation of naphthalene illustrates the method of disulfonation in one step where the time of reaction must be taken into consideration.

A cast-iron kettle with moderately good stirring facilities, a thermometer, charging and discharging holes, and a jacket for heating are required. The kettle is charged with 800 pounds of naphthalene flakes of good quality and heat is applied to melt it. Then the temperature is raised rapidly to 150° C.; between 150° and 160° C., 3600 pounds of 98 per cent sulfuric acid are added. This should take 2 hours. When all the acid has been added, the temperature is kept at 160° C. for 3 hours more. It is then dropped into 20,000 pounds of water and neutralized with milk of lime. The calcium salts of 2,6- and 2,7-disulfonic acids must now be separated. In order to do this, the difference in solubility of the calcium salts in brine is utilized. The limed mixture is brought to a volume of 4000 gallons, heated to boiling, and filtered from the gypsum. The filtrate together with the washings are evaporated to a volume of 1440 gallons; 3200 pounds of common salt are dissolved in the liquor which is then cooled, with stirring, to 20° C., whereupon both the 2,6- and 2,7-calcium disulfonates crystallize out. The batch is then heated to boiling to dissolve the 2,7-salt, and the 2,6-salt is filtered off. Most of the 2,7-salt crystallizes from the filtered solution upon cooling at least 24 hours. The crystallized sulfonate is filtered off, and the filtrate is evaporated in order to obtain another crop by another cooling. After a second crop has been separated, the filtrate is discarded. The

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[2] Forster and Keyworth, *J. Soc. Chem Ind.*, 46, 29T (1927).

yield of the 2,7-isomer is 50 per cent of theory; of the 2,6-isomer, 35 per cent.

Monosulfonation of Nitrobenzene. A cast-steel jacketed kettle, provided with moderately good stirring, a thermometer, and discharging and charging holes are required. Into the kettle are run 1350 pounds of good-quality commercial nitrobenzene; this is heated to 70° C., and the addition of 20 per cent oleum is started with stirring. The temperature rises to 90° C. during addition of the oleum over a period of 2 hours, then to 110° C. during the addition of the last half of the oleum during the next hour. A total of 4730 pounds of nitrobenzene is required. After heating at 110° for 30 minutes longer, a sample is taken for control of the sulfonation. Upon diluting with water, no nitrobenzene should separate. Longer heating and possible addition of oleum may be required to finish the sulfonation. The sulfonation product is dropped into 5600 pounds of ice water, and 2200 pounds of common salt are added with stirring and cooling. The sodium salt of the sulfonic acid separates in 90 per cent yield.

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Recent Progress in Amination by Ammonolysis

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Although the greater number of ammonolysis reactions are carried out in the liquid phase with aqueous ammonia, the ammonolysis of alcohols, aldehydes, and oxides may often be done most advantageously in the vapor phase.

During the past few years marked progress has been made in improving the operating technic in the manufacture of amines from practically all classes of compounds susceptible to ammonolysis. Of importance also has been the fundamental research leading to a better understanding of these reactions. Recent investigations correlate the use of oxidants and reducing agents with the susceptibility of the amine to oxidation. The influence of ammonia ratio on the proportions of primary, secondary, and tertiary amines has been studied and gives information of great practical and theoretical value. The effect of ammonia concentration on practical ammonolysis and in reaction rate studies has also been reported.

In organic synthesis, amination by ammonolysis relates to those reactions where an amino compound is formed as a result of the action of ammonia. To a limited extent such agents as urea and ammonium carbamate which, during the course of the reaction undergo decomposition with the liberation of ammonia, may be employed. When an organic ammonia derivative—e. g., an alkyl- or arylamine—is used as the reactant, the product will be the corresponding substituted secondary or tertiary amine. Most frequently a univalent substituent, chloride, hydroxyl, or sulfonic acid group is replaced by the amino group during ammonolysis, but reactions involving simple addition and the replacement of oxygen are known, and some of these are economically important.

For convenience, the compounds that are susceptible to ammonolysis may be divided into four classes:

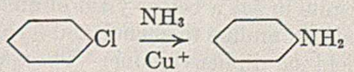
- Halogeno compounds
- Sulfonic acids
- Oxygen-containing compounds:
  - Phenols and alcohols
  - Aldehydes and intranuclear ketones
  - Aliphatic ring oxides
  - Carbon dioxide
- Compounds possessing a labile nitro group

Although the preponderant number of reactions are carried out in the liquid phase with aqueous ammonia, the ammonolysis of alcohols, aldehydes, and oxides may often be carried out most advantageously in the vapor phase.

During the past few years a considerable number of new syntheses have been developed, and marked progress has been made in improving the operating technic in the industrial manufacture of amines from halogeno and oxygen-containing compounds. Of importance also has been the fundamental research leading to a better understanding of these reactions. In this brief review mention will be made only of those syntheses of each class in which substantial progress has been made.

Replacement of Halogen

Aniline from Chlorobenzene. Although the patent literature (*19*) and trade journals have given ample evidence of activity and progress in the manufacture of aniline from chlorobenzene,



there have been until recently no adequate published operating data regarding this important amination process. Vorozhtzov (*48*) reported the results of an investigation based on methods disclosed in Dow patents (*19*). The procedure consists in reacting chlorobenzene with aqueous ammonia in the presence of cuprous oxide at 190° to 230° C. The reaction mass from the autoclaves is cooled and permitted to settle, whereby the charge separates into two layers—a dark brown layer comprising principally aniline and an almost colorless upper aqueous layer which rapidly becomes blue on exposure to air. The volume of the water layer will, of course, be considerably greater than that of the aniline layer and will vary with the ammonia liquor ratio. When 5 moles of 32 per cent ammonia and 0.1 mole of cuprous oxide were used per mole of chlorobenzene, Vorozhtzov found that the products of reaction were distributed as follows (in per cent by weight):

Component	Aniline Layer	Water Layer
Aniline	81.55	4.9
Phenol	4.9	0.33
Diphenylamine	0.85	...
Chloride ion (NH_4Cl)	Trace	8.84
Cu_2O	Trace	2.9
NH_3	...	13.8

To recover the aniline and other products from the crude aniline, 50 per cent sodium hydroxide is added to the charge in an amount corresponding to 0.2 per cent of its volume. The batch is then subjected to fractional distillation, using jacket heat. The first fraction is aniline-water, and this is followed by a technically pure aniline of 97 to 99 per cent purity, which contains neither phenol nor diphenylamine. The weight of aniline thus recovered corresponds to 90 per cent of the amine originally present. After the removal of the aniline, the charge still contains sodium phenolate and diphenylamine. The latter is separated by distillation with steam; the phenol is recovered by acidifying the residue and distilling.

Alkali is also added to the water fraction in an amount sufficient to react with all ammonium compounds and with phenol. Upon fractional distillation, ammonia is first expelled and then recovered in a suitable absorption system. An aniline-water fraction is next distilled from which an aniline layer separates out on cooling. The supernatant aqueous portion containing a small quantity of amine can be used advantageously in the ammonia absorption system. The residual solution of sodium phenolate and sodium chloride is then filtered from the precipitated copper oxides. The recovered copper oxide catalyst is washed and again used along with fresh copper in subsequent operations (*11*).

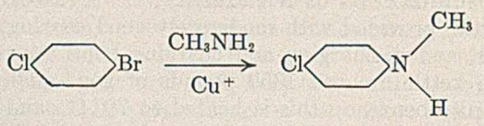
TABLE I. EFFECT OF AMMONIA RATIO ON ANILINE PREPARATION[a]

Mole Ratio NH_3/ Chlorobenzene	Temperature	Decomposition	Aniline Yield: % to C_6H_5Cl used	Aniline Yield: % to C_6H_5Cl which reacts	Phenol Yield	Ratio, Aniline/ Phenol	Diphenylamine Yield, % of Theoretical
	° *C.*	%	% of theoretical	% of theoretical	% of theoretical		
3	187–244	89.1	78.3	87.8	5.2	15.1	1.7
4	188–239	98.5	89.0	90.5	5.3	16.8	1.8
3	193–242	84.2	72.2	85.7	5.5	13.1	1.5
4	193–237	95.5	83.5	87.5	5.5	14.8	1.9
5	192–230	99.1	88.2	88.9	5.6	15.8	1.5
6	196–229	99.6	89.8	90.2	5.5	16.6	1.0
8	194–222	99.5	90.0	90.4	5.2	17.3	1.0
12	192–215	98.2	90.6	92.3	5.0	17.9	0.0

[a] 0.2 mole CuO per mole chlorobenzene; operating pressure 70 atmospheres or 980 pounds per square inch. Size of charge adjusted for 21 per cent freeboard at room temperature according to Vorozhtzov (*48*).

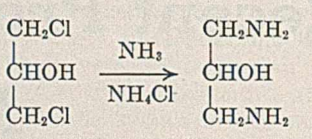
The data in Table I (*48*) show that an increase in the ammonia ratio results in (*a*) a better yield of aniline, (*b*) an increase in the ratio of aniline to phenol, and (*c*) a slight diminution in the yield of diphenylamine. These characteristics are especially marked in proceeding from 3 to 5–6 moles of ammonia per mole of chlorobenzene. A further increase in the ratio of aqueous ammonia has only a relatively small effect on the conversion and yield of aniline.

PREPARATION OF CHLOROANILINES. The comparative ease in replacing the bromine atom of 4-chlorobromobenzene can be taken advantage of in the preparation of 4-chloroaniline as well as 4-chloro-(*N*-methyl-) aniline (*34*):



For the preparation of the substituted amine, 19.2 parts by weight of 4-chlorobromobenzene are reacted with 45 parts of aqueous monomethylamine (33 per cent) in the presence of 2 parts of cuprous chloride for 5 hours at 110° C.

1,3-DIAMINOPROPANOL-2 FROM GLYCEROL DICHLOROHYDRIN. In this synthesis,



$$\begin{matrix}CH_2Cl\\|\\CHOH\\|\\CH_2Cl\end{matrix}\xrightarrow[NH_4Cl]{NH_3}\begin{matrix}CH_2NH_2\\|\\CHOH\\|\\CH_2NH_2\end{matrix}$$

the principal precautions to be observed, according to Bottoms (*8*), are: (*a*) use of methanol or ethanol as a solvent for the 1,3-dichloropropanol-2, (*b*) use of a large excess of concentrated (50 to 60 per cent) aqueous ammonia, (*c*) the introduction of ammonium chloride, and (*d*) the gradual introduction of the dichlorohydrin into the reaction vessel containing the ammoniacal solution. Under such conditions the formation of secondary and tertiary amines and 1-amino-2,3-dihydroxypropane is inhibited.

The method of operation is as follows: 375 grams of ammonium chloride are dissolved in 1750 grams of water, and the mixture is placed in a jacketed autoclave equipped with a mechanical stirrer. Thirty-five hundred grams of anhydrous ammonia are added, and the temperature is brought up to 45–55° C. A solution consisting of 450 grams of glycerol dichlorohydrin and 300 grams of methanol is then pumped into the autoclave. The reaction is complete in 45 minutes.

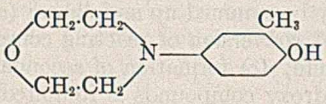
After removal of the excess ammonia, the charge is transferred to a still, and 560 grams of sodium hydroxide are added. The liberated ammonia is distilled, and the remaining solution is concentrated to a small volume. Subsequent to removal of the precipitated salt by filtration, the amine is taken up in 500 cc. of ethanol and then distilled. The 1,3-diaminopropanol-2 distills over at 145–165° C. and 20-mm. pressure.

Pure 1,3-diaminopropanol-2 is a white crystalline solid melting at 42° C. and boiling at about 235° C. Because of its pronounced basic properties, high degree of stability over a wide temperature range, ready solubility in water, and low vapor pressures at low and high temperatures, it is an effective absorbent for acidic gases such as carbon dioxide and hydrogen sulfide. It combines chemically with such gases at comparatively low temperatures and is regenerated at elevated temperatures, during which process the absorbed gases are liberated. The apparatus shown in Figure 1 was suggested by Bottoms (*7*) for the absorption of acidic gases by amines.

MORPHOLINE FROM β,β'-DICHLORODIETHYL ETHER. When the 2 chlorine atoms of *sym*-dichlorodiethyl ether are replaced by the imino group through the action of anhydrous ammonia, morpholine is obtained (*14*):

The synthesis is carried out as follows: 400 parts by weight of *sym*-dichlorodiethyl ether dissolved in 500 parts of benzene are introduced into a nickel-lined autoclave, and 286 parts of liquid anhydrous ammonia are added. The total pressure is increased to about 1500 pounds per square inch (105.5 kg. per sq. cm.) by the addition of nitrogen gas. The temperature of the charge is brought to 50° C., corresponding to a pressure of 1750 pounds (123 kg.) and thus maintained for 24 hours. The ammonia is vented and reliquefied. The benzene and unreacted β,β'-dichlorodiethyl ether remain in the autoclave along with aliphatic amines and ammonium chloride. After filtering off the ammonium chloride, the constituents of the liquid are separated by fractional distillation. Based on dichlorodiethyl ether consumed, the yield of morpholine is 80 per cent.

When the β,β'-dichlorodiethyl ether is reacted with hydroxyamino compounds—e. g., 2-methyl-4-aminophenol—instead of ammonia, the resultant product is 3-methyl-4-hydroxy-*N*-phenylmorpholine (*39*):



Ammonolysis of Alkylene Dihalides. The preparation of ethylenediamine and the polyamines obtained concomitantly through condensation have been reported by a number of investigators. Curme (*16*) described a continuous process where ethylene dichloride is added to a large excess of aqueous ammonia maintained at 110° C. and 10 atmospheres pressure. Lauter (*32*) reported a process involving the use of sufficient metal salts to form a ternary complex with ammonia and dichloroethane, from which ethylenediamine is obtained upon hydrolysis. Bersworth (*6*) preferred to inject ethylene dichloride under pressure into a heated pressure system containing anhydrous ammonia vapors at 150° C. Anhydrous needles of ethylenediamine dihydrochloride are obtained which, on hydrolysis with alkali, yielded the free amine.

Mnookin (*35*) used a dilute aqueous ammonia and obtained the expected mixture of polyamines. When 1600 grams of water, 340 grams of 28 per cent ammonia liquor, and 200 grams of ethylene dichloride are heated at 140° to 150° C. for approximately 1 hour, all of the halide has entered into reaction. The product consists approximately of the following:

Component	B. P., ° C.	Formula	Per Cent
Ethylenediamine	118	$H_2N{\cdot}CH_2{\cdot}CH_2NH_2$	40
Diethylenetriamine	208	$H_2N{\cdot}CH_2{\cdot}CH_2$ >NH $H_2N{\cdot}CH_2{\cdot}CH_2$	30
Triethylenetetramine	266	$H_2N{\cdot}CH_2{\cdot}CH_2$ >NH / $CH_2{\cdot}CH_2$ HN \ $CH_2{\cdot}CH_2NH_2$	20
Higher polyamines	...	....	10

Nafash (*36*) developed a cyclic process for the preparation of ethylenediamine and other primary alkylamines from the corresponding bromine derivatives. A combination of well-known chemical reactions is employed according to the following equations:

$$C_2H_4Br_2 \xrightarrow{NH_3} C_2H_4(NH_2)_2{\cdot}2HBr$$

$$C_2H_4(NH_2)_2{\cdot}2HBr + 2NaOH \longrightarrow C_2H_4(NH_2)_2 + 2NaBr + 2H_2O$$

$$2NaBr\ (aq.) + Cl_2 \longrightarrow 2NaCl + Br_2$$

$$NaBr\ (aq.) + Cl_2 \longrightarrow NaCl + BrCl$$

$$C_2H_4 \xrightarrow{Br_2} C_2H_4Br_2$$

$$C_2H_4 \xrightarrow{BrCl} C_2H_4BrCl$$

The alkyl bromides are more costly than the corresponding chlorine derivatives, and their use necessitates additional operating steps. These economic handicaps are, to a substantial extent, offset by certain advantages as follows: (*a*) the practicability of using weaker ammonia liquor, (*b*) the feasibility of operating at lower temperatures and pressures, and (*c*) the production of comparatively pure primary amines as the principal product.

For the preparation of ethylenediamine, the following procedure may be employed: Ethylene dibromide, preferably as a vapor, is introduced into a vertical autoclave partially filled with aqueous ammonia at 180° C. Reaction apparently occurs in the vapor phase with the formation of the solid dihydrobromide of ethylenediamine. During the course of the amination, the solid particles fall into the ammonia liquor, creating a slurry which is periodically removed. The solid ethylenediamine dihydrohalide is then treated with sodium hydroxide, whereupon the base is liberated and is recovered by subjecting the alkaline mass to distillation. The residue which is essentially an unsaturated solution of sodium bromide is treated with chlorine gas, and the bromine is set free. The continued bubbling of chlorine into the solution apparently effects the solution of bromine, presumably as bromochloride. Although bromine and chlorine are soluble in their saturated salt solutions only to about 4 per cent by weight, 40 parts by weight of bromine, when treated with chlorine, will dissolve in 75 parts of saturated sodium chloride solution. When ethylene is introduced into the vessel containing the liberated bromine, ethylene dibromide is immediately formed, admixed with some of the corresponding bromochloride or dichloride.

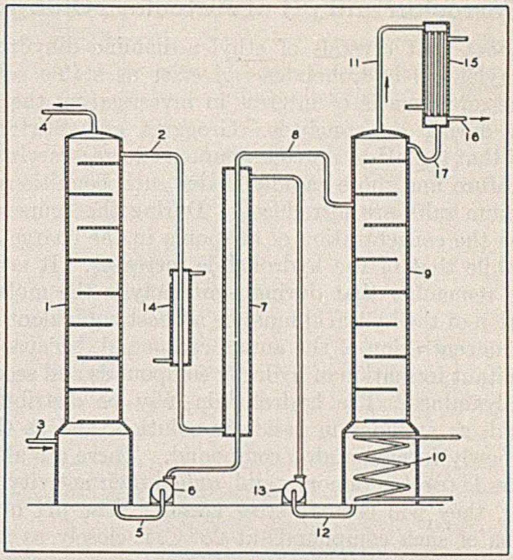


Figure 1. Plant Layout for Absorbing Acidic Gases by Amino Compounds

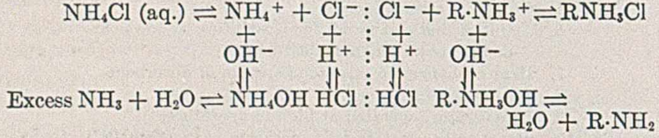
1. Absorber, containing solution of amino compound and provided with contact filler and baffles
2. Inlet for absorbing agent—e. g., diaminopropanol and triethanolamine
3. Inlet for acidic gases
4. Outlet for stripped gases
5, 6. Outlet line and pump for circulating amino compound containing absorbed gases
7. Heat exchanger to raise temperature of absorbent
8. Inlet pipe to regenerator
9. Regenerator, operated at high temperatures
10. Steam coil to maintain temperature of regenerator
11. Outlet for gas driven from absorbent agent
12, 13. Outlet line and pump for regenerated amine
14. Heat exchanger to cool absorbent agent
15. Condenser for vapors of absorbent agent
16. Outlet for cooled acidic gases
17. Return trap to regenerator

Corrosion and pH of Autoclave Charge

The fact that crystals of ethylenediamine dihydrohalide and alkylamine hydrohalides can exist as stable solids in aqueous ammonia is of interest in investigating the roll of amines during ammonolysis. Groggins and Stirton (*23*) showed that the pH of aqueous ammonia decreases with rising temperature and more rapidly under such conditions when ammonium salts are introduced. During the course of the reaction the concentration of ammonia in the charge diminishes while that of the hydrohalide increases. It is important to remember that during ammonolysis the molar concentration of the hydracid must be at least equivalent to the molar concentration of the amino compound, because of the concomitant formation of hydroxy compounds and secondary and polyamines. The hydrohalide may be distributed as free acid, as ammonium halide in solution, and as the salt of the newly formed amino compound. These are all acidic compounds (proton donors), and, unless their activity is neutralized, they will corrode steel vessels. The pH of molar solutions of such compounds at 25° C. is closely as follows:

NH_4Cl, 4.7; $CH_3NH_2\cdot HCl$, 5.5; $C_2H_5NH_2\cdot HCl$, 6.0; $C_6H_5NH_2\cdot HCl$, 2.3; $C_5H_5N + NH_4Cl$, 7.1

In closed systems containing an excess of aqueous ammonia in addition to corresponding molal concentrations of hydrochloric acid and primary amine, the equilibria involved may be represented as follows:



$$\begin{array}{l}
\qquad\quad NH_4Cl\ (aq.) \rightleftharpoons \overset{\displaystyle NH_4^+}{} + Cl^- : Cl^- + R\cdot NH_3^+ \rightleftharpoons RNH_3Cl \\
\qquad\qquad\qquad\qquad\quad + \qquad\quad + \ : \ + \qquad\quad + \\
\qquad\qquad\qquad\qquad OH^- \qquad H^+ : H^+ \qquad OH^- \\
\qquad\qquad\qquad\qquad\ \ \downarrow\uparrow \qquad\quad \downarrow\uparrow \ : \downarrow\uparrow \qquad\ \ \downarrow\uparrow \\
\text{Excess } NH_3 + H_2O \rightleftharpoons NH_4OH\ HCl : HCl\quad R\cdot NH_3OH \rightleftharpoons \\
\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad H_2O + R\cdot NH_2
\end{array}$$

The available information regarding these reactions at high temperatures is inadequate, and our knowledge relates only to certain segments of the whole. There is little doubt, however, that the principal factors which affect the equilibria are (1) the temperature of the system, (2) the relative basicity of the amine, and (3) the solubility of the amine.

Because of its volatility, ammonia can be displaced from $[H(NH_3)]Cl$ by basic substances of higher boiling point, for this reaction is practically independent of the strength of the base. The rate at which such displacement occurs, however, obviously depends on the strength of the base—e. g., calcium hydroxide, alkylamine, etc.—the reaction temperature, and the counter influence of free ammonia. It is known, however, that with increasing temperature ammonia has a diminishing capacity to form the ionogen, ammonium hydroxide, and at 290° C. the union of ammonia to hydrogen chloride in aqueous $[H(NH_3)]Cl$ is so weak that the two components react as if they were alone, and ammonium chloride in aqueous solution can be employed to convert methanol to dimethylamine (*9*) and *sym*-xylenol to dixylylamine. The fact that the charge and free space in the autoclave contain a large excess of gaseous ammonia does not, therefore, signify that the hot aqueous ammonia has the capacity to hydrolyze all amino hydrohalides, for there is evidence to the contrary (*36, 44*). When the amino hydrohalide is insoluble, then the concentration of the phenyl ammonium ions in solution is diminished.

From the extensive literature on inhibitors, it would be expected that the amino compound being synthesized should serve as its own inhibitor, and indeed it would if sufficient free base were available. It is well known that the addition of aniline to aniline hydrochloride will reduce the dissociation and, consequently, the corrosive action of the latter (*10*). This probably explains why it has been found efficacious to add acid inhibitors—e. g., alkylamines, secondary amines, and pyridine—to the autoclave charge in the preparation of nitroamines (*17*). It is probable that the reintroduction of some of the amine (any subspecification material) being synthesized would accomplish the same purpose, for this procedure would ensure the presence of free base during ammonolysis.

Two other useful methods of controlling the pH of the autoclave charge are the introduction of copper-ammonio hydroxides (*11*) and the use of buffer oxidants (*24*), such as chlorates which are attacked and decomposed when the concentration of the hydracid is sufficiently great. The oxidants cannot be used to advantage, however, when the amino compound—e. g., aniline—is readily susceptible to oxidation.

EFFECT OF AMMONIA CONCENTRATION. Extensive investigations in the ammonolysis of halogeno compounds have shown that the practical advantages to be obtained by utilizing a more concentrated ammonia solution for noncatalytic aminations may be summed up as follows: (*a*) Amination is more rapid; (*b*) conversion of reacting compound to amine is more complete; (*c*) formation of secondary and tertiary amines and hydroxy compounds is inhibited; (*d*) lower reaction temperatures can be used; and (*e*) since larger batches can be treated with the same quantity of liquor, economies in the number of pieces of equipment can be effected.

The effect of ammonia concentration in catalytic ammonolysis has been investigated by Vorozhtzov and Kobelev (*48*) and by Groggins and Stirton (*25*). The practical benefits of employing higher ammonia concentrations are brought out clearly by the data in Table II. In these experiments, as in plant practice, a constant ratio of ammonia and copper to 4-chloroxenene was provided. From the tabulated data it can be concluded: (*a*) For any particular ammonia concentration, within limits, the rate of conversion is a function of the copper-ammonio concentration; (*b*) most of the generalizations relating to the noncatalytic ammonolysis of halogeno compounds are equally valid; (*c*) the difference between conversion—i. e., decomposition of halogeno compound—as determined by chloride ion, and amination, for 18 per cent copper, is approximately twice as great as that for 12 per cent copper; and (*d*) as the ammonia concentration is increased, this "difference" becomes less, despite the fact the reaction has proceeded further.

TABLE II. INFLUENCE OF AMMONIA CONCENTRATION IN PREPARATION OF XENYLAMINE[a] (*25*)

Expt. No.	NH_3 Concn.	Aqueous NH_3	4-Chloroxenene	$Cu(NO_3)_2\cdot 3H_2O$	Catalyst Concn.	Conversion, *A*	Amination, *B*	100 × Mole Ratio Cu/R·Cl	Mole Ratio NH_3/R·Cl	Difference *A* − *B*
	%	*Grams*	*Mole*	*Mole*	*Gram atom Cu/liter*	%	%			
1	14	304	1/6	0.03	0.0932	55.31	45.14	18	15	10.17
2	21	304	1/4	0.045	0.1360	66.20	57.68	18	15	8.52
3	28	304	1/3	0.06	0.1770	86.35	80.15	18	15	6.20
4	35	292	2/5	0.072	0.2169	93.26	88.77	18	15	4.49
5	21	304	1/4	0.072	0.2175	85.56	73.82	28.8	15	11.74
6	14	304	1/6	0.02	0.0621	41.20	35.73	12	15	5.47
7	21	304	1/4	0.03	0.0906	58.38	53.44	12	15	4.94
8	28	304	1/3	0.04	0.1180	74.10	71.35	12	15	2.75
9	35	292	2/5	0.048	0.1446	87.02	84.41	12	15	2.61
10	35	292	1/4	0.048	0.1446	98.92	88.99	19.2	24	9.93
11	21	304	1/4	0.048	0.1450	73.38	64.06	19.2	15	9.32

[a] 16 hours at 200° C.

Reaction rate studies showed that the effect of ammonia concentration on the rate of conversion in catalytic ammonolysis depends upon: (*a*) the ammonia ratio, (*b*) the reaction temperature, and (*c*) the halogeno compound (*25*). This is to be expected because the solubility of the organic compound is not the same in all ammonia solutions. It would be the same for the various systems only if there were no significant differences in solubility in 21, 28, and 35 per cent aqueous ammonia; but the solubility of the halogeno compound, like the respective partial pressures, is an intrinsic property of the ammonia used, and there is no satisfactory way of disassociating this factor in comparing the reactivity of ammonia solutions. When comparisons are made at comparatively high temperatures or with excessive ammonia ratios (Figure 2), the advantageous properties of concentrated ammonia are obliterated; consequently, the conclusions drawn from reaction rate studies in homogeneous systems ignore the penalty that technical operations must pay for employing weak ammonia.

The results in Table III relating to the preparation of 1-naphthylamine show that at 180° C. an increase in conversion and amination rates is brought about by the use of stronger ammonia. When the reaction temperature is raised to 200° C., the conversion rate for 28 per cent aqueous ammonia is still better than that for 21 per cent ammonia, but the 35 per cent solution no longer has an advantage. The amination rates are, however, better with increased ammonia concentration.

TABLE III. REACTION RATE STUDIES IN AMINATION OF 1-CHLORONAPHTHALENE[a] (*25*)

Expt. No.	NH_3 Concn. %	Cl^- %	1-Naphthylamine %
Temp. 180° C.; Chloronaphthalene Taken, 0.2 Mole; Mole Ratio NH_3/Chloronaphthalene, 18.75; *b* = Gram Atom Cu/Liter = 0.12085			
1[b]	28	0.21	0
2	21	5.54	2.32
3	28	7.84	4.90
4	35	8.62	5.66
Temp., 200° C.; Chloronaphthalene Taken, 0.3 Mole; Mole Ratio NH_3/Chloronaphthalene, 12.5			
5	21	12.02	10.91
6	28	14.43	12.38
7[c]	28	14.59	12.93
8	35	14.44	13.16

[a] Time, 5 hours; catalyst, CuCl.

[b] No catalyst. [c] $Cu(NO_3)_2 \cdot 3H_2O$ as catalyst.

Treatment of Sulfonic Acids

No technical advances in the well-known method of preparing 2-aminoanthraquinone from sodium anthraquinone-2-sulfonate have been reported recently.

Of considerable economic significance, however, is the preparation of "silver salt" from the sulfoketo acid by cyclization. When 4′-chloro-2-benzoylbenzoic acid, which is readily prepared according to the Friedel and Crafts reaction from chlorobenzene and phthalic anhydride, is reacted with a sodium sulfite solution under pressure, the corresponding 4′-sulfo-2-benzoylbenzoic acid is obtained (*46*). On cyclization with concentrated sulfuric acid, this leads solely to anthraquinone-2-sulfonic acid from which 2-aminoanthraquinone of high purity is readily obtained by ammonolysis.

Oxygen-Containing Compounds

Undoubtedly the greatest recent research progress in the field of ammonolysis has been made in the conversion of oxygen-containing compounds. The amines derived from alcohols, aldehydes, alkylene, and other oxides have wide technical application, and new industries are taking root in this soil, tilled by the tools of chemical exploration.

CONVERSION OF ALCOHOLS. The literature reveals that practically the whole range of primary alcohols from methyl and butyl to cetyl and stearyl alcohols has been investigated. The synthesis of low-molecular-weight alkylamines from alcohols is almost always carried out in the vapor phase, according to the method of Sabatier and Maihle (*40*) in which the reacting alcohol and ammonia are passed over a dehydrating catalyst. Compounds of aluminum or phosphorus—e. g., alumina (*2*, *43*), aluminum silicate (*2*, *33*), aluminum phosphate (*1*), and diammonium phosphate (*1*)—are most frequently employed for this purpose. As in the amination of alkyl halides, the product of reaction may comprise primary, secondary, and tertiary amines, depending on the specific alcohol, the ammonia ratio, and other conditions employed. The net reaction may be expressed thus:

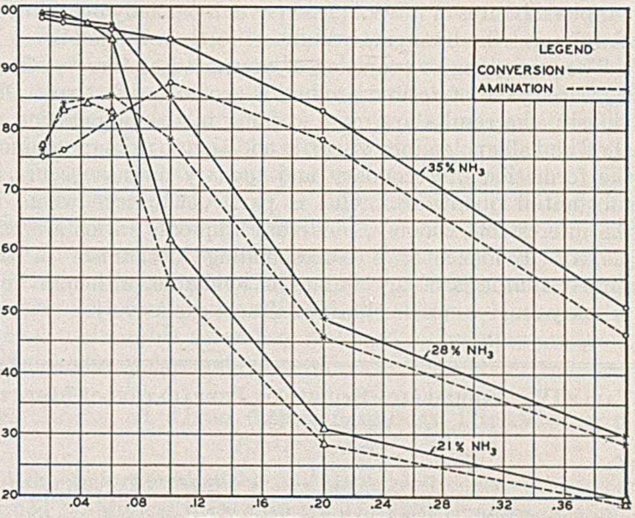
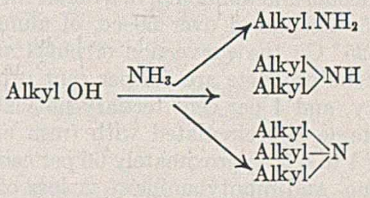


FIGURE 2. AMINATION OF 4-CHLOROXENENE

20 hours at 200° C., 0.12 mole of $Cu(NO_3)_2 \cdot 3H_2O$.

% NH_3	Moles Taken
21	3.75
28	5
35	6



A typical mode of manufacture of methylamines is as follows: Absolute methanol at the rate of 0.75 to 1.5 cc. per cc. of catalyst per hour, together with sufficient anhydrous ammonia to give a molecular ratio of 3–4 methanol to 1 ammonia is preheated to 325° C. and passed over an alumina gel catalyst maintained at 450° C. Under these conditions the initial conversion to total amines, based on ammonia input, is 85 per cent, of which 57 per cent is tertiary and 28 per cent secondary with no primary amine. The tertiary amine is separated from the secondary and recirculated with fresh reactants; the resultant product then contains only about 8 per cent tertiary amine, whereas the conversion to secondary amine is 45 to 50 per cent, based on ammonia consumption. When the ratio of ammonia to methanol is in the order of 4–5 to 1, then the product consists primarily of monomethylamine with only small amounts of the secondary and tertiary amines.

Since it is difficult and often uneconomical and impracticable to arrange operating conditions for the production of one of the amines, it is customary to rework the products under suitable conditions or to reintroduce them into the amination system along with fresh reactants (*28*, *45*). Swallen and Martin (*45*) showed that primary methylamine can be converted to dimethylamine and trimethylamine by repassing it through the catalytic chamber in the absence of ammonia. The results obtained when methylamine and various mixtures of it were passed over a partially dehydrated aluminum trihydrate catalyst are set forth in Table IV.

The reworking or recycling of unwanted amines to afford a greater yield of desired product is generally effective. Obviously, the results are more striking in the preparation of alkyl and alkanolamines where, in addition to primary amines, the formation of secondary and tertiary amines occurs in substantial quantities. This is particularly true when, in the interest of economy, moderate ammonia ratios are employed. Evidence of a corresponding mechanism in the similar synthesis of arylamines is available, although here primary amines can be obtained almost exclusively.

TABLE IV. EQUILIBRIUM STUDIES ON PREPARATION OF METHYLAMINES (*45*)

Compn. of Feed	Temperature	Space Velocity, Ratio Gas/Catalyst	Compn. of Product			
			NH_3	CH_3-NH_2	$(CH_3)_2$-NH	$(CH_3)_3$-N
	° *C.*	*Cc.*	%	%	%	%
100% CH_3NH_2	450	550	33.2	31.8	31.4	3.6
	450	550	31.8	31.3	32.6	4.3
87.0% CH_3NH_2 + 13.0% $(CH_3)_3N$	425	400	27.0	25.3	33.1	15.6
	425	400	25.4	29.8	27.7	17.1
	450	670	35.2	27.6	24.4	12.9
	450	630	39.0	33.6	16.3	11.1
	450	550	29.2	26.5	29.8	14.5
	450	550	30.4	26.4	28.6	14.6
	475	510	40.0	28.2	16.4	15.3
	475	420	38.0	26.6	17.4	18.0
65% CH_3NH_2 + 20.2% $(CH_3)_2NH$ + 14.8% $(CH_3)_3N$	450	680	38.6	23.6	17.4	20.4
	450	350	32.0	25.8	26.2	15.9

In contrast to and supplementing the data of Table IV, showing the formation of di- and trimethylamines from monomethylamine, are the results obtained by Arnold (*3*) in the conversion of *tert*-butylamine to the more basic amines. When butyl alcohol and ammonia, in a molar ratio of approximately 1 to 5, are passed over 50 cc. of alumina-silica gel catalyst at 325° C., the conversion of butyl alcohol is 25.2 per cent and the products are 5.2 per cent primary, 16 per cent secondary, and 4 per cent tertiary butylamine. When the tributylamine is recirculated with fresh ammonia in a molar ratio of 1 to 6.5, approximately 66 per cent of it is converted to mono- and dibutylamines. A loss of about 3 per cent is sustained through the formation of butylene. Hale (*26*) showed that also in the liquid-phase synthesis of butylamines from the corresponding halogeno derivative, the *sec*- and *tert*-butylamine can be successfully recycled for the production of primary butylamine.

The amines of the high-molecular-weight fatty acids are best prepared in a pressure system. Cetylamine is thus obtained by conducting cetyl alcohol and ammonia through a catalytic reaction chamber containing aluminum oxide which is kept at 380–400° C. (*42*) and under a pressure of 125 atmospheres. The vented vapors are condensed and yield an oily liquid containing some water. Upon distillation of the oil, cetylamine is obtained. Oleyl and stearyl alcohols react in a similar fashion. When alkylamines are employed instead of ammonia, the corresponding alkylamino compounds are formed. Thus, monoisobutyl dodecylamine is prepared from 1 part *n*-dodecyl alcohol and 10 parts monoisobutylamine (*42*). It is also possible to carry out the ammonolysis of the higher fatty alcohols in the vapor phase (*4*). A mixture of primary, secondary, and tertiary alcohols is usually obtained.

TAURINE FROM HYDROXYETHANESULFONIC ACID. Taurine, along with some ditaurine, can be obtained by reacting 256 parts by weight of sodium hydroxyethanesulfonate with 800 parts of 25 per cent ammonia liquor at 210° C. for 3 hours. The addition of 10 parts of sodium sulfite aids materially in increasing the conversion, which falls off as the quantity of sodium sulfite is reduced:

$$OH{\cdot}CH_2{\cdot}CH_2{\cdot}SO_3Na \xrightarrow[Na_2SO_3]{NH_3} H_2N{\cdot}CH_2{\cdot}CH_2{\cdot}SO_3Na$$

The synthesis is of particular interest because it shows that, in aliphatic compounds containing both sulfonic and hydroxyl groups, the —OH group can be replaced preferentially by —NH_2 (*38*) and $—N\begin{matrix}\diagup \text{alkyl}\\ \diagdown H\end{matrix}$ (*37*). In addition to sodium sulfite, other salts such as sodium carbonate can be used. In the preparation of the alkylamino derivatives—e. g., methyltaurine—the introduction of potassium hydroxide is found to be advantageous.

AMMONOLYSIS OF ALDEHYDES. The conversion of aldehydes to amines is generally carried out in the presence of a hydrogenation catalyst—e. g., nickel—for here the intermediate reduction of the aldehydic group necessitates the presence of hydrogen. When unsaturated aldehydes such as acrolein are reacted, saturation as well as amination takes place, and a normal primary amine—viz., propylamine—will be obtained.

GLUCAMINE AND RELATED PRODUCTS FROM MONOSACCHARIDES. Stable hydroxyamino compounds can be prepared readily by reacting ammonia or an aliphatic amine with monosaccharides in the presence of hydrogen and a suitable reducing catalyst:

$$CH_2OH(CHOH)_4CHO \xrightarrow[Ni]{NH_3 + H_2} CH_2OH(CHOH)_4CH_2NH_2$$

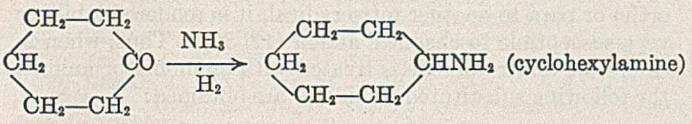
These reactions are exemplified by the following synthesis of glucamine (*22*): Twenty-five hundred grams of commercial glucose are charged into an autoclave containing 2500 grams of 21 per cent aqueous ammonia and 250 grams of a reduced nickel catalyst. Hydrogen is then introduced until a pressure of about 100 atmospheres is obtained, and the charge is stirred rapidly without heating for 0.5 hour to effect solution of the glucose. With the application of heat, hydrogen absorption begins at 63° to 65° C., and the temperature is brought up to 95° C. Hydrogen is introduced periodically during a 0.5-hour period to replenish that consumed in the reaction. The charge which is then free from reducing sugars is filtered and concentrated. Glucamine is obtained in good yields as a viscous noncrystalline sirup. From the anhydrous sirup, glucamine can be crystallized out of methanol as a white crystalline compound melting at 127° C.

By treating glucose, xylose, fructose, and other monosaccharides with monomethylamine, the corresponding methylamino sugars are obtained. Any alkylamine with a replaceable hydrogen can be substituted for the methylamine to give a wide variety of alkylaminomonosaccharides (*21*).

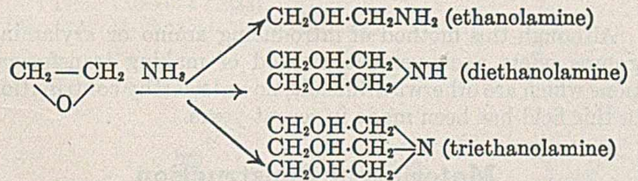
CONVERSION OF ALDEHYDES. Saturated and unsaturated aliphatic and aromatic aldehydes and intranuclear ketones can be converted to amines in the vapor phase by passing their vapors along with equal volumes of ammonia and hydrogen over a heated nickel catalyst (*5*). A reaction temperature of 125° to 150° C. has been found satisfactory. To avoid resinification of unstable unsaturated aldehydes or ketones before their contact with the catalyst, they are preferably vaporized separately and their vapors, admixed with fresh hydrogen, are led into the reaction system where they are mixed with the circulated preheated mixture of ammonia and hydrogen. The ammonolysis of acrolein, crotonaldehyde, and cyclohexanone, respectively, is as follows:

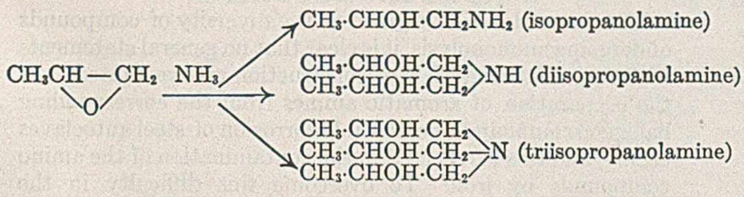
$$CH_2{:}CH{\cdot}CHO \xrightarrow[H_2]{NH_3} CH_3{\cdot}CH_2{\cdot}CH_2NH_2 \text{ (}n\text{-propylamine)}$$

$$CH_3{\cdot}CH{:}CH{\cdot}CHO \xrightarrow[H_2]{NH_3} CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2NH_2 \text{ (n-butylamine)}$$



Conversion of Alkylene Oxides to Alkanolamines. The alkylene oxides—e. g., ethylene (*29*), isopropylene (*29*, *50*), and isobutylene (*29*) oxides—can readily be converted to alkanolamines:



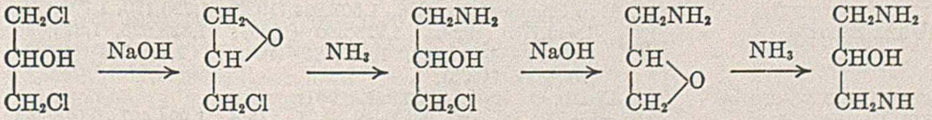


These reactions are exothermic, and an operating temperature of 50° to 60° C. usually suffices. When ordinary 28 per cent aqueous ammonia is employed, primary, secondary, and tertiary amines are obtained, the proportions being dependent on the ammonia ratio.

When propylene oxide is bubbled into aqueous ammonia at 40° to 50° C. in a sealed agitated vessel, the isopropanolamines are formed and can be separated by fractional distillation. Wickert (*50*) showed that it is feasible to control the proportions of the various amines by adjusting the relative concentration of the reactants. The curves in Figure 3 show clearly the relation of the reactants to the products. The physical properties of the ethanol- and propanolamines which find use as wetting agents, rubber accelerators, and absorbents for acidic gases, are as follows (*50*):

Amine	Specific Gravity, 20°/20° C.	Boiling Point at 5 Mm. ° C.	Freezing Point ° C.	1% Soln. Alkalinity pH
Monoisopropanol	0.981	45	−5	11.4
Diisopropanol	1.0089	116	32	11.1
Triisopropanol	1.0196	144	45	10.2
Monoethanol	1.0180	58	10.5	11.50
Diethanol	1.0984	156	28.0	11.75
Triethanol	1.1258	201	21.2	11.30

Although the alkylene oxides on ammonolysis give rise to amines with one to three alkanol groups, the epichlorohydrins derived from glycerol yield mono- and diaminopropanols. When 1 mole of glycerol dichlorohydrin is added to 2 liters of aqueous ammonia containing 2 moles of sodium hydroxide at 30° to 50° C., the conversion to diamine takes place according to the following scheme (*8*, *20*):

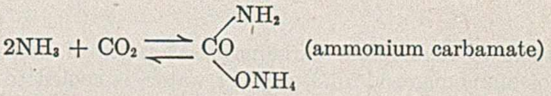


The first reaction that takes place probably is one between the dichlorohydrin and the sodium hydroxide in which one chlorine atom is removed with the formation of epichlorohydrin. This immediately reacts with a molecule of ammonia to form a glyceryl aminochlorohydrin, which then reacts with sodium hydroxide to form sodium chloride, releasing water and producing epiaminohydrin. The epiaminohydrin forthwith reacts with a further quantity of ammonia to produce the 1,3-diaminopropanol-2. The intermediate formation of epihydrins makes it necessary to have ammonia present in large excess and at the operating temperature, 50° C., in order to prevent the amino derivatives which are first formed from reacting with further quantities of the chlorohydrin and producing undesirable secondary and tertiary reaction products and complex polymers.

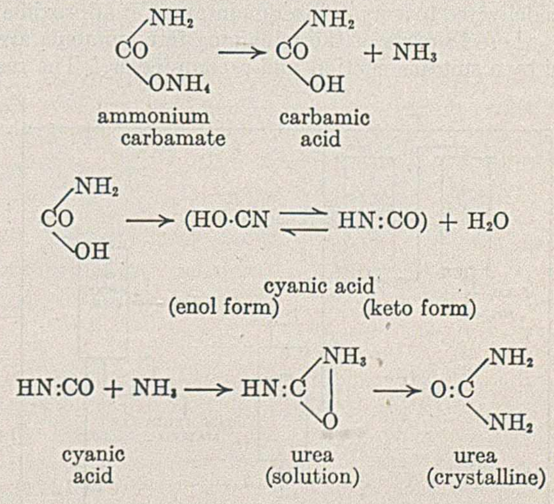
Synthesis of Urea from Carbon Dioxide and Ammonia

Although urea was the first of the organic compounds to be formed synthetically, its commercial production had to await the development of the synthetic ammonia process. Here the principal product, ammonia, and a by-product, carbon dioxide, which constitute the raw materials for urea production, are prepared cheaply.

The reactions involved in the formation of urea from carbon dioxide and ammonia are as follows (*49*):



At elevated temperatures urea is formed from ammonium carbamate by a series of reactions:



(*27*)

Although the transformation of ammonium carbamate to urea is not a direct dehydration, the presence of water is a limiting factor with respect to the extent that the reaction occurs. It has been found that at any temperature a definite equilibrium is established which can be approached from either direction (*15*). Krase and Gaddy (*31*) showed that a real shift in the carbamate-urea-water equilibrium is obtained by employing an excess of anhydrous ammonia, which functions as a strong dehydration agent. The employment of ammonia up to 280 per cent of that combined as carbamate gives conversions to urea between 81 and 85 per cent of the carbamate ammonia.

The commercial production of urea from carbon dioxide and ammonia is carried out as a continuous process, Figure 4 (*18*). Approximately 102 parts of ammonia and 44 parts of carbon dioxide are compressed and delivered separately as liquids (or compressed gases) into a steam-heated autoclave at 190° C.; maintaining an internal autoclave pressure of approximately 200 atmospheres. About 2 hours are required for the passage of the materials through the autoclave, during which interval the reactants are almost wholly converted to ammonium carbamate, which in turn is transformed largely to urea. From the autoclave the melt, consisting of 11.7 parts of ammonium carbamate, 51 parts of urea, 68 parts of ammonia, and 15.3 parts of water, is cooled to approximately 150° C. and is then admitted to a urea still which is maintained at 60° C. Here 42.3 parts of unconverted ammonia and any unreacted carbon dioxide are removed and collected for return to the system. The urea-water solution is then delivered to a crystallizer maintained at approximately 15° C. where 18 parts of the remaining free ammonia are removed by a suitable suction pump compressor. The resultant magma is passed to a continuous centrifuge where 30 parts of crystalline urea are obtained. The mother liquor, comprising 11.7 parts of ammonium carbamate, 21 parts of urea, 7.7 parts of ammonia, and 15.3 parts of water, may be variously used in the manufacture of mixed fertilizer.

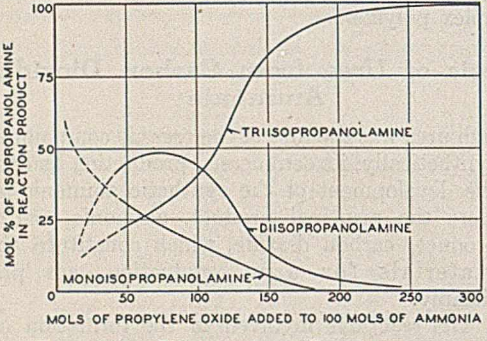


FIGURE 3. RELATION OF REACTANTS TO PRODUCTS

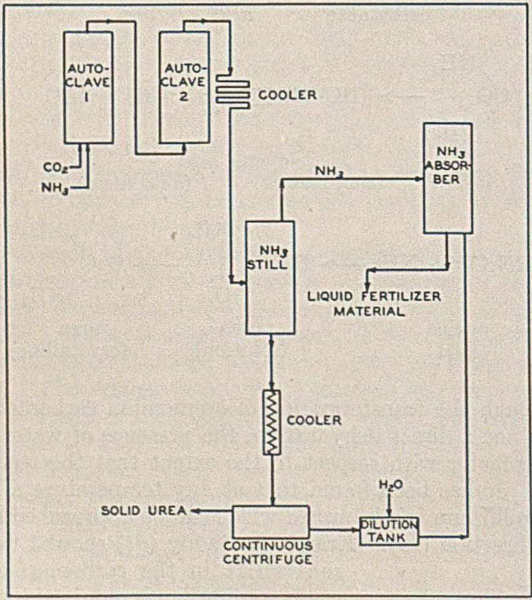
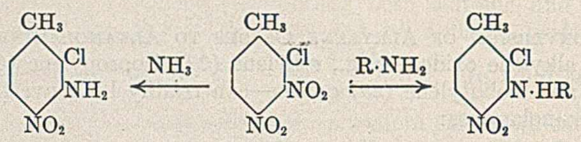


FIGURE 4. FLOW DIAGRAM IN THE UREA SYSTEM

Replacement of Labile Nitro Groups

It has long been known that, when a nitro group is found ortho or para to another nitro radical, it is rendered labile or very susceptible to chemical action (*12*, *30*). Thus, when 2-chloro-3,4-dinitrotoluene is treated with ammonia or aniline, the following substituted toluidines are obtained:



Although this method of introducing amino or arylamino groups offers a convenient method of making transformations which are otherwise difficult, no noteworthy contribution in this field has been made in recent years.

Materials of Construction

When consideration is given to the diversity of compounds undergoing ammonolysis, it is clear that no general statements with respect to materials of construction are warranted. In the preparation of aromatic amines from the corresponding halogeno compounds, perceptible corrosion of steel autoclaves occurs, and this is reflected in the contamination of the amino compounds by iron. To overcome this difficulty in the preparation of *p*-nitroaniline from *p*-nitrochlorobenzene, Saunders (*41*) advocated the use of acid-resistant stainless-steel alloys in the fabrication of the autoclave. The same material of construction is also endorsed for the similar preparation of other amines (*13*). In the preparation of urea, the liquid in the autoclave, consisting of a mixture of urea, water, ammonium carbamate, and free ammonia, is highly corrosive to ordinary materials of construction (*47*). Iron and steel are rapidly dissolved in it, and chromium steel and many alloys are rapidly attacked. Lead and silver are two of the most resistant materials and these metals are employed as linings for the autoclaves and stills used in this process. Resistant steel alloys are, however, used in the construction of parts where lower temperatures are encountered.

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Amination in Liquid Ammonia

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As a result of the present comparatively low price for liquid ammonia and the fact that amines are increasing in industrial importance, a study is being made of the use of liquid ammonia as a solvent for the unit process of amination. This paper reports some of the chemistry involved.

The reaction of alkyl halides, including isoamyl chloride, isoamyl bromide, isoamyl iodide, *n*-hexyl bromide, and 2-ethyl butyl bromide upon sodium amide and potassium amide, suspended in liquid ammonia, has been studied. Yields of 50 to 60 per cent of isoamylamine have been obtained from isoamyl bromide and iodide, and 30 to 40 per cent yields of isoamylamine from isoamyl chloride. With *n*-hexyl bromide 75 per cent yields of *n*-hexylamine have been obtained; 2-ethyl butyl bromide has given only about 10 per cent of 2-ethyl butylamine, along with 75 per cent yields of 2-ethylbutylene. These yields of amine are considerably higher than those reported in the literature for compounds of neighboring molecular weight. The fact that 50 up to 75 per cent yields of amines have been obtained from isoamyl and *n*-hexyl halides points out that this method may be valuable for the preparation of certain amines.

LEBEAU in an early article (*7*) described the reaction between a liquid ammonia solution of sodium and alkyl halides. Methyl iodide gave methane, ethyl iodide gave ethane, and propyl iodide gave propane. Chablay (*3*), in a later and more extensive investigation of the same type of reaction, gave the reactions as:

$$C_2H_5I + 2Na + NH_3 \longrightarrow C_2H_6 + NaI + NaNH_2$$
$$C_2H_5I + NaNH_2 \longrightarrow C_2H_4 + NaI + NH_3$$
$$C_2H_5I + NaNH_2 \longrightarrow C_2H_5NH_2 + NaI$$

n-Propyl iodide gave 71.4 per cent propane, 9.4 per cent propylene, and 21.2 per cent propylamine; isobutyl iodide yielded 69.8 per cent isobutane, 14.6 per cent isobutylene, and 15.6 per cent isobutylamine. Isobutyl chloride yielded only isobutane; isoamyl chloride yielded only isopentane; isoamyl iodide yielded isopentane, isoamylene, and isoamylamine.

Chablay (*2*, *3*) added alkyl halides gradually to suspensions of sodium amide in liquid ammonia at its normal boiling point. With methyl iodide the reaction was very vigorous and was said to lead to the formation of methylamine. The higher alkyl halides react with sodium amide to produce unsaturated hydrocarbons in amounts increasing with the molecular weight of the halide. Thus, ethylene was obtained in 5.4 per cent yield from ethyl iodide, propylene in 37 and 69.6 per cent yields from *n*-propyl iodide and *n*-propyl chloride, respectively, and isobutylene in 62.4 per cent yield from isobutyl iodide or in 83.6 per cent yield from isobutyl chloride.

Picon (*8*), Bergstrom (*1*), and White, Morrison, and Anderson (*11*) have also worked in this field.

Experimental Procedure

Suspensions of sodium amide were made in liquid ammonia, using ferric nitrate as a catalyst, according to Vaughn, Vogt, and Nieuwland (*10*), Franklin (*4*), and Kraus (*6*):

A 500-ml. three-neck flask was fitted with a mechanical stirrer, a dropping funnel, an air outlet through a drying tube containing soda lime, and a pentane thermometer with a range of −200° to +20° C. (Figure 1). The flask was cooled by means of a solid carbon dioxide–alcohol bath. (For lower temperature, ether was used as the solvent.) Approximately 300 ml. of am-

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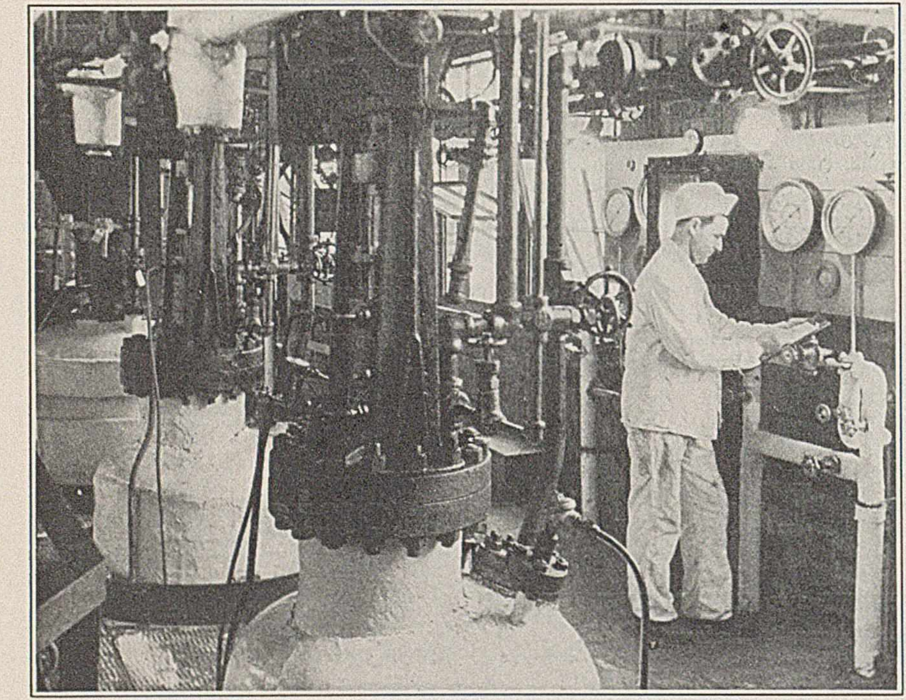

Courtesy, Monsanto Chemical Company

AMINATION CONTROL DEVICES

monia were condensed in the 500-ml. flask, and 0.15 gram of finely powdered ferric nitrate was added. With the stirrer running slowly, one-half molecular equivalent of the metal to be used was added in small portions slowly enough to prevent a too rapid rise in the temperature of the mixture. The mixture was stirred slowly for 15 to 20 minutes after addition of the last of the metal or until the blue metallic color had completely disappeared. The mixture was cooled to the desired temperature by means of the solid carbon dioxide–alcohol bath. With the mixture agitated thoroughly, one-half molecular equivalent of alkyl halide was added from the dropping funnel at a rate that would allow the temperature of the mixture to be maintained at the desired point. If the halide was added more rapidly than 30 to 40 drops per minute, the temperature of the mixture rose so rapidly that it could not be controlled by the cooling bath. The stirring and cooling were continued for about an hour after completion of halide addition.

The ammonia was evaporated slowly (about 24 hours for complete evaporation) by leaving the cooling bath around the reaction flask but not adding any more solid carbon dioxide. When the ammonia was all distilled, the contents of the reaction flask was hydrolyzed by dropwise addition (at the start) of water; 150 ml. of water were added in all. The mixture was then treated with 20 grams of sodium hydroxide to ensure the freeing of any amine present in the reaction product. Organic material was extracted from the mixture with three 75-ml. portions of ethyl ether. The ether extract was placed over solid sodium hydroxide to dry for about 15 hours in preparation for distillation.

In runs where isoamylene was formed, this compound (boiling at 20.5° C.) passed out of the reaction flask during evaporation of ammonia and hydrolysis of the reaction mixture. In order to identify the isoamylene, the ammonia and other gases passing from the reaction flask were led through a condensing coil which was cooled by means of an alcohol–solid carbon dioxide bath at −10° to −20° C. The cooling coil terminated in a 200-ml. round-bottom flask, its end dipping below the level of about 75 ml. of carbon tetrachloride contained in the flask. After completion of hydrolysis, the contents of the reaction flask was stirred and warmed to about 30° C. in order to drive over any remaining isoamylene. With the carbon tetrachloride solution maintained at 0° C., one-half equivalent of bromine, dissolved in 75 ml. of carbon tetrachloride, was added dropwise with shaking. The cooling bath was maintained at 0° C. for 2 hours and then gradually allowed to rise to room temperature with frequent shaking. The contents of the flask was treated with sodium bicarbonate to decompose excess bromine. The carbon tetrachloride solution was washed with water and placed over calcium chloride to dry. The solution was analyzed by distillation.

Analysis of Product

In every case the analysis was performed by distilling the dried ether extract through a Purdue modification of the Podbielniak column. The column consisted of a Pyrex glass reflux tube 8 mm. in diameter and approximately 110 cm. long. The reflux tube contained a Nichrome wire in the form of a spiral which provided for intimate contact between downgoing liquid and upcoming vapor. A dead-air jacket was provided by means of another and larger Pyrex glass tube (diameter, 25 mm.) surrounding the reflux tube. Upon this second glass tube was wrapped a spiral of Nichrome resistance wire for maintaining the desired column temperature. A third and larger glass tube (diameter, 45 mm.) provided another air jacket around the heating coil. The column was equipped for regulation of reflux and was connected to a vacuum line in order to provide for distillation under reduced pressure. The distillate was received in an inverted buret which allowed the quantity of distillate to be read to an accuracy of 0.1 ml.

All compounds which boiled at temperatures much over 100° C. were distilled under reduced pressures. In order to determine the boiling point at standard pressure of such compounds and thus the identity of the compound, the equation given by Hass and Newton (*5*) was used:

$$2.8808 - \log p = \frac{\phi\, dt}{273.1 + t - 0.15\, dt}$$

$\log p$ = log of observed pressure in mm. of Hg
t = observed b. p., ° C.
ϕ = entropy of vaporization at 760 mm.
dt = b. p. at 760 mm. minus t, ° C.

Figure 2 is a distillation curve for the product of reaction between sodium amide and isoamyl bromide in liquid ammonia solution at −50° C. The calculation of the yield for each run was made by use of a distillation curve of this type. The ether was first distilled from the ether extract, and then a record was made of millimeters of distillate *vs.* boiling temperature as the product came over.

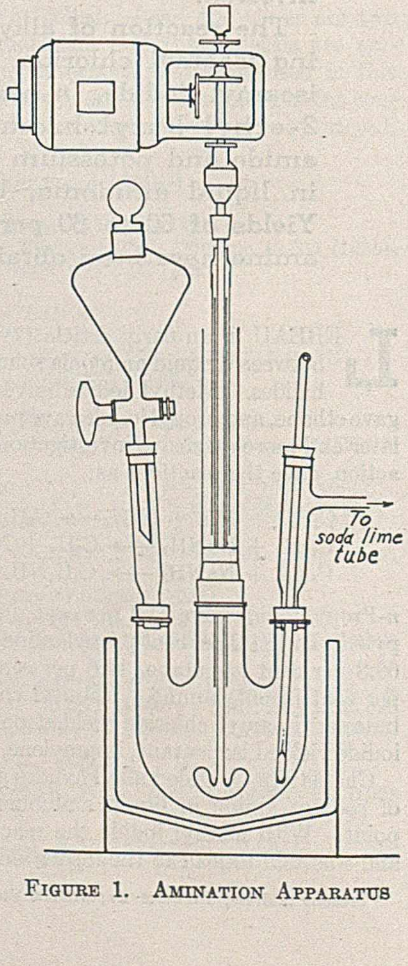

FIGURE 1. AMINATION APPARATUS

Use of Different Metallic Amides

In a preliminary investigation (in conjunction with A. R. Padgett), the difference in reaction of the amides of the four metals, sodium, potassium, barium, and calcium, with isoamyl bromide in liquid ammonia at −34° C. was studied. The following table shows the results obtained (in per cent):

Metal Amide	Isoamyl Bromide Recovered	Primary Amine	Secondary Amine	Total Amines
Na	0.0	53.2	0.0	53.2
K	0.0	27.4	13.7	41.1
Ba	39.1	0.0	0.0	0.0
Ca	28.4	0.0	0.0	0.0

Sodium and potassium amides were much superior to barium and calcium amides for the preparation of amines. The low percentage of halide recovered in the barium and calcium runs was due to the difficulty encountered in separating the reaction products. The difference in reaction between sodium and potassium is not a true indication, as shown in subsequent work where the reaction conditions were more closely regulated.

Effect of Variation in Reaction Temperature

In order to determine whether there was any difference in the ratio of amine and unsaturate with variation in reaction temperature, several runs were made at temperatures ranging from −34° to −70° C. The alkyl halide used in this series of experiments was isoamyl bromide. The results are as follows:

Reaction Temp.	Metal	Monoamine	Diamine	Total Amines
° *C*		%	%	%
−34	Na	50.0	2.0	52.0
−34	K	48.8	2.1	50.9
−40	Na	50.0	3.9	53.9
−40	Na	48.5	5.9	54.4
−40	K	48.5	4.0	52.5
−50	Na	54.3	2.9	57.2
−50	K	53.0	5.8	58.8
−70	Na	56.1	3.9	60.0
−70	K	53.5	3.8	57.3

Although there is not a wide variation in yield of amine over the temperature range, the yields at temperatures below −50° C. are from 4 to 6 per cent greater than those at temperatures above −50° C. This may be due to loss of product by evaporation of ammonia at temperatures nearer its normal boiling point.

Effect of Reactant Concentration in Solvent

Sodium metal and isoamyl bromide were used in varying concentrations in liquid ammonia in order to determine concentration effect. All of the reactions were carried out at −55° C.:

Reactant per 100 Grams NH_3	Monoamine	Diamine	Total Amines
Mole	%	%	%
$^1/_{12}$	48.3	1.9	50.2
$^1/_{12}$	45.0	3.9	48.9
$^1/_6$	55.0	3.0	58.0
$^1/_6$	54.0	2.0	56.0
$^1/_3$	57.4	11.4	68.8
$^1/_3$	59.5	8.9	68.4

Probably the increased yield with higher concentrations was due to the higher ratio of reaction products present to the solvent ammonia; thus a smaller proportion of amine would be carried over with the evaporating ammonia. Vaughn, Hennion, Vogt, and Nieuwland (*9*) found that as high as 10 to 30 per cent of organic products of molecular weight comparable to the compounds obtained in this work were lost during evaporation of ammonia and hydrolysis after reaction. There is a noticeable increase in the proportion of diamine at the highest concentration.

Comparison of Chloride, Bromide, and Iodide

Several runs were made under exactly similar conditions, except for the use of different isoamyl halides. The reactions were all carried out at −50° C.:

Isoamyl Halide	Metal	Monoamine	Diamine	Halide Recovered
		%	%	%
Cl	Na	37.8	0.0	10.0
Cl	Na	43.1	0.0	9.2
Cl	K	30.7	3.9	0.0
Cl	K	33.6	3.6	0.0
Br	Na	54.3	2.9	0.0
Br	K	53.0	5.8	0.0
I	Na	55.0	6.9	0.0
I	K	47.5	7.9	0.0

It seems significant that in the case of sodium amide and isoamyl chloride not all of the halide reacted. This was borne out by the fact that the reaction did not proceed nearly as violently as with the bromide. Also some of the sodium amide remained unreacted as evidenced by the heat given off upon hydrolysis. The yield of amine with potassium amide and isoamyl chloride was much lower than that with sodium amide; however, no isoamyl chloride was recovered, indicating that the potassium amide tends to form unsaturates more readily than sodium amide in the case of reaction with isoamyl chloride.

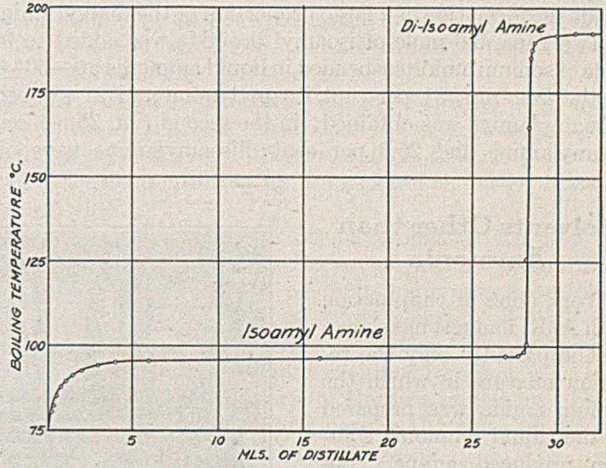

FIGURE 2. DISTILLATION CURVE FOR THE PRODUCT OF REACTION BETWEEN SODIUM AMIDE AND ISOAMYL BROMIDE IN LIQUID AMMONIA SOLUTION AT −50° C.

The reaction with metal amide and isoamyl bromide and iodide proceeded with a great deal more rapidity than with the isoamyl chloride. The iodide had more heat of reaction than the bromide but, as shown in the table, there was little difference in yield of amine whether the bromide or iodide was used.

Balance on Isoamyl Group

An attempt was made to identify as nearly as possible the complete course of the reaction by identification of the isoamylene formed in the reaction. Several runs were made, using the procedure given for isoamylene determination. All were carried out with sodium amide and isoamyl bromide at −55° C.:

Run No.	Monoamine	Diamine	Isoamylene Dibromide	Isoamylene	Total Identified
	%	%	*Ml.*	%	%
1	55.4	4.6	7.3	11.0	71.0
2	54.3	4.9	8.2	12.4	71.6
3	55.1	5.9	10.0	15.1	76.1

Difference in Reaction of *n*-Hexyl and 2-Ethyl Butyl Bromides

The best yield of amine in any runs was obtained from *n*-hexyl bromide. The smallest yield of amine was obtained with 2-ethyl butyl bromide. All of the following reactions were carried out at −55° C.:

Metal	*n*-Hexylamine	1-Hexylene	2-Ethyl Butyl-amine	2-Ethyl-butylene
	%	%	%	%
Na	74.3	4.8	11.4	41.4
Na	73.5	4.0	9.2	44.7
K	74.3	5.6	4.6	74.5
K	71.3	6.4	6.1	71.0

It is probable that a considerable amount of *n*-hexene (boiling at 64° C.) and 2-ethylbutylene (boiling at 66.2° C.) was lost during evaporation of ammonia and hydrolysis. The large proportion of unsaturate formed in the reaction with 2-ethyl butyl bromide is doubtless due to the reactivity of the tertiary hydrogen atom present in the molecule on the carbon atom next to the carbon atom holding the bromine atom, allowing hydrogen bromide to be split out of the molecule as in the case of the reaction of alcoholic potash upon halides to give unsaturates. The potassium amide here, as in the case of isoamyl chloride, shows a greater tendency to form unsaturates than sodium amide.

Effect of Excess Alkyl Halide

The use of a slight excess of halide throws the reaction towards the formation of a large proportion of the dialkyl amine. In two runs, 0.6 mole of isoamyl bromide was added to 0.5 mole of sodium amide suspended in liquid ammonia at −50° C. In the first run, 31 per cent isoamylamine and 21 per cent diisoamylamine was obtained; in the second run, 25 per cent isoamylamine and 25.3 per cent diisoamylamine were obtained.

Solvents Other than Ammonia

Work done in conjunction with A. R. Padgett has shown that apparently only the reaction mixture in which the sodium amide was prepared in the liquid ammonia solution produced amine. Sodium amide, prepared in another vessel, ground, and suspended in liquid ammonia, seemed relatively inactive. The use of other solvents for the reaction, including petroleum, ether, and benzene instead of liquid ammonia, led to the formation of little or no amine.

Discussion of Results

It has been shown that amines can be prepared in good yield by the action of alkyl halides upon suspensions of alkali metal amides in liquid ammonia solution at atmospheric pressure and temperatures at and below the boiling point of ammonia.

The results reported in this paper are in disagreement with the work of Chablay (*2*) whose results indicate that the principal compounds formed in this reaction are alkenes. Chablay does not mention the method by which he prepared the sodium amide used in his experiments. Since it has been shown in this work that only sodium amide prepared in the reaction mixture yielded amines, the difference in yields obtained is probably due to the difference in sodium amide used. The iron nitrate used as a catalyst in the work here described for the preparation of amide may also have catalyzed the formation of amine. The indication that the yield of unsaturates increases with the molecular weight of the halide, shown by Chablay's results, was shown not to hold under the conditions of the present experiment. Higher yields of amine were obtained with *n*-hexyl bromide than those with isoamyl bromide. Low yields of amine were obtained with 2-ethyl butyl bromide. The conclusion is that the ratio of unsaturate to amine formed does not depend on molecular weight but upon characteristics of the particular halide.

Sodium amide was found to be most desirable for carrying out the reaction, not only because of the lower price of sodium over potassium, but also because of the fact that in every case sodium gave as good, or in some cases better, results than potassium. As soon as the chemistry of the process is more fully determined, the plan at Purdue is to apply these reactions under conditions that will point to commercial application.

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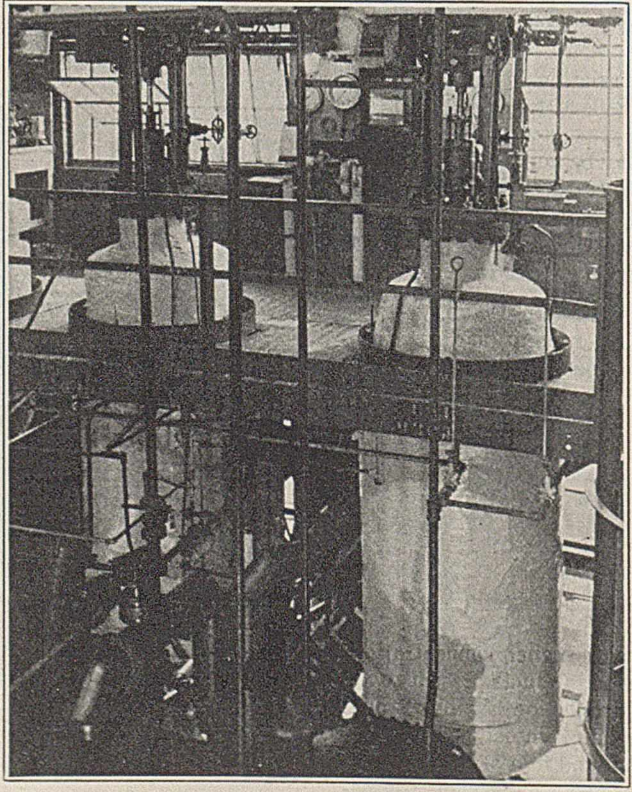

Courtesy, Monsanto Chemical Company

Typical Amination Equipment

Drying Oils

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CHARACTERISTIC of the drying oils is their interchangeability. This important fact is neglected by those whose interests have led them to emphasize the merits of a particular oil as against others. Because of interoil competition, perspective in this field occasionally becomes somewhat distorted and this survey has been made to suggest some of the corrections that must be applied to give a more accurate view of the whole field.

Industrially the applications of drying oils divide themselves naturally into three major fields: (1) protective and decorative coatings, (2) printing inks, and (3) linoleum and oilcloth. There are other uses outside these fields, but either their economic importance for the present purpose is small or they depend primarily on properties of the oils other than their drying qualities, which allow us to omit them from present consideration.

Although a great many oils have been used and suggested for their drying qualities, only six are of present economic significance: linseed, tung (China wood), perilla, fish, oiticica, and soybean oils.

LINSEED oil is our most important drying oil. It is expressed from flaxseed from domestic sources (48.8 per cent) and from imported seed (51.2 per cent) largely from the Argentine and Canada. The seed is processed in this country. The plant itself is of a variety less suitable than others for fiber production and, despite oft repeated attempts to that end, no large linen industry has grown up in this country to assist in increasing flax acreage. Domestic production at present tends to decrease. The following table shows United States production and imports of flaxseed:

U. S. production:	*1000 bushels*[a]	U. S. imports:	*1000 bushels*
1921–1925 (av.)	17,749	1922–1926 (av.)	18,198
1926–1930 (av.)	20,084	1927–1931 (av.)	18,659
1930–1935 (av.)	9,991	1932–1936 (av.)	13,357
15-year av.	15,941 (48.8%)	15-year av.	16,738 (51.2%)
U. S. consumption:			
15-year av.	32,679 (100.0%)		

[a] 1 bushel = 56 pounds.

Exports and imports of oil are small and are as follows:

Year	U. S. Imports *1000 pounds*	U. S. Exports *1000 pounds*	Year	U. S. Imports *1000 pounds*	U. S. Exports *1000 pounds*
1931	235	1094	1934	2781	653
1932	25	824	1935	2232	986
1933	9375	828			

Tung oil, also called China wood oil, is second in importance. The oil itself is imported from the Far East, and a small but growing domestic production from plantations of tung trees along the Gulf Coast is entering the market. Domestic production is still small compared with imports. During the present year young groves of American tung trees are expected to yield about 1.5 per cent of the total amount of oil used in the United States. Unlike flaxseed grown on an annual crop plant, tung nuts grow on trees which begin to bear about their sixth year; hence with greater and greater numbers of trees bearing each year, the domestic production may be expected to increase in the near future.

Perilla oil is of comparatively new economic importance in the drying oil industries here. Like linseed oil it is expressed from the seeds of an annual plant, and like tung oil it is imported from the Far East. Attempts to grow seed in this country are still in the early experimental stages. Perilla oil illustrates forcibly the interchangeability of drying oils for industrial use. The rapid increase of imports shows how rapidly a new valuable oil can be utilized to replace accepted standards when its properties are those desired.

The fish oils, notably menhaden and sardine oils, have become increasingly valuable as the technic of refining and handling them has developed within the past two decades. Their fishy odor formerly kept these oils outdoors, and they were principally used in roof paints and similar applications. Refining methods have now been so improved that odor is much less objectionable, and their valuable drying qualities are making these oils useful in a variety of special finishes.

Oiticica oil is the newest addition to the list of commercially important drying oils. In many ways it is similar to tung oil both as to properties and source. However, it has the important advantage from an American point of view of being produced in Brazil, which is nearer and less likely to be subject to the political and social revolutions that disturb the Far East. The importation of oiticica oil began only about two years ago, and it has not yet become an established member of the drying oil family. Presumably its importance will increase within the next few years.

Finally, soybean oil must be added to the list despite the facts (1) that it is not, in the strictest sense, to be classed with the foregoing in drying properties, and (2) that its major uses lie in other fields utilizing its fatty character rather than its drying ability.

Numerous other oils with drying properties are used for special purposes and to limited extents. Walnut oil, lumbang oil, rapeseed oil, hempseed oil, and numerous others have their fields which are, in one sense, competitive with the major oils but actually represent fractions of the market too small at present to be important in this discussion.

The production and imports of the five important drying oils (in 1000 pounds) and their uses in the three important divisions of industry are as follows:

Year	Linseed	Tung	Perilla	Soybean	Fish	All Drying Oils
			Paint and Varnish Industry			
1931	231,608	72,853	2,904	6,256	12,107	328,390
1932	173,816	59,158	3,226	7,485	7,565	254,251
1933	192,959	76,714	6,529	8,568	8,753	297,560
1934	205,743	88,184	9,898	10,451	11,654	329,894
1935	230,146	98,435	27,164	13,003	28,951	404,705
1936	233,340	94,642	53,222	14,471	35,780	441,282
			Linoleum and Oil Cloth Industry			
1931	47,886	7,303	725	2,612	14,837	73,473
1932	32,375	7,299	1,651	4,061	11,988	57,515
1933	33,015	11,746	5,826	5,641	13,223	69,938
1934	32,108	12,854	4,481	2,843	13,282	67,811
1935	41,809	10,391	9,650	4,816	13,865	81,031
1936	50,076	7,131	17,717	2,886	16,235	101,882
			Printers' Ink Industry			
1931	11,782	965	34	33	45	13,284
1932	9,078	713	143	47	63	10,431
1933	10,863	1,523	419	65	113	13,419
1934	12,606	1,660	582	59	103	15,544
1935	14,266	2,013	828	52	354	18,000
1936	14,968	2,331	1,940	62	235	20,206
			All Uses			
1931	520,735[a]	82,314[b]	4,722[b]	...	...	...
1932	326,569	67,948	5,693	...	...	...
1933	405,948	91,549	14,186	...	...	...
1934	370,769	105,978	16,108	...	...	...
1935	502,043	114,287	41,809	...	...	...
1936	?	107,875	80,019	...	...	...

[a] U. S. production. [b] U. S. imports.

It is important to note that large quantities of untreated linseed oil are used directly in paints by painters in addition to the quantity used in the paint and varnish industry proper. All other oils require industrial processing for use, and hence quantities used in industry correspond to consumption.

TO UNDERSTAND the present situation, it is necessary to go back to the time before the World War and trace subsequent developments up to the present. A little over two decades ago, linseed oil was to all intents and purposes *the* drying oil. Tung oil was being imported, and paint and varnish makers were still learning how to use it. Their troubles were less chargeable to tung oil itself than to the variability of shipments from China, resulting from lack of uniformity on the part of the producers and handlers in the Orient in their practice of adulterating tung oil with other oils. Fish oil was at that time a malodorous product whose disability carried over through the ordinary cooking and processing steps into the finished job. Even a coat of paint in which fish oil was used retained the odor of its origin more or less permanently, and because of this and the refusal of fish oils to dry completely tack-free, their use was greatly restricted. Perilla, rapeseed, walnut, and hempseed oils were used but were of minor commercial importance then.

Linseed oil had always been the standard. Paint, varnish, printing ink, linoleum, and oil cloth had reached their important places in the scheme of industrial things because their makers were able to buy and to use linseed oil. Paints were universally ground in it. Varnishes for use as finishes and as vehicles for enamels were made by "running" natural resins—kauri, manila, congo, and Zanzibar copals—with linseed oil. For printing inks, linseed oil was cooked to the desired consistency and used with or without the addition of varnish for grinding ink. Linoleum and oilcloth similarly depended upon linoxyn derived universally from linseed oil.

In each of these industries, technic was in a sense a guild matter passed from father to son and known only to the initiated. A new and strange oil, particularly one so uncertain in character as the early China wood oil, was heartily resented by the artisans asked to handle it. The change in traditional methods required was stubbornly resisted. Had it not been that China wood oil could yield an excellent varnish with rosin (common pine rosin) instead of requiring expensive copals as linseed oil did, it is possible that development of the oriental oil here might never have taken place. However, the profit motive for the early development was supplied by the cheapness of rosin-wood oil varnishes and their excellence in service, and the first important change in the drying oil industries was underway.

Tung oil had scarcely attained respectability as a varnish oil when the development of quick-drying lacquers based on nitrocellulose solutions appeared. The impact of these newcomers on the field of industrial finishes was tremendous. Although their cost was higher than customary finishes they replaced, the extraordinary speed with which work normally requiring many coats could be completed produced a substantial net saving. Further, lacquers gave all users of protective and decorative coatings reason to complain of the slow drying of the materials offered them.

At this time phenolic resins were being developed for use with tung oil, and the combination yielded a varnish that could be applied alone or used in the vehicle of enamels, having the ability to dry tack-free in a few hours. This gave oil vehicles a new lease on life in their competition with lacquers. Later the extension of the same principles to other oils—linseed, perilla, and oiticica—produced similarly quick-drying vehicles. Not only do phenolic resin varnishes possess the invaluable property of rapid film formation but they can be given a high degree of brilliance for fine finishes. Combinations including natural resins and alkyds are also possible.

For exterior work, varnishes of this type made with tung are notably waterproof and form films of special value in the newer practice of painting for corrosion prevention on steel.

The next important development in the coating industry was that of the alkyd resin varnishes. These are based on resins of the polybasic acid (phthalic anhydride)-polyhydric alcohol (glycerol) type and are formed in the presence of fatty oils. For industrial use the speed of drying of alkyd vehicles and the excellent properties of the coating formed have made them active competitors of the lacquers from this field. Under suitable temperature conditions, alkyd resin coatings can be dried in a matter of minutes to a couple of hours where baking is practicable. The finished coat has an excellent appearance, a hardness meeting reasonable requirements, and a high resistance to destructive agencies. Furthermore, and this has been a most important consideration, the solvents required in alkyd finishes are far cheaper than the esters and alcohols necessary in dissolving nitrocellulose to form lacquers.

The alkyds are made with drying oils and impart to the oils in which they are dissolved the peculiar property of drying throughout the film, apparently by polymerization, instead of from its surface as ordinary oil and varnish films dry, presumably by a combination of polymerization and oxidation. This fact is important in industrial finishing, since it obviates the formation of pouches of partly dry coating which has run beneath the dried surface.

Throughout this shifting of emphasis on vehicles, there has had to be a similar shifting of emphasis between different pigments to fit their compatibilities. For use with linseed oil, both alone and in varnishes, white lead and zinc oxide are the leading white paint pigments. Lithopone, sublimed white lead (sulfate), and titanium oxide are equally compatible with linseed oil vehicles, and numerous other pigments, both white and colored, offer no difficulty. The advent of tung oil vehicles forced lithopone to the fore and both white lead and zinc oxide into the background. The extreme sensitivity of nitrocellulose to alkalies gave further impetus to chemically inert pigments, lithopone and titanium oxide, and these are still increasing in importance.

One thus finds throughout the drying oil industries frequent shifting of emphasis from one oil to another and a growing tendency to use mixtures and combinations to produce desired effects. One may almost set up a table of interchangeability based on costs of oils, but its figures necessarily change with conditions. Whenever under present conditions the order of increasing cost changes from linseed, perilla, and tung, the shift will be toward the cheaper oil. Suggestively, one may assume a price of 100 per cent for linseed oil and, from that as a yardstick, place perilla at 110 per cent and tung at 120 per cent. If one or the other oil departs from this approximate price scale, the trend of the industry is toward or away from it, depending on the direction of the price change. Naturally there are many exceptions to such a rule. Some results are to be had only with one oil or another and may be so important as to overbalance an adverse price change of 100 per cent. Necessarily substitutions require re-formulation and changes of practice which the industry seeks to avoid. Hence, changes are preferably on permanent rather than transitory market shifts.

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COAL HYDROGENATION[1]

Chemistry

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A discussion is presented of the relative importance of rank of coal, nature of vehicle, type of catalyst, agitation, temperature, and pressure in coal-hydrogenation processes. Wherever possible, the discussion is conducted to show the interplay of the rates and equilibria involved, and to indicate where additional data would help in formulating the mechanism of the reactions involved.

TWO excellent detailed reviews of the literature on the hydrogenation of coal appeared in 1931 (*25, 28*). The important contributions made from 1931 to the present have been briefly summarized every year by Fieldner (*9*). The purpose of the present paper is to present a critical discussion of the important physical and chemical factors involved in the conversion of coal to useful liquid hydrocarbons by destructive hydrogenation.

Rank of Coal

The reactivity of coals to hydrogenation is, roughly, inversely proportional to their carbon content. In laboratory investigations using small bombs at 450° C., about 100 atmospheres initial (cold) pressure of hydrogen, and 2 hours at reaction temperature, the yield of distillable oils (boiling below 360° C. at atmospheric pressure) was found to show an approximately linear relation to the carbon content of the coal (*5*). In experimental continuous plants, however, this relation is apparently much more complex. For example, a coal which gives a fair yield of oil in the bomb tests may be totally unsuited for use in a continuous hydrogenation plant because of any one of a number of factors that do not affect the operation of a small bomb but are of critical importance in continuous operation (*5*). Perhaps the most important of these critical variables is the optimum temperature range for the primary liquefaction of the coal. If this range is too narrow, the continuous plant may give markedly inferior results because temperature control is not so precise as in the bomb tests. Other factors that make it difficult to translate small bomb tests in terms of a continuous plant are the fusain and resin content of the coal, and the specificity attached to the peptization of the coal by the vehicle which determines the ease of pumping of the mixture.

The variation in oil yield from hydrogenation tests on various coals with the constituents of the coal, as determined by petrographic analysis, has not yet been completely investigated. However, it is generally agreed that the fusain content of coal cannot be readily hydrogenated (*27*). Some experiments on the hydrogenation of durain and vitrain are reported by Graham and Skinner (*15*). There is little, if any, difference between the results described for clarain and durain from the South Staffordshire white-seam thick coal. The results for vitrain from the Warwickshire slate seam indicate a considerably lower yield of oil than is obtained from the Staffordshire clarain and durain. The yield of oil from Lancashire Arley seam coking coal of 84 per cent carbon content was about 70 per cent greater than that from the clarain and durain of 81 to 82 per cent carbon from the noncoking Staffordshire coal.

The products of the hydrogenation of bituminous coals are largely aromatic in nature, whereas appreciable yields (about 12 per cent) of the paraffin hydrocarbons are reported in the hydrogenation of brown coals (*37*). A high-pressure extraction of the brown coal with benzene, followed by hydrogenation of the extract thus obtained, is the procedure used for the production of paraffin wax.

Nature of Solvent (or Vehicle)

Laboratory studies on the extraction of coal by various solvents indicate that depolymerization, followed by colloidal solution, occurs when an appreciable fraction of the coal is dissolved by solvents such as tetrahydronaphthalene or coal-tar fractions; and that organic liquids of high boiling point, medium dipole moment, and medium dielectric constant are the best solvents (*1, 3, 11, 13*).

All of the experiments (*4, 24*) on solvent extraction of coal under conditions comparable with those used in coal-hydrogenation practice indicate that solution of the coal constituents, except ash, fusain, and some attrital matter, is rapid and complete (*24*). In all of these experiments, however, it is probable that, despite the absence of added catalysts and hydrogen gas, some hydrogenation occurred by transfer of hydrogen atoms from the solvent to the solute.

The data of Pott and Broche (*24*) show that, for each of the coals investigated, an optimum maximum temperature of extraction exists. At temperatures higher than this optimum, reprecipitation of polymers occurs. The optimum temperature for most bituminous and brown coals was between 390° and 410° C. when equal parts of coal and solvent (tetrahydronaphthalene:phenol:naphthalene = 2:1:2) were used. The product of this extraction resembles a primary coal tar.

A survey of the efficiencies of various types of organic compounds as vehicles in the primary liquefaction of coal by mild hydrogenation was made by Fisher and Eisner (*11*). Their results indicate that completely saturated hydrocarbons are generally poor vehicles. Tetrahydronaphthalene was found to be an excellent hydrogenation medium; and mixtures of it with naphthalene, toluidine, cresol, and quinoline were equally satisfactory or superior to tetrahydronaphthalene alone. Methylnaphthalene was found to be a much better vehicle than naphthalene. In general, the addition of polar compounds, such as phenols and amines, increased the effectiveness of all aromatic and hydroaromatic vehicles.

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[1] This series of three papers was presented before the Division of Gas and Fuel Chemistry at the 94th Meeting of the American Chemical Society, Rochester, N. Y., September 6 to 10, 1937. Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

Importance of Vehicle, Agitation, and Catalyst

One would expect that in a heterogeneous reaction, such as that between coal-oil paste and hydrogen, agitation would be of paramount importance. The experiments of Horton, King, and Williams (*19*) indicated that this expectation is justified. Some of their data are given in Table I.

Comparisons of experiments 3 with 5, 2 with 6, and 4 with 7 show that an increase in yield of 15 to 24 per cent is to be ascribed to agitation. Comparisons of experiments 2 with 4 and 6 with 7 indicate an increase of 6 to 13 per cent due to the addition of a vehicle when a catalyst is also present. Comparison of experiment 1 with 3 shows an increased yield of 13 per cent due to the addition of a vehicle in the absence of a catalyst. Comparisons of experiments 3 with 4 and 5 with 7 indicate an increased yield of 10 to 16 per cent due to the addition of a catalyst when a vehicle is also present. Comparisons of experiments 1 with 2, 1 with 3, and 5 with 6 indicate that the addition of a catalyst results in a greater increase in oil yield than the addition of the vehicle. From the comparisons indicated, it is perhaps safe to list the following order of importance: agitation > catalyst > vehicle. This discussion applies only to the early stages of coal hydrogenation—that is, the liquefaction to produce a "heavy" oil. Furthermore, these three variables are probably not independent. It is likely that the function of catalysts such as stannous oxide and germanium monoxide in the early stages of the reaction includes the rapid production of liquid material from a portion of the coal; this liquid subsequently acts as a dispersion medium for the remaining solid material. Similarly, agitation will result in a dispersion of remaining solids in the earliest liquefied products formed. However, the much larger increase in yields, which must (on the basis of the data of Table I) be attributed to agitation as compared with either vehicle or catalyst addition, is probably significant in indicating a measure of the relative independence of this variable.

TABLE I. SMALL AUTOCLAVE TESTS ON INFLUENCE OF VEHICLE, CATALYST, AND AGITATION

Expt. No.	Autoclave Contents			Agitation	Oil Yield
	Coal	Vehicle[a]	Catalyst[b]		% *on coal*
1	+	−	−	−	23
2	+	−	+	−	49
3	+	+	−	−	36
4	+	+	+	−	46
5	+	+	−	+	54.4
6	+	−	+	+	64.4
7	+	+	+	+	70.3

[a] Coal-tar distillate.
[b] 0.1 per cent (on weight of coal) of SnO or GeO.

The importance of agitation in determining the rate of coal hydrogenation has not been the subject of any experimental work other than that of Horton, King, and Williams (*19*). Some recent patents (*29, 33, 38, 46, 49, 53*) describe mechanical arrangements for this purpose. It would be desirable to determine whether the rate of solution of hydrogen in the liquid phase is a rate-controlling factor in coal hydrogenation. In general, it has been recognized that the rate of hydrogen circulation is an important factor in the process, but the data at hand do not permit a decision as to whether such circulation is important, mainly because of the mechanical agitation produced or because of the increased rate of hydrogen solution. Only one recent patent (*59*) mentions the rate of hydrogen circulation and specifies 10,000 to 30,000 cubic feet per hour per barrel of coal-oil mixture. This rate is 1700 to 5100 cubic meters per hour per ton of coal (assuming equal parts by weight of coal and oil). This rate is about the same as that used by Warren (*26*) for the hydrogenation of Canadian coals.

Catalysts

The nature of the catalysts employed in coal hydrogenation has been the subject of numerous patents. The presence of appreciable quantities of sulfur compounds and organic substances of high boiling points makes impractical the use of the well-known active hydrogenation catalysts such as reduced nickel. Moreover, the latter frequently show a negative temperature coefficient at temperatures of 400° to 500° C. in hydrogenation reactions where sulfur and high-boiling organic substances are absent; because of this, they are not so active as other catalysts which are inferior to them at lower temperatures (*2*).

The numerous recent patents disclosing catalysts for the destructive hydrogenation of coal and other carbonaceous materials may, for convenience, be classified in four groups as follows:

(1) Those emphasizing the desirability of the addition of some volatile chloride or compound which will yield a volatile chloride upon decomposition at process temperatures (*31, 34, 36, 41, 47, 51*).
(2) Promoted heavy metal sulfide catalysts (*35, 39, 42, 44, 48, 50, 52, 54, 56, 58*).
(3) Finely divided metals (*34, 45, 47, 55*).
(4) Alkali and alkaline earth metals and their compounds, along with finely divided iron or other metals (*30, 40, 43, 57*).

This survey of the recent patent literature shows the outstanding importance of volatile chlorine compounds as catalysts in the primary liquefaction of coal by hydrogenation. This fact may be correlated with the ability of halogens, alkyl halides, and halogen acids to function as catalysts in the thermal decomposition of oxygenated organic compounds such as ethers (*14*) and aldehydes (*17*).

A few amphoteric sulfides—namely, molybdenum and tungsten disulfides and stannous sulfide—are the most active of the metal sulfide catalysts. Stannous sulfide is reported to be particularly effective in the primary liquid-phase hydrogenation; molybdenum and tungsten disulfides are preferred for vapor-phase hydrogenation of tars or liquid primary coal-hydrogenation products. The metal sulfides are, in general, more active than the oxides, and it is desirable to maintain a minimum partial pressure of about one atmosphere of hydrogen sulfide in order to avoid conversion of metal sulfides to oxides or to metals.

A series of investigations concerning the action of promoters for molybdenum oxide as a hydrogenation catalyst has recently been published. The experiments of Hollings, Bruce, and Griffith (*18*) on the influence of silica as a promoter for molybdic acid in the hydrogenation of tars showed that, when the yield under a given set of conditions was plotted against the atom percentage of silicon, a curve was obtained containing two maxima at 3.0 and 5.5 per cent and a minimum at 4.5 per cent. Their interpretation of this curve is as follows:

> The curve appears to be the observed result of two simultaneous processes: one, a straightforward promoting influence of silica on the catalyst activity, and the other, a change in adsorptive power, which becomes so pronounced that either unchanged material or reaction products retard the activity between the silicon ratios of 3.0 per cent and 5.5 per cent. As every type of hydrocarbon appears to be adsorbed vigorously, the same effect would be produced either by complex cyclic hydrocarbons originally in the tar, or by fully hydrogenated reaction products of perhaps high molecular weight which would be stable under the experimental conditions.

These authors also studied the adsorption, at temperatures up to 450° C., of hydrogen, benzene, hexane, and cyclohexane by molybdic acid containing varying amounts of silica. The data for hydrogen are given in Table II.

The adsorption curves (atom per cent silicon *vs.* cc. adsorbed per 100 grams of catalyst) for hexane at 400° C., cyclohexane at 450° C., and benzene at 450° C., are all of the same form, showing a pronounced maximum at about 4.5 per cent silicon. The rates of decomposition of hexane and cyclohexane at low pressures (about 200 mm.) and at 500° C. when plotted against the atom per cent of silicon yield curves with a pronounced maximum at about the same point—namely, 4.5 per cent silicon.

TABLE II. AMOUNT AND RATE OF HYDROGEN ADSORPTION BY 100 GRAMS OF CATALYST AT ABOUT 550 MM. PRESSURE

Si	—H_2 Adsorbed (N. T. P.)—			—Time for Half-Satn.—			Heat of Activation at 400–450° C.
	350° C.	400° C.	450° C.	350° C.	400° C.	450° C.	
Atom %	*Cc.*	*Cc.*	*Cc.*	*Sec.*	*Sec.*	*Sec.*	*Kg. cal.*
0.0	9.1	9.7	9.6	528	210	51	29.0
3.0	24.0	22.5	22.1	372	157	44.4	23.9
4.4	25.9	25.6	25.6	330	125	34.0	23.5
5.5	50.0	44.9	38.0	156	57.5	23.0	17.6
10.0	63.0	57.6	50.0	180	52.5	22.0	16.9

However, it should be noted that the high-pressure experiments with coal tar gave a minimum at 4.5 per cent silicon. The authors' explanation of the high-pressure coal tar results can be amplified somewhat by a consideration of the data of Table II. It is apparent that large decreases in heat of activation of the hydrogen adsorption occur between 0.0 and 3.0 per cent silicon and between 4.4 and 5.5 per cent, whereas this heat is practically constant between 3.0 and 4.4 per cent. If one assumes a steadily increasing retardation by coal tar or its hydrogenation products with increasing atom per cent of silicon, it is reasonable to predict on the basis of the changes in heats of activated adsorption of hydrogen precisely the form of curve actually obtained—that is, two maxima, one somewhere between 0.0 and 3.0 per cent silicon, and the other between 4.4 and 5.5 per cent. From this point of view the adsorption tests for hydrogen, if carried far enough to locate the points of maximum change of slope of the curve (heat of activation *vs.* atom per cent silicon), constitute a good criterion of the optimum concentrations of silicon. This is not in accord with the authors' conclusions which are that the adsorption data for hydrogen are of no value as a laboratory test for catalyst efficiency in tar hydrogenation.

It is perhaps unfortunate that this work has apparently led to the omission of rates of activated adsorption of hydrogen in subsequent similar investigations on the effect of promoters for molybdenum catalysts for hydrogenation reactions. The efficiency of various promoters in increasing the catalytic activity of molybdenum oxide in the catalytic hydrogenation of phenol to benzene was studied by Kingman and Rideal (*21*). They found that phosphorus, nickel, chromium, aluminum, or silicon enhanced the activity, whereas tin and thorium compounds depressed it.

A detailed study of promoters for the dehydrogenation of hexane and the hydrogenation of phenol was recently published by Griffith (*16*). The optimum promoter concentration for hexane decomposition at 500° C., using a molybdenum oxide catalyst, is found to be 4.3 atom per cent for sodium, chromium, cerium, aluminum, barium, boron, and thorium, and 2.2 atom per cent for iron, copper, and lead. The metal oxides of the first group are not reducible under the operating conditions, whereas iron, copper, and lead oxides are reduced to the respective metals. For the hydrogenation of phenol at 440° C., the optimum promoter concentrations for a molybdenum oxide catalyst were 16 atom per cent for cerium, 16.5 for aluminum, and 15.0 for silicon. No adsorption measurements for phenol or hydrogen are reported.

Griffith (*16*) also gives a series of dehydrogenation rate determinations for decahydronaphthalene, decane, hexane, and cyclohexane, using chromic oxide gel plus various amounts of magnesia. For decahydronaphthalene the activity is constant from 0.0 to 90.0 per cent magnesia, and then it drops off linearly with increasing magnesia content. For decane the constant activity range is 0.0 to 50.0 per cent, for hexane 0.0 to 20.0 per cent, and for cyclohexane the activity drops continuously with increasing magnesia content. Griffith (*16*) explains these data by assuming that the larger hydrocarbon molecules cover many active centers upon adsorption, and hence the dilution effect due to the inert carrier magnesia is not apparent until the active centers are farther apart than the necessary distance for activation and reaction. Similar experiments using a chromic oxide-silica catalyst and adding various amounts of magnesia showed an immediate dilution effect with all hydrocarbons. Griffith (*16*) concludes from this that chromic oxide promoted with silica presents a surface which is qualitatively different from unpromoted chromic oxide and not merely one with a larger number of active centers.

This research will unquestionably be of importance in developing the chemistry of vapor-phase hydrogenation. It would, however, be desirable to have catalytic rate studies on the destructive hydrogenation of larger molecules. There is also a dearth of rate measurements on destructive hydrogenation in liquid phase of pure compounds of high molecular weight. Where relatively large molecules are involved, it seems probable that adsorption of such molecules will, beyond a certain limit, retard destructive hydrogenation reactions. Especially in liquid-phase hydrogenation of large molecules, one would expect the rate to be largely determined by that of the activated adsorption of hydrogen on a surface almost completely covered by the other reactant. It would, perhaps, be more logical to search for hydrogenation catalysts which do not strongly adsorb the organic molecule that it is desired to hydrogenate destructively, or for hydrogenation catalysts which are soluble in the liquids to be hydrogenated, thus avoiding the necessity of a contact catalytic reaction. Tetrahydronaphthalene probably functions in part as a liquid-phase catalyst for coal hydrogenation, and it is likely that the desirability of compounds such as methylnaphthalene, phenols, quinoline, etc., in liquid-phase coal hydrogenation systems may also be a matter of labile hydrogen atoms in these molecules, in addition to their well-known solvent action on coal.

Somewhat extraordinary hydrogenation catalysts are phthalocyanine and its copper salt. These are active in the para-to-ortho hydrogen conversion, and in the combination of hydrogen and oxygen (*7, 8*). This organic nitrogen compound is apparently capable of functioning as a hydrogenation catalyst at temperatures of about 300° C. A study of its applicability in the hydrogenation of organic compounds should be made.

Temperature and Pressure

It is commonly supposed that one of the important reasons for the necessity of a temperature above 400° C. for the liquid phase of coal hydrogenation is the fact that active pyrolysis of coal does not occur until such temperatures are employed. This explanation is probably too simple, for there are other factors involved, such as the positive temperature coefficient of the solubility of hydrogen in most liquids, the decrease in retardation of the reaction rate at high temperatures due to decreased adsorption of bituminous materials on the contact catalyst, and the effect of temperature and particle size on the rate of depolymerization and solution of the coal substances.

Maxted and Moon (*23*) showed that the temperature coefficient of the molar solubility of hydrogen in all the liquids tested by them is positive. With a given gas-liquid interfacial area (which is largely determined by the rate and manner of hydrogen recirculation), both the rate and the total equilibrium amount of hydrogen dissolved by a given weight of liquid will increase with the temperature.

The work of Fischer, Peters, and Cremer (*10*) showed that, when bituminous coal is ground to less than 1 micron in size and extracted with benzene at 260° C. in the presence of 160 atmospheres pressure of hydrogen and a molybdenum oxide catalyst, 80 per cent of the coal substance was dissolved in 120 hours of refluxing. The usual contact time in liquid-phase coal hydrogenation is 2 hours at 450° C. If one assumes that the difference in vehicles did not greatly affect the speed of primary liquefaction, then the temperature coefficient of the hydrogenation reaction is not greater than 60 for a temperature difference of 180° C. It is unlikely that such an extraordinarily low temperature coefficient is characteristic of the chemical reactions involved; but is probably due to a combination of a diffusion process in the solution of the coal and to a very slow increase in catalyst activity with temperature as a result of decreased absorption of large molecules. Further experiments are needed on the temperature coefficient of liquid-phase hydrogenation of coal using the same vehicle in all experiments.

The rates of removal of oxygen, nitrogen, and sulfur atoms from coal during hydrogenation at 385° and 400° C. have recently been determined by Fisher and Eisner (*12*) in this laboratory. Since the hydrogen concentration was kept practically constant throughout their experiments, the rate curves may be treated as those of a first- or zero-order reaction. Such treatment shows that about 60 per cent of the oxygen of the coal is removed rapidly at both temperatures, and the difference in rate at the two temperatures indicates an activation energy of about 55 kg-cal. The remaining 40 per cent of the oxygen is removed much more slowly, and the temperature coefficient for its removal indicates an activation energy of about 30 kg-cal. The slow removal of oxygen is probably a contact catalytic reaction, and the fast removal a homogeneous reaction. It is therefore apparent that at least two types of oxygen linkages in the coal substance are indicated by these data. The rates of organic sulfur removal also indicate the possibility of more than one type of linkage, but the differences are not so pronounced as in the oxygen case. The rate of nitrogen removal is slow at these temperatures and is approximately constant.

Pressures of at least 200 atmospheres of hydrogen are found to be essential in liquid-phase hydrogenation of coal at temperatures of about 450° C. At appreciably lower pressures, repolymerization and coke formation occur. The function of the high hydrogen pressure is not entirely clear. Its necessity cannot be due to reversible hydrogenation reactions, for Boomer and Saddington (*4*) found it possible, in a small bomb test, to obtain good yields of oil using tetrahydronaphthalene as vehicle and 150 atmospheres pressure of natural gas. Since the equilibrium partial pressure of hydrogen for the tetrahydronaphthalene-naphthalene equilibrium at 450° C. is reported to be only 1 atmosphere (*22*), it is apparent that high-pressure hydrogen is not thermodynamically necessary for the liquid-phase hydrogenation of coal. Two other possible functions of high-pressure hydrogen are (1) to keep the bulk of the vehicle in the liquid phase and (2) to increase the amount of dissolved hydrogen.

In connection with the second factor the results of Ipatieff and Levin (*20*) are of interest. They found that hydrogen is more soluble in alicyclic than in aromatic compounds and the solubility in the latter decreases with increase in number of side chains. At low temperature and pressures the solubility obeys Henry's law, but at higher pressures the solubility coefficient increases with increasing pressure.

In the vapor-phase hydrogenation of oils obtained from coal, high-pressure hydrogen is probably a thermodynamic necessity, for reversible[2] hydrogenation reactions are predominant (*5*, *6*). The necessity of temperatures as high as 480° C. for vapor-phase hydrogenation is, however, not obvious. In fact, recent patent literature (*32*) indicates that much lower temperatures may be satisfactorily employed when sufficiently active catalysts are available.

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[2] The thermal decomposition of large molecules and subsequent saturation of the fragments may not be a reversible process, but the products of such a reaction can be dehydrogenated at lower hydrogen pressures, yielding organic compounds which may not be the same as the original molecules.

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Primary Liquefaction by Destructive Hydrogenation of the Oxygen, Nitrogen, and Sulfur Linkages

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To obtain information regarding the elimination of the inorganic elements in the coal substance during the primary liquefaction, a Pittsburgh bed coal was hydrogenated in tetrahydronaphthalene for different lengths of time (3, 6, 9, and 12 hours) at 385°, 400°, and 415° C.

The most marked changes occurred in the first 3-hour period when about 60 per cent of the oxygen was removed. The remaining 40 per cent of the oxygen was eliminated with much greater difficulty. These results appear to indicate that at least two types of oxygen linkage are present in coal. The elimination of nitrogen was very slow and approximately constant. Sulfur removal, which occurred to the greatest extent in the first 3 hours, was also slow.

Several conclusions, which must be regarded as tentative until confirmed by later work, were drawn from the analytical and yield data concerning the mechanism of the primary liquefaction and the nature of the oxygen linkages in coal.

ONE part of the coal-hydrogenation program at the Bureau of Mines is concerned with primary liquefaction, which consists principally in effecting dissolution of the coal substance, hydrogenating some of the carbon-carbon bonds, and converting considerable quantities of the coal oxygen, nitrogen, and sulfur into their hydrogen derivatives. A previous paper (*3*) described the primary liquefaction of coal in various types of vehicle. The present paper presents a study of the removal of oxygen, nitrogen, and sulfur from coal by hydrogenation under comparatively mild conditions. The rates of removal of these inorganic elements during the destructive hydrogenation are of interest because some approximations as to the number of different types of linkage and the bond strengths may be obtained from such data. Information of this kind should be valuable in studies of coal constitution and in engineering practice in coal-hydrogenation plants. The results obtained in the present experiments have thrown light also on other features of primary hydrogenation. Since the coal was hydrogenated stepwise at three different temperatures (385°, 400°, and 415° C.), the data give some indication of the effect of temperature and time on the yields and nature of products.

Hydrogenation Procedure

The hydrogenation experiments were carried out with the apparatus (18–8 stainless steel converter of 1200-cc. capacity rotating on its horizontal axis) described previously (*3*). The same coal, a Pittsburgh bed coal obtained at the Bureau of Mines experimental mine at Bruceton, Pa., was used in all the experiments. Its proximate analysis is as follows (per cent by weight): moisture, 1.6; volatile matter, 35.7; fixed carbon, 56.4; ash, 6.3. The ultimate analysis is given in Tables II and III.

Other analytical data obtained with this coal have been given in a previous paper (*3*). Tetrahydronaphthalene, purified by extraction with dilute alkali and acid and redistillation, was employed as the vehicle. This method of purification failed to remove traces of a reactive hydrocarbon, possibly dihydronaphthalene, which could be converted into an insoluble solid by treatment with 82 per cent sulfuric acid (Table VII).

The following stepwise hydrogenation procedure was used at each of three reaction temperatures (385°, 400°, and 415° C.):

A mixture of 1 gram of stannous sulfide and 100 grams of coal (200 mesh) was placed in the bomb, and 100 grams of tetrahydronaphthalene were added. After the bomb was flushed successively with nitrogen and hydrogen, hydrogen was introduced until the pressure was 1000 pounds per square inch (70.3 kg. per sq. cm.). After 0.5 to 1 hour had elapsed, the pressure again was brought to 1000 pounds, replacing the hydrogen which had dissolved in the coal-oil paste. The temperature of the converter was then brought to the desired value at the rate of approximately 2° per minute, and held at reaction temperature for 3 hours. After the converter had cooled to room temperature, the gaseous contents were passed through wash bottles (containing about 15 per cent solution of sulfuric acid and sodium hydroxide) and a wet test meter into a gas holder. In the experiments of only 3-hour duration (L1, I1, and H1 at 385°, 400°, and 415° C., respectively), the converter was opened at this stage and its contents (as well as gas samples from the gas holder and solutions from the wash bottles) were analyzed by the methods described below. In the other experiments (L2, L3, L4 at 385°; I2, I3, I4 at 400°; and H2, H3, H4 at 415° C.) the converter was not opened but was recharged with hydrogen to a pressure of 1000 pounds (after bleeding and flushing the bomb with hydrogen), and the 3-hour hydrogenation experiment was repeated until the total time of treatment at each reaction temperature was 6, 9, or 12 hours.

TABLE I. LIQUEFACTION YIELD DATA

Expt. No.	Temp.	Total Time	Products: Liquids, Solids	Products: Gases	Loss	Oil Centrifuged	Oil from Centrifuge	Conversion of Pure Coal: Based on residue	Conversion of Pure Coal: From ash content
	° C.	Hr.	Grams	Grams	Grams	Grams	%	%	%
L1	385	3	191	3.5	8.1	174.1	44	83.6	80.7
L2		6	190.6	6.0	6.8	172.1	81	91.0	89.8
L3		9	191.3	7.6	5.2	178.6	81	92.2	91.3
L4		12	189.1	9.5	6.3	175.5	83	94.4	93.2
I1	400	3	191.7	5.5	5.8	178.4	78	91.5	89.0
I2		6	193.4	7.5	3.1	173.3	82	93.6	92.3
I3		9	185.8	9.9	9.4	167.9	84	95.4	93.7
I4		12	186	12.3	7.6	167	87	95.4	94.8
H1	415	3	188	6.9	8.5	172.7	80.7	93.7	89.7
H2		6	186.5	11.4	7.1	176.9	84.2	95.0	93.5
H3		9	187.2	15.7	3.3	177	85	95.0	95.1
H4		12	176.8	17.9	12.2	166.9	84.2	95.8	93.5
P4	400	12	191	...	...	181	95	99.2[a]	98.6[a]

[a] Based on starting material (100 grams of pitch obtained by hydrogenating Bruceton coal for 3 hours at 400° C.).

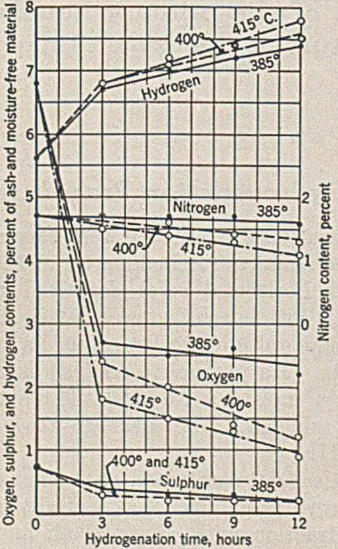


FIGURE 1. OXYGEN, HYDROGEN, NITROGEN, AND SULFUR CONTENT OF PITCHES

After the hydrogenation had proceeded the desired number of hours, the liquid and solid contents of the converter were transferred to a weighed bottle and centrifuged for 1.5 to 2 hours at about 3500 r. p. m. The ash-free oil (the amount of this oil, calculated as per cent of the material centrifuged, is given in Table I) thus obtained was transferred to a flask with a 6-inch (15.2-cm.) Vigreux-type column and distilled to 215° C. to remove the vehicle, water, and any low-boiling oil formed during the hydrogenation. The distillation residue (the principal product) was poured from the flask while hot. The distillate was analyzed for tar acids and bases and neutral oil constituents. To determine the olefin content, the oil was shaken for 5 minutes with 3 volumes of 82 per cent sulfuric acid and then distilled to 220° C., the distillate being taken as olefin-free oil. Aromatics were determined in the olefin-free oil by successive extractions with 3 volumes of 96 per cent sulfuric acid (60 cc.) and about 5 cc. of 98 per cent acid.

The products not removed manually from the bomb were washed out with acetone and added to the main residue in the centrifuge bottle. The bomb was weighed before and after the acetone washing on a Troemner bullion balance to determine the amount thus removed. The combined residues were washed with four or five 140-cc. portions of acetone (centrifuged each time) at room temperature and dried at 110° C. for 24 hours to obtain the weight of acetone-insoluble material (Table III). This procedure of washing the residue with acetone extracts nearly as much organic material as does long refluxing with benzene. In previous experiments it was found that about 84 per cent of the acetone residue was recovered after extraction with benzene in the Soxhlet apparatus for 48 hours. The amount of pure coal (ash-, moisture-, and fusain-free) liquefied was calculated from the acetone-insoluble residue and, as a check, from the ash content of the residue (Table III).

The sodium hydroxide solutions used to absorb acidic material from the hydrogenation gases were diluted, and aliquot portions were analyzed for hydrogen sulfide (iodine titration) and for carbon dioxide (gravimetrically by acidifying the caustic solutions and passing the liberated gases through anhydrous copper sulfate and collecting the carbon dioxide in potassium hydroxide solution). The ammonia absorbed in the sulfuric acid solution was regenerated by treatment with excess alkali, passed into a standard sulfuric acid solution, and titrated in the usual manner. Samples of the gas from the gas holder were analyzed in the Orsat apparatus (Table V).

Destructive Hydrogenation of Inorganic Linkages

The changes in oxygen, nitrogen, and sulfur contents during the 3-, 6-, 9-, and 12-hour intervals are indicated in Figure 1 and Table II, which contain data describing the composition of the original coal and of the products (pitches or very viscous oils) obtained in highest yield. These data indicate that the most marked changes take place in the first 3-hour interval.

Since the partial pressure of hydrogen in all these experiments was the same (within ±5 per cent for the 3- to 12-hour period) the rates of oxygen removal should be first or zero order. The rate of oxygen removal during the first 3 hours is very rapid, but during the 3- to 12-hour period it is much slower than would be expected for either a first- or zero-order

TABLE II. COMPOSITION OF PITCHES

Pitch No.	H	C	N	O	S	Available H	Calorific Value	C/H Ratio
	%	%	%	%	%	%	G. cal.	
L1	6.7	88.4	1.7	2.7	0.4	6.0	8861	13.19
L2	7.0	88.4	1.7	2.5	0.3	6.3	9183	12.63
L3	7.2	88.1	1.7	2.6	0.3	6.5	9233	12.24
L4	7.4	88.5	1.6	2.2	0.2	6.8	..	11.96
I1	6.8	88.7	1.7	2.4	0.3	6.1	9156	13.05
I2	7.1	89.1	1.6	2.0	0.2	6.5	9322	12.61
I3	7.4	89.5	1.4	1.4	0.2	6.9	9483	12.09
I4	7.5	89.8	1.3	1.2	0.2	7.1	9522	11.97
H1	6.8	89.6	1.5	1.8	0.3	6.2	9206	13.18
H2	7.2	89.7	1.4	1.5	0.2	6.7	9396	12.53
H3	7.4	89.8	1.3	1.3	0.2	7.0	9517	12.09
H4	7.8	90.0	1.1	0.9	0.2	7.4	9517	11.54
P1[a]	6.5	88.7	2.3	2.1	0.4	5.7	..	13.65
P4	7.6	90.0	1.4	0.8	0.1	7.2	9561	11.84
Coal[a]	5.6	84.2	1.7	6.8	1.7	4.4	8361	15.04

[a] Ash- and moisture-free basis.

reaction. Hence, it is probable that at least two types of oxygen linkages exist in the coal substance. It appears unlikely that the original oxygen linkage in the coal yields, upon destructive hydrogenation, a second type that is more difficult to hydrogenate for the following reason: Extrapolation of the slow rates to zero time shows that the original fast reaction is too slow to yield the necessary amount of the postulated second type of oxygen linkage. The possibility that the two types of oxygen linkage are located in different coal constituents instead of being uniformly distributed throughout the coal substance was not investigated.

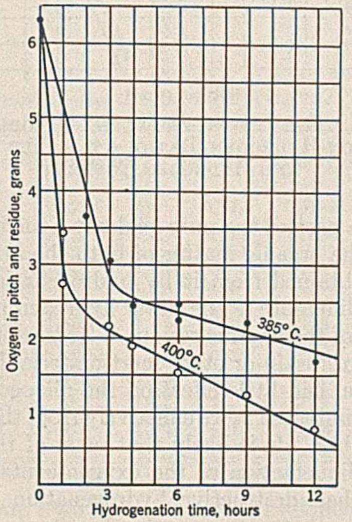


FIGURE 2. RATES OF DESTRUCTIVE HYDROGENATION OF OXYGEN LINKAGES IN BRUCETON COAL

The rates of oxygen removal at 385° and 400° C. are shown in Figure 2. These curves were made on the assumption that oxygen contained in phenols boiling below 215°, as well as the oxygen in carbon dioxide, carbon monoxide, and water, had been eliminated by destructive hydrogenation. Calculations made from the data thus far available (Figure 2), which are offered tentatively until more accurate results are obtained, indicate activation energies of 55 and 32 kg-cal., respectively, for the fast and slow reactions.

The rate of nitrogen removal was very slow and approximately constant (Figure 1, Table II). The data in Figure 1 show that the complete removal of nitrogen by hydrogenation at 400° C. or lower temperatures would be extremely difficult. The curves for organic sulfur content (Figure 1) are of the same qualitative shape as those for oxygen, but the differences between the first and later 3-hour intervals are smaller.

The amounts of available hydrogen—that is

$$\text{Per cent H} - \frac{\text{per cent O}}{8} - \frac{3\ (\text{per cent N})}{14}$$

in the original coal and in the pitches obtained by hydrogenation are shown in Figure 3. The differences between available hydrogen are greater than the corresponding differences between the actual hydrogen content (Figure 1). The curves showing the carbon contents (Figure 3) indicate that hydrogenation after the first 3 hours had little effect on the carbon contents of the products obtained at 385° and 415° C., but increased considerably the carbon content of the products obtained at 400°. It may be concluded from these facts that at 385° and 415° more hydrogen is consumed in the saturation or cleavage of carbon-carbon linkages than at 400°. At the latter temperature, a greater proportion of the hydrogen was utilized in the removal of inorganic constituents.

Effect of Time and Temperature on Liquefaction Yields

The greatest amount of liquefaction at all reaction temperatures was achieved in the first 3 hours of hydrogenation (Figure 3, Table I). This was especially true for the 400° and 415° C. experiments, in which the first 3-hour periods effected 90.3 and 91.7 per cent conversions, respectively. The second 3-hour period was important in the 385° experiments, since the conversion was increased from 82.2 to 90.4 per cent of the pure coal. However, the last two 3-hour periods at 385° were similar to those at 400° and 415° in that the average conversion per period was very small (Figure 3). It is interesting that straight lines are obtained when the liquefaction yields are plotted against inverse time of hydrogenation (Figure 4). These straight lines should be useful in predicting conversion yields for any desired time of hydrogenation.

As was expected, the liquefaction of coal was greater at 415° and 400° than at 385° C. However, the beneficial effect of the higher temperatures diminished with the time of experiment. For example, the differences in percentage yields (385° and 400° experiments) after 3 and 12 hours are, respectively, 8.8 and 1.3 (Figure 3). The extent of the liquefaction was calculated in all cases from the amounts of acetone-insoluble material obtained. Since the amounts of this residue actually isolated agree well with the values calculated from ash contents (Table III), it is believed that the liquefaction yield data are reliable.

Nature of Products

In all experiments except one (L1), the products as removed from the converter were colloidal solutions of moderately low viscosity, which could be poured and centrifuged with ease. Ultramicroscopic examination indicated that even the solution produced by hydrogenation for 12 hours at 400° C. was colloidal, although less so than the product removed from the converter after 3 hours of hydrogenation. The product obtained at 385° during 3 hours of hydrogenation (experiment L1) was a soft pitch as taken from the converter. This difference in fluidity is roughly indicated by the fact that centrifuging gave only 44 per cent yield of oil, whereas the oil yields from the centrifuge in the other experiments ranged from 78 to 87 per cent (Table I). The great difference in viscosity and physical appearance of the L1 product indicates that its

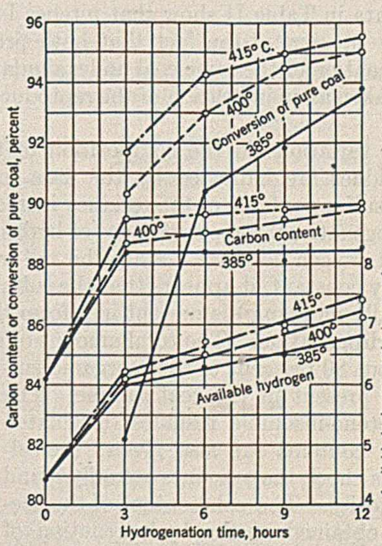


FIGURE 3. CONVERSION OF PURE COAL, CARBON CONTENT, AND AVAILABLE HYDROGEN CONTENT

average molecular weight is considerably higher than those of the other products.

The composition of the principal products of the hydrogenation experiments (pitches or viscous oils) has already been considered (Figures 1 and 3, Table II). The calorific values of the coal and the various pitches also are recorded in Table II. As was expected, these values are related to the hydrogen content, the carbon-hydrogen ratio, and the available hydrogen (Figure 5).

Table II also gives the composition of a very viscous oil (designated as P4) which may be compared with pitch I4. This viscous oil was prepared by hydrogenating a mixture of pitches (P1, Table II) which had been obtained in a previous investigation (*3*) by hydrogenating Bruceton coal for 3 hours at 400° C. The mixture of pitches (P1) was subjected to hydrogenation in tetrahydronaphthalene for 9 hours (three 3-hour periods) at 400° C., using stannous sulfide as a catalyst. The data in Table II show that pitches I4 and P4 are very similar; in view of the fact that both products arose from hydrogenation of the same coal under similar conditions, this may be taken as an indication of the reproducibility of the results.

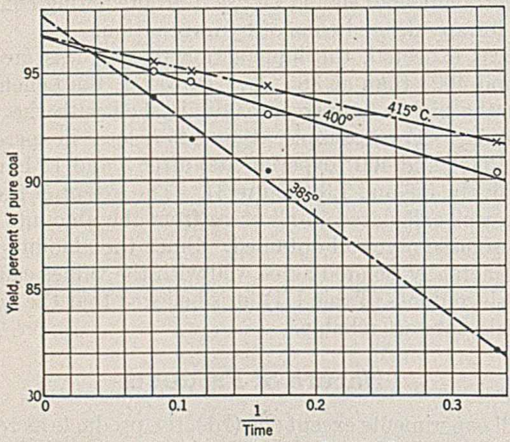


Figure 4. Rates of Pure Coal Conversion

Consistent variations in the composition of the acetone-insoluble residues are indicated by the data in Table III. The ash and sulfur contents of the residues increase with the time of hydrogenation; the percentages of hydrogen, carbon, nitrogen, and oxygen decrease. Since the sulfur-ash ratio is approximately constant, it appears that the sulfur in the residue (principally inorganic) is present in a form that is stable to further hydrogenation. The total amount of sulfur in the residue is about 80 per cent of the inorganic sulfur originally present in the coal sample. The yields of acetone-insoluble residues (calculated from the ash content) are also given; the calculated values check the amounts actually found very satisfactorily. The ash content of the acetone residue obtained in the hydrogenation of a mixture of pitches (P1, Table II) for 9 hours approximates that of the residue (I4) prepared from coal by hydrogenation during 12 hours.

The analyses in Table III were used to calculate the composition of the organic material in the acetone-insoluble residues (Table IV). Since organic sulfur was not determined in the residues, the calculations were made on the assumption that hydrogenation and dissolution had removed nearly all the organic sulfur. This assumption cannot cause any appreciable error, since the organic sulfur of the original coal was only 0.713 per cent. Judging from the calculations in Table IV, the part of the pure coal not liquefied is quite different from the organic matter of both the original coal and the pitches obtained from it by hydrogenation. The most conspicuous difference is the lower hydrogen and higher carbon contents of the organic residue. This probably indicates the presence of fusain or other inert material high in carbon. Hydrogenation had little effect on the nitrogen content, but oxygen was eliminated more effectively from the residues than from the pitches. It is likely that most of this oxygen was removed by liquefaction of the oxygen-containing constituents rather than destructive hydrogenation of the oxygen linkages.

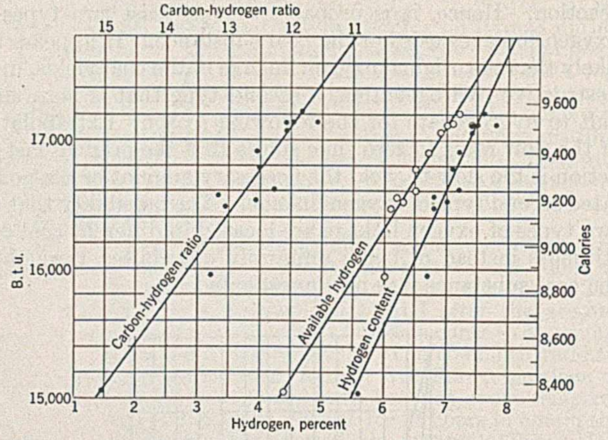


Figure 5. Relations between Calorific Value and Carbon-Hydrogen Ratio, Available Hydrogen, and Hydrogen Content

The quantities of constituents found in the hydrogenation gases are recorded in Table V. Since the converter was bled and recharged with hydrogen at the end of each 3-hour interval, the gases analyzed were those formed in the last 3 hours of hydrogenation. Excluding the gas obtained from the 3-hour experiments at 400° and 415° C. (which were 87.9 and 85.9 per cent hydrogen, respectively), the hydrogen contents ranged from 91 to 95 per cent by volume. The hydrogen content of the gas samples increased with the total time of hydrogenation, another indication that the greatest consumption of hydrogen occurred in the early stages of the hydrogenation. The percentages of saturated hydrocarbons in the gases decreased with increase of hydrogenation time. Small and almost constant amounts of alkenes were found. The quantities of carbon dioxide, hydrogen sulfide, and ammonia found in the alkaline and acidic wash solutions (Table V) show definite trends that are in agreement with the other ex-

Table III. Composition of Acetone-Insoluble Residues

Residue No.	Acetone-Insol. Residue Found Grams	Acetone-Insol. Residue Calcd. from ash content Grams	H %	C %	N %	O %	S %	Ash %	S/Ash Ratio
L1	24.2	26.8	3.5	61.9	1.3	2.9	3.2	27.2	0.114
L2	17.5	18.6	2.9	51.1	0.9	1.4	4.4	39.3	0.113
L3	16.4	17.2	2.7	48.6	0.9	0.7	4.7	42.4	0.111
L4	14.4	15.5	2.4	44.4	0.8	0.1	5.1	47.2	0.108
I1	17.1	19.3	2.7	52.6	1.0	1.6	4.2	37.9	0.111
I2	15.2	16.3	2.5	46.3	0.9	0.6	5.0	44.7	0.112
I3	13.5	15.1	2.2	42.4	0.9	0.3	5.7	48.5	0.117
I4	13.5	14.1	2.1	39.4	0.8	0.0	5.9	51.8	0.114
H1	15.1	18.7	2.5	51.0	1.0	2.3	4.2	39.0	0.108
H2	13.9	15.2	2.3	43.1	0.9	0.2	5.6	47.9	0.117
H3	13.9	13.8	1.9	37.3	0.8	0.0	6.9	53.1	0.130
H4	13.2	13.6	2.0	37.1	0.9	0.0	6.4	53.6	0.119
P4	2.5	3.1	...	...	...	...	...	53.9	
Coal[a]	...	...	5.2	78.8	1.6	6.4	1.6	6.4	

[a] Moisture-free basis.

perimental data. Most of the carbon dioxide and hydrogen sulfide were liberated early in the hydrogenation; the converse was true for ammonia.

TABLE IV. ORGANIC MATTER IN INSOLUBLE RESIDUES

Expt. No.	Per Cent by Weight H	C	N	O
L1	5.1	88.1	1.9	4.4
L2	5.2	90.2	1.6	2.5
L3	5.1	91.3	1.7	1.3
L4	5.0	92.4	1.7	0.2
I2	4.9	91.1	1.8	1.6
I3	5.0	90.8	1.9	1.5
I4	4.9	92.5	1.9	0.0
H1	4.4	89.3	1.8	4.0
H2	4.9	92.0	1.9	0.4
H3	4.7	92.8	1.9	0.0
H4	5.0	92.0	2.2	0.0
Coal[a]	5.7	85.0	1.7	6.9

[a] Calculated organic matter in coal (omitting sulfur).

TABLE V. COMPOSITION OF HYDROGENATION GASES (IN GRAMS)

Expt. No.	CO_2	C_nH_{2n}	H_2	CH_4	C_2H_6	H_2S	NH_3
L1	0.566	1.04	4.43	1.11	0.60	0.215	0.002
L2	0.153	1.12	5.17	0.94	0.16	0.090	0.007
L3	0.134	0.60	5.26	0.60	0.16	0.039	0.016
L4	0.088	0.83	5.24	0.82	0.16	0.013	0.019
I1	0.654	0.74	4.00	2.11	1.65	0.289	0.006
I2	0.111	0.36	4.98	1.07	0.46	0.025	0.014
I3	0.056	0.50	4.96	1.23	0.61	0.006	0.040
I4	0.039	0.82	5.21	0.26	1.20	0.003	0.047
H1	0.614	0.17	3.62	2.89	2.96	0.306	0.006
H2	0.129	0.61	4.39	2.58	1.02	0.051	0.035
H3	0.061	0.99	4.75	1.11	2.09	0.006	0.058
H4	0.096	0.16	5.36	0.13	1.74	0.004	0.081

The maximum hydrogen pressures developed in the experiments and volumes of hydrogenation gases are given in Table VI. It is interesting that both the maximum pressures and gas volumes increased with the time of hydrogenation. The increasing gas volumes resulted from decreased rates of hydrogenation. It is likely that a lowering in average molecular weight of the pitches was responsible for the increased pressures.

The distillates were found to be the recovered vehicle, tetrahydronaphthalene, somewhat contaminated with small amounts of hydrogenation products (Table VII). The specific gravity of the distillates and of the neutral oils obtained from them decrease with increase in time of hydrogenation, and the neutral oils were lower in specific gravity than their antecedent distillates. The distillates contained small amounts of phenols and traces of tar bases, but carboxylic acids were absent. Because of the formation of emulsions in some instances and the inherent errors of the analytical method, great significance cannot be attached to the small variations in the tar acid and base contents. In spite of the inaccuracies involved in the determination of neutral oil constituents, it appears that there is a gradual increase in the content of saturated hydrocarbons with increase in time of hydrogenation. This conclusion is supported also by the specific gravities of the neutral oils, which decrease slightly with increase in reaction time (Table VII). The olefin contents of the original vehicle and the neutral oils were found to be similar, but the neutral oils, unlike the tetrahydronaphthalene, did not give a precipitate with 82 per cent sulfuric acid.

Discussion of Results

Studies of the elimination of oxygen from coal by hydrogenation offer several attractive avenues of approach to investigators of coal constitution. Although the present study, as yet incomplete, does not cover all phases of destructive hydrogenation of oxygen, several interesting possibilities are discussed here in connection with the results thus far available. It is hoped that similar and other experiments now in progress in this laboratory will throw more light on the constitution of coal and the nature of its primary liquefaction.

The primary liquefaction, especially in the early stages, is characterized by the elimination of coal oxygen, principally as water, and by a decrease in molecular weight of the coal substance, which, after liquefaction, is recovered as a colloidal solution in the vehicle. Whether the removal of coal oxygen and the lowering of molecular weight are mutually independent or the manifestation of one single reaction is extremely important in investigations bearing on coal structure and the mechanism of coal hydrogenation. It appears from coal extraction studies (*1*, *4*), in the absence of hydrogen, that the average molecular weight may be reduced considerably without much loss of oxygen (assuming that dissociation or lowering of molecular weight precedes dissolution). It is quite likely that a part of the primary liquefaction by hydrogenation proceeds in a similar manner, giving a solution of the coal substance which later loses oxygen, principally as water. However, there is little or no evidence regarding the converse situation—namely, the lowering of molecular weight brought about by elimination of oxygen. If removal of oxygen has a profound influence on molecular weight, the oxygen thus removed is probably of the linear ether type, since loss of oxygen from the other types of linkage would have little effect. On the other hand, elimination of linear ether oxygen would cause tremendous lowering of molecular weight. For example, complete elimination of oxygen from the coal used in the present work (assuming that all the oxygen is of the linear ether type) would reduce the average molecular weight to about 220. Since precise information as to the lowering of molecular weight caused by oxygen elimination is lacking,

TABLE VI. HYDROGEN ABSORPTION AND MAXIMUM AND FINAL PRESSURES (FOR LAST 3 HOURS)

Expt. No.	Hydrogenation Period	Hydrogen Consumed	Pressure Max.	Pressure Final (cold)	Vol. at 0° C.
	Hours	*Grams*	*Lb. per sq. in.*		*Cu. ft.*
L1	0 to 3	1.57	2400	800	1.844
L2	3 to 6	0.83	2525	930	2.120
L3	6 to 9	0.74	2455	930	2.125
L4	9 to 12	0.76	2590	940	2.130
I1	0 to 3	2.00	2450	770	1.743
I2	3 to 6	1.02	2615	880	2.036
I3	6 to 9	1.04	2670	895	2.043
I4	9 to 12	0.79	2710	940	2.119
H1	0 to 3	2.38	2480	730	1.663
H2	3 to 6	1.61	2685	815	1.921
H3	6 to 9	1.25	2815	910	2.027
H4	9 to 12	0.64	2870	950	2.186

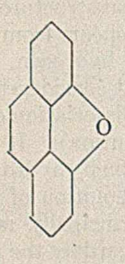
TABLE VII. COMPOSITION OF DISTILLATE

Expt. No.	Oil Distilled	Boiling below 215° C. Water	Boiling below 215° C. Oil	Distillate Sp. gr. (15.6° C.)	Distillate Tar bases	Distillate Phenols	Neutral Oil Sp. gr. (15.6° C.)	Neutral Oil Olefins	Neutral Oil Aromatics	Neutral Oil Saturates
	Grams	*Cc.*	*Cc.*		*% by volume*			*% by volume*		
L2	135	Trace	76	0.972	0.8	2.2	0.968	3.5	96.3	0.2
L3	144.5	1.3	80	0.971	0.1	1.6	0.969	3.0	96.8	0.2
L4	145.9	0.8	85	0.967	0.1	3.5	0.966	2.5	96.4	1.1
I1	139.1	0.4	79	0.974	0.5	2.0	0.971	3	96.8	0.2
I2	142.1	1.5	87.5	0.970	1.0	2.5	0.965	3	96.2	0.8
I3	141	3.5	77.5	0.961	1.5	2.5	0.960	3.5	95.5	1
I4	145	3.0	92	0.963	0.6	2.4	0.961	3	96.4	0.6
H1	133	Trace	79.5	0.971	1.4	2.7	0.969	4.6	94.9	0.5
H2	145	2.5	83.5	0.965	0.7	3.0	0.964	3.4	95.9	0.7
H3	146.9	2.0	93.0	0.958	1.0	3.2	0.957	3	95	2.0
H4	152.7[a]	...	84[b]	0.955	0.0	4.5	0.951	4.6	94.2	1.2
P4	172	...	103	0.957	2.2	2.0	0.954	4	94	2
Vehicle	...	...	..	...	0.0	0.0	0.971	4	96	0.0

[a] This included oil washed from the converter with acetone.
[b] Boiling at 175–215° C.

this interesting relation has not been used in investigations of the oxygen linkage in coal.

Complete elimination of the inorganic elements and saturation of the carbon-carbon bonds by hydrogenation under mild conditions (*2*) should also furnish information as to the nature of the oxygen linkage. The connection between the nature of the original oxygen linkages and the hydrocarbon products obtained by complete saturation of the carbon skeletons may be described as follows: Although the production of completely cyclic hydrocarbons from coal containing linear ether linkages is easily explained, completely cyclic hydrocarbons could arise from other types of oxygen linkage only in special cases. For example, cyclic hydrocarbons could result from structures, such as I and II



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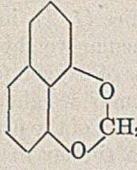
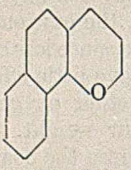
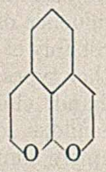


II

but other types of heterocyclic rings, such as III and IV



III



IV

would be expected to yield hydrocarbons with aliphatic side chains. The hydrocarbon products obtained from bituminous coals containing considerable oxygen of the latter type should have appreciable amounts of aliphatic side chains.

The present work appears to indicate that oxygen elimination and molecular weight lowering, although usually occurring simultaneously, are largely independent. In the 3-hour experiment at 385° C., almost as much oxygen was eliminated as at 400° C. (Figures 1 and 2, Table II), but the lowering of molecular weight was much less. (This conclusion is based on the high viscosity of the product as removed from converter.) This result would appear to indicate that oxygen may be removed without the occurrence of a commensurate change in molecular weight of the coal substance. It is planned to obtain more information on this point by determining both molecular weights and oxygen contents of the products.

In the second 3-hour period at 385° C., the molecular weight was considerably lowered but little oxygen was removed. This result also may be taken as support of the hypothesis that oxygen removal and decrease in molecular weight are largely independent and that cleavage of carbon-carbon linkages or rupture of secondary valence forces is chiefly responsible for lowering of molecular weight.

The addition of hydrogen to carbon-carbon double bonds or the cleavage of carbon linkages is indicated also by the changes in carbon and oxygen contents of the pitches obtained by more than 3-hour hydrogenation at 385° C. Since the oxygen was removed without increase in carbon content in the 385° experiments, a compensating amount of hydrogen must have been absorbed. In the experiments at 400° the carbon content increased slowly during the removal of oxygen; therefore, at this temperature more of the hydrogen was utilized in removing the inorganic elements. The carbon content of the 415° C. pitches also increased very little with time of hydrogenation. Saturation of carbon-carbon double bonds at 385° and cracking at 415° could have been responsible for the small increase of carbon contents at these temperatures.

It has been pointed out already that there is some evidence for believing that the coal oxygen consists of two broad types (Figure 2). If the current belief (*5*) that nearly all the oxygen in Pittsburgh bed coal is present as ether linkages is correct, it follows that the two types of oxygen linkage are both ether linkages. Since diphenyl ether retains its oxygen under the conditions of the present work [such experiments (*3*) have been carried out at 400° C.], it is possible that ether linkages of this type represent the oxygen removed slowly in the latter stages of the liquefaction; other and more reactive types of oxygen are responsible for the considerable loss of water during the first 3 hours.

The demonstration that two broad types of oxygen linkage are present in coal is of great interest, and further work to confirm this view is desirable. If other coals are found to behave in the same manner, the determination of these types should be included in a complete analysis of coal. Extrapolation of the slower rate curve to zero time (Figure 2) would give the amount of one type, and subtraction of this value from the total oxygen would give the other. Significant results might be obtained by correlating the contents of the two types of oxygen with rank of coal, yield of phenols on coking, etc.

The peculiar composition of the residue resistant to liquefaction (Table IV) and the fact that the last 3-hour periods at 400° and 415° C. effected only a negligible increase in yield indicate that the liquefaction yield is limited by the presence of a material quite different from the rest of the coal substance. In this connection Figure 4 is of interest because it indicates that hydrogenation for an infinite time would leave some of the "pure coal" unconverted. Since the fusain content of Pittsburgh bed coal usually is 2 to 3 per cent, it appears that some constituent of the coal other than fusain is unusually resistant to hydrogenation. This conclusion was verified by microscopic examination, which revealed the presence of spore remains as well as fusain.

Acknowledgment

The authors are indebted to H. H. Storch, in charge of the coal hydrogenation program at the Bureau of Mines, for suggesting the problem and for kind advice during the work and preparation of the manuscript. R. Thiessen of the Coal Constitution Section made the microscopic examinations. The authors are grateful to H. M. Cooper and other members of the Coal Analysis Section for analyses of the coal, pitches, and insoluble residues.

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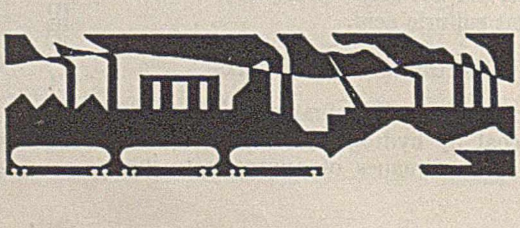

U. S. Bureau of Mines Experimental Plant

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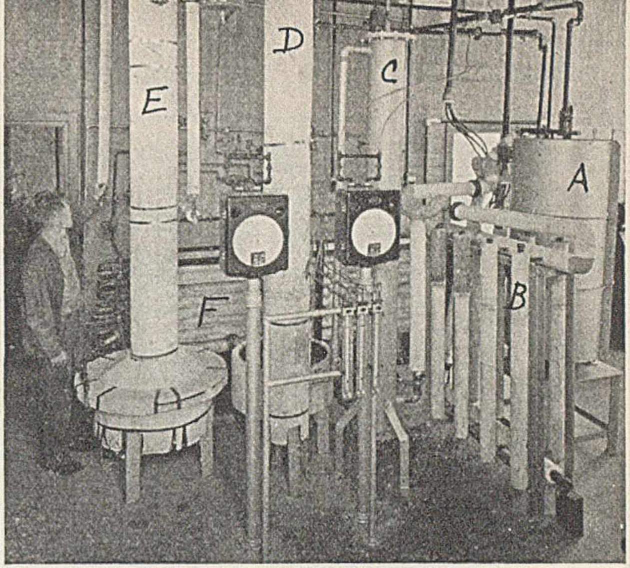
I. I. PINKEL, R. L. BOYER, J. R. SCHAEFFER,
AND R. H. KALLENBERGER

A description is given of an experimental plant for the continuous hydrogenation of about 100 pounds of coal per 24 hours. The major difficulties experienced in operation of the plant and the solutions adopted are discussed. Typical results on the liquid phase hydrogenation of Pittsburgh seam coal are given.



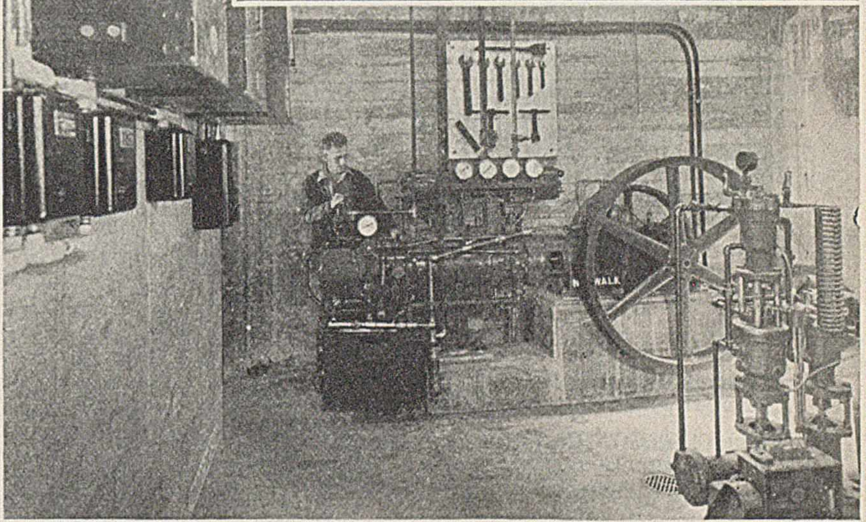


Figure 1 (*Top*). Hydrogen Plant
Figure 2 (*Bottom*). Hydrogen Compressor

THE U. S. Bureau of Mines experimental coal-hydrogenation plant was built to obtain information regarding the amenability of the various types of United States coals to hydrogenation for the production of liquid fuels. Owing to the absence of detailed information concerning the construction and operation of existing European coal-hydrogenation plants, it appears desirable to publish a description of the bureau's plant at the present time and to present a discussion of some of the preliminary experiments.

Hydrogen Production Plant

The hydrogen plant shown in Figure 1 consists of a water-gas generator *A*, water-gas shift chamber *B*, water-spray tower *C*, carbon dioxide scrubber *D*, amine regenerator *E*, and heat exchangers *F*. A four-stage horizontal compressor (Figure 2) is used for compressing the hydrogen. Hydrogen is stored in a battery of 25 high-pressure cylinders, each 200 cubic feet in capacity (measured at atmospheric pressure).

The water-gas generator consists of two concentric tubes, 7 and $4^1/_2$ inches o. d. and 60 inches long made of high chromium-nickel alloy (25 per cent chromium, 20 per cent nickel). The 1-inch annulus between these tubes is filled with pure nickel stampings, $^1/_4 \times {}^1/_8$ inch, which serve as catalyst for the reaction between the steam and natural gas. This reaction zone is maintained at 1050° C. (1920° F.) by two sources of heat—namely, a 1.5-inch Glowbar unit in the center of the inner tube, and a high-temperature resistance heater surrounding the outer tube. Equal volumes (about 100 cubic feet per hour) of steam and natural gas are used. The analysis of the natural gas varies somewhat with time but averages about 90 per cent methane, 8 per cent ethane, and 1.5 per cent nitrogen. The water gas produced by the generator contains about 75 per cent hydrogen, 21 per cent carbon monoxide, 1 per cent carbon dioxide, 2 per cent nitrogen, and 1 per cent methane.

The water-gas shift tubes (Figure 1*B*) have been replaced by a more compact catalyst chamber to reduce heat losses. The new water-gas shift chamber consists of a 24-inch section of 6-inch steel pipe containing at its center a 2-inch copper rod. Attached to the latter are eight copper plates or vanes which divide the chamber into eight catalyst spaces. This arrangement permits rapid heat conduction and avoids excessive channeling of the water gas–steam mixture. A copper-cobalt catalyst, the preparation of which was recently described (*1*), was used for accelerating the water-gas reaction,

$$H_2O + CO = CO_2 + H_2$$

the temperature being maintained at about 350° C. (660° F.). Approximately five parts of steam are mixed with the water gas as it issues from the water-gas generator. The exact amount of steam added is determined by the desired temperature gradient in the column of copper-cobalt catalyst. This gradient is preferably kept below 50° C. (90° F.)—that is, a catalyst temperature of 300° to 350° C. (570° to 660° F.).

Water-spray tower *C* condenses the excess steam in the off-gas from the cobalt-copper catalyst. Carbon dioxide scrubber *D* is an 8 inch × 12 foot tower packed with $^1/_4$-inch car-

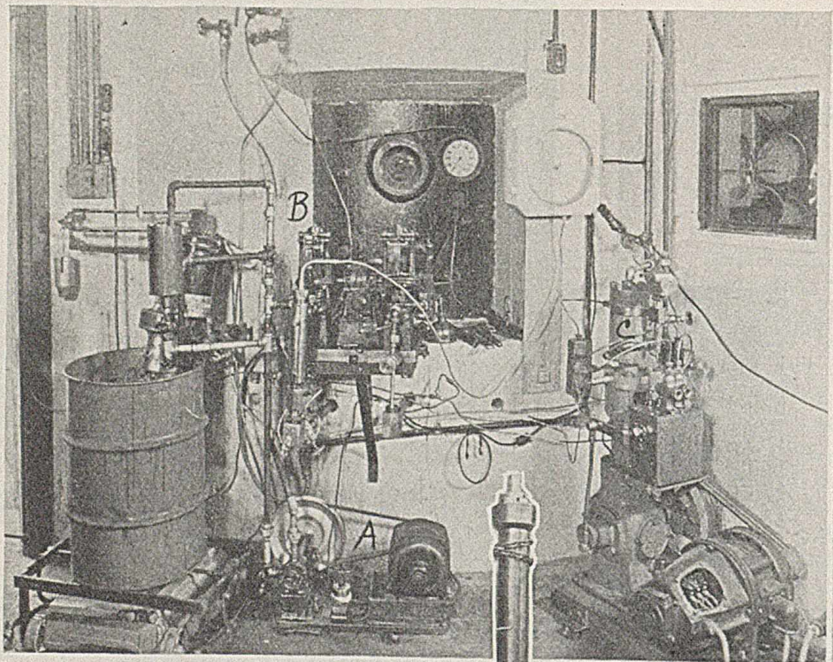
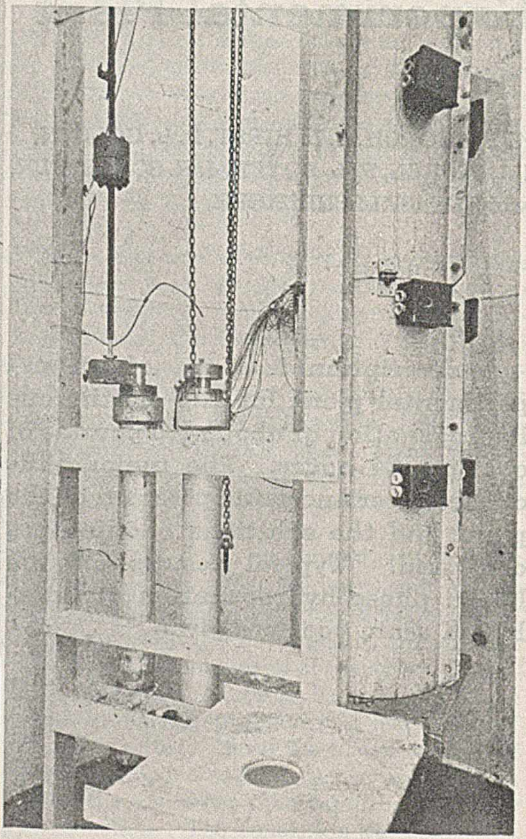


Figure 3 (*Above*). Paste Pumping and Hydrogen Recirculation

Figure 4 (*Right*). Coal Hydrogenation Converter

Figure 5 (*Below*). Condensation Traps and Furnace



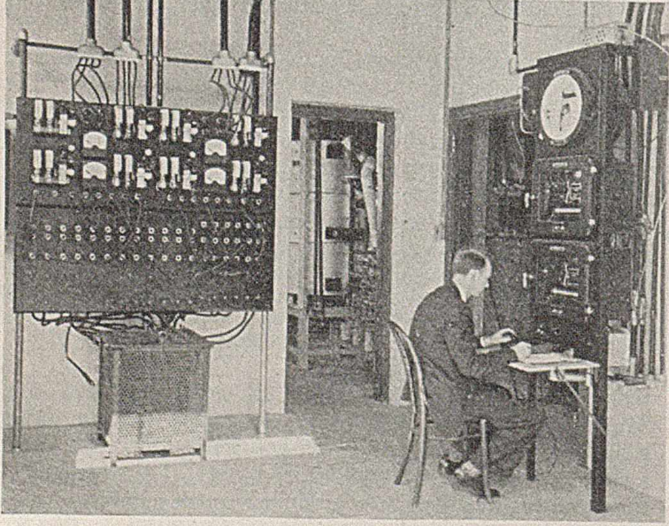
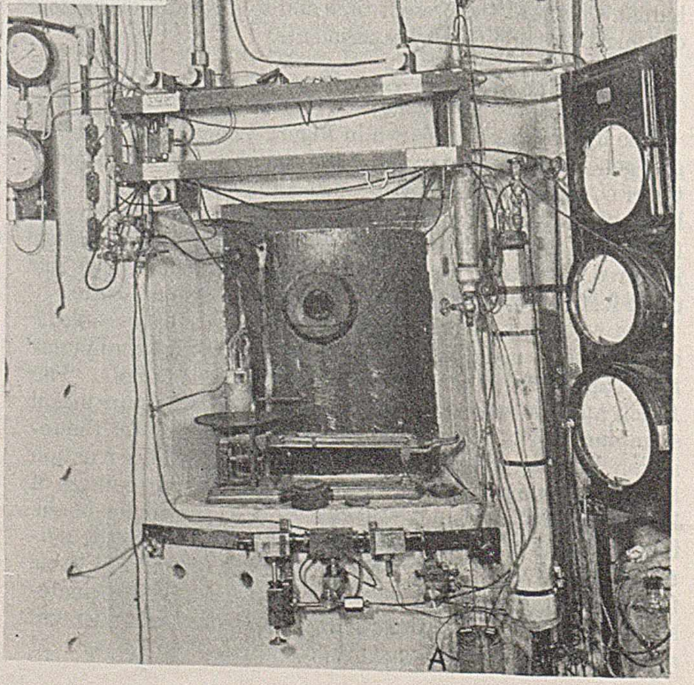


Figure 6 (*Above*). Switchboard and Control Instruments

Figure 7 (*Below*). Control Valves and Discharge Coil



bon Raschig rings. A spray of 10 per cent Tetramine (Carbide and Carbon Chemicals Corporation) is used to scrub out the carbon dioxide. The amine regenerator, *E*, consists of a boiler 12 × 30 inches, attached to a distillation column 8 inches × 11 feet, packed with 1/4-inch carbon Raschig rings. The spent amine is heated in the heat exchanger, *F*, by transfer of heat from regenerated amine, and is then pumped through a spray head in the center of the distillation column of *E*. A reflux coil carrying cooling water is located in the top of this column.

The hydrogen plant has functioned satisfactorily during the production of about 25,000 cubic feet of hydrogen. The percentage analysis of the hydrogen produced is approximately as follows: 96.0 hydrogen, 0.5 carbon monoxide, 0.2 carbon dioxide, 1.2 methane, 0.2 oxygen, and 1.9 nitrogen.

Coal-Hydrogenation Plant

The coal-hydrogenation plant is shown in Figures 3, 4, and 5. The coal-oil paste is delivered under several pounds pressure by the gear-type oil pump *A* (Figure 3) to the paste pump *B*. The latter is a vertical piston pump with steel ball check valves and adjustable stroke. The paste is forced into the converter shown in Figure 4 and contained in the furnace of Figure 5. This converter is a tube 5 inches o. d. × 3 inches i. d., made of 18 per cent chromium–8 per cent nickel alloy-steel. The converter closures are the same as those described by Warren and Gilmore (*2*), except that Monel metal sealing rings are used in place of copper. Hydrogen is pumped in through the top of the converter and preheated by passage through a heat exchanger. The latter consists of several coils of aluminum tubing through which the incoming hydrogen passes before being mixed with the paste. The light oil and hydrogen off-gas pass around these coils before leaving the converter. Heat is supplied to the converter by a cylindrical electric resistance furnace (Figure 5). Temperatures are measured by thermocouples inserted in a well attached to the top closure of the converter and extending the full length of the latter. Surface temperatures on the outer wall of the converter are measured at four equidistant points.

The light oil and hydrogen off-gas pass through the two traps shown in Figure 5. The light oil condenses in the first trap, and hydrogen sulfide, water vapor, and carbon dioxide are removed from the hydrogen gas by a layer of sodium hydroxide in the second trap. From the latter the gas is picked up by the recirculation pump and pumped back into the converter.

The switchboard and temperature-recording instruments are shown in Figure 6, and the control valves and discharge coil in Figure 7. Figure 8 is a floor plan of the present arrangement of the apparatus in the coal-hydrogenation building.

TABLE I. OPERATING DATA

(Temperature, 410° C. (770° F.); pressure, 3200 pounds per square inch; hydrogen recirculation rate, 200–300 cubic feet (atmospheric pressure) per hour; total time of run, 18 hours; time of contact, 3 hours; catalyst 0.25 per cent stannous sulfide, 0.25 per cent molybdenum oxide)

	Total Weight, Lb.	Total % of Ash- and Moisture-Free Coal		Total Weight, Lb.	Total % of Ash- and Moisture-Free Coal
Paste	94.0	..	Heavy oil	50.1	..
Coal	46.5	..	Light oil	34.5	..
Hydrogen absorbed	2.7	6.3	Water	2.7	4.7
Liquid products	88.3	..	Solids	3.5	..
Gaseous products	8.4	19.6	Oil yield	..	74.7

TABLE II. ANALYTICAL DATA ON PRODUCTS

	Light Oil		Vehicle (Anthracene Oil)		Heavy Oil	
	%	Sp. gr.	%	Sp. gr.	%	Sp. gr.
Sample as received	..	1.103	..	1.103	..	...
Distn. temp. of product:						
Under 200° C. (390° F.)	18.5	0.880	1.5	...	3.0	...
200–270° C. (390–520° F.)	45.0	0.993	30.5	Solid	..	...
270–300° C. (520–570° F.)	16.5	1.054	15.0	1.090	..	...
300–330° C. (570–625° F.)	10.0	1.075	14.0	Solid	..	...
Over 330° C.	10.0	...	39.0	...	..	...
To 200° C. at 5 mm.	..	...	..	...	53.0	1.057
Tar bases	4.2	...	6.4	...	3.8	...
Phenols	9.2	...	4.4	...	7.4	...
Carboxylic acids	0.4	...	0.0	...	0.2	...
Neutral oil	86.2	0.990	89.2	1.064	..	
Components of neutral oil, %:						
Olefins	7.5	...	8.0	...	..	...
Aromatics	82.6	...	92.0	...	..	...
Saturates	9.9	...	0.0	...	..	...
Acetone insol.	..	...	..	...	6.7	...
Tetrahydronaphthalene insol.	..	...	..	...	5.7	...

being converted to normally gaseous hydrocarbons. The product consists of about 50 per cent of light oil, distilling mainly between 180° and 300° C., and 50 per cent of a heavy oil that resembles a low-temperature tar. This heavy oil is centrifuged to remove the ash and other solid matter, such as fusain and catalyst material, and the liquid is then used for pasting an additional quantity of coal. The light oil is to be sent to the second hydrogenation stage, where it will be converted to gasoline. As an example of the data collected, Tables I and II give the details of run C-4.

Several runs have been made recently and will be reported in detail in later publications. In these runs contact time was decreased from 3 to 1.5 hours and the temperature of the liquid in the converter was varied from 410° to 433° C. Paste was made using heavy oil from earlier runs as the vehicle. Oil yields as per cent of ash- and moisture-free coal varied from 74.7 to 79.3 per cent, with gas yields varying from 17.2 to 19.7 per cent. Light oil from these runs is being accumulated and will be used for charging stock for the second-stage converter.

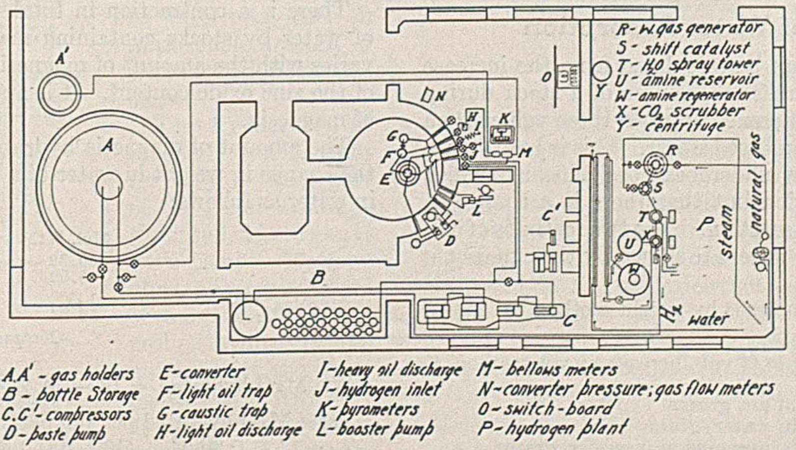


FIGURE 8. PLAN OF COAL HYDROGENATION PLANT

Liquid-Phase Hydrogenation of Pittsburgh Seam Coal

Six single-stage runs, lasting 10 to 48 hours, were made using coal from the bureau's experimental mine at Bruceton, Pa. These show that it is possible to liquefy about 75 per cent of the coal (ash- and moisture-free basis), about 20 per cent

Operating Difficulties

During these experiments the following difficulties were encountered and the indicated solutions adopted:

PASTE PUMPING. Tetrahydronaphthalene-coal mixtures could not be pumped by the Hills-McCanna pump. Anthracene oil-coal mixtures could be readily pumped only of the mixture was heated and agitated for several hours prior to feeding into the pump. The introduction of a gear-type oil pump to agitate the coal-oil paste by recirculation and to feed the paste under positive pressure to the Hills-McCanna pump made the paste-pumping operation much smoother and eliminated the frequent loss of "prime" of the paste pump. It was found, however, that the gear-type oil pump would occasionally cause a "gelling" of the paste. This can be avoided by lowering the temperature of the paste and reducing the speed of the oil pump.

Recently several hundred pounds of paste were made from Bruceton coal and centrifuged heavy oil from the earlier coal hydrogenation runs. With this paste there was little tendency for coal to settle out. It pumped readily and hydrogenated without difficulty.

HEAVY-OIL DISCHARGE. The erosion of ordinary high-pressure valves is very rapid in discharging the heavy oil plus solid residue of the first hydrogenation stage. A long coil of narrow-bore copper tubing *A*, Figure 7, has been found to be a satisfactory discharge apparatus.

LIGHT-OIL DISCHARGE. Clogging of the light-oil discharge line by solid ammonium carbonate caused interruption of a recent run. This was avoided by steam-jacketing the discharge line and, when necessary, continuously injecting a small amount of water just ahead of the discharge valve.

HYDROGEN RECIRCULATION. Injection of hydrogen along with the coal-oil paste is the only means of mechanical agitation that is readily available. It has been found that the amount of cold hydrogen that can be recirculated is limited to about 200–300 cubic feet per hour (measured at atmospheric pressure and temperature). Larger amounts of cold hydrogen remove an excessive amount of heat from the converter and vaporize too much of the pasting fluid. The introduction of a heat exchanger inside the top section of the converter so that the light-oil vapors and hydrogen off-gas will preheat the incoming hydrogen will probably solve this problem. Such a heat exchanger fabricated of aluminum tubing is now being tested.

Acknowledgment

The writers wish to thank C. H. Fisher and Abner Eisner of this laboratory for the distillation of the products and determination of tar bases, phenol, carboxylic acids, neutral oil, etc. They also wish to thank T. E. Warren of the Canadian Bureau of Mines, Fuel Testing Laboratory, and F. S. Sinnatt, Director of Fuel Research, Department of Scientific and Industrial Research, Great Britain, for the advice and help given in the design and operation of the experimental coal hydrogenation plant.

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Water Resistance of Neoprene

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SUPERIOR water resistance of well-cured neoprene, like that of natural rubber, depends upon the absence of water-soluble ingredients and agents that are capable of absorbing water. It has been shown (*1, 2, 3, 5*) that the water resistance of neoprene varies greatly with different activating agents. This paper includes a more detailed study of the water absorption of neoprene–magnesia–zinc oxide compounds and describes certain loaded stocks with improved water resistance. The water absorption was determined by the method already outlined (*5*), using slabs 0.20 cm. thick.

Calculation of Water Absorption

The water absorption can be calculated from the increase in weight or from the increase in volume of a stock during immersion in water. A difference between these values is an indication of chemically combined water. This is based upon the assumption that water undergoes no significant change in volume during absorption but that there is a change in volume during a chemical reaction. The two methods of calculating the absorption of water are shown by the equations:

$$\frac{c - a}{a - b} \times 100 = \%\ \text{vol. increase by weight method, } W$$

$$\frac{(c - d) - (a - b)}{a - b} \times 100 = \%\ \text{vol. increase by vol. method, } V$$

where a = original weight in air, grams
b = original weight in water, grams
c = weight in air after immersion in water, grams
d = weight in water after immersion in water, grams

If there is no change in volume of the water, $b = d$ and both methods give the same result. If, however, there is a decrease in volume, $d > b$ and the calculated results by the weight method will be greater than those obtained by the volume method. The weight method gives, within the limits of the experimental error, the volume of water absorbed per 100 volumes of sample, and the volume method gives the percentage increase in volume of the sample.

Magnesia Stocks

There is a contraction in total volume during absorption of water by stocks containing magnesia. This contraction varies with the amount of magnesia used but is independent of the zinc oxide content. It is apparently due to hydration of magnesia.

The amount of magnesia hydrated can be calculated from the change in weight in water of a specimen after immersion in water as follows:

	Mol. Wt.	Sp. Gr.	Gram Mol. Vol., Ml.
MgO	40.32	3.20	12.60
H_2O	18.02	1.00	18.02
$MgO + H_2O$	...	..	30.62
$Mg(OH)_2$	58.34	2.36	24.72
		Contraction per gram mole	5.90

$$\text{Wt. MgO hydrated} = (d - b) \times \frac{40.32}{5.90}$$

Parts MgO hydrated per 100 parts neoprene (M) =

$$(d - b) \times \frac{40.32}{5.90} \times \frac{\text{stock formula wt. with 100 neoprene}}{a}$$

TABLE I. ABSORPTION OF WATER BY MAGNESIA COMPOUNDS IMMERSED IN WATER AT 100° C.

Formula No.			1					2					3					4		
Neoprene Type E, parts			100					100					100					100		
MgO, parts			10					20					10					20		
ZnO, parts			10					10					20					20		
a, grams			5.301					6.103					6.011					6.565		
b, grams			1.523					1.940					1.985					2.327		
Time in Water at 100° C.	*c*	*d*	*W*	*V*	*M*	*c*	*d*	*W*	*V*	*M*	*c*	*d*	*W*	*V*	*M*	*c*	*d*	*W*	*V*	*M*
Hours	*Grams*	*Grams*	%	%	*Grams*	*Grams*	*Grams*	%	%	*Grams*	*Grams*	*Grams*	%	%	*Grams*	*Grams*	*Grams*	%	%	*Grams*
24	5.890	1.558	15.59	14.66	5.4	6.925	2.021	19.75	17.80	11.8	6.587	2.027	14.31	13.26	6.2	7.380	2.409	19.23	17.29	12.0
48	6.040	1.555	19.56	18.71	5.0	7.089	2.020	23.68	21.76	11.7	6.736	2.027	18.01	16.96	6.2	7.547	2.409	23.17	21.24	12.0
72	6.195	1.557	23.66	22.76	5.3	7.220	2.019	26.83	24.93	11.5	6.891	2.025	21.86	20.86	5.9	7.676	2.404	26.21	24.40	11.2
120	6.367	1.563	28.21	27.16	6.2	7.372	2.024	30.48	28.47	12.2	7.051	2.030	25.83	24.71	6.7	7.834	2.409	29.94	28.01	12.0
330	6.964	1.564	44.01	42.93	6.3	7.774	2.031	40.14	37.95	13.3	7.499	2.037	36.96	35.67	7.7	8.201	2.417	38.60	36.48	13.1
420	7.127	1.564	48.33	47.24	6.3	7.884	2.032	42.78	40.57	13.4	7.633	2.037	40.29	39.00	7.7	8.305	2.418	41.06	38.91	13.3

The results obtained with four different stocks are shown in Table I. Most of the hydration occurs during the first 24 hours; it increases only slightly as the immersion is continued for 420 hours, even though the water absorption continues to increase substantially as shown by the values in the *W* and *V* columns of Table I. The average amount of magnesia hydrated is 68 per cent of the total amount which was supposedly added. The magnesia actually used had been on hand for some time. It analyzed as follows:

MgO	61%
$Mg(OH)_2$	35
$MgCO_3$	4

Since the determinations of both the degree of hydration and the composition of the magnesia involve indirect calculations, these results are in as good agreement as might be expected. Leaching cannot account for the difference, since water in which samples had been exposed at 100° C. contained only traces of magnesium and zinc.

Similar determinations with three stocks which did not contain magnesia, as given in Table II, did not show this change in weight in water even after an appreciable amount of water had been absorbed.

The hydration of magnesia can account for only a small part of the water absorption, and the result with sample 7 shows that the replacement of magnesia by magnesium hydroxide does not improve the water resistance. Since it seemed possible that some of this high absorption might be due to small amounts of magnesium chloride formed during cure, silver abietate and silver stearate where included in a series of compounds to convert the soluble chloride into insoluble silver chloride. These stocks failed to show any improvement over the controls.

> **The contraction in total volume during absorption of water by neoprene compounds containing magnesia is attributed to hydration of the magnesia. Neoprene compounds with a water resistance exceeding that of smoked sheet rubber compounds may be obtained by compounding with litharge and such additional activators as zinc sulfide and catechol. Rosin improves the water resistance of neoprene compounds at elevated temperatures. Sulfur decreases the water resistance of magnesia–zinc oxide and litharge-neoprene compounds in proportion to the amount used. The influence of temperature on the water absorption of both magnesia–zinc oxide and litharge compounds has been determined.**

TABLE II. ABSORPTION OF WATER BY NEOPRENE WITHOUT MAGNESIA

Formula No.	5[a]		6[a]		7[a]	
Neoprene Type E	100		100		100	
PbO	20		20		...	
ZnO	...		10		5	
$Mg(OH)_2$	...		...		10	
Hours in Water at 100° C.	*c*	*d*	*c*	*d*	*c*	*d*
0	4.507	1.427	4.628	1.643	4.842	1.251
24	...	...	...	...	5.372	1.258
48	4.762	1.425	4.866	1.642	5.582	1.255
120	...	...	...	...	5.981	1.255
185	...	...	...	...	6.260	1.258
	% Volume Absorption					
48	8.2		8.1		20.6	

[a] Press-cured 30 minutes at 153° C.

Litharge Gum Stocks

Previous work (*3*, *5*) showed that a litharge compound (Eagle-Picher sublimed litharge) containing zinc oxide, rosin, and sulfur had high water resistance. A disadvantage of this combination is the instability of the uncured compound and the processing difficulty it presents. The stability may be improved if the sulfur is omitted, but its activating influence is lost and the zinc oxide does not activate a litharge compound in the absence of sulfur. Possible activators for use in a litharge compound have been evaluated in a gum stock, and the results are summarized in Table III. Litharge alone gives a fairly stable stock, and the cured slabs have good water resistance but low modulus and tensile strength. The addition of magnesia raises the modulus but decreases the stability in the absence of rosin and lowers the water resistance.

TABLE III. LITHARGE GUM STOCKS

Formula No.	8	9	10	11	12	13	14
Neoprene Type E	100	100	100	100	100	100	100
PbO	20	20	20	20	20	20	20
MgO	...	10	...	...	...	...	...
ZnO	...	...	5	...	...	...	...
ZnS	...	...	...	5	10	...	...
Catechol	...	...	...	...	...	0.1	0.5
	Stability, Plasticity–Recovery Numbers						
Aged at 50° C., Hr.							
0	112–11	153–47	122–14	130–13	143–17	111–12	114–12
24	130–14	168–65	135–13	140–10	147–32	133–12	132–16
48	123–13	179–98	130–16	142–30	148–39	139–16	148–50
96	145–53	190–110	161–48	163–59	161–58	155–47	172–64
	Per Cent Volume Water Absorption, 48 Hr. at 100° C., 30-Min. Cure						
	7.6	17.6	7.2	7.3	7.6	6.4	5.7
Min. of Cure at 153° C.	Stress-Strain Data[a]						
10	14(200) 83(1175) 1130	39(550) 121(1725) 1040	11(150) 105(1500) 1200	9(125) 93(1325) 1190	21(300) 92(1300) 1100	19(275) 109(1550) 1000	35(500) 97(1375) 890
30	25(350) 112(1600) 960	47(675) 155(2200) 1020	19(275) 118(1675) 980	26(375) 134(1900) 1040	37(525) 135(1925) 1000	42(600) 90(1275) 750	58(825) 111(1575) 730
60	21(300) 128(1825) 970	58(825) 151(2150) 940	30(425) 128(1825) 970	33(475) 132(1875) 970	33(475) 142(2025) 1000	54(775) 88(1250) 680	74(1050) 93(1325) 660

[a] The figures for each formula represent stress at 600% elongation in kg. per sq. cm. (lb. per sq. in.), tensile strength in kg. per sq. cm. (lb. per sq. in.), and per cent elongation at break.

TABLE IV. COMPARISON OF CARBON BLACK COMPOUNDS OF NEOPRENE WITH RUBBER

Formula No.	15	16	17	18	19	20
Neoprene Type E	...	100	100	100	100	100
Smoked sheet	100	...	...	...	...	...
FF wood rosin	...	5	5	5	5	5
Litharge	5	20	20	20	20	20
P-33	50	35	35	35	35	35
Thermax	75	52	52	52	52	52
Extra light calcined magnesia	...	...	2	...	...	...
Zinc sulfide (Cryptone)	...	...	...	...	10	...
Catechol	...	...	...	...	...	0.25
Zinc oxide	...	...	...	5	...	...
Sulfur	1	...	1	1	...	...
"Neozone" A (*4*)	1.5	...	...	...	...	...
"Antox" (*4*)	1.5	...	...	...	...	...
"Zenite" (*4*)	2	...	...	...	...	...
"Retarder" W (*4*)	0.5	...	...	...	...	...
	Stability, Plasticity–Recovery Numbers					
Aged at 50° C., Hr.						
0	140–7	156–13	153–11	153–9	155–11	164–14
24	160–6	188–32	187–36	182–39	190–37	241–88
48	172–11	215–78	212–61	213–77	216–79	282–160
96	191–51	272–128	280–105	281–161	274–130	375
Cure[b]	Stress-Strain Data[a]					
1	69(975) 160(2275) 530	90(1275) 116(1650) 500	92(1300) 107(1525) 520	84(1200) 100(1425) 500	86(1225) 107(1525) 540	102(1450) 111(1575) 410
2	72(1025) 149(2125) 540	104(1475) 118(1675) 420	105(1500) 109(1550) 440	116(1650) 121(1725) 330	97(1375) 118(1675) 460	104(1475) 107(1525) 370
3	74(1050) 149(2125) 520	107(1525) 121(1725) 460	112(1600) 114(1625) 400	104(1475) 109(1550) 400	109(1550) 118(1675) 430	107(1525) 112(1600) 320
4	76(1075) 151(2150) 500	107(1525) 118(1675) 420	118(1675) 118(1675) 400	111(1575) 114(1625) 350	109(1550) 120(1700) 450	116(1650) 123(1750) 330
Days of Immersion	Stress-Strain Data after Immersion in Water at 100° C.[a]					
2	93(1325) 137(1950) 450	114(1625) 118(1675) 340	116(1650) 116(1650) 300	111(1575) 111(1575) 300	111(1575) 114(1625) 400	114(1625) 114(1625) 300
4	98(1400) 144(2025) 420	121(1725) 121(1725) 300	118(1675) 118(1675) 300	111(1575) 111(1575) 300	120(1700) 120(1700) 300	118(1675) 118(1675) 300
16	100(1425) 141(2000) 430	...... 135(1925) 260	...... 121(1725) 280	118(1675) 118(1675) 300	...... 127(1800) 250	...... 127(1800) 250
32	95(1350) 137(1950) 410	...... 135(1925) 260	...... 116(1650) 280	125(1775) 125(1775) 300	...... 135(1925) 280	...... 132(1875) 260
	% Loss of Material after Immersion in Water at 100° C.					
32	1.88	0.84	1.88	1.88	0.89	0.92

[a] The figures for each formula represent stress at 300% elongation in kg. per sq. cm. (lb. per sq. in.), tensile strength in kg. per sq. cm (lb. per sq. in.), and per cent elongation at break

[b] Rubber cured 15, 30, 45, and 60 min. at 134° C.; neoprene cured 10, 20, 40, and 60 min. at 153° C.

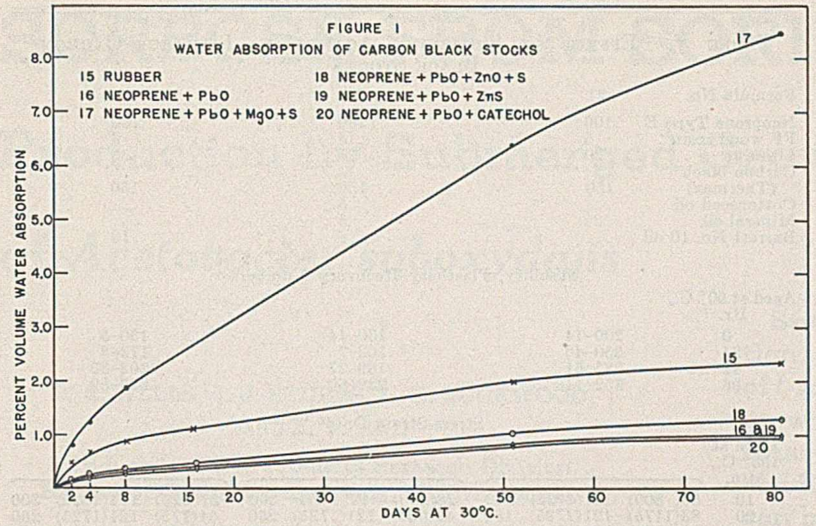


FIGURE 1
WATER ABSORPTION OF CARBON BLACK STOCKS

Zinc oxide without sulfur in the presence of litharge has no significant effect on the stability or water absorption but actually retards the cure and lowers the modulus. Zinc sulfide is a mild activator in combination with litharge, although less effective than magnesia; it has little effect on the stability or water resistance. Catechol is effective in giving a high-modulus gum stock with good water resistance but low tensile strength. In fact, the tighter cure obtained with catechol gives a litharge compound with improved water resistance. Although catechol itself is water soluble, the small amounts used probably exist in the cured compound as an insoluble lead salt.

Litharge–Carbon Black Stocks

A comparison of carbon-black-loaded neoprene, compounded with litharge and additional activating agents, with a practical water-resistant rubber compound showed that the neoprene compounds, except that containing magnesia, have superior water resistance at 30° and at 100° C. Since two soft carbon blacks (P-33 and Thermax) were used in the rubber stock, both were used in the same proportion in the neoprene to give the same volume loading. The compounds and test data are included in Table IV.

The water absorption values at room temperature and at 100° C., as calculated from the gain in weight, are plotted against time in Figures 1 and 2. In each case the water resistance of the loaded neoprene stock is appreciably better than that of the corresponding gum stock (Table III). The effect is greater than that which can be attributed to the dilution of the neoprene by carbon black. At both room temperature and at 100° C. the water resistance of the stock containing zinc oxide and sulfur is slightly inferior to that containing only litharge as activator. The addition of zinc sulfide has little effect, whereas the addition of catechol actually improves the water resistance.

These conclusions regarding the influence of compounding ingredients on water absorption of the 0.2-cm. slabs were substantiated by measurements made with thinner slabs. The thinner the sample, the greater the apparent water absorption of any given compound, especially during the shorter periods of exposure. For example, the apparent volume per cent absorption of compound 16 during 48-hour immersion in water at 100° C. increased from 0.64 to 0.85 to 1.07 as the thickness of the samples varied from 0.21 to 0.14 to 0.08 cm., respectively. The apparent absorption of similar rubber samples (compound 15) under identical conditions increased from 1.92 to 3.02 to 5.65 per cent.

The water resistance of neoprene compounded with a high amount of soft carbon black, with and without softening agents, was measured to determine the advantage in water resistance to be gained by high loading and the influence of the softening agents on the water absorption. The compounds prepared and the test data obtained are given in Table V. The results show that, although the use of an increased amount of carbon black by itself increases the water resistance, the selection of the softening agent employed to produce a stable and processable stock may decrease the water resistance considerably. This is illustrated by compound 22 in which cottonseed and mineral oils were used. An agent such as Barrett No. 10 oil gives a compound (23) with a plasticity and stability comparable to those of the compound containing cottonseed and mineral oils. During the first 24-hour immersion period at 100° C., Barrett No. 10 oil volatilizes, and the net result is an apparent shrinkage rather than a swelling. After the first 24-hour period compound 23 containing the Barrett No. 10 oil shows a definite swelling, due to water absorption. Upon prolonged exposure, especially at elevated temperatures, the apparent water absorption of all the samples is influenced by loss of material due either to leaching or volatilization.

Effect of Wood Rosin

The effect of the addition of 5 parts of rosin per 100 parts of neoprene to both magnesia–zinc oxide and litharge stocks

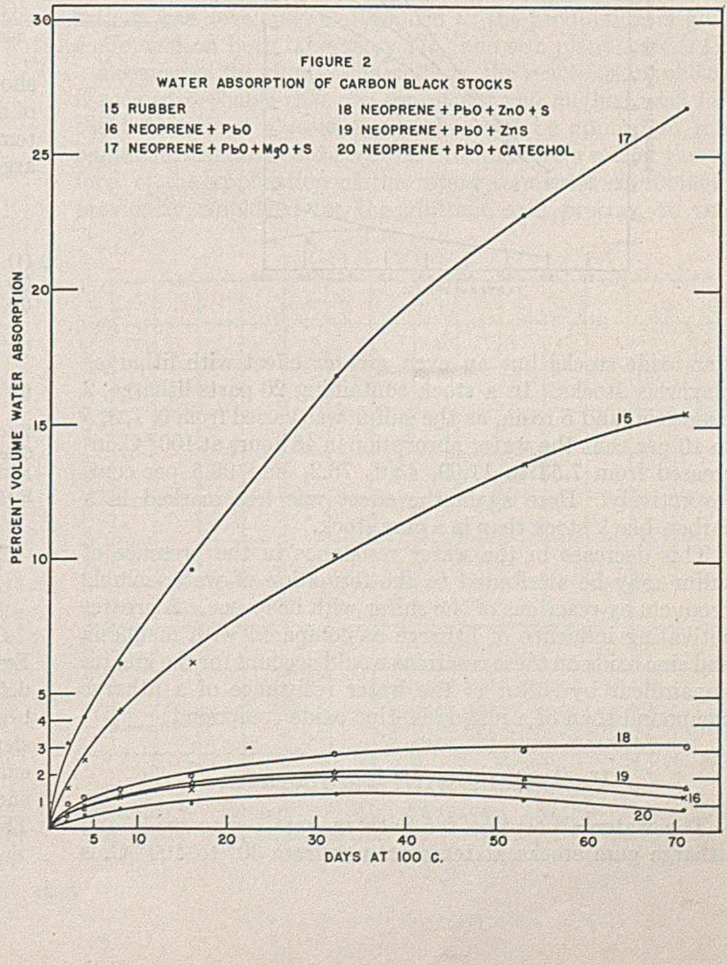


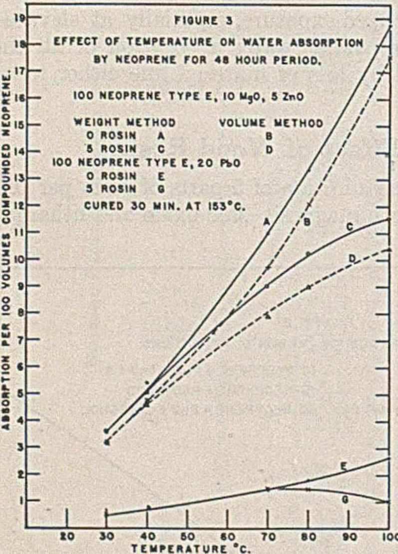
FIGURE 2
WATER ABSORPTION OF CARBON BLACK STOCKS

is shown by the data plotted in Figure 3. The addition of rosin makes no difference on the water resistance of neoprene at room temperature, but it appreciably improves the resistance at elevated temperatures. The litharge stock containing rosin actually appears to be more resistant at 100° C. than at some intermediate temperatures.

Amounts of rosin greater than 5 parts per 100 parts of neoprene do not improve the water resistance; 10 parts are no more effective than 5 parts, but 20 parts of rosin decrease the water resistance.

Effect of Sulfur

M. A. Youker of the du Pont Company observed that the water absorption of a magnesia–zinc oxide gum stock was increased from 16.1 to 26.7 per cent by increasing the sulfur content from 1 to 3 parts per 100 parts of neoprene. The influence of sulfur was less marked in the case of carbon black stocks. N. L. Catton of the du Pont Company investigated in more detail the influence of sulfur and observed not only this effect on the water resistance of magnesia–zinc oxide stocks but an even greater effect with litharge–magnesia stocks. In a stock containing 20 parts litharge, 2 magnesia, and 5 rosin, as the sulfur was varied from 0, 1, 3, 5 to 10 per cent the water absorption in 48 hours at 100° C. increased from 7.53 to 11.09, 43.0, 76.2, and 96.5 per cent, respectively. Here again the effect was less marked in a carbon black stock than in a gum stock.



This decrease in the water resistance in the presence of sulfur may be attributed to the formation of water-soluble products by reactions of the sulfur with neoprene. A greater activating influence of litharge as compared with magnesia and zinc oxide on these reactions would account for the greater impairment by sulfur of the water resistance of a litharge compound than of a magnesia–zinc oxide compound.

Variations with Temperature

The water absorption for both magnesia–zinc oxide and litharge gum stocks at temperatures from 30° to 100° C. is shown in Figure 3. These results indicate that the hydration of magnesia occurs at room temperature as well as at elevated temperatures. They show clearly the superiority of the litharge stocks.

Table V. Effect of Softening Agents on Litharge–Carbon Black Stocks

Formula No.	21	22	23
Neoprene Type E	100	100	100
FF wood rosin	5	5	5
Litharge	20	20	20
Carbon black (Thermax)	150	150	150
Cottonseed oil	...	5	...
Mineral oil	...	5	...
Barrett No. 10 oil	...	...	10

Stability, Plasticity–Recovery Numbers

Aged at 50° C., Hr.			
0	200–14	130–14	130–5
24	250–46	162–7	173–8
48	285–61	189–27	202–30
96	352–116	238–69	270–89

Stress-Strain Data[a]

Cure at 153° C., Min.									
10	56(800)	121(1725)	330	28(400)	97(1375)	260	37(525)	114(1625)	300
20	83(1175)	121(1725)	180	42(600)	121(1725)	290	54(775)	121(1725)	260
40	90(1275)	139(1975)	230	40(575)	121(1725)	290	54(775)	121(1725)	250
60	90(1275)	134(1900)	210	42(600)	125(1775)	250	53(750)	121(1725)	240

Stress-Strain Data after Immersion in Water at 100° C.

Days of Immersion									
4	102(1450)	144(2050)	190	65(925)	127(1800)	200	86(1225)	132(1875)	200
16	118(1675)	135(1925)	130	93(1325)?	128(1825)	180	104(1425)	127(1800)	160
32	111(1575)	146(2075)	160	67(950)	130(1850)	180	93(1325)	127(1800)	160

% Loss of Material after Immersion in Water at 100° C.

32	0.67	4.84	3.34

Apparent % Volume Water Absorption (Weight Method)

Days	30° C.	100° C.	30° C.	100° C.	30° C.	100° C.
2	0.14	0.34	0.39	1.87	0.00	−3.76
4	0.23	0.60	0.52	2.47	0.02	−3.40
8	0.29	0.75	0.64	2.77	0.04	−3.25
16	0.33	0.97	0.76	2.75	−0.09	−3.11
32	..	1.17	..	2.00	....	−2.32
51	0.68	0.98	1.26	1.18	−0.35	−2.20
71	..	0.72	..	0.67	....	−2.53
81	0.72	..	1.4	..	−0.72	....

[a] The figures for each formula represent stress at 100% elongation in kg. per sq. cm. (lb. per sq. in.), tensile strength in kg. per sq. cm. (lb. per sq. in.), and per cent elongation at break.

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Received September 23, 1937. Presented before the Division of Rubber Chemistry at the 94th Meeting of the American Chemical Society, Rochester, N. Y., September 6 to 10, 1937. Contribution 36 from Jackson Laboratory, E. I. du Pont de Nemours and Company, Inc.

Correction

On page 968 of the September, 1937, issue of Industrial and Engineering Chemistry an error occurs in the very important definition of "Molecular Distillation." The sentence which begins on the fifth line of the section on "Apparatus and Methods" should read: "The free path of the majority of the molecules emerging is then *greater* than the distance between the surfaces, and distillation occurs at the lowest possible temperatures." The word "less" was printed instead of "greater."

K. C. D. Hickman

SORBOSE FROM SORBITOL

Production by Submerged Growths of *Acetobacter suboxydans*

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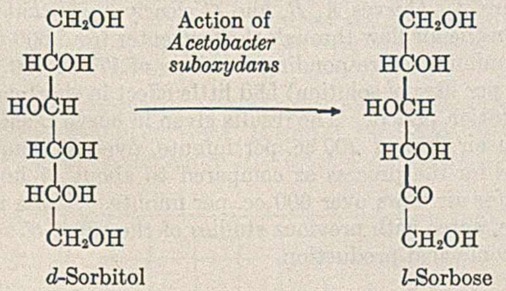
Studies on the effect of air flow, agitation, and air pressure on the production of *l*-sorbose from *d*-sorbitol by submerged growths of *Acetobacter suboxydans* in rotary drum fermenters have revealed conditions under which this conversion can be rapidly and efficiently carried out. Under the best conditions found, using 15 per cent sorbitol solutions, a yield of *l*-sorbose in excess of 93 per cent, based on the sorbitol available, was obtained in 24 hours from the time of inoculation. Sorbitol in concentrations up to 20 per cent was satisfactorily fermented. A method of preparation of a highly active inoculum suitable for use in large-scale operation of the process was developed.

RECENT interest in *l*-sorbose arises from its use in the chemical synthesis of vitamin C (*l*-ascorbic acid), since it is the configuratively correct starting material for the preparation of this important substance. The successful commercial production of *d*-sorbitol from glucose in the past few years has provided a ready source of this essential intermediate, but the biological conversion of *d*-sorbitol to *l*-sorbose, the only practical method available, has been somewhat difficult to accomplish. This difficulty is chiefly due to inherent disadvantages of the surface type of fermentation process which has been used in all previous studies on this problem.

Bertrand (*2*) in 1896 first reported the formation of *l*-sorbose from *d*-sorbitol by the action of the sorbose bacterium, now identified with *Acetobacter xylinum*. The oxidation of *d*-sorbitol to *l*-sorbose by this and other species of Acetobacter was studied by Sazerac (*10*), Boeseken and Leefers (*3*), Kluyver and de Leeuw (*6*), Bernhauer and Görlich (*1*), Maurer and Schiedt (*7*), Fulmer et al. (*4*), and others (*12*, *13*).

The reaction involved is as follows:



$$CH_2OH\text{-}HCOH\text{-}HOCH\text{-}HCOH\text{-}HCOH\text{-}CH_2OH \xrightarrow{\text{Action of } Acetobacter\ suboxydans} CH_2OH\text{-}HCOH\text{-}HOCH\text{-}HCOH\text{-}CO\text{-}CH_2OH$$

d-Sorbitol *l*-Sorbose

In most of this previous work concentrations of sorbitol varying from 2 to 6 per cent were employed, and periods ranging from 3 to 40 days were required for completion of the fermentation. Fulmer and his associates (*4*), however, showed that sorbitol, in concentrations up to 35 per cent, is rapidly oxidized to *l*-sorbose by surface cultures of *Acetobacter suboxydans*. The use of such high concentrations of sorbitol represents an improvement in the process because it makes possible the handling of minimum volumes of solution with attainment of high sorbose yields.

The application of a submerged type of fermentation to this process would offer numerous advantages for large-scale production. Studies made in this division (*8*) on the production of gluconic acid from glucose by submerged mold growths under increased air pressure have shown that such a method is greatly superior to the surface type of fermentation for the same process. Subsequently (*5*) an apparatus suitable for industrial application of submerged mold fermentations was developed and applied to the production of gluconic acid on both laboratory (*15*) and semiplant scale (*14*).

Because of the similar character of the reactions involved, it seemed probable that the equipment and method used for the oxidation of glucose by molds could be applied to the bacterial oxidation of *d*-sorbitol. Studies were made, therefore, of the application of the rotary fermenter equipment, previously employed for the gluconic acid process, to the

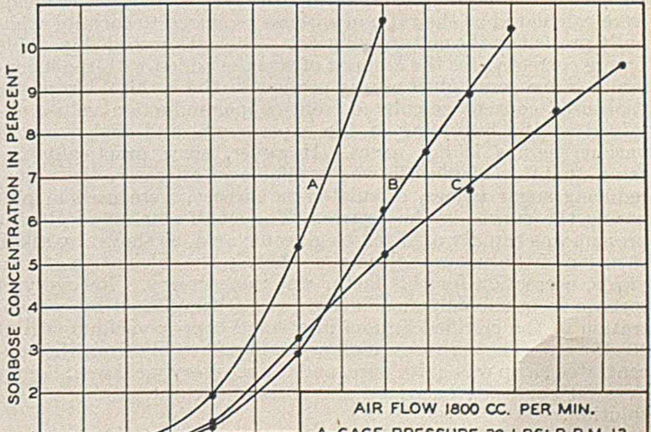


FIGURE 1. EFFECT OF AIR PRESSURE AND OF RATE OF ROTATION OF FERMENTATION OF SORBITOL TO SORBOSE BY *Acetobacter suboxydans*

sorbose fermentation. The present report deals with studies of large-scale inoculum preparation and the effect of certain important factors for the production of *l*-sorbose from *d*-sorbitol by submerged growths of *Acetobacter suboxydans*.

Procedure

The sorbitol sirup used in these experiments was a technical grade containing 75.7 per cent sorbitol, 2.3 per cent glucose, 0.6 per cent sodium sulfate, and 21.4 per cent water. The fermentation solutions were prepared from this sirup by proper dilution with distilled water and the sole addition of Difco yeast extract in the amount of 5 grams per liter of solution. The sorbitol concentrations were checked by refractometer readings. Except when stated otherwise, the sterilized culture solutions (3200 cc. of 10 per cent sorbitol solution for each drum) were inoculated with 200 cc. of a bacterial suspension prepared in the following manner: 200 cc. of solution containing 10 per cent sorbitol and 0.5 per cent of Difco yeast extract were placed in a 500-cc. Jena-glass gas washing bottle (type 101a) and, after sterilization and cooling, were inoculated from a tube culture of the organism grown on an agar slant which contained 5 per cent sorbitol. Sterile air, at about 200 cc. per minute, was passed through the culture for a period of 48 hours. The contents of one flask prepared in this manner was used for inoculating each drum. The experiments were all made at 30° C. The method of operation of the rotary fermenter was described elsewhere (*5*). The course of the fermentation was followed by removing samples at intervals for sorbose analysis. Copper reduction values were determined by the method of Shaffer and Hartmann (*11*), and the sorbose content was calculated by means of a table of copper values prepared from analyses of pure sorbose by this method. Yields were calculated as the ratio of sorbose produced to sorbitol originally present in the culture solution. The data recorded in Table I were corrected for the amount of sorbose added with the inoculum. Since some glucose was present in the sorbitol sirup, the "sorbose" content calculated from copper reduction values obtained at the beginning of the experiments and shown in the various figures is not exact. However, since practically the same quantity of glucose was available in all cases, the actual reducing sugar values, calculated as sorbose, were used in preparing the curves in the figures. The small amount of glucose present was rapidly oxidized to gluconic acid, as shown by alkali titration of the culture solution, so that, in the calculation of final yields, correction for this factor was unnecessary. Recovery of sorbose from the culture solutions was accomplished by concentration of the clarified liquors in a small copper vacuum still at 40–45° C. The sorbose which crystallized readily from the concentrated sirup was quite pure, and the recovery yield was slightly over 80 per cent, based on the sorbose present in the culture solution.

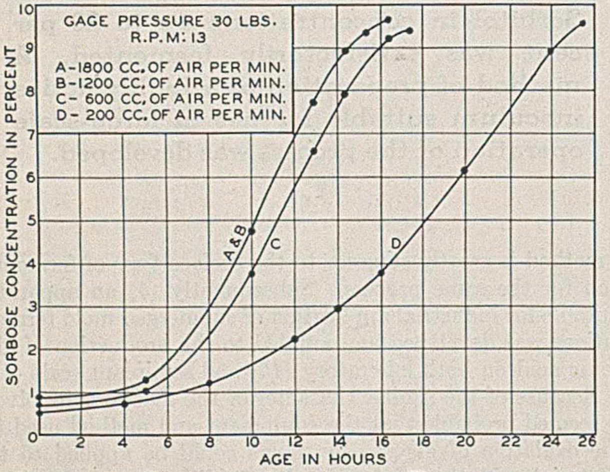


FIGURE 2. EFFECT OF AERATION ON FERMENTATION OF SORBITOL TO SORBOSE BY *Acetobacter suboxydans*

Effect of Agitation and Pressure

Previous work (*15*) showed that increased air pressure and a high degree of agitation and aeration were important factors for the rapid biological oxidation of glucose to gluconic acid. A similar study of the effect of air pressure and the degree of agitation on the production of sorbose from sorbitol was made and the results are shown in Figure 1. Curve *A* shows the course of the fermentation under favorable conditions of air flow, pressure, and agitation. The oxidation was completed in 16 hours. Curve *B* shows the results obtained under a less favorable degree of agitation maintained by a slower speed of rotation of the fermenter. In this case approximately 22 hours were required for complete fermentation. The results shown in curve *C* were obtained when the fermentation was conducted at atmospheric pressure. They demonstrate that a considerably longer period was required for the oxidation under these conditions than for that required when the pressure was increased to 30 pounds per square inch (2.11 kg. per sq. cm.) gage pressure. The beneficial effect of a high degree of agitation and increased air pressure in shortening the time required for the fermentation corresponds, in general, to the same effect observed in studies on the production of gluconic acid by molds.

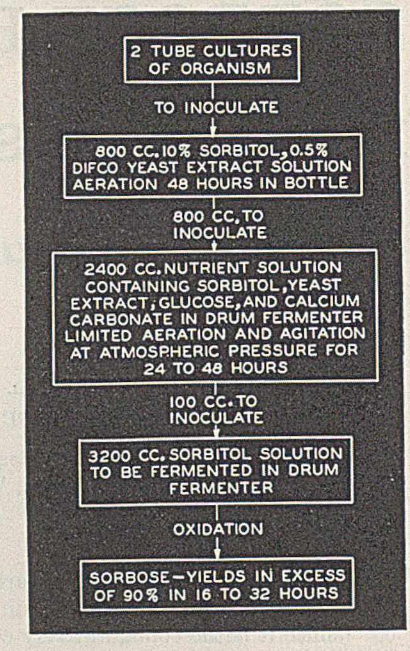


FIGURE 3. DIAGRAM OF LARGE-SCALE INOCULUM PREPARATION METHOD FOR PRODUCING SORBOSE FROM SORBITOL

Effect of Air Flow

The results of a study of the effect of air flow on sorbose production from sorbitol by *Acetobacter suboxydans* are shown in Figure 2. Curves *A*, *B*, and *C* clearly show that an increase in the air flow through the fermenter from 600 to 1800 cc. per minute (corresponding to a flow of 177 to 530 cc. per minute per liter of solution) had little effect in shortening the fermentation period. The results given in curve *D* show that with an air flow of 200 cc. per minute, over 25 hours were required for the process as compared to about 17 hours required for air flows over 600 cc. per minute. These results, likewise, agree with previous studies of the effect of aeration on gluconic acid production.

Effect of Sorbitol Concentration

The production of sorbose by the organism grown on various concentrations of sorbitol was studied and the results are shown in Table I. The total sorbitol available (column 3) was the sum of the sorbitol originally weighed out plus that contained in the inoculum. It is evident that rapid oxidation to sorbose occurred in all cases except where a 30 per cent concentration was used. The poor result in this case was apparently due to the high osmotic pressure. It should be pointed out that the fermentation in which 19.8 per cent sorbitol was used was practically completed in a period of 33 hours but was not harvested until 12 hours later. Fulmer and his co-workers (*4*) found that surface cultures of *Acetobacter suboxydans* were able to oxidize sorbitol in concentrations up to 35 per cent, but the results obtained here for submerged growths of the organism indicate that a sorbitol con-

Table I. Effect of Concentration of *d*-Sorbitol on Production of *l*-Sorbose by Submerged Growths of *Acetobacter suboxydans*

[Air flow, 1800 cc. per minute; r. p. m., 13; gage pressure, 30 pounds per square inch (2.11 kg. per sq. cm.)]

Sorbitol Concentration %	Fermentation Period *Hours*	Total Sorbitol Available *Grams*	Sorbose Produced *Grams*	Sorbose Produced *% by weight*
1	2	3	4	5
10.1	16.5	332	307	92.5
14.5	24	453	423	93.4
19.8	45[a]	632	617	97.6
30.3	69	975	194	19.9

[a] Fermentation practically completed in 33 hours.

centration of 20 per cent was most satisfactory for high practical yields of sorbose.

Large-Scale Inoculum Studies

The preparation of inoculum in the Jena-glass gas washing bottles, previously described, was entirely satisfactory for the small-scale studies reported here, but, in anticipation of adapting the process to large-scale operation, studies were made to develop a suitable method for preparation of large quantities of a highly active inoculum. Since the rotary fermenters had previously (*9*) been used successfully in the preparation of inoculum for the gluconic acid fermentation, they were employed as culture vessels in this study. The method employed, shown diagrammatically in Figure 3, was as follows:

The solutions used had the same composition as indicated previously except when otherwise noted. An 800-cc. portion of sterile nutrient solution contained in a 2-liter Pyrex glass bottle was inoculated with two tube cultures of the organism grown on agar slants containing 5 per cent sorbitol. Sterile air was passed through the culture by means of a Jena glass distribution tube (type 33C) at a rate of 800 cc. per minute for a period of 48 hours. This suspension was used to inoculate 2400 cc. of sorbitol solution, thus giving a total volume of 3200 cc. which was then introduced into the drum fermenter operated in the usual manner. Analyses for sorbose were made at frequent intervals. It was desired that the bacterial suspension thus produced in the fermenter could, in turn, be used for inoculating purposes in the proportion of 1 part to 32 parts of solution to be fermented because of the limited capacity of equipment available for this purpose in connection with the large-scale experimental work. The fermentative activity of the suspension was tested by aseptically removing 100-cc. and 200-cc. samples at intervals and using them to inoculate the solutions to be fermented, in each case 3200 cc. of 10 per cent sorbitol solution.

The results obtained by this procedure are shown in curve *R*, Figure 4, and in curves *A*, *B*, and *C*, Figure 5. In explanation of these results, curve *R*, Figure 4 shows the increase in sorbose concentration in the inoculum prepared in the drum fermenter. Since, in this case, the conditions of air flow, pressure, and agitation were the same as those found to be most favorable for the fermentation, the sorbitol was oxidized completely to sorbose in 13 hours. Samples of this inoculum, which for convenience is designated as inoculum *R*, were removed after intervals of 9 and 13 hours for testing its activity; curves *A*, *B*, and *C*, Figure 5, show the results obtained in the production of sorbose using inoculum *R*. It is evident that the oxidations were not uniform, and the pronounced decrease in activity at 13 hours as compared to that at 9 hours indicated that such an inoculum would be far from satisfactory for practical purposes.

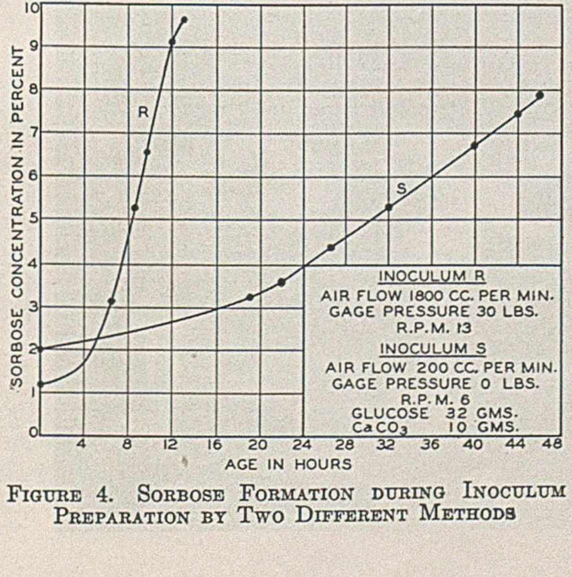


Figure 4. Sorbose Formation during Inoculum Preparation by Two Different Methods

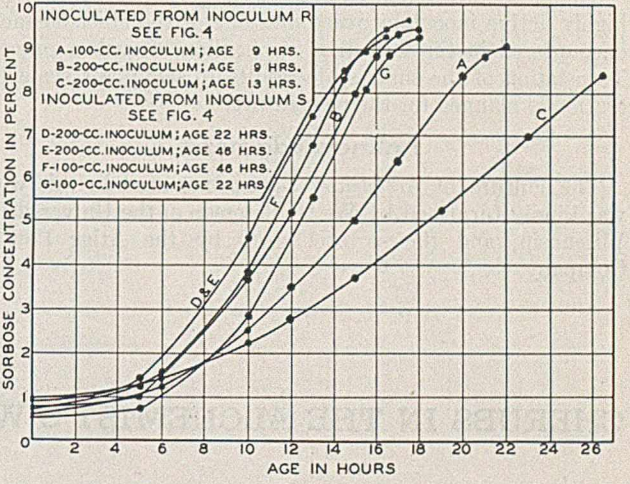


Figure 5. Effect of Age and Different Quantities of Inoculum on Sorbose Fermentation

Gage pressure, 30 pounds; r. p. m., 13; air flow, 1800 cc. per minute

It was thought that the addition of a more readily available carbon source to the nutrient solution used for preparation of the inoculum would provide conditions for a more rapid and suitable growth of the organism. Experiments (not shown) were made in which 1 per cent of glucose was added to this nutrient solution. The formation of free gluconic acid from the glucose in this solution caused a complete cessation of sorbose formation. However, after addition of a slight excess of calcium carbonate to neutralize the acid produced, formation of sorbose was resumed, and samples of this inoculum tested for activity gave promising results.

The nutrient solution for preparation of the inoculum was, therefore, modified by the addition of glucose and a slight excess of calcium carbonate above that required to neutralize the gluconic acid produced. The solution which finally proved satisfactory for inoculum preparation in the drum fermenter had the following composition per liter of solution: sorbitol, 100 grams; Difco yeast extract, 5; glucose, 10; and calcium carbonate, 3.1.

The results obtained using the above solution are shown in curve *S*, Figure 4. Conditions of air flow, pressure, and agitation were maintained which were less favorable for sorbitol oxidation, in order to provide a longer growth period without exhaustion of the sorbitol supply.

The activity of inoculum *S* was tested in the same manner as that described for inoculum *R*. The results are shown in Figure 5, curves *D*, *E*, *F*, and *G*. It is evident that the inoculum was uniformly active at both the 22- and 46-hour periods. Moreover, it possessed a high degree of activity, as shown by curves *F* and *G* where 1 part of inoculum to 32 parts of solution fermented was used. The oxidation of the 10 per cent sorbitol solutions to sorbose was completed in about 18 hours in all cases.

Conclusions

The results of studies on the effect of air flow, air pressure, and the degree of agitation on the production of sorbose from sorbitol by submerged growths of *Acetobacter suboxydans* show that these factors are of great importance in determining the duration of the fermentation period. The combined effect of the proper adjustment of these factors is emphasized by the results shown in Figure 4, curves *R* and *S*. Highly aerobic conditions are most satisfactory for the rapid conversion of sorbitol to sorbose.

The use of 20 per cent sorbitol solutions in the submerged growth process provides a commercially feasible method for sorbose production.

The method developed for the large-scale preparation of a highly active inoculum overcomes one of the chief obstacles encountered in the industrial application of such a process. Translation of the small-scale results to semiplant scale operation is planned for the near future.

Acknowledgment

The culture of *Acetobacter suboxydans* used in this work was kindly furnished by W. H. Peterson of the University of Wisconsin, and the sorbitol sirup by the Atlas Powder Company.

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CHERUBS IN THE ALCHEMIST'S WORKSHOP

By David Teniers, the Younger

Again we return to that reliable old standby of the collector of alchemical prints, the younger and more famous of the two David Teniers.

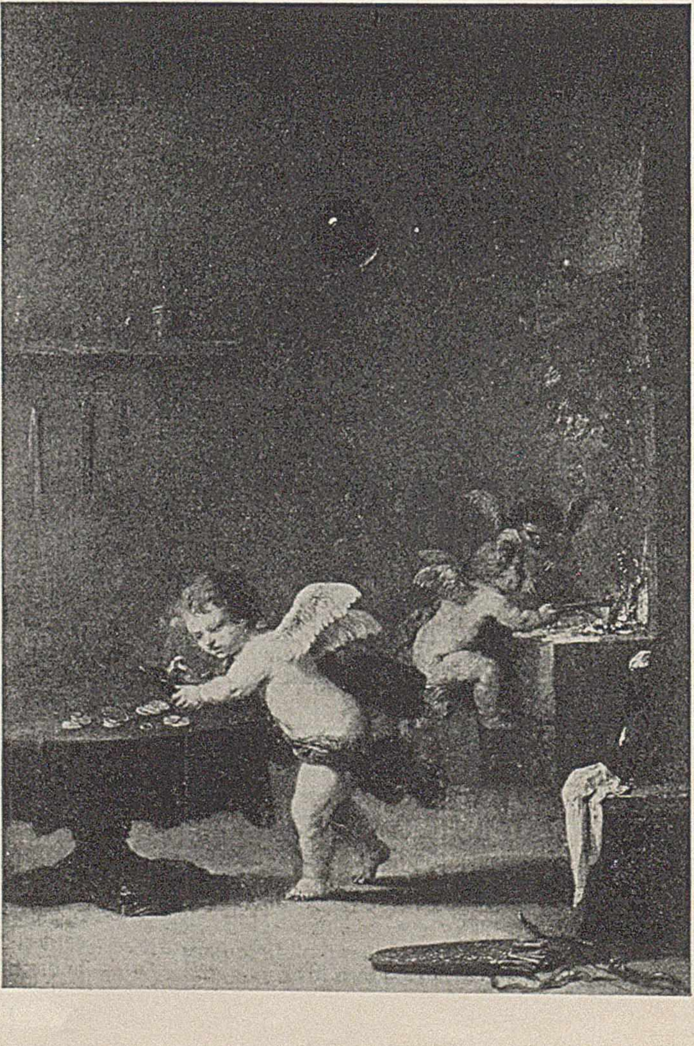
The original of No. 84 in the Berolzheimer Series of Alchemical and Historical Reproductions is in the Staedelsches Kunst-Institut in Frankfort-on-Main, Germany.

The painter, in a lighter vein than usual, has here portrayed the beneficent cherubs furthering the work of the absent alchemist, who, on his return to work, will no doubt find a goodly amount of gold in his crucible after a forced cessation of work because of "lack of funds."

Please note the paucity of equipment and apparatus needed by the cherubs to bring about the transmutation.

●

A detailed list of Reproductions Nos. 1 to 60 appeared in our issue of January, 1936, page 129, and the list of Nos. 61 to 72 appeared in January, 1937, page 74, where also will be found Reproduction No. 73. Reproduction No. 74 appears on page 166, February issue, No. 75 on page 345, March issue, No. 76 on page 459, April issue, No. 77 on page, 554, May issue, No. 78 on page 710, June issue, No. 79 on page 776, July issue, No. 80 on page 945, August issue, No. 81 on page 1039, September issue, No. 82 on page 1134, October issue, and No. 83 on page 1276, November issue.



Recovery of Mercaptans from Cracked Naphtha Fractions

R. W. CRARY AND M. M. HOLM
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Equilibrium data are presented for absorption in caustic of methyl and ethyl mercaptans from the corresponding cracked naphtha fractions. Similar data are given for removal of the same mercaptans from caustic solution by steam stripping. The data are correlated by means of equations derived from the equilibrium constant for the neutralization reaction. Application of the data to the design of commercial equipment is discussed.

SEVERAL articles have described caustic scrubbing of naphthas to remove mercaptans. Birch and Norris (*1*) presented an analysis of the sodium mercaptide solution resulting from caustic treatment of the first 36 per cent fraction distilled from a Persian crude, and interpreted the results in terms of relative strengths of individual mercaptans found. Borgstrom, Dietz, and Reid (*2*) experimented with fourteen known mercaptans varying in composition from *n*-propyl to *sec*-nonyl. Several different naphthas were used as solvent, and the extractions were made with caustic varying in strength from 0.76 to 6.06 normal. Meyer (*11*) discussed the chemical theory of mercaptan scrubbing and presented experimental confirmation of his concepts. Happel and Robertson (*6*) extracted an 83–338° F. cracked naphtha from Luling crude with half its volume of 1.25 normal caustic and determined mercaptan sulfur in narrow cuts of the naphtha before and after such treatment. The data obtained were applied to the operation of a commercial countercurrent scrubbing system.

Regeneration of mercaptide-containing caustic solutions by boiling or steam stripping has been described in general terms (*1, 10, 11*). No quantitative data on the equilibrium relations involved seem to have been reported.

Data on the following specific problems were obtained here:

1. Removal of methyl mercaptan from the butene-butane fraction of cracked naphtha by countercurrent extraction with caustic.
2. Removal of ethyl mercaptan from the pentene-pentane fraction by the same method.
3. Regeneration of the foul caustic solutions by steam stripping.

The purpose of this paper is to report the experimental results and to discuss their meaning in terms of conventional absorption and stripping diagrams.

Materials

The butene-butane used was obtained by fractionation of the reflux liquid available in commercial stabilization of Dubbs cracked naphtha. The 0.40 per cent by weight of mercaptan sulfur present in the crude cut was removed by treatment with a large excess of caustic. The treated product analyzed 1.4 per cent by weight of propylene, 4.0 per cent propane, 14.5 per cent isobutene, 34.4 per cent *n*-butene, and 45.7 per cent mixed butanes.

The pentene-pentane was obtained by direct fractionation of the stabilized naphtha. Mercaptans present in the crude cut were removed with excess caustic, and the final product was analyzed 98+ weight per cent of pentene-pentane cut, less than 1 weight per cent of butane fraction, and less than 1 weight per cent of hexane fraction. Bromine number (*5*) was 0.72 gram per gram, corresponding to 48 per cent olefins and 52 per cent paraffins.

Methyl and ethyl mercaptans were obtained from the Eastman Kodak Company. In most of the tests they were used without further purification. Boiling points and molecular weights were checked roughly to eliminate any chance of gross error.

Caustic used was Baker's C. P. grade, analyzing 0.8 per cent sodium carbonate. Solutions were made up on a total alkalinity basis—in other words, assuming that 1 mole of sodium carbonate was equivalent to 2 moles of sodium hydroxide with respect to mercaptan absorption.

Procedure

Bulk supplies of caustic containing the various desired concentrations of methyl and ethyl mercaptans were prepared. For consistency the solutions used in the absorption tests were identical with those used in making the stripping measurements.

Distribution of methyl mercaptan between butane and caustic was determined with the aid of a one-quart steel bomb. The bomb was charged with about 200 cc. of sodium mercaptide solution and 200 cc. of butene-butane and shaken for 10 minutes; the lower caustic layer was discharged, the bomb was weighed, the butane layer was discharged into a vessel containing several times its volume of mercaptan-free petroleum ether, the bomb was again weighed, and finally the petroleum ether solution was analyzed for mercaptan. In the case of ethyl mercaptan and pentane, the equilibrium between hydrocarbon and caustic layers was effected in an ordinary separatory funnel, and the upper pentane layer was titrated for mercaptan direct. Temperatures were 70° and 75° F. in the cases of methyl and ethyl mercaptans, respectively. Mercaptan concentrations in caustic were determined by iodimetry (*9*). Mercaptan concentrations in hydrocarbon were determined by titration with silver nitrate (*3*).

The stripping measurements were made by the flow method in all cases where the total pressure of mercaptan and water was below atmospheric. The sodium mercaptide solutions were charged to a series of four glass bubblers, about 50 cc. to each vessel. Connections between bubblers were all glass, and the whole unit was immersed in a water bath heated to the desired temperature. A measured volume of dry nitrogen was passed through the series, and the exit gas was scrubbed in a weighed absorption train containing caustic solution and solid calcium chloride. The relation between volume of nitrogen passed and volume of solution tested was such that the change in mercaptan concentration of solution was negligible; further assurance on this point was the separation of the four bubblers and practical establishment of equilibrium in the first unit. Actual proof that equilibrium was established between liquid and gas was obtained by testing pure liquids of known vapor pressure.

The total increase in weight in the absorption train represented mercaptan plus water. Mercaptan was determined by titration with iodine, and water was determined by difference. The principal source of error in these measurements was the temperature, no attempt being made to hold closer than 1° F. to the value reported. The point of particular interest, however, was the ratio of mercaptan to water vapor pressure; therefore minor errors in temperature measurement should cause only a negligible error in the final interpretation of results.

In the single instance where the total pressure was above atmospheric, the stripping vapor pressures were measured by the static method, the sodium mercaptide solution being charged to a steel bomb which was then immersed in an oil bath heated to the desired temperature. As the temperature within the bomb increased, the air was released and finally only mercaptan and water vapor remained. When thermal equilibrium was well established, as evidenced by a pressure gage, a sample of the vapors was absorbed in a weighed caustic–calcium chloride train and analyzed as above. The sample release valve was immersed in the hot oil bath, thus avoiding any chance of refluxing during sampling.

Derivation of Equilibrium Equations

Equilibrium concentrations of methyl or ethyl mercaptan, whether between caustic solution and steam or between caustic solution and naphtha, may be calculated from the equilibrium constant for the following reaction:

$$NaOH + RSH = RSNa + H_2O$$

or, written in ionic form,

$$(OH)^- + RSH = (RS)^- + H_2O$$

The equilibrium constant for this reaction may be written:

$$K = \frac{[H_2O]\ [(RS)^-]}{[RSH]\ [(OH)^-]} \tag{1}$$

The bracketed symbols represent molal concentrations of the various reactants.

The symbols used in the equations have the following meanings:

X_n = mercaptan sulfur per gal. of naphtha, lb.
X_c = mercaptan sulfur per gal. of caustic solution, lb.
Y = mercaptan sulfur per lb. steam, lb.
a = NaOH per gal. of sulfur-free caustic solution, lb.
P_w = vapor pressure of water over caustic solution, lb. per sq. in. abs.
P_r = vapor pressure of pure mercaptan, lb. per sq. in. abs.
M = av. mol. weight of naphtha
d = density of naphtha, lb. per gal.

Stripping Equilibrium

From Equation 1:

$$\frac{[RSH]}{[H_2O]} = \frac{[(RS)^-]}{K[(OH)^-]} \tag{2}$$

Using partial pressures as a measure of the concentrations of RSH and H_2O, and assuming Dalton's law to hold for mixtures of steam and mercaptan vapor:

$$\frac{[RSH]}{[H_2O]} = \frac{18Y}{32} \tag{3}$$

$$[(RS)^-] = \frac{X_c}{32} \tag{4}$$

$$[(OH)^-] = \frac{a}{40} - \frac{X_c}{32} \tag{5}$$

Substituting Equations 3, 4, and 5 in 2:

$$\frac{18Y}{32} = \frac{\frac{X_c}{32}}{K\left(\frac{a}{40} - \frac{X_c}{32}\right)} \tag{6}$$

Solving for Y and simplifying:

$$Y = \frac{40}{18K}\left(\frac{X_c}{a - 1.25\,X_c}\right) \tag{7}$$

Equation 7 is the equation of the equilibrium curve for stripping mercaptan from caustic solution with steam.

Absorption Equilibrium

Again using partial pressures as a measure of concentrations of RSH and H_2O, and assuming that mercaptan dissolved in naphtha follows Raoult's law:

$$\frac{[RSH]}{[H_2O]} = \frac{P_rX_nM}{32dP_w} \tag{8}$$

Substituting Equations 8, 4, and 5 in 2:

$$\frac{P_rX_nM}{32dP_w} = \frac{\frac{X_c}{32}}{K\left(\frac{a}{40} - \frac{X_c}{32}\right)} \tag{9}$$

Solving for X_n and simplifying:

$$X_n = \frac{40dP_w}{P_rMK}\left(\frac{X_c}{a - 1.25\,X_c}\right) \tag{10}$$

Let

$$K' = \frac{40dP_w}{P_rMK} \tag{11}$$

$$X_n = K'\left(\frac{X_c}{a - 1.25\,X_c}\right) \tag{12}$$

Equation 12 is the equation of the equilibrium curve for absorbing mercaptan from naphtha with caustic solution. The relation between K and K' is given by Equation 11.

Results

Experimental results of the absorption tests are presented in Table I. The values of a shown were calculated from data (*7*) on specific gravity of caustic solutions. Values of K' were calculated from Equation 12. In Table II the arithmetic average of values of K' for each mercaptan is shown. Corresponding values of K were calculated from Equation 11. Values of d and M were calculated from the hydrocarbon analyses of the two naphthas. Values of P_r and P_w were obtained from the Chemical Engineers' Handbook (*12*) and the International Critical Tables (*8*), respectively.

Data on stripping equilibria are recorded in Table III. Values of K were calculated from Equation 7. The numerical value of the equilibrium constant, K, depended primarily upon the mercaptan considered, the strength of caustic used, and the temperature. Consequently, in Table III, when several determinations were made with a given mercaptan, using the same strength caustic and a constant temperature, an arithmetic average K has been computed.

Table I. Absorption Equilibria (12° Bé. Caustic Solution)

Mercaptan	Naphtha	Temp. ° F.	Mercaptan S in Naphtha Weight %	X_n	X_c	a	K'
Methyl	Butene-butane	70	0.0030	0.00015	0.110	0.736	0.000896
			0.0060	0.00030	0.180	0.736	0.000852
			0.0148	0.00074	0.320	0.736	0.000777
			0.044	0.0022	0.451	0.736	0.000839
			0.074	0.0037	0.495	0.736	0.000860
Ethyl	Pentene-pentane	75	0.0105	0.000574	0.088	0.736	0.00409
			0.0341	0.00186	0.235	0.736	0.00350
			0.0766	0.00418	0.352	0.736	0.00352
			0.177	0.00967	0.470	0.736	0.00307

Table II. Average Equilibrium Constants Calculated from Absorption Equilibria (12° Bé. Caustic Solution)

Mercaptan	Naphtha	Temp. ° F.	K' (Av.)	d	M	P_r	P_w	K (Av.)
Methyl	Butene-butane	70	0.000845	4.89	56.0	25.5	0.363	58.8
Ethyl	Pentene-pentane	75	0.00354	5.29	71.0	10.0	0.382	32.2

Table III. Stripping Equilibria

Mercaptan	Caustic ° Bé.	Temp. ° F.	X_c	Vapor Pressure Mercaptan Atm.	Vapor Pressure Water Atm.	Y	a	K	K (Av.)
Methyl	12.0	87	0.158	0.00027	0.042	0.011	0.736	59.2	59.2
		120	0.158	0.00069	0.106	0.012	0.736	54.3	54.3
		170	0.158	0.0036	0.345	0.019	0.736	34.3	34.3
	25.0	120	0.175	0.00056	0.113	0.0088	1.89	26.4	26.4
		200	0.066	0.00116	0.612	0.0034	1.89	23.8	
		200	0.175	0.0046	0.621	0.013	1.89	17.9	19.4
		200	0.380	0.0120	0.627	0.034	1.89	17.6	
		289	0.175	0.0225	2.70	0.015	1.89	15.5	15.5
Ethyl	12.0	90	0.235	0.00136	0.046	0.053	0.736	22.3	22.3
		150	0.235	0.0124	0.23	0.096	0.736	12.3	12.3
		190	0.029	0.0018	0.58	0.0055	0.736	16.7	
		190	0.059	0.0048	0.60	0.0142	0.736	13.9	
		190	0.117	0.0114	0.61	0.033	0.736	13.4	14.1
		190	0.235	0.036	0.60	0.106	0.736	11.1	
		190	0.411	0.094	0.62	0.27	0.736	15.3	

It is to be expected that over short ranges of temperature, when the natural logarithm of equilibrium constant K is plotted against the reciprocal of the absolute temperature, a straight-line relation will result. In Figure 1 the values of K in Tables II and III were plotted in this way. The data show clearly that the relation between equilibrium constant and temperature is a function, not only of the mercaptan considered, but also of the strength of caustic used. The various points plotted correspond to averages of from one to five experimental determinations. In drawing the curves, more weight was given to points representing an average of several runs.

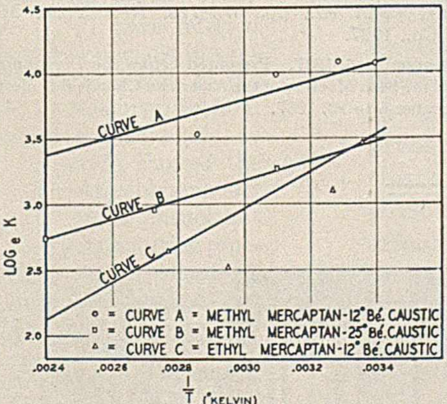

Figure 1

Equations of the three curves are as follows:

$$\text{Curve } A: \quad \log_e K = 698 \left(\frac{1}{T}\right) + 1.70$$

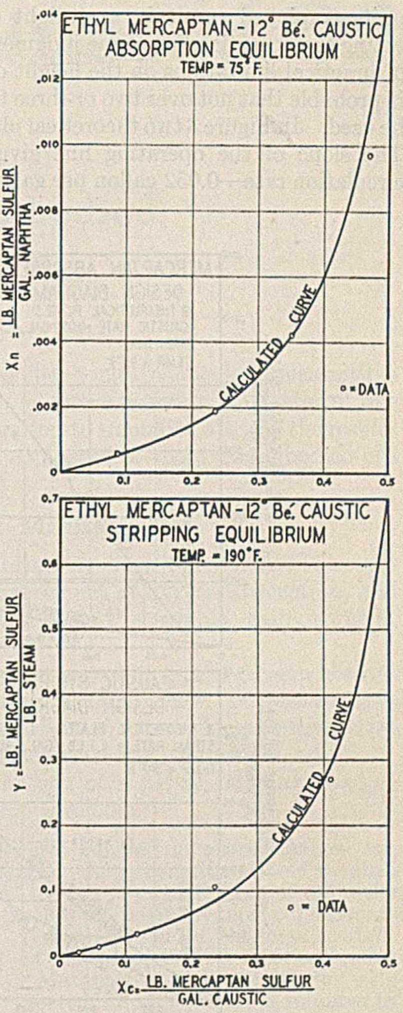

Figure 2

$$\text{Curve } B: \quad \log_e K = 730 \left(\frac{1}{T}\right) + 0.99$$

$$\text{Curve } C: \quad \log_e K = 1400 \left(\frac{1}{T}\right) - 1.24$$

where T = abs. temperature, ° K.

In Figure 2 the calculated equilibrium curve and data for absorption of ethyl mercaptan from pentane-pentene in 12° Bé. caustic at 75° F. are presented. The curve was calculated from Figure 1 and Equations 11 and 12, using appropriate values of a, d, P_r, P_w, and M (*8*, *12*). Figure 2 also presents similar data for stripping ethyl mercaptan from 12° Bé. caustic at 190° F. In both cases the close agreement between the data and the calculated equilibrium curve indicates the validity of the algebraic form of equilibrium Equations 7 and 12.

Design of Equipment

The graphical design methods used were described by Evans (*4*) and by Walker, Lewis, and McAdams (*13*). Let us assume that it is desired to design a caustic-treating system to reduce the mercaptan sulfur content of a liquid pentene-pentane cut from 0.23 to 0.006 weight per cent. Treating is carried out in a countercurrent, packed tower. Design is based on the following assumptions: (*a*) use of 12° Bé. caustic and (*b*) a treating temperature of 75° F.

The design diagram for the present example is given in the upper part of Figure 3. The equilibrium line is calculated as described above. The operating line is fixed by the inlet and the outlet mercaptan concentrations. The stoichiometric units employed result in a straight operating line. In locating the operating line, some judgment is required. In view of practical limitations on the height of the treating tower, it is probable that not over two or three theoretical plates should be used. In Figure 3 two theoretical plates have been assumed. The slope of the operating line gives the required caustic circulation rate—0.052 gallon per gallon of naphtha.

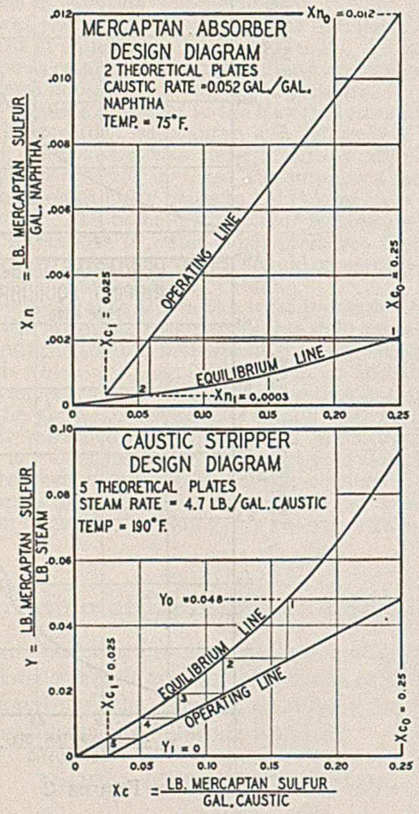

FIGURE 3

Stripping of the mercaptan from the caustic is carried out in a conventional bubble tray column. The stripper design diagram is presented in the lower part of Figure 3. Design is based on the following assumptions: (*a*) use of 12° Bé. caustic and (*b*) operation at 190° F. The operating line is again fixed by the terminal mercaptan concentrations, two of which have already been set in the absorber diagram of Figure 3—namely, the mercaptan sulfur in the caustic entering and leaving the stripper. Five theoretical plates have been assumed. The corresponding steam rate required is 4.7 pounds of steam per gallon of caustic, as obtained from the slope of the operating line.

Figure 3 represents one operable solution to the problem as stated—namely, to reduce the mercaptan sulfur content of a liquid pentene-pentane cut from 0.23 to 0.006 weight per cent. Assuming that the equipment has been built and that the number of theoretical plates available in the absorber and stripper is known, the caustic circulation rate and corresponding stripping steam requirements may be varied over fairly wide limits. The optimum values depend so largely on local costs that their determination is beyond the scope of this paper.

In the example given here the design methods have been applied to ethyl mercaptan. They are equally applicable to the removal of methyl mercaptan from butane-butene fraction. However, ethyl mercaptan is more difficult to remove from naphtha by caustic scrubbing, whereas methyl mercaptan is more difficult to strip from the caustic. It may be desired to remove both methyl and ethyl mercaptan from a butane-pentane fraction. In this case, computation of simultaneous scrubbing or stripping of both mercaptans is somewhat laborious. It is suggested that for this case, absorber design be based on equilibrium for ethyl mercaptan, and stripper design on equilibrium for methyl mercaptan.

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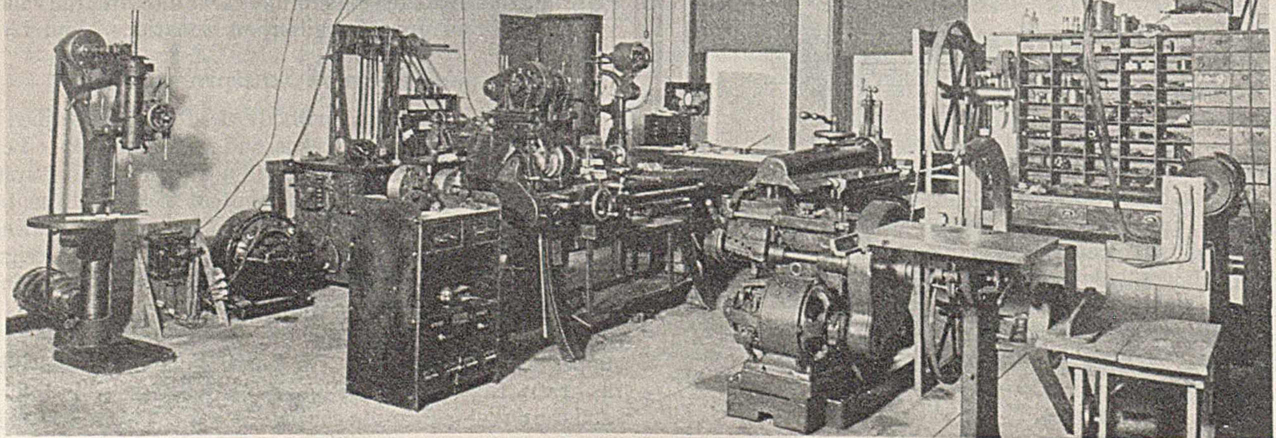

Oxidation of Unbodied Linseed Oil

Antioxidant Influence of Phenol-Formaldehyde Resins on Unbodied Linseed Oil in the Presence of Driers

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This investigation, using commercial materials, showed that the six phenolic resins tested increased the induction period in the oxygen absorption of unbodied linseed oil in the presence of driers, in direct proportion to the amount of resin present. The behavior of the oil after the induction period was apparently unaffected, since it eventually dried completely. Mixtures of synthetic resins with ester gum had the same effect as the pure resins, but to a less degree since the proportion of resin was less. Treatment of two of the three resins that showed the most marked antioxidant effect with an oxidizing agent resulted in a diminution of this effect.

THE phenomenon known as drying of certain unsaturated polymerizable oils has been long known. Many factors govern this drying, and many substances when mixed with oil accelerate or retard it. Many theories have been proposed in an effort to explain this behavior.

It is generally recognized that oxidation and polymerization are the principal factors involved in the process. The oxidation is believed to be confined to addition of oxygen to unsaturated carbon atoms of those acids whose esters comprise the major part of a drying oil. The gain in weight following such addition of oxygen provides an approximate criterion of the rate of oxidation, despite the fact that volatile products are evolved during the drying process, especially at the end of it.

Moureu and Dufraisse (*5*) proposed a theory relative to inhibition of autoxidation processes in general, which has been helpful in planning this study and which has indicated some of the procedures followed. This theory holds that antioxidants are themselves oxidizable substances with the antioxygenic property localized in the oxidizable part of the molecule. Prominent among the antioxidants of Moureu and Dufraisse are phenols, which are used in the production of many synthetic resins. Several investigators (*4, 9, 10*) have shown that phenolic compounds inhibit the oxidation of linseed oil during the induction period. Other investigators (*1, 8*) have inferred the presence of free phenols in synthetic resins. Careful tests of the samples used in this investigation, using diazotized *p*-nitroaniline as well as ferric chloride, showed the absence of any considerable amounts of unreacted simple phenol left there from the manufacturing process. In one instance a somewhat complex phenol was detected and removed.

Synthetic resins have been used in the manufacture of varnishes for some time. Such varnishes have dried satisfactorily, although the effect of the resins on such drying has varied. This behavior must not be confused with the results reported for this study. The oil used in the manufacture of these varnishes was heat-bodied to begin with, became heat-bodied during the process, or else was tung oil which has a conjugated system of double bonds particularly susceptible to polymerization. This study was limited to unbodied oil, and the results attained should not be compared to those where bodied oils were used.

Method

After a study of the limitations of such methods as ultimate analysis, volumetric measurement of oxygen absorption, and blowing with conditioned air, the simple gain-in-weight method was chosen.

This method gave only the apparent rate of oxygen absorption, but in a study such as this one where conclusions were to be drawn from a comparison of data collected under identical experimental conditions, it was considered adequate. It had the further advantage of rapidity, making possible many readings in the time available.

The resin-oil solutions were prepared in concentrations calculated as per cent by weight. Each constituent was weighed to 0.5 mg. on an analytical balance; for each gram of oil in the solutions, 0.0427 gram of naphthenate drier was included, the metal content of which is given in the section headed "Materials." The mixture was heated to 150° C. for 5 minutes to ensure complete dispersion, sealed in vials, and stored in a dark cabinet 2 days before use. The mixture so prepared was then spread on slightly etched, tared glass plates so that an area of approximately 95 sq. cm. was exposed. These plates were weighed immediately and at timed intervals thereafter; the intervals were governed by the rapidity of drying. The initial weights of the films so prepared varied from 0.1000 to 0.2580 gram, depending on the thickness of the film which, in turn, was governed by the viscosity of the original solution. No attempt was made to govern the thickness of the films, except to keep it within the limits prescribed by Wise and Duncan (*11*) who showed that reasonable variation did not appreciably affect the rate of oxidation. The present writers' experience in securing checks with films of the same resin mixture but varying in weight, and therefore thickness, confirmed the finding of these investigators.

Since temperature (*6, 10*), humidity (*7*), and light (*3*) all influence the drying of oils, it was necessary to carry out the experiments under conditions such that these factors were as nearly constant as possible. During the day the films were exposed to diffused light, and the temperature variation for the test periods was held within 2° C. limits. The humidity was much more difficult to control, but it was found that data collected when the humidity varied from 50 to 60 agreed within the limits of experimental error. Most of the data were collected at an average of 55.

Weighings were made over a period of 180 hours, the intervals being longer after 60 hours. The most satisfactory agreements were secured during the first 15 hours, after which time uncontrollable factors caused some variation.

Materials

The resins investigated met the usual industrial specifications and contained the amount of phenolic resin indicated in the following table. The diluent for those resins specified as less than 100 per cent phenolic was ester gum. The numbers given provide the key for reference in the discussion:

Resin No.	Approx. Phenolic Resin Content, %	Test for Free Phenol	Resin No.	Approx. Phenolic Resin Content, %	Test for Free Phenol
1	100	−	4	45	+
2	100	−	5	20	−
3	100	−	6	14	−

The alkali-refined linseed oil used had the following values:

Iodine No., Wijs method	185.3
Acid No.	0.65
Saponification value	193.20
Specific gravity	0.931

The metal content of the naphthenate drier used was 0.30 per cent cobalt, 0.30 per cent manganese, and 4.60 per cent lead; the specific gravity of the drier was 0.855.

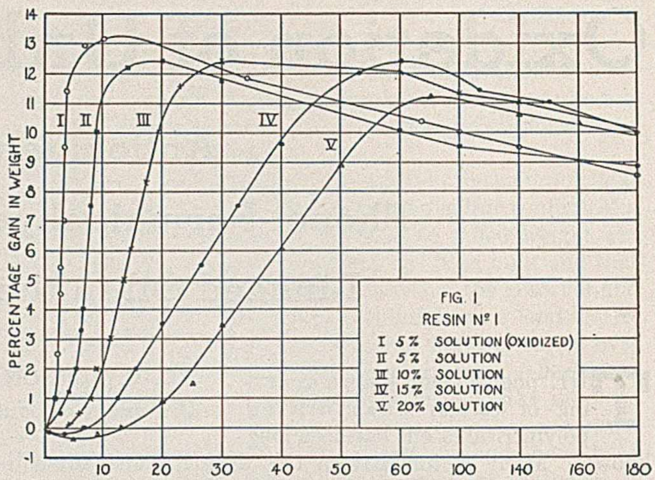
Consideration of Curves

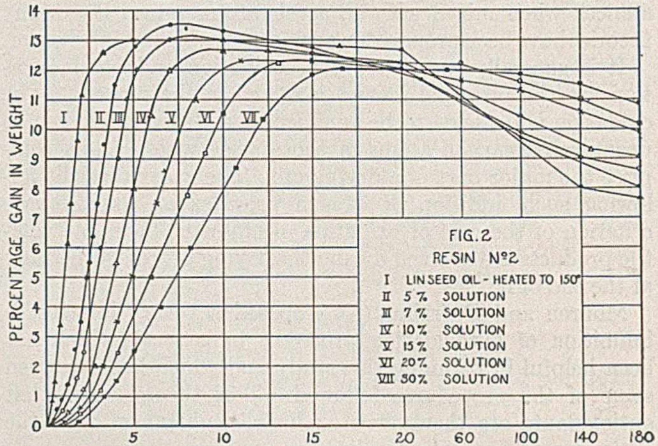
The curves presented represent the percentage gain in weight of the oil in the resin-oil mixtures, not that of the entire mixture. It was shown in preliminary studies that thin films of the resin, spread from ether suspensions or solutions, did not gain in weight when exposed to air under the experimental conditions which prevailed during this study. The amount of oil present in any given sample was easily determined from the original weight of the film and the percentage composition of the solution. The "raw" data were all recalculated by the use of an appropriate conversion factor so that the new data showed the percentage gain in weight of the oil.

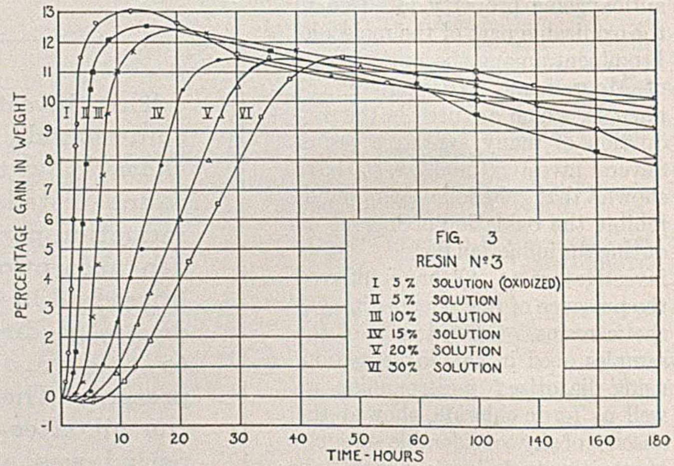
The conclusions were drawn by comparing the curves for the resin-oil mixtures with curves for linseed oil without resin; both curves were from data collected under identical experimental conditions. This method had the advantage that the inherent defects of the gain-in-weight method were eliminated.

Each of these curves represents data collected in several runs under similar conditions and agreeing within the usual experimental limits. In addition to curves representing the resin-oil mixtures is the curve showing the behavior of linseed oil (Figure 2, I) and a curve (Figure 5, I) showing the behavior of ester gum, the diluent for resins 4, 5, and 6. The data for these curves were collected under the experimental conditions prevailing during this study and the curves have been included for comparison with the resin-oil curves.

The curves for the 100 per cent phenolic resins (Figures 1, 2, and 3) show that each of these had antioxidant influence, in direct proportion to the amount of resin present. This effect was confined for the most part to the induction period.



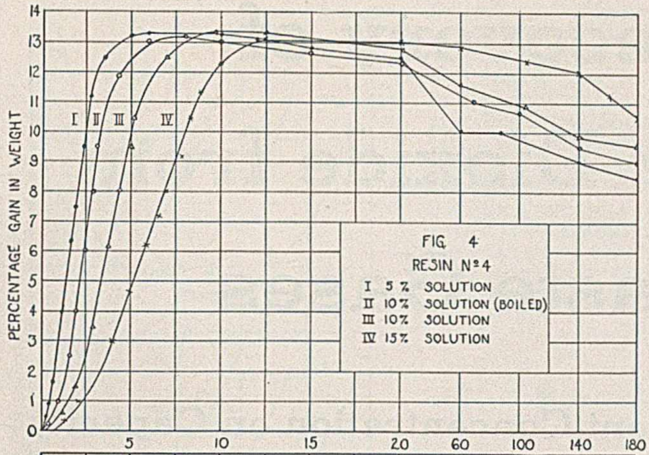


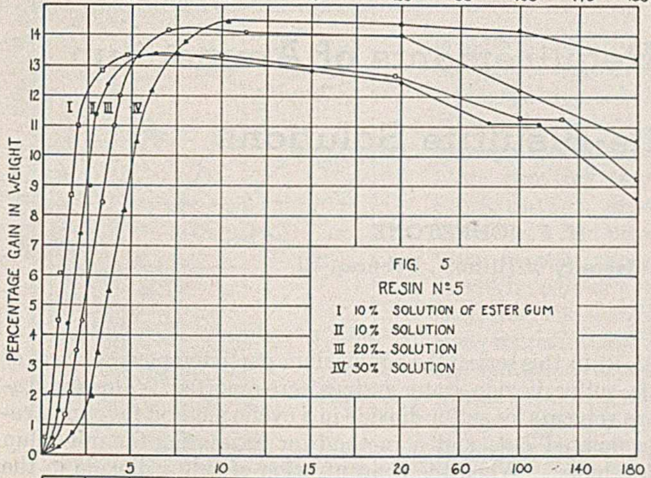


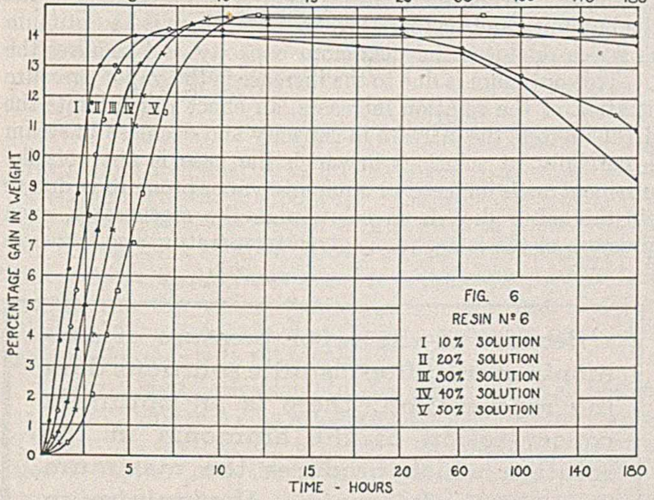
There was a loss in weight after the initial weighing in the higher concentrations of resin 1 and in all concentrations of resin 3. This portion of the curves was checked many times in an effort to determine the cause. It was found that heating the weighed sample of resin to incipient fusion under a vacuum before incorporation in the linseed oil resulted in the elimination of this behavior, without affecting the rest of the curve. Boiling weighed samples of resin in water, drying, and incorporating with oil had precisely the same effect. Naturally, there was a loss in weight of resin by both of these treatments. Some volatile water-soluble substance was eliminated by these treatments, but it could not be identified with certainty, although occluded or adsorbed formaldehyde was suspected. Elm (*2*) noted a similar initial loss of weight in the drying of trilinolenic glyceride, which of course was not due to formaldehyde.

In order to test the applicability of Moureu and Dufraisse's theory to the work in hand, 4.0 grams of resins 1 and 3 were oxidized for one hour with 60 cc. of 30 per cent hydrogen peroxide. After thorough washing and drying, these samples were spread and weighed in the usual manner. Although the antioxygenic properties were not completely eliminated (Figure 1, I, and Figure 3, I), they were sufficiently decreased to substantiate the theory.

This same antioxidant effect was noted when commercial resins made up of mixtures of phenolic resins and ester gum were tested (Figures 4, 5, and 6). Ester gum itself was found slightly oxidizable, gaining 1.7 per cent in weight after







120 hours when spread as a film from an ether solution. It did not, however, show antioxidant properties when incorporated in linseed oil and treated in the usual manner (Figure 5, I). The synthetic resins did not gain in weight when treated in the same manner as the ester gum.

The amount of synthetic resin actually present in these solutions was less than the percentage given for the curves in the figures. Thus a 30 per cent solution of a 20 per cent phenolic resin–ester gum mixture actually contained but 6 per cent phenolic resin. Curves for such mixtures can scarcely be compared to 6 per cent solutions of purely phenolic resins, since the amount of oil exposed at the surface interface of the former was much less than that exposed in the latter case.

The temperature required to disperse resins 4 and 5 was 260° rather than 150° C. The curve for the linseed oil heated to 260° was identical with that heated to 150° within the limits of experimental error, and therefore was not included.

An interesting point concerning resin 4 was that it yielded, on prolonged treatment with boiling water, 19.93 per cent of 4,4-dihydroxydiphenylmethane. When this substance had been removed, the dried residue, incorporated in oil and spread in the usual manner, showed markedly less antioxidant effect (Figure 4, II). The other resins when so treated did not show any change in their antioxidant effect. With resin 3 an initial loss of weight was eliminated by this treatment, as has already been mentioned.

The increased viscosity of the solutions containing the larger amounts of resin was undoubtedly a factor in the rate at which the oil in the mixture absorbed oxygen, in that the diffusion of oxygen was rendered more difficult. No way of eliminating this was found. Then, too, there was less oil exposed at the surface of the more concentrated solutions, which would tend to slow up the oxygen absorption. It was believed that the slope of the curves representing more concentrated solutions was due at least in part to these factors.

Conclusion

The six phenol-formaldehyde resins and mixtures of these resins with ester gum studied in this investigation showed marked antioxidant effect on pure alkali-refined linseed oil in the presence of driers. This effect was specific for each individual resin, and was confined to the induction period. This antioxidant effect was partially due, in two cases, to some oxidizable part or component of the resin, since it was markedly decreased when the resin was treated with oxidizing agents. This last fact was in accord with the theory of Moureu and Dufraisse (*5*) relative to antioxygens, and indicated a possible treatment of such resins should their antioxygenic properties be undesirable.

The resins studied were apparently free from simple phenols used in their manufacture, although one of the resin–ester gum mixtures yielded a considerable amount of a complex phenol. The presence of free formaldehyde could not be demonstrated; yet in one case a behavior was noted which indicated the possibility of its presence.

The results of this investigation must not be compared to those attained with heat-bodied oils, since the oil used here was not heat-bodied. Neither must it be concluded that these resins prevented the complete drying of the oil, for the oil did dry eventually. The results of interest are those shown during the induction period of oxygen absorption.

Acknowledgment

This work was made possible by a fellowship granted to W. W. Rinne, the junior author, by the Louisville Oil, Paint, and Varnish Production Club. The authors wish to express their deep appreciation, not only for the fellowship, but also for the generous coöperation of the members of the club in furnishing materials and helpful suggestions.

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Recovery of Sulfur Dioxide from Waste Gases[1]

Effect of Solvent Concentration on Capacity and Steam Requirements of Ammonium Sulfite-Bisulfite Solutions

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IN PREVIOUS papers (*1*, *2*) in this series[2] the equilibrium partial vapor pressures of solutions in the ammonia–sulfur dioxide–water system were reported. The application of these solutions as solvents for sulfur dioxide in a cyclic method involving regeneration by heating was pointed out, and a method for estimating the minimum steam requirements was developed. When the concentration of sulfur dioxide in the original gases is low and the humidity and temperature are high, there is an optimum concentration of the solvent which produces the maximum capacity and requires the smallest quantity of steam. This optimum is due to the increase in the vapor pressure of ammonia as the concentration of the solution increases, an effect which limits the extent of regeneration and thus offsets the increase in capacity and decrease in steam requirements encountered normally in solutions in which the base is not volatile. The increase in steam requirement with increase in ammonia vapor pressure is due to the greater tendency to hold the sulfur dioxide in solution in the regenerator, even though the actual vapor pressure of the latter at any given temperature also increases with concentration. These relations may be understood by examination of the equilibrium diagrams and equations in the previous paper.

The existence of the optimum concentrations when the absorption temperature

Because of the vapor pressure of ammonia over sulfite-bisulfite solutions during regeneration, there is an optimum concentration of the ammonia in the solution which produces the maximum capacity and requires the minimum quantity of steam for regeneration. This concentration is a function of the composition of the raw gas and of other operating conditions. For dilute gases with high humidity, the optimum concentration may be less than half the concentration of the saturated salt solution.

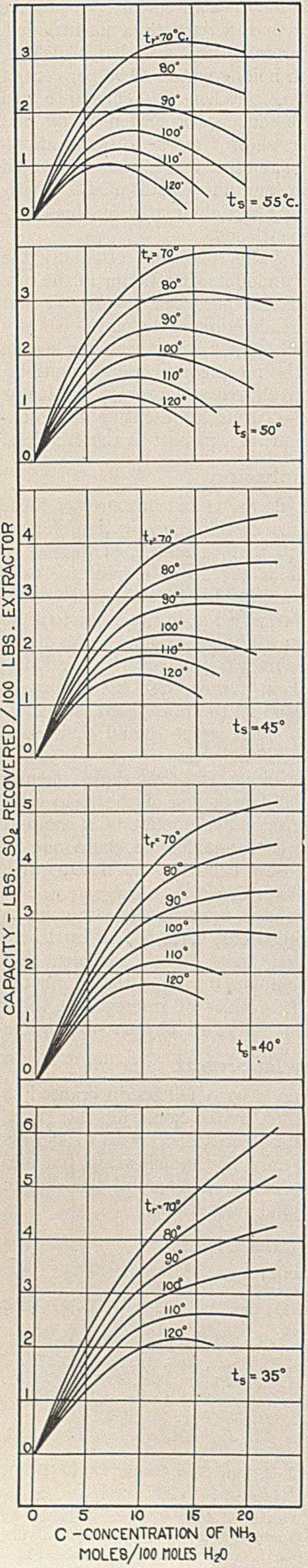

FIGURE 1. EFFECT OF AMMONIA CONCENTRATION ON CAPACITY OF SULFITE-BISULFITE SOLUTIONS FOR ABSORBING SULFUR DIOXIDE FROM GASES CONTAINING 0.3 PER CENT SULFUR DIOXIDE, ASSUMING EQUILIBRIUM IS REACHED IN THE SCRUBBER

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[1] Presented before the Division of Industrial and Engineering Chemistry at the 94th Meeting of the American Chemical Society, Rochester, N. Y., September 6 to 10, 1937. Published by permission of the Director of the Engineering Experiment Station, University of Illinois. This paper contains part of the results obtained on the coöperative research project, Case 34, with the Utilities Research Commission of Chicago.

[2] The third paper in the series appeared in March, 1937, pages 286 to 297.

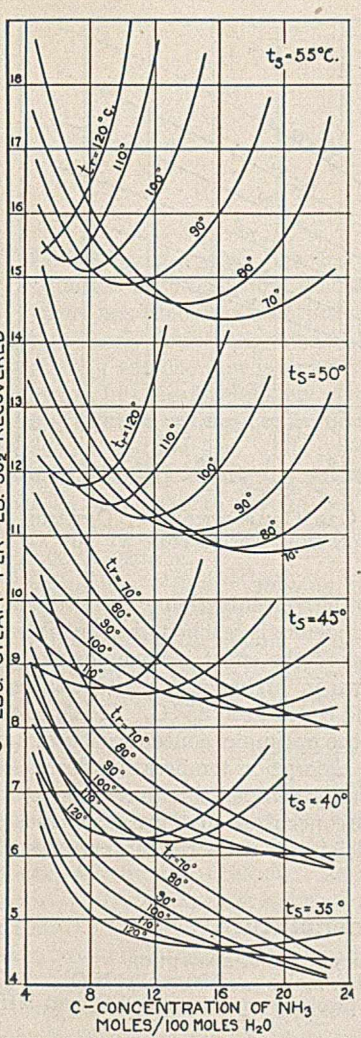

FIGURE 2. EFFECT OF AMMONIA CONCENTRATION ON STEAM REQUIREMENTS FOR REGENERATION OF SULFITE-BISULFITE SOLUTIONS FOR ABSORBING SULFUR DIOXIDE FROM GASES CONTAINING 0.3 PER CENT SULFUR DIOXIDE, ASSUMING EQUILIBRIUM IS REACHED IN THE SCRUBBER

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is at 35° C.(95° F.) or above, is shown in Figures 1 and 2. Many industrial gases, particularly those resulting from combustion, have wet-bulb temperatures in this range. It will be observed that, for the conditions represented, the concentrations of ammonia producing the highest capacity for absorbing sulfur dioxide coincide with those requiring the smallest amounts of steam for regeneration.

The curves in Figures 1 and 2 are based on an arbitrary set of operating conditions chosen only for comparison. The solution is assumed to leave the scrubber saturated with respect to gases containing 0.3 per cent sulfur dioxide. Regeneration is carried to the point where the vapor pressure of ammonia over the lean solution at the stated temperature equals that of sulfur dioxide. The vapors leaving the regenerator are assumed to be in equilibrium with the influent solution.

The graphical derivation of these curves is tedious and inexact, involving as it does reading off data from several graphs. The derivation given in this paper of the optimum concentration is applicable to the general case and may be used in predicting the capacity of any solution of ammonium sulfite-bisulfite for absorbing sulfur dioxide from dilute gases.

The operating conditions affecting the optimum concentrations of ammonia in the solvent are: (1) concentration of sulfur dioxide in the gases being treated, (2) efficiency of the scrubber, (3) temperature of solution leaving the scrubber, (4) temperature of regeneration, and (5) efficiency of regeneration.

The solution cannot leave the scrubber completely saturated with the sulfur dioxide in the entering gas. The degree of saturation depends on the size and on the efficiency of the scrubber. Items 1 and 2, however, may be combined by designating the equilibrium sulfur dioxide pressure over the solution leaving the scrubber at the scrubber temperature. As previously shown, the relation between this equilibrium pressure and the composition of the solution over the ranges in question is as appears in Equation 1.

$$p_{SO_2} = M \frac{(2S - C)^2}{C - S} \qquad (1)$$

where M is a function of the temperature only,

$$\log M = 5.865 - \frac{2369}{T} \qquad (2)$$

The maximum concentration of sulfur dioxide in the solution leaving the scrubber, then, is given by:

$$\frac{(2S_m - C)^2}{C - S_m} = \frac{p_{SO_2}}{M} = a \qquad (3)$$

Solving for S_m:

$$S_m = \frac{4C - a \pm \sqrt{a^2 + 8aC}}{8} \qquad (4)$$

Only the positive root is of interest.

The operation of the regenerator is somewhat arbitrary, but it will be assumed here that regeneration will be carried to the point at which the vapor pressure of ammonia equals the vapor pressure of sulfur dioxide over the solution. As shown in the previous paper (*2*), this represents the approximate limit of regeneration. The equilibrium vapor pressure of ammonia is given by an equation analogous to Equation 1,

$$p_{NH_3} = \frac{N \cdot C(C - S)}{2S - C} \qquad (5)$$

where N is also a function of temperature only,

$$\log N = 13.680 - \frac{4987}{T} \qquad (6)$$

Equating (1) and (5) for the value of S_e:

$$\frac{(1 - S_e/C)^2}{(2S_e/C - 1)^3} = \frac{M}{N} \qquad (7)$$

The ratio S_e/C, therefore, is a function of temperature only and is independent of the value of C. Although Equation 7 indicates that the effect of temperature is a complex function, it happens that in the range of practical interest—viz., from 70° to 120° C., a linear relation exists (Figure 3).

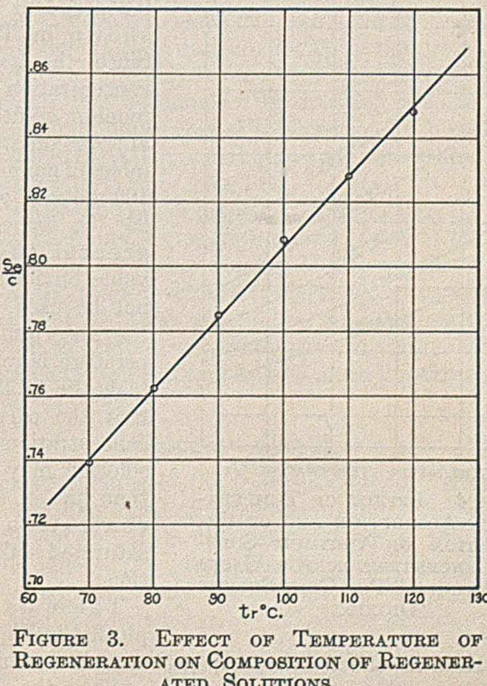

FIGURE 3. EFFECT OF TEMPERATURE OF REGENERATION ON COMPOSITION OF REGENERATED SOLUTIONS

The equation of the line is:

$$S_e/C = 0.00219t_r + 0.587 \quad (8)$$

The capacity of the solution is defined as the pounds of sulfur dioxide recovered per 100 pounds of solution entering the scrubber, or

$$W = \frac{6400\ (S_m - S_e)}{1800 + 17C + 64S_e} \quad (9)$$

Substituting the values of S_m and S_e from Equations 4 and 8,

$$W = 800\left(\frac{\sqrt{a^2 + 8aC} - C(0.696 + 0.0175t_r) - a}{1800 + 0.14t_rC + 54.6C}\right) \quad (10)$$

Equation 10 may be used for determining the capacity of any solution of known ammonia concentration under fixed conditions of operation, giving the values of the parameters a and t_r.

TABLE I. OPTIMUM CONCENTRATIONS OF SOLUTIONS FOR ABSORBING SULFUR DIOXIDE FROM GASES CONTAINING 0.3 PER CENT SULFUR DIOXIDE

Regeneration Temp., ° C.	Moles NH_3/100 Moles H_2O at Absorption Temp. of: 35° C.	40° C.	45° C.	50° C.	55° C.
70	(28.8)[a]	(24.3)	20.4	17.1	14.0
80	(25.7)	21.2	17.7	14.7	12.0
90	22.4	18.5	15.2	12.5	10.2
100	19.4	15.9	13.0	10.4	8.6
110	16.8	13.6	10.9	9.0	7.1
120	14.2	11.3	9.0	7.3	5.8

[a] Values in parentheses are above the saturation concentration of ammonium sulfite.

Differentiating Equation 10 in respect to C and equating to zero, we have, after simplifying,

$$\frac{7200a - 0.14a^2t_r - 54.6a^2 - aC_{\text{max.}}\ (0.56t_r + 218.4)}{1250 + 31.5t_r - 0.14\ at_r - 54.6a} = \sqrt{a^2 + 8aC_{\text{max.}}} \quad (11)$$

Although Equation 11 appears to be complicated, numerical examples can be solved easily for $C_{\text{max.}}$, so that the optimum concentration can be found for any conditions of operation. A table of values covering practically all such conditions when the vapor pressure of sulfur dioxide over the solution leaving the scrubber is 2.3 mm. (corresponding to equilibrium with a 0.3 per cent gas) is shown in Table I. Since the saturated concentration of ammonium sulfite exists at approximately 22.5 moles of ammonia per 100 moles of water at 25° C. values of C greater than this value obviously cannot be used. When the absorption temperature is relatively high, the table shows that the optimum concentration of the solution may be less than half of the concentration of the saturated salt solution.

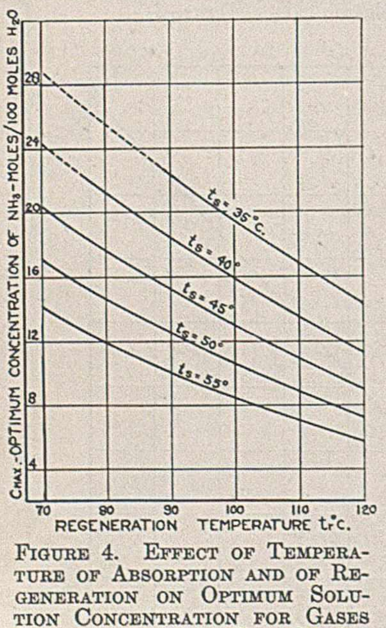

FIGURE 4. EFFECT OF TEMPERATURE OF ABSORPTION AND OF REGENERATION ON OPTIMUM SOLUTION CONCENTRATION FOR GASES CONTAINING 0.3 PER CENT SULFUR DIOXIDE

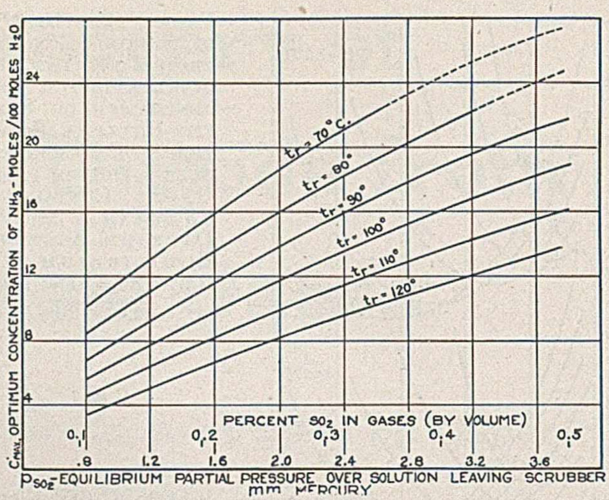

FIGURE 5. EFFECT OF GAS COMPOSITION ON OPTIMUM SOLUTION CONCENTRATION FOR ABSORPTION AT 45° C.

These data are plotted in Figure 4 in order to show the effect of the temperature of absorption and of regeneration on the optimum value of C. Since the constant a is directly proportional to the concentration of sulfur dioxide in the gases, assuming equilibrium is reached, it is possible to use the data of Table I to show the effect of changing the gas composition. This is shown in Figure 5, for which the absorption temperature is held constant at 45° C. It is evident from Figures 4 and 5 that the optimum concentration of ammonia (a) decreases as the absorption temperature decreases, (b) decreases as the regeneration temperature decreases, (c) increases as the sulfur dioxide concentration of the gas increases, and (d) increases as the efficiency of the scrubber increases the saturation of the solution.

Nomenclature

a = ratio p_{SO_2}/M at temperature of absorption
C = concentration of NH_3, moles per 100 moles H_2O
M, N = constants in vapor pressure equations for SO_2 and NH_3, respectively
p_{SO_2} = equilibrium vapor pressure of SO_2, mm. Hg
p_{NH_3} = equilibrium vapor pressure of ammonia, mm. Hg
S = concentration of SO_2, moles per 100 moles H_2O
S_m = concentration of SO_2 in solution leaving the absorber
S_e = concentration of SO_2 in solution for which $p_{SO_2} = p_{NH_3}$ at regeneration temperature
t_s = temperature of solution leaving absorber, ° C.
t_r = temperature of solution leaving regenerator, ° C.
W = capacity of solution for abosrbing SO_2, lb. per 100 lb. solution entering scrubber

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(1) Johnstone, IND. ENG. CHEM., 27, 587 (1935).
(2) Johnstone and Keyes, *Ibid.*, 27, 659 (1935).

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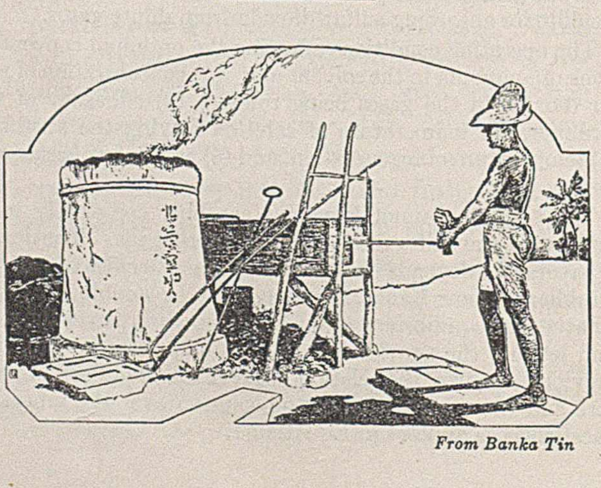


From Banka Tin

ACETONE

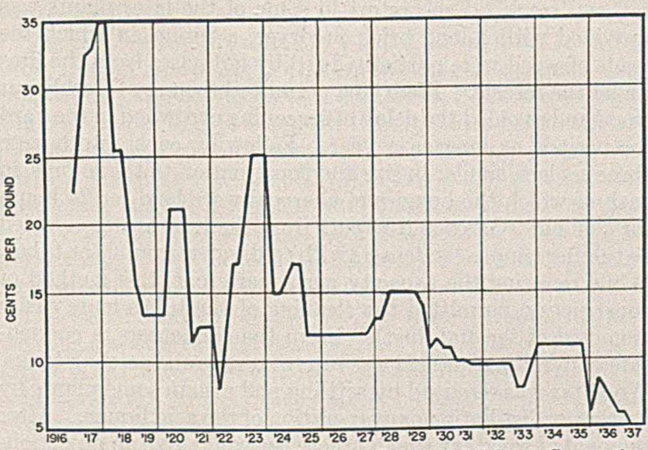
LLOYD C. COOLEY
706 Straus Building, Chicago, Ill.

FROM being a vitally needed munition of war with production lagging behind demand and at a high price, acetone has become a plentiful solvent with production of one year nearly double the sales and at a low price. The consumption of acetone now is somewhere near twice that of the war period, but the development of synthetic methods of manufacture from practically unlimited amounts of raw material has flooded the market. The price is at the lowest level in history (Figure 1). Before discussing the future possibilities it will be of interest to develop background by reviewing the older methods, both obsolete methods and those still in use for making acetone.

Acetone is a pleasant smelling liquid, water-white, boiling at 56.1° C., completely miscible with water, and weighing about 6.6 pounds per gallon. The liquid is inflammable and the vapors form explosive mixtures. The manufacturers issue complete specifications of the numerous properties.

History

It has been stated (*2*) that cordite in Great Britain during part of the war period was produced at the rate of 2000 tons per week. This amount would require, without solvent recovery, 440 tons of acetone. As solvent recovery methods became perfected, the net amount of acetone required per 100 pounds of cordite was reduced to 15 or 17 pounds. The latter figure would call for 600,000 pounds of acetone on the weekly output of 2000 tons of cordite. Cordite was the name given the British propellant used in army and navy cannon. It was made from gun cotton (13.2 per cent nitrogen) of higher nitration than that used in the United States, and was characterized by its low solubility in ether-alcohol mixtures such as were used in this country. Mixed with the gun cotton was nearly half its weight of nitroglycerin and 8 per cent petrolatum. The presence of nitroglycerin added to the risk of solvent recovery operations although no serious trouble was reported. To make collodion from the above mixture prior to forcing through macaroni presses, 35.5 pounds of a solvent mixture were added to 100 pounds of mixed gun cotton, nitroglycerin, and petrolatum. The solvent was approximately 60 per cent acetone and 40 per cent denatured alcohol (formula 2B).



Courtesy, Commercial Solvents Corporation

FIGURE 1. PRICES OF ACETONE IN TANK CARS, 1917–37
(Source, *Oil, Paint and Drug Reporter*)

Prior to the war the only commercial source of acetone was calcium acetate obtained from wood distillation. Its use was scattered over a large number of items, but only a few took large volumes—for dissolving compressed acetylene, for use in the production of photographic film, and in pharmacy as a denaturant for rubbing alcohol where it was said to have some specific benefit. The manufacture of iodoform and chloroform was based on acetone, and acetone was used in paint and varnish removers and for making celluloid and artifical leather.

The amount of acetone needed to supply war demands for the manufacture of British cordite and airplane dopes or lacquers could not be produced by increasing the number of wood-carbonizing plants because of the amount of time and capital involved and the number of wood cutters that would have been required from a nonexistent supply of idle labor. Therefore, new processes were studied and started; among them were fermentation of grain, molasses, and kelp from the Pacific Ocean, fermentation of ethyl alcohol to vinegar, and conversion of acetylene to acetic acid.

Ocean Kelp

From the kelp which was harvested from narrow beds or fields stretching parallel to and half a mile or so from the beach of the Pacific Coast, fermentation produced acetic acid in the presence of suspended calcium carbonate; the resulting calcium acetate was evaporated in long-tube evaporators, dried, and roasted in standard acetate retorts. A simple continuous column still was used to rectify the crude acetone, and some pure acetone was made and shipped, as well as a nearly equal quantity of methyl ethyl ketone.

The development of this process had its share of wartime development troubles. One of the first striking accomplishments was the construction of a mechanical cutter or sickle bar like a giant hay mower, which was used for harvesting the kelp. The first fermentations were conducted in the presence of sodium carbonate, possibly from a California lake, and the sodium acetate was decomposed by roasting with niter cake. The high maintainance cost of this part of the process led to its abandonment; calcium carbonate was substituted for soda and acetate retorts were installed.

Later when the task of disposing of spent kelp became almost overwhelming, owing to the need for acres of dumping ground and the enormous number of flies which bred in the mass, a method was developed for fermenting the kelp almost to a liquid so that the waste could be run back into the ocean. In addition to acetone, other ketones and various fatty acids were obtained ("taffy salts") as well as an important proportion of potash salts.

Calcium Carbide

The most startling of the wartime methods for producing acetone was developed at Shawinigan Falls, Quebec, by H. W. Matheson and H. S. Reid at the plant of the Canadian Electro-Products (*48*). Acetylene was piped from the neighboring carbide plant and bubbled through a hot mixture of sulfuric acid and mercuric oxide in Duriron kettles:

$$\begin{aligned} CaC_2 + 2H_2O &= C_2H_2 + Ca(OH)_2 \\ C_2H_2 + H_2O &= CH_3CHO \end{aligned}$$

Distilled acetaldehyde was converted to acetic acid under pressure in aluminum-lined steel kettles by bubbling air through the liquid in the presence of manganese acetate catalyst:

$$2CH_3CHO + O_2 = 2CH_3COOH$$

The acetic acid thus formed was distilled to make glacial acetic acid, and shipped as such or revaporized for use in the catalytic formation of acetone in converters:

$$2CH_3COOH = (CH_3)_2CO + CO_2 + H_2O$$

The catalyst used for converting acetylene to acetaldehyde was mercuric oxide which was made in a cast-iron or concrete electrolytic cell, using 5 per cent solution of sodium hydroxide and provided with a steel cathode and a mercury anode. The cell contained about 1240 pounds of mercury per charge. In the earliest days there was an unpleasant amount of caustic fume in the air and a few men had sore gums, but that condition was soon cured by ventilation.

The conversion of acetylene to acetic acid was carried out in Duriron kettles with hot water jackets, Duriron paddle agitators, and mercuric oxide paste feeders. The catalyst was kept in suspension in 6 per cent sulfuric acid at about 60° C.; a batch was added every half-hour while acetylene was bubbled through. As the kettle filled with water and catalyst, a portion was drained from the bottom to large wooden storage tanks where the sludge was settled out and then dried in a steam-jacketed agitator pan.

The gas and aldehyde from the kettles passed through a water-cooled and then a brine-cooled condenser and a scrubbing tower to a gas holder. The condensed aldehyde and scrubbing water flowed to large steel tanks provided with brine coils and covered with insulation. Supply pumps from storage to still house feed tank were controlled by a float in the tank operating an electric switch. The acetaldehyde was distilled free of water and some paraldehyde in a cast-iron continuous still column with a combined rectifying and exhausting column about 6 feet in diameter and a short 5-foot-diameter auxiliary purifying column. The still was provided with a partial and a final condenser, a cooler, a feed-slop heat exchanger, and a vapor-pressure-operated steam regulator.

For converting the acetaldehyde to acetic acid, a battery of aluminum-lined steel kettles was used and the unconverted aldehyde and acetic acid were condensed in aluminum tube condensers followed by scrubbers. Back pressure was maintained on the kettle and reflux condenser system by suitable valves.

To refine the acetic acid, pot stills were used which were about 7 × 7 feet in size, built of 0.5-inch copper and provided with a copper steam coil and a 40-inch-diameter aluminum column, with aluminum-tube partial and final condensers.

At the time of the first distillation of acetic acid a small amount of unconverted material got into the kettle so that when a little heat was applied there was quite an evolution of vapor and foam which blew through the column and condensers and caused a little excitement among the operators, besides giving the traveling-crane operator a shower bath just as he passed the building.

To convert acetic acid to acetone, small copper vaporizers were used which were heated by steam. The vapor passed into converting tubes packed with small iron balls, all coated with lime. The resulting acetone was first condensed in a water and then a brine condenser, followed by a scrubber.

The resulting acetone was purified in a four-column continuous still provided with the usual partial and final condensers, cooler, feed-slop heat exchanger, oil cooler, decanter, and steam regulator. The columns varied from 66 to 46 inches in diameter.

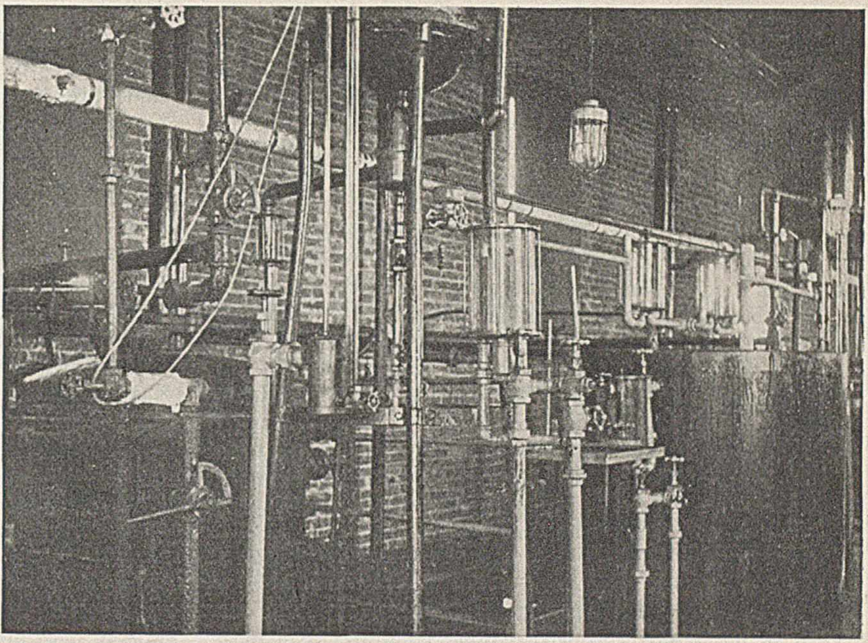
During the development of this process, an oxidation kettle was used which had a large explosion relief head held down by bolts with large springs. Many times until the control was perfected, the head lifted and sprayed aldehyde and acid around the landscape. In fact, once or twice during the early days of plant operation the pressure ripped open an aluminum reflux condenser with consequent fire. Fortunately, the supply of aldehyde was protected in insulated tanks in the cellar.

Bookkeeping indicated poor yields, and yet sampling showed no losses from the bases of the continuous stills; a search was therefore made and suspicion was cast on a float feed tank which contained a cooling coil. Nothing appeared to be wrong, but a cooling coil outlet was found to be piped to a water drain without a sight glass or an open top funnel. As soon as the change in piping arrangements was started by opening the pipe union, the odor of aldehyde was strong. Here was the leak. A cracked fitting inside the tank, possibly caused by the freezing of residual testing water, had permitted acetaldehyde to escape through a closed drain and into the river under the ice.

While all the new process plants were being built and put into operation, the wood distillation plants were "sawing wood" literally and figuratively; the conversion of molasses alcohol to acetone and the fermentation of corn to acetone and butyl alcohol were yielding great volumes.

Wood Distillation

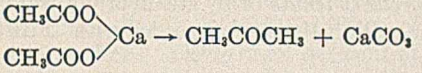
Better prices due to war demand enabled the wood distillers to invest in better equipment for the existing plants and to build additional carbonizing capacity with equipment which gave better yields and at lower operating costs. The standard method of carbonizing wood with recovery of by-products, or in fact any products other than charcoal, consisted of heating, in a sheet steel retort, cord wood which was piled in strap iron buggies as wide as the wood sticks were long. A retort could hold three or four buggies and was built over a narrow-gage railroad track. Each retort in some of the later plants was provided with a long brick predryer, a tunnel in which the loads of wood were partially dried by hot gases from the fires under the retorts. Predrying permitted the use of freshly cut wood and avoided the delay of seasoning cordwood in the yard for periods as long as a year. Following each retort were three coolers, similar in size and construction to the retorts, in each of which the buggies of charcoal were held for 24 hours for cooling. Gases and vapors from the retorts were carried to tubular copper condensers with cold water around the tubes. While reducing the capacity per square foot, this method of construction permitted the cleaning of the tubes more easily (removal of tar and dust). From the condensers, a condensate of pyroligneous acid was run to storage and settling tanks. Wood tar was removed by settling and also in some plants by a primary distillation or evaporation of the acid liquor. After removal of wood tar which otherwise would give an objectionable color, the crude was treated with lime "to a rich wine red," the volatile portion (methanol and ketones) was removed in a lime lee still or column, and the water residue which contained calcium acetate was evaporated in double- or triple-effect evaporators and then finished to a paste on drum dryers or in pans with steam-jacketed bottoms. From the pans the semicrystalline and nearly dry mush was spudded and then shoveled out onto drying floors which were steel plates over waste gas flues; or, as in the case of drum dryers, the paste was carried by screw conveyors to apron dryers, such as the Huillard. The usual calcium acetate of commerce was 82 per cent acetate.



Courtesy, T. C. Albin, Newberry Lumber Chemical Co.

Figure 2. Operating Floor of a Wartime Acetone Plant

Calcium acetate is heated dry to produce acetone:



$$(CH_3COO)_2Ca \rightarrow CH_3COCH_3 + CaCO_3$$

An approximate yield of 20 pounds of acetate per 100 pounds of 82 per cent acetate is obtained.

In early methods large direct-fired kettles were used with attendant dust troubles (*36*) and difficulties of good temperature control. The industry finally settled on the method of loading shallow trays with the acetate from an overhead hopper or weigh scale and then pushing buggy loads of trays along a transfer car into retorts similar to those built for carbonizing wood, with rails laid in them. The acetate retorts were heated with tar, wood gas, or coal. One wartime plant which was typical of its kind had an oven house, still house, barrel house, and chemical storage. The oven house was 55 feet wide and 366 feet long, holding twenty-four acetone retorts in pairs; they, in turn, could hold ninety-six cars or buggies. The ovens were built of brick, each setting carrying two retorts with a separate firebox for each. The hot gases from burning fuel were distributed along the bottoms of the retort and then up around the sides and out to the stack.

The retorts were built of 0.5-inch boiler plate about 41 inches square and 21 feet 6 inches long, containing rails for the four acetate buggies and a perforated steam pipe for blowing out residual vapors before the retort could be opened safely. The door was of cast iron, usually hinged to a cast-iron frame which was riveted to the retort. Some of the early jobs had welded frames and the closed end had a welded head, but many cracked and were replaced with cast-iron frames riveted on to the steel retorts.

The cars were approximately 9 feet 4 inches long, 38 inches wide, and 38 inches high, with seven angle-iron guides, each supporting two acetate pans, 1 inch deep, 37.75 inches wide, and 56.5 inches deep. Each car held fourteen pans with 500 pounds of dry calcium acetate. The heating period was about 8 hours at 450° to 500° C. The crude acetone with water, oils, and other ketones was condensed and run to storage. Some operators used to blow steam into a retort during the heating period to sweep out the acetone faster and prevent tar formation.

The still house was 55 × 90 feet with six pot stills and columns and twelve steel storage tanks for fractions, two horizontal tanks with agitators for washing acetone, and twelve small test tanks (two for each still for holding the product until chemical tests were completed and each tank of acetone was passed or rejected).

Some plants had four-column copper continuous stills provided with feed-slop heat exchangers, vapor heaters, chemical treatment plates and sections, and continuous oil decanters; others had batch stills. Returning to the typical example of a plant with twenty-four retorts and six stills, the kettles were of steel 8 feet in diameter and 12 feet high, with copper coils, 8-inch vapor pipes, and approximately 4-foot-diameter columns. Two stills were set aside for refining acetone and were so connected by pipes to the rest of the system that no crude but only partially refined materials could be run into them or to the washer which was devoted to the refining end. Figure 2 shows the top of a column, the lower end of a condenser with regulating bottle from which reflux returned to the column, pressure-indicating bottle, sensitive regulating cocks for condenser water, and sampling cocks.

Experience determined that acetone "cuts" from the crude stills could not be set aside for refining unless they remained pink with potassium permanganate solution at least 20 minutes. This was called "20-minute acetone." Twenty-minute acetone was diluted in the washer to about 60 per cent with cooled condensate from the steam traps, 10 or 15 pounds of aluminum sulfate in solution were added, and the agitator was run for about 30 minutes; then the contents was pumped to the charging tank to settle for 2 hours. About an hour was required to heat the still and column. Heads and 20-minute acetone were set aside for further treatment. When a sample from the still stood the permanganate test for 50 minutes and had less than 0.002 per cent carbon dioxide the condensate was switched into one of the "cut" tanks. By waiting until the acetone was of this quality, contamination of a cut tank could be avoided. Cut tanks were filled and tested alternately and dumped to the pure acetone tank as long as each cut tank passed the tests. Near the end of the run, as the vapor temperature at the base of the column began to rise, the run was switched to a 20-minute tank and later to an oil separator until the run was over. Yields and fuel consumption were as follows:

Yields per 100 lb. acetate, lb.:		
Acetone		18.37
Ketone oil		4.77
Consumption of chemicals per ton of acetone, lb.:		
Aluminum sulfate		2.2
Sodium chloride		245.0
Sodium hydroxide		70.2
Crude acetone from retorts, per 100 lb. acetate, gal.		6
Steam consumption in still house per lb. acetone, lb.	Approx.	8
Coal used under retorts per 100 lb. calcium acetate, lb.		37.5

Vinegar

The manufacture of acetone from vinegar was carried out in conjunction with the production of ethyl alcohol from molasses by the Curtis Bay Chemical Company, Baltimore. The alcohol was fermented to vinegar in generators built like wooden stave tanks in which the alcohol was automatically fed at intervals and filtered down over coke or beech shavings.

It took a 40-car train from Oregon to bring the lumber. Special shavings were required and could not be brought in fast enough, so coke breeze was substituted. Nine hundred sixty of the generators were 18 feet tall and 10 feet in diameter. Two hundred more were 18 feet high and 25 feet in diameter. Air circulated through the generators due to natural draft, which gave lower production in summer than in winter, and oxidized the alcohol to acid by vinegar bacteria. After neutralizing with lime, the solution was evaporated in horizontal-tube quadruple evaporators. One strange feature of the evaporation was the fact that the acetate solution made from vinegar from beech chips behaved differently in the evaporators from the solution made from vinegar from the coke-filled generators; one solution foamed much more than the other. The partially concentrated solution was dried to a mush on drum dryers and finished on Huillard dryers (long wire screen aprons which traveled in tunnels against hot air). At first, hot flue gases were tried but had to be changed to air heated by steam coils because the flue gases deposited sulfur dioxide compounds which spoiled the permanganate test of the acetone from the stills.

From the dryers, the dried acetate was conveyed to rotary retorts for dry-distilling in batches, and the crude acetone was refined in large pot stills with copper columns. Chemical treatment was accomplished by trickling dilute sulfuric acid down each column from near the top and feeding dilute caustic solution on one of the plates a short distance from the bottom of the column.

Fermentation

The production of acetone by fermenting corn mash has been fully described (*25*, *35*). The first operation in North America was in Toronto using cultures brought over from England by Speakman and Legg. Strict attention to details of cleanliness and correct propagating and operating conditions made a success of the process. The firm of Gooderman and Worts, Ltd., turned over part of their Toronto whisky distillery with fermenters and beer stills to the Imperial Munitions Board. A continuous acetone refining still was bought in the United States and production was carried on. This was one of the war industries where girl students or graduates of Toronto colleges acted as fermenter and still operators. Between observations they found time to do their knitting. The hydrogen and carbon dioxide gases evolved from the fermenters were passed through water seals to vents on the roof. A large tank was used to store the then little used "butyl," while experiments were carried on seeking to convert butyl alcohol to methyl ethyl ketone which was later produced on a manufacturing scale.

Soon after the United States entered the war, Colonel Gooderham assisted in the purchase of a distillery in Terre Haute, where the process was carried out as in Toronto and later became the foundation of the Commercial Solvents Corporation.

As the different methods for making acetone are reviewed, it is evident that comparatively few patents have been taken out recently relating to the wood distillation, vinegar, or kelp processes, but a great many have been issued to describe the fermentation and the catalytic conversion methods, the latter based on such raw materials as ethyl alcohol, acetylene, acetic acid, still gases, and natural gas.

Except for the fermentation method, little information is made available by the manufacturers so that patent literature is the only source from which to obtain ideas as to how the more modern methods are carried out.

One of the earliest fermentation patents is that of Fernbach and Strange (*22*) which describes a process for the production of acetone and higher alcohols from starch, sugars, and other carbohydrate material. Either maize, potatoes, or glucose are mashed and sterilized; then yeast is added which has been degraded by either *Tyrothrix tenuis* or by steam or hot water under pressure. After cooling, the mash is seeded with "Fitz" butyl bacteria.

The process was started by Strange and Graham, Ltd., in England about 1910 as part of an effort to make synthetic rubber (*2*). When the World War broke out, Strange and Graham contracted to supply acetone to the British Government but their output was small and the government took over the plant, later putting in Weizmann's process and obtaining better yields. Since the grain supply in England was short because of submarine warfare, plants for producing acetone were constructed in Canada and India. The Canadian plant which has just been described turned out about a million gallons in two years.

The Weizmann patent (*58*), which was the basis of the large-scale processes just mentioned, states that Fitz had to carry on the fermentation under anaerobic conditions; Weizmann claims that his bacteria did well with or without air. A process for isolating the bacteria is described, and although their spores stand some heat, it was specifically stated that they would not stand the test mentioned by Scheckenbach (*49*) of resisting saturated steam at 100° C. for 30 minutes. Weizmann's bacteria were found on cereals or in the soil.

Delbruck and Meisenburg (*13*) obtained a patent for fermenting sugar in 1916, but it is not known how widely the process was used.

A process for producing acetone from either starch or sugar was patented in 1919 by Northrup (*40*). The organism was called *B. acetoethylicum* and was derived from old potatoes. From a corn mash containing calcium carbonate a yield was obtained of 8 to 10 per cent acetone on the dry weight of the corn and the 12 to 20 per cent ethyl alcohol. If molasses was used, a solution was made up containing 8 per cent sugar. The fermentation was completed in about 40 hours with a yield of 8 to 10 per cent of the weight of the sugar as acetone and 12 to 20 per cent ethyl alcohol. No added nitrogenous substance was needed for feeding the bacteria.

Naturally, attempts were made to broaden the field of available raw materials and to improve the yields from corn. The Commercial Solvents Corporation was the leading producer of of acetone during the period from 1924 up to recent years and naturally led in the number of patents taken out concerning methods of producing acetone; a few will be reviewed.

Pike and Smyth (*43*) used an organism, *Clostridium butyricum*, for the fermentation of blackstrap molasses, which is described minutely according to the methods of the Society of American Bacteriologists. Acid, gas, and alcohols are formed in dextrose, lactose, sucrose, and starch. The acid is principally butyric and the gas is mixed carbon dioxide and hydrogen. The optimum temperature is 30° to 40° C.

Clostridium butyricum was originally derived from corn meal according to the method of Weizmann but was thereafter propagated by several successive subcultures in deep tubes of dextrose agar; the material for the subcultures was taken from the tubes after cutting open the bottoms with a file. Just before being cut open, the tubes were heated at 100° C. for 2 minutes before incubation. After a pure culture was obtained, the bacteria were retained in 5 to 10 per cent corn-meal mash. In order to use blackstrap molasses, it was diluted to 5 per cent sugar and sterilized for 30 minutes at 15 pounds per square inch steam pressure. The several steps are described. The fermentation should be conducted without the presence of copper and there is no need to add nitrogenous substances as food for the organism.

Considerable illumination is cast on the fermentation process for producing acetone and butyl alcohol by Legg (*37*); he refers to Weizmann's patent (*58*) and describes the usual methods previously in use on starch. A method of observing the progress of the fermentation makes use of the rise in the acidity of the mash which normally reaches a peak of 4 to 6 cc. of 0.1 *N* sodium hydroxide per 100 cc. of mash and then falls off to 2 or 3 cc. Yields of 24 per cent of solvents based on the weight of the raw material were ordinarily obtained but were frequently followed by recurrent periods of lowered yields due to abnormal fermentations in which acidity did not rise and fall in the usual way. There are two kinds of abnormal fermentation, one is due to contamination by lactic acid bacteria and the other to a filterable virus or bacteriophage which appears to be parasitic on the acetone butyl alcohol bacillus. The former can best be controlled by rigid aseptic precautions; the latter, according to the patentee, has been successfully dealt with by immunizing the acetone organism against the virus. One-millionth part of the Berkfeld filtrate from a sluggish mash induces sluggish fermentation in a new sterile mash. A process was discovered to render the bacteria resistant to the disease of sluggishness. They were repeatedly subcultivated in the presence of filtrate from a sluggish culture until they became immune. The cultures were heat-shocked before each subcultivation in order to eliminate vegetative forms of the bacteria, leaving only the spores to germinate. The result of using immunized high-yielding strains of the bacteria was to eliminate the periods of sluggishness in which yield was often between 7 and 22 per cent and also to raise the normal yield from 24 to 25 per cent on the dry corn.

Fernbach (*21*) describes an acetone–butyl alcohol fermentation process and gives methods for fermenting saccharose. In previous methods the bacteria which were used fermented starch but did not fully ferment saccharose as in beet or cane molasses. The object of the patented method is to invert the sugar, provide available nitrogen for the bacteria, and remove caramel.

Hydrolysis of the molasses is accomplished by invertase or preferably by yeast (1 or 2 pounds per 100 pounds of sugar). The dilute molasses is heated to 50–55° C. to prevent proliferation of yeast and alcoholic fermentation, maintaining the temperature until inversion is complete at a pH of 4.3 to 4.5. During the hydrolysis, protein in the mash undergoes proteolysis thereby enriching the solution in nitrogen. The mash is then boiled to destroy the yeast, and the caramel is removed by filtering through activated carbon. Finally, the pH is adjusted to 5 or 6, and a culture of acetobutylic bacteria is added.

According to the United States Bureau of the Census, the principal producers of acetone since 1929 are Commercial Solvents Corporation, Publicker, Inc., Carbide and Carbon Chemicals Corporation, and Shell Chemical Company. Two of these companies use fermentation and two use methods to be described later.

Two other interesting patents were issued to Viljoen (*57*) and Schorger (*51*). Viljoen's method is for use with mashes of high sugar content. He discovered that, by adding a comparatively large number of *Clostridium acetobutylicum* to a properly buffered sugar solution, it is possible to ferment mashes of 4 to 6.5 per cent sugar concentration with yields of 30 to 33 per cent on the sugar in the ratio of 5 parts butyl alcohol to 2.5 parts acetone to 1 part ethyl alcohol. Briefly, the method consists of using a sterile starter mash of molasses equivalent to 2 per cent sugar, adding sufficient proteolyzable protein, and allowing the mixture to ferment to a maximum bacterial concentration. A second mash of 8 per cent sugar concentration is then added in such quantity that the sugar concentration of the combined mashes is 5 per cent. Haner (*27*) uses a primary and secondary fermentation to ferment all the sugar. After the butyl organism has become fully active, yeast is added to ensure complete utilization of the sugar which is left over by the butyl bacteria. Starch mashes, if used, must be hydrolyzed to sugar.

To increase the proportion of butyl alcohol in the acetone–butyl alcohol fermentation Hutchinson (*29*) suggested that ammonium lactate be added to the fermenting mash; to increase the proportion of acetone, ammonium acetate may be added to the mash.

Izsak and Funk (*32*) describe a new organism *Clostridium saccharobutylicum* (gamma) for fermenting sugar and producing isopropyl alcohol and acetone in different proportions from those of previously discovered bacteria. The beta form of the organism (*31*) is claimed to produce from five to ten times as much isopropyl alcohol as acetone; the gamma form reverses the action and goes farther, producing ten to twenty times as much acetone as isopropyl alcohol. Identification charts are given according to the Society of American Bacteriologists. The spores stand 100° C. for 5 minutes, are incapable of unaided fermentation of cereal starch, but are capable of fermenting molasses at 24° to 40° C.

Clostridium propyl butylicum (*38*) should be noted and also a process (*53*) for producing butyl and isopropyl alcohols with minor amounts of acetone from inverted sucrose in molasses.

Arroyo (*3*) was allowed a patent for producing butyl alcohol and acetone from molasses by an organism found on the root of sugar cane.

Ethyl Alcohol

Allied to the fermentation processes of making acetone is the use of ethyl alcohol as a starting material, especially where the ethyl alcohol used is a fermentation product, as in the plant of British Industrial Solvents, Limited, at Salt End near Hull (*30*). For making acetone the process used is that of reacting ethyl alcohol (made from molasses) with steam and a catalyst:

$$2C_2H_5OH + H_2O = (CH_3)_2CO + 4H_2 + CO_2$$

Some of the hydrogen is used under the furnaces; the balance of the heat is furnished by oil burners. In the furnaces are contact chambers containing the catalyst through which the alcohol and steam pass. The gases, coming out together with a small amount of uncondensed alcohol, pass through condensers and scrubbers. The weak acetone is concentrated and fractionated in batch stills.

A patent for the use of ethyl alcohol as a source of acetone under reduced partial pressure was issued to Bloomfield, Swallen, and Crawford (*6*). The partial pressure is reduced by using nitrogen, carbon dioxide, gaseous reaction product, or a vacuum pump. The catalysts are oxygen compounds of the first long period of the periodic table. Unlike the British process just mentioned, no water vapor is used.

A patent was issued to Dreyfus (*15*) which relates to the production of ketones from aliphatic primary alcohols containing at least 2 carbon atoms, especially the production of acetone from ethyl alcohol. Alcohol and water vapor are subjected to high temperature in the presence of zinc or zinc compounds and alkaline earth oxides, hydroxides, or salts (zinc acetate, zinc oxide, zinc carbonate, etc.). The temperature may range from 200° to 700° C., but 400° to 550° C. is particularly suitable. Vacuum, atmospheric pressure, or 3–10 atmospheres may be used. A ratio of two to ten times as much steam as alcohol and of two to five times as much air as alcohol should be utilized.

Acetylene

In addition to the production of acetone from acetylene by catalytic conversion of the latter to acetaldehyde and thence to acetic acid, a method of using acetylene and steam with a catalyst at high temperature has been patented. Schlecht's method (*50*) for producing acetone is similar to the one for producing acetaldehyde except that a longer time is allowed. The catalysts contain metals or their compounds, the acetates of which decompose to form acetone when heated. The inventor also found that good yields of acetone could be obtained from aldehyde (instead of acetylene) and steam over the same catalysts which consist of zinc or the oxides, carbonates, or acetates of zinc, tin, or aluminum. The best temperature is 400° to 450° C. The ratio of acetaldehyde to steam is less than 1 to 1. Part or nearly all of the steam can be replaced with air. A high velocity should be maintained through the apparatus to avoid polymerization or decomposition. The reaction is

$$2CH_3CHO + H_2O = (CH_3)_2CO + CO_2 + 2H_2$$

Anderson's patent (*1*) covers similar methods but is not specific as to velocity, which should be about 30 liters per hour and per liter of catalyst.

Two other recent patents cover the conversion of acetylene or acetaldehyde to acetone (*46, 47*). The first states that it has been found better for the catalyst to consist of basic oxygen compounds of metals with at least one heavy metal. The use is recommended of iron shavings or iron sponge with a superficial oxide layer. Calcium acetate was dried on rusty iron shavings. The second patent mentions troubles in earlier catalytic processes with poor yield, loss of efficiency, etc. These troubles are avoided, according to the later patent. The catalysts are not affected by poisons so that it is not necessary to purify the acetylene. Economy is improved by using less steam and lower temperatures with the improved catalysts. The patent claims the new principle of adjusting the composition of the catalyst to yield a partial pressure of oxygen within the limits 10^{-25} to 10^{-30} atmosphere at 400° to 500° C. and with 5 to 10 parts of water vapor to 1 of acetylene.

Petroleum Oil or Gas

When petroleum is cracked, gases are evolved which contain propylene. Propylene is obtainable from natural gas also but, whatever the source, it is the basis for the manufacture of acetone and isopropyl alcohol.

When oil cracking is used as a source of propylene, a propane-propylene fraction is obtained from the pressure distillate. For the removal of impurities, especially sulfur compounds, the propylene fraction is subjected to intensive purification and is then brought into contact with sulfuric acid whereby propyl hydrogen sulfate is formed and dissolved in the acid layer. The acid layer is separated and diluted with water, hydrolyzing the sulfuric acid ester to produce isopropyl alcohol. From the acid mixture isopropyl alcohol is distilled and then the pure distillate is subjected to either the dehydrogenation or oxidation process at high temperature to convert it to acetone. After the usual refining distillation, the acetone is marketed as a very pure material having over 99.5 per cent dimethyl ketone which holds the permanganate test for at least 60 minutes. The minimum initial boiling point is 55.9° C.; the maximum dry point is 56.6° C. The total distillation range is not more than 0.5° C. The bromine color is not completely decolorized in 15 minutes, and the acetone is free from all fogging or photographically active substances. The acidity is less than 0.002 per cent as acetic; after carbon dioxide removal, there is no acidity.

The foregoing description of a process for making acetone is similar but not quoted from a portion of a patent issued to Ellis and Wells (*19*). The patent relates to oxidation products of alcohols, etc., which are derived from petroleum, especially such products from alcohols obtained by cracking an oil to produce unsaturated hydrocarbons, and sulfating the latter with sulfuric acid of 1.8 specific gravity in a packed tower. By diluting with two volumes of water and distilling, alcohols may be obtained in the boiling range from 75° to 100° C. The distillate can be oxidized by sodium bichromate in dilute solution yielding ketones. Instead of converting the acid extract to alcohols and then oxidizing them to ketones, one may convert the olefins of the acid extract direct to ketones. The reactions are illustrated as follows (*17*):

$$C_{10}H_{22} = C_5H_{10} + C_5H_{12}$$
$$C_5H_{10} + H_2SO_4 = C_5H_{11}(HSO_4)$$
$$C_5H_{11}(HSO_4) + H_2O = C_5H_{11}OH + H_2SO_4$$

$$C_5H_{11}(HSO_4) + CH_3COONa = CH_3COOC_5H_{11} + NaHSO_4$$
$$(CH_3)_2CHHSO_4 + H_2O = (CH_3)_2CHOH + H_2SO_4$$
$$2(CH_3)_2CHOH + O_2 = 2(CH_3)_2CO + 2H_2O$$

Wells (*59*) claims some improvements for the process just described. The gases should be dried. In addition to sulfuric acid, other dibasic or tribasic acids may be used—for example, selenic or phosphoric. For oxidation, air is preferred and nitrogen or carbon dioxide may be added to dilute the oxygen and to control the vigor of the reaction. The various alcohols obtained may be cracked to ketones at high temperature, in which case no oxygen is needed. Iron and copper are good catalysts; copper tubes become spongy on the surface. Other metals are mentioned. The temperature may range from 700° to 900° C., and a cooling coil may be needed in the catalyst bed.

Naturally many laboratories are at work on the problem of improving these processes and particularly to obtain catalysts of greater activity and longer life. For example, Lorany (*39*) describes the addition of a promoter (about one per cent) to the catalyst for dehydrogenating isopropyl alcohol in order to prolong its life. Zinc oxide, thorium oxide, etc., may be used for the purpose.

The term "dehydration" is restricted to compounds containing oxygen and olefins, according to Taylor and Lazier (*54*). The formation of mesityl oxide and pharone from acetone and the preparation of ethers or olefins from alcohols are cited.

On the other hand, dehydrogenations cover a broader field and are applicable to hydrocarbons and to compounds containing the hydroxyl radical. The invention of Taylor and Lazier makes it possible to select a catalyst suitable for these two classes of reactions from the standpoint of durability, activity, and insensitivity to poisons and then so to alter the qualitative performance of the mass as to suit the needs of the process in question.

As an example, when isopropanol is vaporized at 400° C. over a catalyst consisting of zinc oxide, 0.05 mole of propylene and 0.95 mole of acetone are obtained. But if zinc oxide is triturated with a solution of sodium carbonate and dried so that the product contains 4.5 per cent sodium carbonate, less than 0.01 mole of olefin and 0.99 mole of acetone are obtained.

Frolich (*24*) writes fully about the discovery of the hydrogenating power of a variety of metallic oxides which offer a great degree of selectivity with respect to chemical reactions and show marked resistance to poisons as well as to changes in temperature. Examples are nickel, platinum, and palladium. Among other products, aldehydes, ketones, acids, and esters may be formed.

Uses

After the war the demand slackened somewhat for a short period but the growth of the lacquer industry and especially the need for acetone in the use of cellulose acetate again increased the consumption of acetone to an important status.

The prewar uses still exist; in many, the proportion of acetone used has increased and new uses have been developed as follows: Dissolving compressed acetylene; special denaturant for alcohols (rubbing, etc.); artificial leather solvent; basis for manufacture of diacetone alcohol, plastics and resins, and ketene; cellulose acetate and nitrate (solvent); celluloid solvent; confection glaze; cosmetics solvent (nail polish remover, etc.); dehydrating agent; explosives solvent; extractions (vitamins, fats, etc.); film; lacquer solvent; paint and varnish remover; petroleum dewaxing and lubricating oil refining; plastics solvent; safety glass; shoe and rubber cements; and textile specialties.

It is practically impossible to obtain a reliable estimate as to the relative tonnages used in the various processes, but it is safe to say that cellulose acetate and petroleum dewaxing are near the top, along with the use for dissolving compressed acetylene. The principal manufacturers issue very complete descriptions of the various properties, together with charts of viscosity, vapor pressure, specific gravity at various temperatures, specific heats of solutions, low-temperature characteristics, and evaporation rates compared with other solvents.

The use of acetone for dissolving compressed acetylene is responsible for the vast commercial development of the use of acetylene in burning and welding. It is practically impossible to compress acetylene gas for commercial use because it explodes. However, when acetone is distributed over kapok (*23*), asbestos, or similar inert material, it is capable of dissolving twenty-five times its own volume of acetylene at normal temperature and for every atmosphere of pressure so that, at 15 atmospheres, one volume will hold 375 volumes. The efficiency of acetone as a solvent depends on its purity. Claude and Hess (*10*) show that the increased solubility of acetylene in acetone is nearly proportional to the increase in pressure. Butler (*8*) discusses the effect of pressures above 75 pounds per square inch. Freeman writes (*23*) that the heat of combustion of acetylene is approximately 1500 B. t. u.; for coal gas the heat of combustion is 500 B. t. u. and for hydrogen, 350—hence the advantage in using acetylene for welding. The kapok fills about 20 per cent of the cylinder.

One of the large users states that acetone is employed in considerable quantities for denaturing rubbing alcohol and as a solvent for artificial leather. As to its use in rubbing alcohol, the opinion has been expressed that acetone itself is somewhat effective in bringing blood near the surface of the skin.

As a basis for the manufacture of several materials, acetone has the advantage of being easily obtainable at a price which is moderate, of uniformly great purity, and of a pleasant odor.

A resin can be prepared from *o*-cresol or a mixture of cresols with a ketone, which can be used for coating a plastic compound containing cellulose or cellulose derivatives. This is claimed by Seymour (*52*). The resin is compatible with derivatives of cellulose and can be used to make yarn. Some of the catalysts which can be employed are strong hydrochloric, sulfuric, or phosphoric acid.

Werner (*60*) mentions resins made from acetone and formaldehyde in the presence of alkali, likewise from acetone and acetaldehyde, paraldehyde, aldol, and furfural.

Ketene ($CH_2{:}CO$) is a useful acetylating agent for many organic syntheses, although it is extremely active and unstable and must be used at closely controlled temperatures. For the manufacture of ketene from acetone, Reid's patent (*43A*) specifies the pyrolysis of acetic anhydride and acetone:

$$CH_3COCH_3 = CH_2{:}CO + CH_4$$

In the presence of iron, nickel, or alloys, the reaction may be

$$CH_3COCH_3 = H_2 + CO + CH_4 + C$$

so that the choice of catalysts is limited. Copper has been used but the difficulty is that it oxidizes readily at the temperatures used, so that up to the cracking zone the tube is made of iron-chromium alloys. In the pipe furnace the tube is made of different alloys, depending on temperature conditions. The different sections are composed first of iron, then chromium-iron with copper lining, and then chromium-iron. No nickel or nickel alloys can be used.

Ketene is also made from hydrogen and carbon monoxide under pressure and heat in volumes proportional to the molecular properties required. The process is covered by a patent granted to Dreyfus (*14*):

$$3CO + H_2 = CO_2 + CH_2CO$$

Examples of catalysts are zinc oxide, copper oxide, copper chromate, zinc chromate, zinc aluminate, potassium zincate, or mixtures of any of these. Temperatures between 200° and 300° C. and pressures up to 200 atmospheres are preferred, depending on the catalyst. The velocity of the gas has an influence.

Ketene vapors can be absorbed in glacial acetic acid to form acetic anhydride (*9*):

$$CH_2CO + CH_3COOH = (CH_3CO)_2O$$

Acetone can be used as a precipitant in the manufacture of a prepared resin according to Thomas and Hochwalt (*55*). From a cracking process an unsaturated hydrocarbon is obtained which reacts with pulverized aluminum chloride. Other catalysts which can be used are chlorides of iron, boron, zinc, antimony, indium, titanium, and tin, propyl alcohol saturated with hydrogen chloride, ethyl sulfate, and aniline hydrobromide. The viscous reaction product is neutralized and steam-distilled, removing unconverted hydrocarbon. Particles of aluminum hydroxide or salt give a putty color. The mass left in the still is dissolved in benzene, carbon tetrachloride, or ethylene dichloride and dumped. To the solution is added a water-soluble liquid such as acetone or ethyl alcohol which precipitates the resin. The latter is then decanted and filtered.

Acetone and an aldehyde can be used in the presence of sodium hydroxide to form an "amorphous product," a plastic according to Ellis (*18*). For example, when 20 pounds of acetone and 50 pounds of formaldehyde (37 per cent) are reacted with 5 pounds of soda ash in a heated kettle with a reflux condenser, 29 pounds of sirup are obtained. This is quite thick when cold and is soluble in alcohol or alcohol and benzene. If more alkali is used, the mass is harder.

Acetone is called "not the best but the most suitable solvent for acetylene" by Remler (*45*); he gives a table of the advantages of acetone as a solvent and several tables of the solubilities in acetone of resins, fats, oils, greases, mineral oils, asphalts, and bitumens (*44*).

Wire with a thin textile insulation was covered with a thin film of cellulose acetate dissolved in acetone by a prominent wire manufacturer (*4*) continuously and in very large amounts.

Aliphatic ketones as solvents (*42*) have been fully described by Park and Hofmann, and the evaporation rates of organic liquids are thoroughly covered by Hofmann (*28*).

Petroleum dewaxing is an application of acetone developed at the Indian Refining Company by Govers; it was started in 1927 and later taken over by the Texas Development Company (*26*). There are eight installations in the United States and six in Europe. Wax-bearing stock is dissolved in solvent, chilled to the required temperature depending on the desired pour point, and filtered to remove the precipitated wax, and the wax-free oil is recovered by distilling the solvent. The solvent used is a mixture of an oil solvent and a wax antisolvent. The proper composition of the solvent involves a balance between wax precipitation and oil solubility. Acetone and benzene were the first solvents used to replace the conventional straight-run solvent naphtha commercially in dewaxing operations. Recently some advantage has been found in using methyl ethyl ketone instead of acetone because the former has greater solvent power for oil without increasing wax solubility. The latest improvements involve introduction of continuous processes such as continuous stills and rotating disk- or drum-type filters operating under pressure and covered with insulation instead of being installed in refrigerated rooms.

In ketone-benzene mixtures the ratio of ketone to benzene is limited at two extremes. One extreme is that benzene crystallizes with low ketone concentration, and with high ketone concentration there is a liquid-phase separation (heavy oil).

Anderson (*1*) points out that acetone is an antisolvent for wax in petroleum to such a great extent that oil will separate with the wax so that the acetone must be blended. Benzene is a good secondary solvent; an effective mixture is 62 per cent benzene and 38 per cent acetone. For treating heavy oils, the latter mixture is not satisfactory; a third ingredient is needed, preferably naphtha (initial boiling point 165° F.; end point 250° F.). When using naphtha the percentage of benzene is slightly increased and the percentage of acetone is decreased. One volume of oil to 2.5 volumes of diluent is used in the exact ratio depending on the nature of the oil to be dewaxed. The mixture is chilled at about −10° F. and filtered. An object of this invention is to provide means of using an acetone-benzene mixture for dewaxing heavy oils without causing benzene to freeze out or heavy oil to separate from the diluent.

Ba Thi and Strang describe with charts the principles of solvent dewaxing (*5*) but make no mention of acetone.

Acetone can be used to distribute a plasticizer in making plastics (*16*). "Plasticizers make cellulose esters less elastic and more plastic, more extensible." The work described shows that even volatile solvents are, in small part, long retained. A chart shows the percentage of several solvents evaporated over a period of five days. It is believed that loss of solvent in the last stages is responsible for the cracking of old celluloid. There seems to be some evidence that nitrocellulose combines chemically with acetone.

In combination with either benzene or carbon tetrachloride, amyl or ethyl acetate, ether, chloroform, and alcohols, acetone is used for spraying rubber solutions or lacquers or for making rubber cement. Sufficient acetone is used in the rubber industry to have interested the assistant medical director of the Goodyear Tire and Rubber Company in investigating the health hazard (*12*). It was determined that the toxicity of acetone is very slight and that it occurs normally in small amounts in the blood but is increased to a pathological extent in the following conditions: diabetes (mellitus), certain forms of malignancy, starvation, autointoxication, certain metabolic changes which produce acetonuria, and fevers of prolonged duration.

Proper ventilation is necessary to keep acetone vapors away from workers. This is especially true where, as is usual, acetone is associated with substances such as benzene which are definitely toxic. The conclusions reached as to the health hazard of acetone were as follows:

> Acetone is safe to use in well-ventilated and guarded systems.
> Acetone is a fire hazard.
> Acetone is toxic but much less so than any of the other usual solvents used in the rubber industry.
> There are no characteristic blood findings.
> Individuals who show slight symptoms can be removed and are all right in 24 hours.

Recovery of acetone from gas or air mixtures can be accomplished by scrubbing with water in packed or spray towers or in bubble-cap columns such as were used in the war period. In recent years activated carbon has been used almost exclusively (*4, 20*). A recovery system consists of active carbon absorbers, a condensing tower, and a batch still for removing acetone from water. Air and vapor from the wire-coating machines pass through tubular coolers to the absorbers which are large horizontal tanks carrying active carbon. Air stripped of acetone goes to the roof. After one hour of operation, the flow is cut off and switched into another tank while low-pressure steam is admitted to the first tank to drive off acetone. The mixed steam and acetone vapor are condensed in about equal parts and stored underground. Recovered acetone from the still is sampled to be sure that it is dry and pure. The over-all recovery is 85 to 86 per cent.

Precautions for preventing explosion and fire are fully described (*4*), including the use of lead and aluminum diaphragms in explosion relief openings on the tanks and coating machines and a carbon dioxide fire-extinguishing system.

Fire is a real hazard where acetone and other solvents are used. Static was apparently responsible for an explosion which occurred when a vacuum shelf dryer was opened for unloading golf balls or similar goods. Since that time residual acetone vapors have been swept out with steam before the doors are opened. In Great Britain a fire occurred in a vacuum stove (shelf dryer) in a solvent recovery house (*11*) during unloading. Nitrocellulose was dried in Uralite trays with wooden rims which rested on hollow iron shelves for heating with steam. It had been the custom to admit air when the vacuum was at a certain height, then open the door, and pull the trays. A flash occurred while the door was open, apparently because of the friction of a tray on warm dry nitrocellulose dust on an iron shelf. In the future it is proposed to blow in steam with the air in order to sweep out the vapors and to help discharge the static by the presence of high humidity. Also a door will be installed on the back of the stove as well as the front for better inspection and cleaning. Trays half as long will be used, and a pair of brass wheels will be provided at the inner end of each tray.

To prevent serious damage from the explosion of vapors, vents (*7*) with hinged automatic shutters are used at a ratio of 1 square foot per 10 cubic feet of room. Self-closing shutters are desirable because they help to retain the inert atmosphere which results from the first explosion.

The United States Bureau of Mines and the Western Electric Company made a study of the use of diaphragms (*33*). One of the wire-coating machines was set up in a special building and used in testing the upper and lower limit of explosibility of acetone. The effect of humidity was investigated, and studies were made of flame propagation. In another paper (*34*) studies of solvent mixtures were reported. Nuckolls reports on the propagation of flames in pipes and the effectiveness of arresters (*41*).

Production

Data on acetone production from 1919 to 1929, inclusive, are as shown in Table I (*2, 56*).

Since about 1927 little or no acetone has been produced from calcium acetate originating in a hardwood distilling plant. The two sources of supply have been the fermentation of grain or molasses and by catalytic methods from petroleum-still gases containing propylene.

The outstanding point of interest regarding acetone in 1929 was the production of commercial quantities of acetone from propylene in natural gas. This method and fermentation accounted for nearly all of the 1929 production.

Table I

Year	Pounds	Source
1914	10,425,817	Wood distn.
1919	6,045,914	Wood distn.
1921	4,380,085	Wood distn.
1923	10,927,841	Wood distn.
1925	13,348,229	Commercial Solvents Corp. only
1926	21,466,483	Commercial Solvents Corp. only
1927	25,519,506	Commercial Solvents Corp. only
1928	25,058,000	Commercial Solvents Corp. only
1929	32,000,000	Commercial Solvents Corp. and Carbide and Carbon Chemicals Corp. (estd.)
1930	Not published	....
1931[a]	25,853,902	....
1932	Not published	....
1933	42,205,443[b]	....
1934	42,615,312[b]	(6,456,865 gal.)[d]
1935	56,124,000[b]	(8,503,000 gal.)[e]
1936	64,651,128[b]	(9,795,625 gal.)[f]
1936	94,565,000[c]	....
1935	5,607,176 gal.	Ethyl acetate sales

[a] Figures from 1931–1936, inclusive, obtained from U. S. Tariff Comm. (*56A*).

[b] Sales, previous figures show production.

[c] Preliminary estimate of production.

[d] Sales (compared with 73,868,000 gal. of benzene and motor fuel).

[e] Sales (compared with 82,486,000 gal. of benzene and motor fuel).

[f] Sales.

Summary

The downward trend in the price of acetone has halted at 5 cents per pound in tank car lots. Will it go lower? No one can predict. Certain facts suggest that there is little profit in acetone for the lowest cost producers, who make it from petroleum process gases. The gases which can be used for the manufacture of acetone are chargeable in most plants at the cost of fuel except where special effort has been made to modify the cracking process in order to increase the proportion of propylene for its derivatives. To 4 cents per therm (100,000 B. t. u.) or about 64 cents per 1000 cubic feet of propylene (equivalent to 0.5 to 0.6 cent per pound) might be added an estimated 2.5 to 3.0 cents per pound for conversion or a total of 3 to 3.6 cents per pound of propylene processed. At 90 per cent yield, then, acetone would cost 2.4 to 3.0 cents per pound at the plant; therefore, with freight, sales costs, and taxes, a 5 cent price does not leave much profit.

How far can the fermentation companies go in order to meet competition is another guessing game. When the price of acetone goes below the cost of production, butyl alcohol and the by-products of the fermentation gases, carbon dioxide and hydrogen, will have to carry the burden of making a profit for the plant or else acetone will have to be converted into products which have a better price or a large enough market to take a large volume of acetone. The butyl price cannot go up much without danger of competition from substitutes. Naturally, the low price of acetone is causing many people to experiment with it in place of more expensive solvents but progress in that direction is slow. Vigorous research to find new outlets for acetone are not at present producing the desired results. The shadow of overproduction still looms.

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Boiling Points and Critical Properties of Hydrocarbon Mixtures

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KNOWLEDGE of the critical properties of hydrocarbon mixtures, particularly as a function of properties readily determinable, is of great value for estimating the physical and thermal properties necessary for intelligent design of petroleum refining equipment. Many of these properties are directly correlatable on the basis of the critical temperature and pressure by application of the theorem of corresponding states.

The most easily determined properties definitive of a hydrocarbon are the specific gravity and the boiling point. Many other properties, such as molecular weight, chemical character, cracking reaction velocity constants, hydrogen content and heats of combustion, are correlatable as functions of these simple inspection data. However, petroleum problems almost always involve mixtures of great numbers of components which it is usually impracticable to treat separately, even to the extent of determining individual boiling points and gravities. In such cases it is customary to measure the gravity of the entire mixture and to report the boiling point in the form of a batch distillation curve. For the higher boiling substances, the distillation must be carried out at sufficiently low temperatures to avoid decomposition, necessitating pressures lower than atmospheric and correction to the equivalent atmospheric pressure values by means of vapor pressure relations. Since the true boiling point distillation is not yet in general use by the industry, boiling point curves obtained by the A. S. T. M. and Engler distillations will be considered in the following discussion and correlations.

Additive Properties of Mixtures

Many properties of mixtures may be estimated by assuming that the properties of the individual components are directly additive. For example, such properties as the weight or hydrogen content of a mixture are equal to the sums of the corresponding properties of the components. Similarly, it may be satisfactorily assumed that in liquid hydrocarbon mixtures at atmospheric temperature and pressure the volume of the mixture is equal to the sum of the volumes of the components, neglecting volume changes in mixing. On the basis of these principles of additivity, it is possible to establish conditions which must be met by correlations of various properties that are to be mutually applicable to mixtures and pure components.

Watson and Nelson (7) introduced the following boiling point and gravity ratio, termed the "characterization factor," as an indication of the chemical character of a hydrocarbon and as a correlative factor:

$$K = \frac{(T_B)^{1/3}}{d} \qquad (1)$$

where K = characterization factor
d = specific gravity at 60° F.
T_B = atmospheric boiling point, ° Rankine

This factor is valuable in that it is reasonably constant for chemically similar hydrocarbons. It is useful as a quantitative means for expressing the effect of variation in chemical type and, in conjunction with one other property, serves as a basis for correlating properties of pure components of widely varying chemical types and boiling points.

Application of the characterization factor was extended to mixtures by considering the boiling point of the whole mixture to be the "molal average boiling point," which was less than the volumetric average by a correction which was a function of the Engler distillation curve slope. It was pointed out that the boiling point so obtained was actually higher than the true molal average boiling point and was established in an effort to obtain a single, simple average boiling point which would eliminate dependence on width of boiling range from the characterization factor and correlations of other physical properties. However, more complete data and application of the principle of additivity of the properties of mixtures indicate that for wide boiling mixtures the Watson-Nelson "molal average boiling point" represents an unsatisfactory approximation to the proper variable for correlation of many properties.

If components of the same chemical character or characterization factor, K, are mixed, the resultant blend should have the same K. From the above definition of K, since d varies linearly with volume per cent, $(T_B)^{1/3}$ must also vary linearly with volume per cent.

$$K_{\text{mix.}} = \frac{f_{V1}(T_{B1})^{1/3} + f_{V2}(T_{B2})^{1/3} + \ldots.}{d_{\text{mix.}}} \qquad (2)$$

where f_{V1} = volume fraction of component 1 in mixture

Thus, the proper boiling point to use for calculation of K is:

$$T_B(\text{av.}) = [f_{V1}(T_B)^{1/3} + f_{V2}(T_{B2})^{1/3} + \ldots.]^3$$

This boiling point will be termed the "cubic average boiling point." For petroleum fractions it may be obtained by subtracting from the volumetric average a correction expressed as a function of Engler distillation curve slope and volumetric average boiling point. This correction is presented graphically by the series of curves in Figure 1, designated as cubic average.

If two components of different K and the same or different boiling points are mixed,

$$K_{\text{mix.}} = \frac{f_{V1}(T_{B1})^{1/3} + f_{V2}(T_{B2})^{1/3}}{f_{V1}d_1 + f_{V2}d_2} = \frac{f_{W1}(T_{B1})^{1/3}}{d_1} + \frac{f_{W2}(T_{B2})^{1/3}}{d_2}$$

or $$K_{\text{mix.}} = f_{W1}K_1 + f_{W2}K_2 \qquad (3)$$

where f_{W1} = weight fraction of component 1

Therefore, the characterization factor, K, when based on the correct cubic average boiling point, is additive with weight fraction in all mixtures where changes in volume with mixing are negligible.

It may be similarly demonstrated that A. P. I. gravity is also additive with weight fraction in all mixtures where volume changes in mixing are negligible:

$$\text{A. P. I.}_{\text{mix.}} = f_{W1} \times \text{A. P. I.}_1 + f_{W2} \times \text{A. P. I.}_2 + \ldots \qquad (4)$$

Application of Pure-Component Correlations to Mixtures

If a correlation of any dependent variable is developed as a function of two definitive properties, it may be validly applied to both mixtures and pure components only if the average definitive properties of the mixture are so defined that the dependent variable for any mixture is the same as that of a pure component having the same definitive properties as the average definitive properties of the mixture. This principle may be used to determine directly the proper average definitive properties for mixtures when pure-component data are available. When only data on mixtures are available, the principle may be applied, by trial-and-error assumptions of average property, to determine the correct average definitive property and consequently establish a valid pure-component correlation if the range of variation in each mixture is small relative to the total range covered by the correlation.

As an application of the above principle, the correlation of molecular weight with boiling point and A. P. I. gravity may be considered. The molecular weight of a mixture is additive with the mole fractions of its components as is also its true molal average boiling point. However, if molecular weights of pure components are plotted against boiling points with lines of constant A. P. I. gravity, it is found that the molecular weight of a pure component, having an A. P. I. gravity and boiling point the same as the A. P. I. gravity and true molal average boiling point of a mixture, is not the same as the molecular weight of the mixture. Therefore, the true molal average boiling point cannot be the proper definitive property for applying the pure-component correlation to mixtures. Similar consideration shows that the cubic average boiling point is also unsound as a correlating variable. However, an average boiling point which is the arithmetic average of the true molal and cubic averages does form a sound basis for correlation of molecular weights. This average, which will be termed the "mean average boiling point" of a blend, corresponds to a molecular weight on the pure-component correlation, which is equal to the actual molecular weight of the mixture.

In Figure 1 are plotted curves for obtaining true molal average boiling points of petroleum fractions from Engler distillation curve slopes and volumetric average boiling points. Midway between these curves and those establishing the cubic average boiling point are plotted similar corrections for obtaining the mean average boiling point. When working with mixtures of pure components or narrow cuts, for which the distillation curve slope is meaningless, the mean average boiling point is directly calculated as the arithmetic average of the true molal and cubic average boiling points of the components.

A similar analysis may be applied to the published correlation (*8*) of hydrogen content with boiling point and specific gravity. Again it is found that the mean average boiling point is the proper definitive variable for application of this pure-component correlation to mixtures and that correlations involving the characterization factor and cubic average or true molal average boiling point are not sound for mixtures of wide boiling range.

Examination of the mean average boiling point shows it to approximate closely the original Watson-Nelson "molal average," which was developed initially for molecular weight correlations. In general, the previously published correlations employing the Watson-Nelson average boiling point are satisfactory for the pure components and relatively narrow cuts for which they were developed, but break down when applied to mixtures of extremely wide boiling range, except where the proper correlating variable is the mean average boiling point as defined above.

The viscosities of blends of petroleum fractions cannot be calculated by directly additive methods, as are molecular weights and hydrogen contents. However, the recommended A. S. T. M. viscosity blending procedure, together with the unpublished results of a fuel oil blending investigation, have been used for predicting empirically the relations between the viscosities of components and their blends. These relations indicate that the cubic average boiling point is the proper variable for use in the correlation of viscosity with gravity and boiling point. Therefore, the published correlations between characterization factor and viscosity are sound and independent of width of boiling range when the characterization factor is based on the correct cubic average boiling point. However, measurement of viscosity alone permits estimation of only the cubic average boiling point, and data must be available on the Engler distillation curve slope to permit calculation of either mean or true molal average boiling points.

Critical Temperatures

Several methods of correlation of the critical temperatures of pure hydrocarbons have been proposed, based on extrapola-

Consideration of the principles of additivity of mixtures shows that, for the application to mixtures of correlations of properties of pure components with specific gravity and boiling point, no one type of average boiling point is suitable for all properties. The following different average boiling points have been developed for application to correlations of the various physical properties: (*a*) cubic average boiling point—characterization factor, viscosities; (*b*) true molal average boiling point—pseudocritical temperature; (*c*) mean average boiling point—molecular weight, hydrogen content, heat of combustion, pseudocritical pressure; (*d*) weight average boiling point—true critical temperatures.

Using these average boiling points, new correlations of true and pseudocritical temperature and pressure data are presented which are applicable both to pure components and wide boiling mixtures.

tions of measurements of low-boiling materials together with experimental data on petroleum fractions. In attempting to apply these correlations to mixtures, the problem is complicated by the lack of additivity of critical properties. It has long been recognized that the true critical pressure of a mixture may be much greater than the critical pressure of a pure component having the same definitive properties, and ordinarily is greater than the critical pressure of any component present in it. It has been assumed, however, that the critical temperature of a mixture was the same as that of a pure component of the same gravity, in conjunction with either characterization factor, molecular weight, or molal average boiling point. However, the recent investigations of Roess (*5*) indicate that the true critical temperature of the mixture is also higher than that of a corresponding pure component having the same gravity and molecular weight.

True critical properties of mixtures are of particular value in the calculation of phase relations and vaporization equilibrium data. However, for the equally important problem of vapor volume and compressibility calculations, it has long been recognized that use of the true critical properties of a mixture for calculating reduced temperatures and pressures renders the theorem of corresponding states inapplicable. Thus the compressibility factor of a mixture at specified reduced conditions is generally greater than the corresponding value for a pure component at the same reduced conditions.

Kay (*4*), as a result of careful measurements of the P. V. T. relations of vapor mixtures, introduced the ingenious and simplifying concept of the pseudocritical point; he defined it as that temperature and pressure which, used as critical properties to calculate reduced pressure and temperature, produce the same reduced compressibility factor correlation as that of pure components.

Although there is no theoretical certainty of the existence of such a point, Kay proved its existence, within experimental accuracy, for those mixtures that he studied; it will be assumed that every mixture has a definite pseudocritical point, and it is the same as the critical point of a pure component having the same definitive properties as some type of average definitive properties of the mixture.

The correlation presented by Kay plots pseudocritical temperature against molecular weight for lines of constant characterization factor, *K*. Several considerations indicate that the extrapolated portion is incorrect, and that *K* and molecular weight are probably not the proper correlating variables. If, as Kay stated, pseudocritical temperature is additive with mole fraction, his constant *K* lines must be straight since molecular weight is also additive with mole fraction, but the plot actually shows deviations from linearity of more than 100° F. Also, since it has been shown in the foregoing discussion that *K* is properly a function of the cubic and molecular weight of the mean average boiling point, it appears that two different average boiling points have been used in the pseudocritical temperature correlation. Furthermore, constant-boiling-point lines through the extrapolated portion of Kay's pseudocritical temperature plot show a decrease to a minimum and then a rise in the values of pseudocritical temperature as *K* increases. The minimum value and the rise are contrary to available pure component data, though this phenomenon in Kay's correlation may be only apparent, due to possible inaccuracies in boiling point–molecular weight correlations.

An indication that boiling point is a better correlating factor than molecular weight lies in the fact that hydrocarbon isomers having the same molecular weight and practically the same characterization factor may possess widely different boiling points and critical temperatures. Consequently critical temperatures of isomers do not correlate well with molecular weight and *K*. They do, however, with boiling point and A. P. I. gravity, though this gives no indication of the proper average boiling point.

If a correct plot of pseudocritical temperature against boiling point and gravity is developed, it is necessary that this plot be applicable to pure components, for which the pseudocritical temperature is equal to the true critical temperature. This same correlation must be correct for true critical temperatures of mixtures of this property can be correlated on the basis of only boiling point and gravity, using the proper average boiling point. Conversely, a plot developed from true critical temperatures must be correct for the pseudocritical temperatures, using proper average boiling points. This must follow from the fact that a pure component is the limiting case of mixtures, for which the pseudocritical and the true critical temperature correlations must agree and for which all average boiling points are identical.

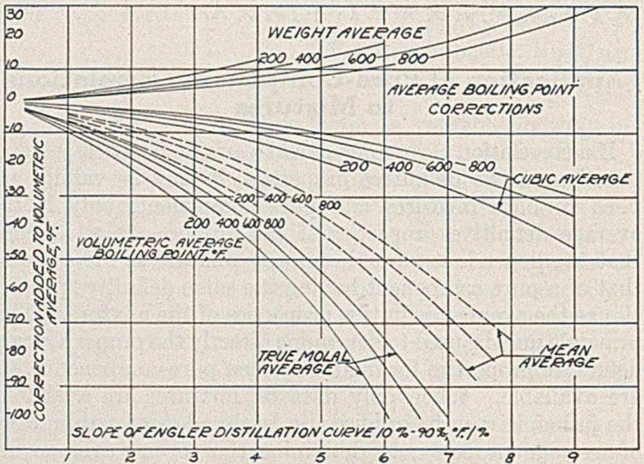

FIGURE 1

Because of the scarcity of pseudocritical data on wide-boiling mixtures, it is difficult to determine with certainty the proper average boiling point for a correlation. However, the principles of valid pure-component-mixture correlations, applied to those mixtures studied by Kay that have a wide enough range to be significant, indicate that the true molal average boiling point is the proper correlating variable for pseudocritical temperatures. The mean average boiling points or molecular weights of the mixtures give, in all cases when used with a pure-component correlation, pseudocritical temperatures considerably higher than the experimental values. The true molal average boiling point used in the same manner gives values only slightly higher than, or the same as, the experimental. Kay's correlation, although agreeing well with his experimental values, does not agree well with pure-component data in the region he investigated.

Roess (*5*), by an ingenious flow method, made accurate determinations of true critical temperatures and pressures of a great number of mixtures; many were at temperatures considerably above the cracking range. Unfortunately the inspections of his samples probably have a lesser degree of accuracy than his critical data, since the atmospheric Engler distillation was the only boiling point data obtained. For the higher boiling stocks it is certain that average boiling points calculated from these atmospheric pressure distillations are too low as a result of decomposition. However, by means of a correlation obtained by comparing a great number of vacuum and atmospheric pressure distillations, an approximate correction may be obtained to be added to the atmospheric pressure Engler distillations as a function of the temperature and the per cent distilled over. Roess' distillation curves were corrected in this manner to approximate the results of vacuum distillation. Fortunately these corrections were small in the majority of cases, and in the worst significant case the correction affected the average boiling point by 25° F.

Roess correlated true critical temperatures as a function of volumetric average boiling point and A. P. I. gravity. The volumetric average was selected because data on wide-boiling-range blends of relatively narrow cuts indicated that the true critical temperature was more nearly proportional to volume per cent than to mole per cent, and that, using volumetric average boiling point as the correlating factor, better agreement was obtained between the experimental critical temperatures on these blends with those predicted from a correlation of the data on narrow cuts. However, continuation of this same type of reasoning favors the use of the weight average boiling point as opposed to the volumetric, though the discrepancies between the two are much less than between the volumetric and the molal. Moreover, true critical data on methane-propane mixtures (*6*) and pentane-heptane mixtures (*3*) show that, for this low-boiling region where Kay found pseudocritical temperature to be nearly linear with mole per cent, true critical temperatures are more nearly linear with weight per cent than with liquid volume per cent. From these considerations it appears that true critical temperature is the same function of weight average boiling point that pseudocritical temperature is of true molal average boiling point.

The weight average boiling point is readily calculated for blends of pure components or narrow boiling cuts. For petroleum fractions with smooth Engler distillation curves, the weight average boiling point may be obtained by adding to the volumetric average boiling point a correction which is a function of Engler distillation curve slope and volumetric average boiling point. These corrections are presented graphically in Figure 1.

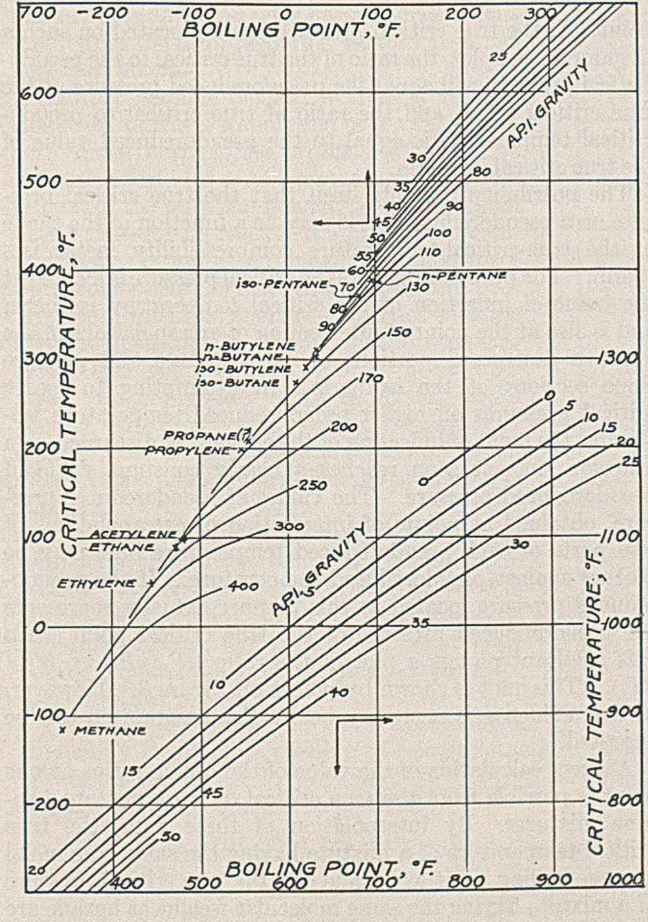

FIGURE 2

The data of Roess on true critical temperatures were plotted against weight average boiling points together with the pseudocritical temperature data of Kay against true molal average boiling points on the same plot with all available data on pure hydrocarbons. Lines of constant A. P. I. gravity were drawn through these points, resulting in the chart shown in Figure 2.[1] Table I gives values from this chart in comparison with some experimentally determined true and pseudocritical temperatures of mixtures and pure components. The average deviation of the correlation of all available data of these three different types is ±4.5° F., with a maximum deviation of 31° F. Figure 2 is also in close agreement with a chart published by Watson and Nelson (*7*), which was derived by mathematical extrapolation of the then-existing data on pure compounds. The good agreement between the true and pseudocritical temperature data, together with those on pure compounds, gives further justification to the choice of the weight average boiling point for true critical temperatures and the true molal average boiling point for pseudocritical temperatures as described above.

Critical Pressures

True critical pressures of mixtures present a problem of a different nature from any of those considered above in that, for mixtures of any two components of appreciably different boiling points, the true critical pressure attains a maximum value at some intermediate composition. Because of this maximum value, greater than the critical pressure of either component, it is evident that true critical pressures cannot be correlated as a function of only two average properties, such as an average boiling point and characterization factor or gravity. However, Kay's data on pseudocritical pressures indicate that no such maximum exists for them, and that the pseudocritical pressure is approximately proportional to mole fraction in binary mixtures.

If pseudocritical pressure can be correlated with two properties definitive of a hydrocarbon, such as boiling point and gravity, it follows that this same correlation must apply to pure components which are merely a limiting case of mixtures. On this basis a correlation of pseudocritical pressures may be built up from three sources of data: critical pressures of pure components, measured pseudocritical pressures, and estimated critical pressures obtained by extrapolating vapor pressure data to the critical temperature. Unfortunately these three methods are limited to materials of low boiling point, since true and pseudocritical pressures of pure components have not been measured for high-boiling substances, and since vapor pressure extrapolations in the high boiling range are uncertain.

The Roess measurements of true critical pressures of relatively high-boiling-point narrow cuts constitute the best basis for estimating the critical pressures of high-boiling compounds. However, for these data a relation between true and pseudocritical pressures must be developed for translation of the true critical data to pseudocritical.

[1] The authors did not at first intend to present their original, somewhat doubtful extrapolations of constant A. P. I. lines for the light hydrocarbon gases, but the location of these lines has since been verified by true critical data of W. B. Kay on ethane-heptane mixtures (to be published in INDUSTRIAL AND ENGINEERING CHEMISTRY under the title "Liquid-Vapor Phase Equilibrium Relations in the Ethane-*n*-Heptane System").

TABLE I. BOILING POINTS AND TRUE AND PSEUDOCRITICAL TEMPERATURES AND PRESSURES OF REPRESENTATIVE MIXTURES AND PURE COMPONENTS

	Roess Data								Kay Data		Pure Components				
Sample No.	1452	1454	1419	1482 (75% 1452 plus 25% 1454)	1483 (50% 1452 plus 50% 1454)	1484 (25% 1452 plus 75% 1454)	1471 (50% 1452 plus 50% 1419)	1472 (25% 1452 plus 75% 1419)	6	11 (26.62 mole % ethane plus 73.38 mole % *n*-heptane)	*n*-Pentane (C_5H_{12})	*n*-Octane (C_8H_{18})	Diisobutyl (C_8H_{18})	Benzene (C_6H_6)	Toluene (C_7H_8)
° A. P. I. (60°/60° F.):															
Obsd.	55.4	19.6	35.3	45.3	34.9	26.7	44.5	39.8	52	..	91.1	68.6	71.4	29.0	31.2
Calcd.	..	..	..	45.2	35.7	27.2	44.8	39.9	..	87.7	..	..	..	..	..
Corrected distillation, ° F.:															
10%	222	442	500	228	245	295	254	280	188	..	..	..	..	..	..
30%	252	488	535	..	..	..	..	..	221	..	..	..	..	..	..
50%	273	538	568	..	..	..	..	..	250	..	..	..	..	..	..
70%	293	604	604	..	..	..	..	..	278	..	..	..	..	..	..
90%	317	739	692	568	678	720	640	674	318	..	..	..	..	..	..
Engler slope	1.19	3.71	2.4	(4.25)	(5.4)	(5.3)	(4.83)	(4.77)	1.63	..	..	..	..	..	..
Av. boiling point, ° F.:															
Volumetric	271	562	580	..	..	..	..	..	251	..	97	258	229	175	231
Weight	274	570	584	360	437	507	438	513	255	176	97	258	229	175	231
Cubic	267	550	574	329	399	471	410	493	245	145	97	258	229	175	231
True molal	261	527	561	311	370	441	365	445	237	113	97	258	229	175	231
Mean	264	538	567	320	385	456	388	469	241	129	97	258	229	175	231
Mol. weight	116	205	245	132	152	176	160	195	107–106	81.4	72.1	114.13	114.13	78.05	92.06
K	11.88	10.70	11.92	11.54	11.23	10.95	11.9	11.91	11.55	13.12	12.94	12.65	12.66	9.75	10.16
T_c, ° F.:															
True, obsvd.	590	941	903	688	787	870	764	836	..	..	..	..	..	..	..
True, correlation	597	938	899	694	783	863	762	833	..	..	..	..	..	..	..
Pseudo, correlation	584	904	881	650	725	810	700	779	573	410	387	565	533	551	608
Pseudo, Kay correlation	600	919	939	670	749	830	740	830	581	410	377	561	560	580	610
Pseudo, obsvd.	..	..	..	..	..	..	..	..	573	413	387	565	531	551	609
tT_c/pT_c (abs.)	1.013	1.0245	1.014	1.04	1.0495	1.0415	1.0535	1.0435	..	..	..	..	..	..	..
tP_c/pP_c (abs.)	1.113	1.213	1.122	1.348	1.43	1.36	1.466	1.378	..	..	..	..	..	..	..
P_c, lb./sq. in. abs.:															
True, obsvd.	476	399	275	547	556	501	493	405	..	..	..	..	..	..	..
Pseudo, obsvd.	..	..	..	..	..	..	..	..	463	450	485	362	361	704	611
Pseudo, calcd. (from obsvd. tP_c)	427	329	245	406	389	369	336	294	..	..	..	..	..	..	..
Pseudo, correlation	407	336	238	401	385	365	332	288	456	450	486	359	380	704	611
Pseudo, Kay correlation	406	297	230	384	359	330	316	274	452	420	477	365	364	740	611
True, correlation	454	408	268	541	550	496	487	397							
True, Roess correlation	448	437	247	554	600	560	493	440							

Relation between True and Pseudocritical Pressures

Development of a correlation between true and pseudocritical pressures is particularly difficult with the data now available because of the fact that no measurements of both properties are reported for any mixture. In Kay's work with low-boiling mixtures, pseudocritical but not true critical properties were measured. Roess, on the other hand, measured true but not pseudo properties.

Qualitative consideration of the variation of true critical temperatures and pressures of mixtures suggests that there should be a relation between the ratio of the true critical to the pseudocritical temperature (tT_c/pT_c) and the ratio of true critical to pseudocritical pressure (tP_c/pP_c). Considering a binary mixture, these ratios are both equal to unity for the two pure components and increase to maximum values at intermediate compositions.

An approximate quantitative relation which would be expected to exist between these two ratios may be predicted from the reduced compressibility factor diagram for pure substances. According to Kay's postulate of pseudocritical properties, any compressibility factor isotherm of a vapor mixture when plotted on a reduced basis will coincide with the isotherm of the same reduced value on the compressibility factor plot for pure components, if the reduced properties of the mixture are based on its pseudocritical properties. Thus the pseudocritical temperature isotherm of the mixture will coincide on the reduced compressibility factor chart with a $T_r = 1$ line for pure components. However, the true critical temperature isotherm of a mixture when plotted on a pseudoreduced basis will coincide with some pure component compressibility-factor isotherm greater than $T_r = 1$. At some point on this isotherm occurs the true critical point. If the true critical pressure can be located on such a pseudoreduced plot, the ratio of the true critical to the pseudocritical pressure will equal the pseudoreduced pressure at the true critical point, and the ratio of true critical to pseudocritical temperature is equal to the pseudoreduced value of the true critical isotherm.

The possibility presents itself that the true critical pressure on a pseudoreduced basis may be a function of the shape of the true-critical-temperature compressibility factor isotherm. For pure components the critical pressure is located at the point of inflection of the critical temperature isotherm and is also at the point of intersection of extrapolations of the concave downward portions of the negative and positive slope sections of the isotherm. In attempting to locate critical pressures on higher pseudoreduced temperature isotherms, the point of inflection of the curve was discarded as a criterion since it soon reaches a nearly constant value of pseudoreduced pressure. The values of pseudoreduced pressure, obtained at points of intersection of extrapolations of two parts of each pseudoreduced temperature line, may be plotted against pseudoreduced temperature. If the pseudoreduced pressure located in this manner actually represents the pseudoreduced pressure of the true critical point, then this resultant plot is a plot of the ratio (tP_c/pP_c) vs. (tT_c/pT_c). This plot is shown by points on Figure 3. However, further evidence is necessary before this assumption can be accepted.

A direct calculation of the value of the above ratios at one point is possible from the true critical data on pentane-heptane mixtures. By interpolation of these data, the true critical temperature of a mixture having the same true molal average boiling point as hexane and the true critical pressure of a mixture having the same molecular weight as hexane are determinable. Assuming that true molal average boiling

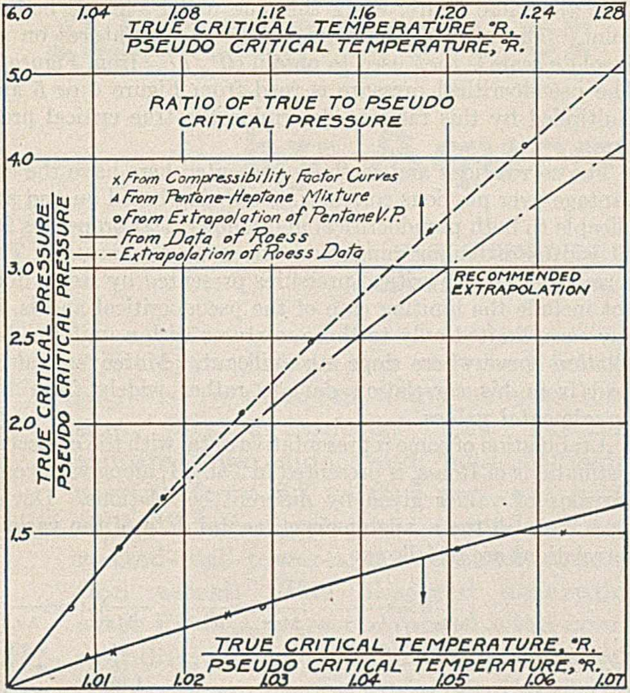

FIGURE 3

point and molecular weight are, respectively, the proper correlating variables for pseudocritical temperature and pressure, the pseudocritical properties of this mixture will then be equal to the critical properties of hexane. As shown in Figure 3, the point calculated in this manner falls almost exactly on the curve calculated from the compressibility factor curves, as described above.

Another possible method evolves from consideration of the extrapolation of a vapor pressure curve beyond the critical. It might be supposed that, for any temperature above the critical of the pure component, the extrapolated vapor pressure represents the pressure of complete liquefaction of an imaginary liquid for a pure component, or the critical pressure of a mixture of the same average properties with the given temperature as its true critical temperature. If true, a plot of P_r vs. T_r of the extrapolated vapor pressure curve is, again, also a plot of (tP_c/pP_c) vs. (tT_c/pT_c). Points calculated from the Brown-Coats (*2*) extrapolation of the vapor pressure of *n*-pentane are shown in Figure 3.

Application of the principles of valid pure-component-mixture correlations to pure component data and the pseudocritical pressure of Kay's wider boiling mixtures indicates that molecular weight, or the mean average boiling point, is the proper correlating variable for pseudocritical pressures.

From precise data on mixtures of the type studied by Roess, it is possible to calculate the true relation between the ratios (tP_c/pP_c) and (tT_c/pT_c) if the proper average boiling points are known. Since

$$\log (tP_c/pP_c) = \log tP_c - \log pP_c$$

log tP_c may be plotted against (tT_c/pT_c) for various constant values of pP_c, the slope of these constant pP_c lines may be calculated,

$$\left[\frac{d \log tP_c}{d\left(\frac{tT_c}{pT_c}\right)}\right]$$

may be plotted against (tT_c/pT_c), and the best line drawn. Since $(tP_c/pP_c) = 1.0$ at $(tT_c/pT_c) = 1.0$, integration of the differential curve from 1.0 gives (tP_c/pP_c) as a function of (tT_c/pT_c). Points with the same pseudocritical pressure are located at the point of intersection of lines representing the mixtures on a plot of A. P. I. gravity against the proper average boiling point. A plot of the relation so calculated using true molal average boiling point as the variable for pseudocritical temperatures and mean average for pseudocritical pressures is shown in Figure 3. This line coincides almost exactly with points determined by the various other methods. The use of either the true molal or mean boiling point as the correlating variable for both pseudocritical constants gives relations that differ widely from one another and from any of the above relations. Thus further evidence is adduced as to the validity of the relation as presented and in favor of the average boiling points selected. For values of (tT_c/pT_c) greater than those investigated by Roess, extrapolation of the relation becomes necessary. In Figure 3 two extrapolations are presented as broken lines. The higher line is calculated from extrapolated pentane vapor pressures and the lower, which is the one recommended for use, results from a direct extrapolation of the function as calculated from Roess' data.

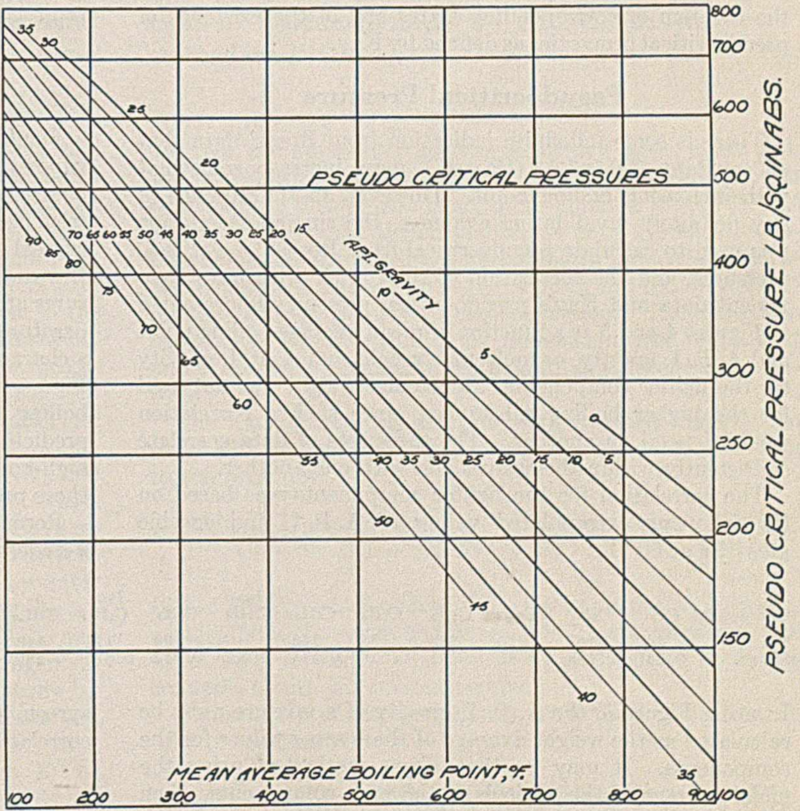

FIGURE 4

It may be that the relation between (tP_c/pP_c) and (tT_c/pT_c) is not the same for all types of mixtures. The assumption that it is the same is tantamount to any one of the following statements, and verification of any one of these statements would validate the assumption: (*a*) The compressibility factor must be the same at the true critical point for all mixtures with the same value of (tT_c/pT_c); (*b*) the compressibility factor isotherms for the true critical temperature, when plotted against log P, must be exactly similar at the true critical point for all mixtures with the same value of (tT_c/pT_c); and (*c*) the true critical temperature isotherms on the true reduced basis must coincide for all mixtures with the same value of (tT_c/pT_c). All of these statements seem reasonable. They are similar in nature to the assumption of the theorem of corresponding states and of the existence of pseudocritical properties as defined by Kay.

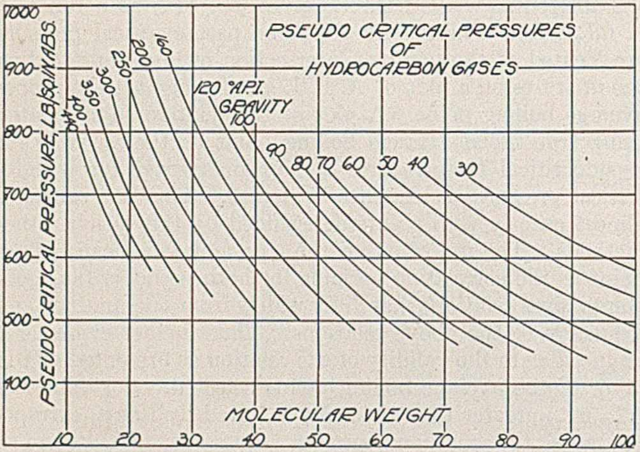

FIGURE 5

Pseudocritical Pressure

There is some indefinite indication from Roess' data that at constant (tT_c/pT_c), (tP_c/pP_c) may increase somewhat with increasing boiling point. However, in the absence of any definitely invalidating evidence, the single-line relation was used to calculate pseudocritical from Roess' true critical pressures, and the correlation of the former with pure component data and Kay's pseudocritical pressures is presented in Figures 4 and 5 as a function of mean average boiling point and A. P. I. gravity, or molecular weight and A. P. I. gravity for the lighter components. Molecular weight was not used for the higher boiling substances, since such a correlation would depend on another. The three sets of data correlate consistently within themselves and with one another.

The correlation for the lighter components was based on the following extrapolated values of A. P. I. and specific gravities at 60° F.:

Component	CH_4	C_2H_2	C_2H_4	C_2H_6	C_3H_6	C_3H_8	Iso-C_4H_8	*n*-C_4H_8	Iso-C_4H_{10}	*n*-C_4H_{10}
° A. P. I.	440	167	213	213	138	145	104	99	114	110
Sp. gr.	0.247	0.473	0.41	0.41	0.526	0.511	0.600	0.613	0.576	0.585

In using Figure 5, the A. P. I. gravity of a mixture must be calculated as the weight average of these same values for the components. It may be that Kay's method of using the molal average of the criticals of the pure components, when known, is as satisfactory as any other for substances lighter than pentane.

Calculation of Complete Critical Data

By means of Figures 1 to 5 the critical properties, both true and pseudo, of any mixture are readily calculated. The true molal, mean, and weight average boiling points and A. P. I. gravity are first determined. The true critical temperature is then read from Figure 2, using the weight average boiling point. The pseudocritical temperature is then read from the same figure, using the true molal average boiling point. The ratio of these two critical temperatures on an absolute scale is then used to obtain (tP_c/pP_c) from Figure 3. The pseudocritical pressure is read from Figure 4 or 5 and multiplied by this ratio to determine the true critical pressure.

The correlations and methods presented here have the advantage over previous correlations of being based on and applicable to both pseudocritical and true critical properties for all widths of boiling range and any type of mixture. The correlation of true critical pressures presented by Roess does not include the limiting case of the pseudocritical and is, in any case, limited only to those mixtures with a uniform distillation curve where slope is significant. Moreover, values read from his correlation deviate rather widely from his experimental values.

A tabulation of some representative data, with the corrected distillations of Roess, is presented in Table I, along with comparisons of values given by different correlations. Deviations from all the available experimental data of the various correlations are as follows:

	Roess		Kay		Authors	
	Max.	Av.	Max.	Av.	Max.	Av.
tP_c, lb./sq. in.	130	±26.7	..	...	94	±9.9
pT_c, ° F.	...	...	29	±7.3	15	±3.9
pP_c, lb./sq. in.	...	...	36	±10.2	30[a] 45[b]	±6.5

[a] Above butane. [b] Below butane.

Pure components are included with the pseudos.

Vapor Pressure Relations

For high-boiling materials the Brown-Coats and all other vapor pressure extrapolations become uncertain and cannot be used with confidence to determine pseudocritical pressure from pseudocritical temperature. Comparison of the pseudocritical pressures of Figure 4 with those estimated from the Brown-Coats chart (*2*) indicate that the extrapolated pressures are too low for the higher boiling materials at high temperatures and pressures on the chart. For substances with a characterization factor of about 12.0, critical pressures from Figure 4 agree almost exactly with those of Kay for the high-boiling materials. Critical pressures for aromatic substances predicted from Figure 4 are higher than those of Kay in the high-boiling region; they are closer to, but still higher than, those predicted from the Brown-Coats chart.

Recently data were obtained (*1*) on the vapor pressures of *n*-dodecane from very low pressures to the critical point. These data indicate that the vapor pressure lines on the Brown-Coats chart are not straight or horizontal, but should slope first upward at very low pressures with increasing pressure and temperature, and then downward to the critical, in agreement with predictions of the present critical pressure correlation.

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Absorption of Nitrogen Dioxide by Aqueous Solutions

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Nitrogen dioxide was absorbed from a mixture in nitrogen using caustic solutions varying from 2.7 to 34.1 per cent sodium hydroxide, and acid solutions varying from 5.7 to 69.8 per cent nitric acid. Similar tests were carried out in a wetted-wall tower and in a batch absorption vessel. The observed absorption rates for NO_2 were compared with corresponding rates of evaporation of water in the same apparatus under similar conditions.

The rate of absorption was found to go through a maximum for pure water, and to be much less in strong acid or strong caustic. Even in the strong solutions the rate of absorption was found to be proportional to approximately the 0.8 power of the gas velocity, indicating the gas-film diffusional resistance to be controlling. The results are explained by the hypothesis of reaction in the gas phase, with the deposition of a nitric acid mist in the gas film.

New data are presented on vaporization of water, desorption of ammonia from aqueous solution, absorption of ammonia by water and by acid, and absorption of sulfur dioxide by caustic in the wetted-wall tower.

THE absorption of nitrogen oxides to form nitric acid, nitrates, and nitrites has long been a subject of much scientific and industrial interest. The chemistry of the important oxides, their reactions with one another, with oxygen, and with various aqueous solutions have been subjects of extensive investigations reported in the chemical literature, but the possible importance of diffusional resistances in the absorption process has received relatively little attention. The present paper presents the results of a study of the significance of diffusional resistances in the absorption of nitrogen dioxide by water and by aqueous solutions of nitric acid and of alkali.

Of the various oxides of nitrogen, only NO, N_2O_3, NO_2, and N_2O_4 appear to be involved in the absorption process. Nitric oxide (NO) is stable and relatively inactive, although it reacts with oxygen to form the dioxide (NO_2) and with NO_2 to form the trioxide (N_2O_3). These latter are absorbed by water and by caustic solutions. NO_2 polymerizes rapidly to an equilibrium mixture of NO_2 and the tetroxide (N_2O_4), and this equilibrium mixture will be referred to as nitrogen dioxide. This equilibrium was the subject of careful study by Bodenstein (*3*), Verhoek and Daniels (*23*), and others (*16, 19, 20, 24*), and the equilibrium constant is known as a function of temperature over the range from 0° to 90° C. The reaction of NO and NO_2 is believed to be very rapid, although the data show that even at moderate temperatures very little N_2O_3 exists in the equilibrium mixture.

The reaction of NO with oxygen to form nitrogen dioxide has been the subject of much study, partly because of its industrial importance and partly because of its scientific interest as a trimolecular reaction with a negative temperature coefficient. The reaction is relatively slow, as shown by the rate constants determined in the classical studies of Bodenstein (*2*). These data, amplified by the results of other workers, are apparently good only for dry gases, since with wet gases, with paraffin-coated vessels, or in contact with charcoal, the rate constants are quite different (*5, 6, 14*). It seems unlikely that Bodenstein's rate data are exactly applicable under the conditions obtaining in industrial absorption equipment, although Taylor, Chilton, and Handforth (*22*) found them of value in this connection. The oxidation equilibrium was also studied by Bodenstein, who found that under ordinary conditions the oxidation is essentially complete.

The dioxide and the trioxide were formerly believed to react with sodium hydroxide in aqueous solutions according to the reactions:

$$2NO_2 + 2NaOH = NaNO_2 + NaNO_3 + H_2O \qquad (1)$$

$$N_2O_3 + 2NaOH = 2NaNO_2 + H_2O \qquad (2)$$

In the absorption of nitrogen dioxide an excess of nitrate is usually found, however, and in reaction 2 some nitrate as well as nitrite is formed. This point will be discussed further in connection with the present results.

The reaction of nitrogen dioxide with water is believed to take place in two steps:

$$2NO_2 + H_2O = HNO_2 + HNO_3 \qquad (3)$$

$$3HNO_2 = HNO_3 + 2NO + H_2O \qquad (4)$$

The nitrous acid decomposes rapidly (*11, 15*), and only a fraction of one per cent nitrous acid is found in the nitric acid formed. The over-all reaction may be written as

$$3NO_2 + H_2O = 2HNO_3 + NO \qquad (5)$$

Equilibrium constants for reaction 5 have been obtained by Burdick and Freed (*7*), Abel, Schmid, and Stein (*1*), and by the authors (*8*).

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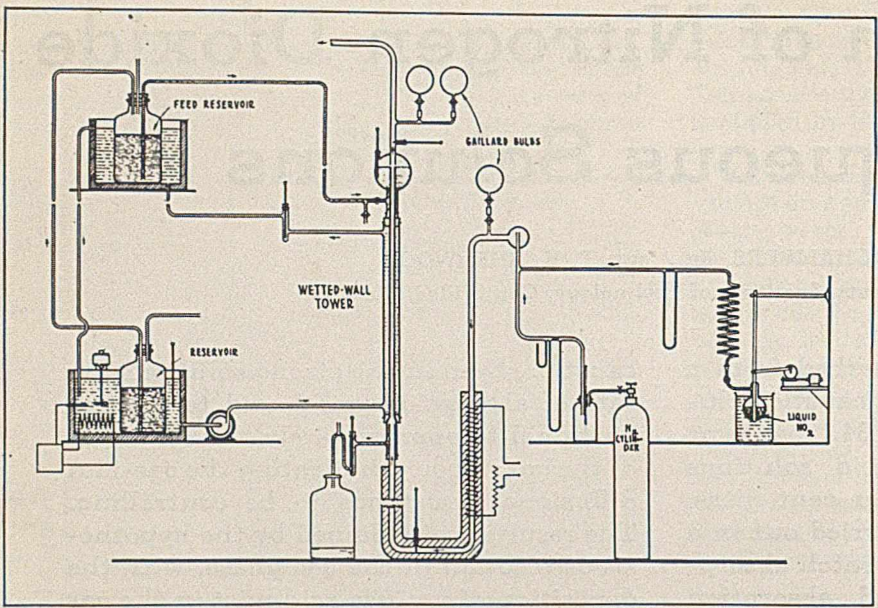

FIGURE 1. WETTED-WALL TOWER AND AUXILIARY EQUIPMENT

The absorption of the dioxide in water has been studied by various workers, notably by Foerster and Koch (*10*), who showed that the rate of absorption fell off to zero in the vicinity of 68 per cent nitric acid, and that stronger acid could not be obtained by absorption of NO_2 at atmospheric temperatures and pressure. The observed maximum acid strength was first explained by Burdick and Freed (*7*) on the basis of their equilibrium data for reaction 5, which showed that at high acid strengths equilibrium would be reached with only traces of NO present in the gas phase.

Assuming that reactions 3 and 4 represent fairly the process of absorption of NO_2 it would appear evident that the general mechanism is as follows: (*a*) NO_2 diffuses in the gas phase through the surface gas film at the interphase boundary; (*b*) NO_2 diffuses in the liquid phase from the gas-liquid interface to the point in the liquid where the formation of nitrous acid occurs, (*c*) nitrous acid decomposes with the liberation of NO, and (*d*) the NO formed is either returned to the gas phase, or is oxidized in the liquid phase by oxygen diffusing in along with the NO_2. If the gas is originally a mixture of NO and oxygen, then the oxidation to NO_2 must occur before absorption can take place. It seems clear that either a diffusional resistance or the speed of one of the chemical reactions involved might control the rate of the over-all process. Partington and Parker (*17*) treat the process as though the physical absorption were the controlling step and apply their treatment to the performance of commercial towers. Taylor, Chilton, and Handforth (*22*) conclude that nitric oxide oxidation is the controlling step in absorption of gas from ammonia oxidation, although realizing the limitations on acid strength imposed by the equilibrium of reaction 5. Bolshakoff (*4*) found the rate of absorption from a mixture of nitrogen dioxide and nitrogen to increase approximately as the 0.8 power of the gas velocity over the liquid surface. This result suggests strongly that diffusion through the gas film was controlling. Bolshakoff also found that NO oxidation was controlling when absorbing from a mixture of NO and air, as evidenced by the fact that the rate of absorption decreased with increased gas velocity through the apparatus.

Roberts (*18*) applied the Stefan diffusion equation to the diffusion of NO_2 and N_2O_4 through the stagnant gas film, with the assumption that the two come to equilibrium with each other instantly at each point in the film. The resulting equation is:

$$N_G = \frac{P}{RT\ p_B\ x}\left[2D_A p_A + D_c p_c\right] \qquad (6)$$

Although the rapid reaction of NO_2 and N_2O_4 in the film has been allowed for in the derivation, the result is the same as for the diffusion of the two gases unaffected by the presence of each other. The equation as given is valid only for the condition of no NO_2 vapor pressure over the solution, as may be seen from the outline of the derivation, described previously by one of the authors (*21*). The applicability of the general Stefan equation to interphase diffusion of vapors, as in evaporation of liquids and absorption of gases, was shown by Gilliland (*13*), who also presented a general correlation of diffusivities in gaseous systems (*12*).

Procedure

With a view to investigating the important variables separately, the present investigation was planned as a study of NO_2 absorption only, thus eliminating NO oxidation from the problem. The first type of equipment employed was a wetted-wall column (Figure 1) through which gas and absorbing solution passed in a countercurrent direction, the solution flowing by gravity down the inner wall of a 1.46-cm. i. d. glass tube. The NO_2 disappearing from the gas stream was calculated from the gas flow and gas analyses. Liquor analyses served to show the amount of NO_2 absorbed in those runs in which dilute sodium hydroxide solution was used as absorbent. The second type of equipment was a cylindrical glass vessel in which the absorbing liquid was placed and through which gas was passed continuously. Both gas and liquid were stirred, the whole arrangement being indicated by Figure 2.

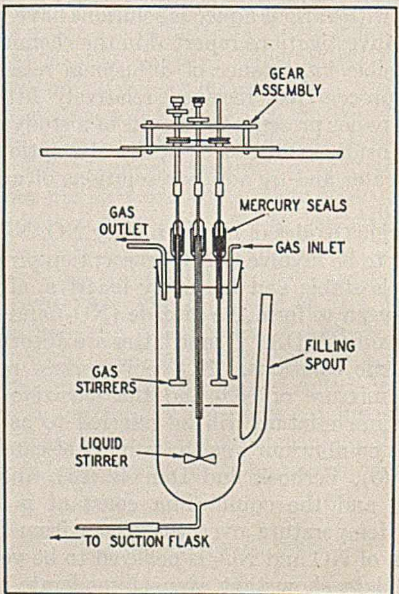

FIGURE 2. BATCH ABSORPTION VESSEL

Both pieces of equipment were designed to be "calibrated" by carrying out a standard absorption or evaporation experiment in which diffusion through the gas film was the controlling process. Comparison of NO_2 absorption rates with the results of these tests served to indicate the importance of diffusion in the more complicated process.

Wetted-Wall Tower

Figure 1 shows the tower absorber with auxiliaries as set up for the experiments with NO_2:

The supply of liquid NO_2 was contained in a glass flask placed in a heated water bath, and connected through a glass stopcock to a spiral of glass tubing. This spiral had sufficient flexibility so that the flask could be rocked mechanically and eliminated the necessity of rubber connections for this purpose. The vaporized NO_2 passed through a calibrated flowmeter to an 800-cc. gas mixing vessel into which nitrogen was fed from a cylinder and flowmeter. Samples of the inlet gas were withdrawn into a Gaillard bulb from a point in the line shortly after the mixing vessel. The mixed gases passed down through a section of electrically heated tubing and up through a vertical lagged calming section, approximately 95 cm. long below the inlet to the tower.

The absorption tower proper consisted of a jacketed length of 1.46-cm. i. d. glass tube, flared at the bottom to permit the entry of the gas feed tube of the same size. The inner tube was ground level at the top, and this upper end served as a weir feed device to supply the absorbing liquid in a smooth film on the inner wall. The flare at the bottom guided the liquid out past a thermometer into a measuring vessel and prevented liquid from falling into the gas supply tube. A thermometer was placed in the liquid in the inverted 300-cc. round-bottomed liquid feed vessel, and another was inserted in the gas line leaving the tower. Gas samples were withdrawn from the exit gas line into two Gaillard bulbs as indicated in Figure 1. The main liquid feed reservoir was placed in a water bath at an elevation of several feet above the top of the tower, and an auxiliary supply was placed in a thermostat at a lower level. Water was circulated from the thermostat through the jacket on the tower to the upper water bath, whence it returned to the thermostat bath.

The tower absorber was also used to measure rates of absorption and desorption of ammonia in water, absorption of ammonia in dilute acid, absorption of sulfur dioxide in 2 N sodium hydroxide and evaporation of water from water and from strong caustic solutions. These were the "calibration" tests carried out for the purpose outlined above. Compressed air was supplied in place of nitrogen and was run through a glass wool filter and a simple pressure-regulating device. Ammonia or sulfur dioxide was introduced at the bottom of the glass spiral shown at the right of Figure 1. In the evaporation tests this line was closed.

For the tests on rates of vaporization of water, wet- and dry-bulb thermometers were placed in the gas line between the air flowmeter and the gas mixing bulb. These served as a rough check on the humidity of the outlet air, measured by absorption trains using anhydrous magnesium perchlorate as the desiccant. The air was sufficiently preheated before entering the tower so that its wet-bulb temperature agreed closely with the temperature of the water running down the walls of the tower. Since a thermometer in the air stream at the bottom of the tower would defeat the purpose of the calming section, the inlet air temperature was not measured during the course of a run. However, it was found that the variation in this temperature was negligible, and it was measured at the beginning and end of each run of this series by lowering a thermometer on a string through the tower. The water film on the inner surface of the tower was somewhat irregular, and annular ripples moved down the tower. The addition of a small amount of wetting agent (Alphasol) to the water eliminated these ripples and produced a smooth regular film which wetted the glass wall perfectly.

Batch Absorption Vessel

This apparatus consisted of a cylindrical round-bottomed glass flask fitted with a large coated rubber stopper. One stirrer in the liquid and two in the gas space were arranged as shown in Figure 2 and connected to suitable electric drives. The liquid stirrer speed was 200 r. p. m. and the gas stirrers were driven at 375 r. p. m. in all tests. A mixture of NO_2 and nitrogen was prepared as for the wetted-wall absorber and introduced to the flask through a bent glass tube directed at the inner wall at the gas stirrer level. The gas leaving was withdrawn from a point about 1 cm. from the top of the gas space. In each run 800 cc. of liquid were used, this being easily introduced through the filling spout without wetting the sides of the flask in the gas space. When the liquid level was filled it was approximately 1 cm. below the gas stirrers and 8 cm. above the liquid stirrer. The stirring shafts passed through mercury seals, and the liquid stirrer shaft revolved in a fixed sleeve which extended below the liquid level and eliminated the effect of a rotating shaft on the liquid surface. The inside diameter of the flask was 9.6 cm. and the diameter of the central sleeve 1.1 cm. so that the exposed liquid surface area was 71.5 sq. cm. The whole absorber was immersed in a thermostat maintained at 25° ± 0.05° C. Gas entered at approximately 66 liters per hour, passing first through a glass coil in the thermostat bath in order to adjust its temperature.

As in the case of the wetted-wall absorber, this apparatus was "calibrated" by measuring the rate of vaporization of water from caustic solutions. The air from the compressed air line was thoroughly dried and purified by sulfuric acid, sodium hydroxide pellets, and P_2O_5 tubes. It was metered by passage through a calibrated flowmeter, and the humidity of the exit air determined gravimetrically using Anhydrite and P_2O_5. The results of these tests served as a basis for calculating the effective film thickness for vaporization of water.

Absorption of NO_2 was measured in this apparatus, using both nitric acid and caustic solutions. Since the volume of liquid was large relative to its surface, the change in the average liquid concentration during a run was negligible. A sample of the inlet gas was drawn into a single Gaillard bulb for determination of total nitrogen oxides, and the result interpreted as NO_2 (and N_2O_4) only, since negligible impurities were found in the NO_2 supplied.

Samples of the exit gas were taken into two Gaillard bulbs, one containing permanganate and the other water for determination of both NO and NO_2. The NO_2 disappearance in passing through the absorber was calculated from these analyses and the measured gas rate.

Preparation of Materials

Most of the NO_2 was obtained as a liquid from the Explosives Department of E. I. du Pont de Nemours & Company, Inc., and the rest was prepared by thermally decomposing lead nitrate in a stainless-steel tube and condensing the vapor. Each lot was purified by oxygen distillation, and the product gave pure white crystals when frozen with solid carbon dioxide.

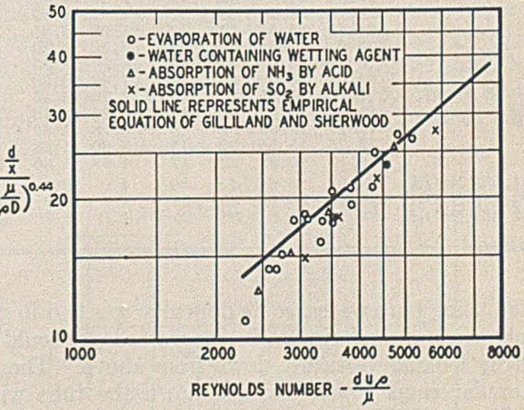

FIGURE 3. DATA OF PRELIMINARY ABSORPTION AND EVAPORATION TESTS IN WETTED-WALL TOWER

Acids, alkalies, etc., used as reagents and as absorbents were C. P. reagent grade. Nitrogen, ammonia, and sulfur dioxide were obtained from commercial cylinders.

Analytical Procedures

The analysis of the gas samples by withdrawal and titrating in Gaillard bulbs was described in detail elsewhere (8). Total nitrogen oxides plus nitric acid were determined by oxidation and titration of the sample in the bulb containing water, and the ratio of nitrogen dioxide to nitric oxide was determined by titration of the sample collected in the bulb containing permanganate.

Water vapor in air was determined gravimetrically by absorption on solid magnesium perchlorate, using two weighed U-tubes in series, and a gas washing bottle for humidifying the air before measuring its volume over water in a large bottle.

Ammonia in air was determined by titrating a weighed sample collected in an evacuated Gaillard bulb containing 25 cc. of water. Sulfur dioxide in air was determined in a similar way using barium hydroxide as absorbent. Excess barium hydroxide was titrated with standard acid.

Water Vapor, Ammonia, and Sulfur Dioxide in Wetted-Wall Column

The data obtained in the calibration runs are reported in Tables I and II. The results (except those with ammonia and water) are plotted in Figure 3 as $d/x/(\mu/\rho D)^{0.44}$ vs. Re for comparison with the empirical equation of Gilliland and Sherwood (*13*), where x, the effective film thickness, is calculated from the Stefan diffusion equation. This equation, based on the data of Gilliland for vaporization of various liquids in a wetted-wall tower, is represented by the solid line shown. The agreement is good, and it is apparent that the empirical equation referred to can be used to calculate the gas film resistances in the present tower.

Table I. Evaporation of Water in Wetted-Wall Tower

Run No.	Liquid	Temperature Liquid inlet	Temperature Liquid outlet	Temperature Gas inlet	Temperature Gas outlet	Partial Pressure Water Vapor gas inlet	Partial Pressure Water Vapor gas outlet	Barometer	Air Flow	Reynolds No.	d/x
		° *C.*	° *C.*	° *C.*	° *C.*	*Mm. Hg*	*Mm. Hg*	*Atm.*	*G. moles/sec.*		
6	Alphasol soln.	24.4	24.4	58	30	1.72	18.10	1.000	0.0353	4580	18.7
7		24.3	24.45	59	31	4.05	18.58	1.022	0.0269	3500	14.6
8	Water	24.85	24.8	60	31	3.46	19.18	1.020	0.0269	3500	14.3
9		24.8	24.9	60	32	3.34	20.02	1.020	0.0269	3500	16.6
10		24.9	25.0	58	30	10.26	20.78	0.987	0.0373	4840	21.8
11		25.0	25.2	60	32	10.50	20.40	0.987	0.0330	4280	16.8
12		25.1	25.3	57	33	6.27	20.10	0.987	0.0295	3820	16.8
13		24.4	24.5	54	30	3.22	18.72	1.000	0.0259	3350	14.3
14		24.6	24.65	51	30	2.58	19.65	1.000	0.0233	3100	14.6
15		24.75	24.8	55	32	2.54	19.08	1.000	0.0198	2570	11.3
16		24.6	24.85	51	35	2.07	16.95	1.000	0.0150	1950	6.7
17		24.8	24.8	52	32	2.20	18.10	1.000	0.0179	2300	8.8
18		24.25	24.45	53	32	1.37	16.80	1.012	0.0161	2090	7.6
19		24.45	24.55	54	32	1.28	16.85	1.012	0.0169	2180	7.7
20		25.0	25.3	59	32	6.52	21.30	1.012	0.0216	2900	14.4
21		25.0	25.1	59	31	7.70	21.35	1.012	0.0228	3050	14.8
22		24.8	25.0	59	32	7.48	20.50	1.012	0.0205	2750	12.2
23		15.75	15.65	23	18	7.70	12.45	1.006	0.0308	4300	20.0
24		15.6	15.6	23	18	8.75	12.35	1.006	0.0273	3850	15.5
25		16.1	15.95	23	18	8.78	12.62	1.006	0.0236	3300	13.0
26		15.25	15.55	22	17	3.90	11.43	1.012	0.0187	2650	11.3
27		16.15	15.9	22	17	4.68	11.85	1.012	0.0368	5180	21.3
28	24.6% NaOH	24.9	25.6	55	30	4.0	12.1	1.007	0.0329	4300	17.0
29	22.4% NaOH	24.85	25.1	55	31	2.9	12.2	1.013	0.0291	3750	14.0
30	22.4% NaOH	24.3	24.8	55	29	3.1	12.4	1.013	0.0243	3120	12.0

When using pure water, some difficulty was had in wetting the tube surface, and ripples in the water layer could be observed by looking vertically down from above. These were flat annular rings which traveled down the tube with the water film. Addition of a small amount of commercial wetting agent (Alphasol) to the water caused it to wet the glass surface readily and eliminated the ripples. As shown by Figure 3, the tests with and without the wetting agent gave the same results, and it may be concluded that the ripples were of negligible importance.

In order to eliminate temperature gradients in the water film caused by temperature change of the water passing through the tower, a number of runs (Table I) were made with inlet feed and jacket water maintained nearly at the temperature of adiabatic saturation of the inlet air. This condition was obtained by varying the temperature of the inlet air, depending on its humidity. The temperature change of the water in passing through the tower was accordingly never more than 0.3° C. The data obtained when this precaution was observed agreed with the absorption data and with the Gilliland equation, indicating that the temperature gradient effect was probably negligible in Gilliland's tests using liquid and air at the same inlet temperatures.

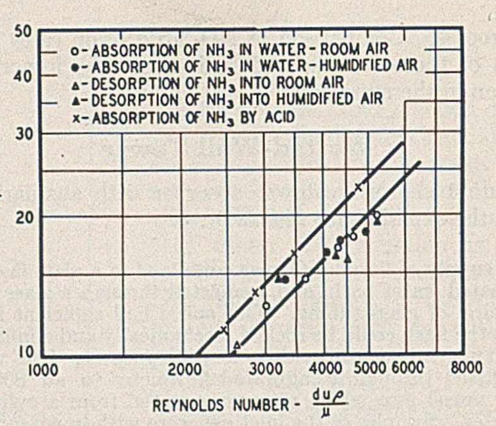

Figure 4. Data on Absorption and Desorption of Ammonia in Wetted-Wall Tower

The data obtained with ammonia and with sulfur dioxide are shown in Table II. Ammonia was absorbed by water and desorbed from an 8–11 per cent aqueous ammonia solution. In each case tests were made using air of ordinary room humidity, and with air humidified to more than 80 per cent relative humidity at the inlet temperature. The agreement of these various results is indicated on Figure 4, where d/x is plotted against Re. The effect of air humidity, suspected by Chilton (*9*), is not observable. Similar tests absorbing ammonia from room air by 2 N sulfuric acid gave higher values of d/x, as shown in the upper curve of Figure 4. These same data are plotted on Figure 3, where they are seen to agree with the water data and with the Gilliland equation. It seems reasonable to conclude that the discrepancy of the two lines of Figure 4 is due to a small liquid film resistance in the case of ammonia with water as the solvent.

Data on absorption of sulfur dioxide by 2 N sodium hydroxide solution, tabulated in Table II, are also plotted on Figure 3. The agreement with the other data indicate that this also is a case of gas film resistance wholly controlling.

Diffusivity of Nitrogen Dioxide

In order to calculate the effective film thickness from data on NO_2 absorption, it is necessary to have reliable values for the diffusivities D_A and D_C of N_2O_4 and NO_2 to be substituted in Equation 6. These values can be estimated by the empirical equation for diffusivities proposed by Gilliland (*12*), but it was deemed desirable to obtain experimental values if possible. Data were accordingly obtained by the method of Stefan, using liquid nitrogen dioxide in small tubes.

A small graduated tube about 3 mm. in internal diameter and 18 cm. long, closed at one end, was filled to within about 2.5 cm. from the open end with liquid NO_2. The tube was then suspended in a large test tube through which nitrogen was passed slowly at atmospheric pressure. The test tube was placed in a cooled bath, and the nitrogen was precooled approximately to the bath temperature. It was assumed that the partial pressure of NO_2 was zero at the mouth of the small tube and equal to the vapor pressure at the bath temperature at the liquid surface. By a material balance and Equation 6, the following relation is obtained:

Table II. Absorption and Desorption in Wetted-Wall Tower

Run No.	Temperature				NH_3 in Liquor		Partial Pressure Solute in Gas		Barometer	Liquor Flow	Air Flow	Reynolds No.	d/x
	Gas inlet ° *C.*	Gas outlet ° *C.*	Liquid inlet ° *C.*	Liquid outlet ° *C.*	Inlet %	Outlet %	Inlet *Mm. Hg*	Outlet *Mm. Hg*	*Atm.*	*G./sec.*	*G. moles/sec.*		
						Absorption of Ammonia in Water							
31	22	25.5	24.6	27.8	0	1.92	106.8	40.8	1.030	..	0.0295	4300	17.0
32	22	25	24.6	26.7	0	1.10	75.4	27.3	1.030	4.00	0.0357	5200	19.9
33	22	24	24.2	26.7	0	1.38	82.5	30.3	1.020	..	0.0317	4650	17.9
34	22	24.5	24.4	26.7	0	1.31	84.7	30.0	1.020	2.78	0.0247	3650	14.6
35	22	24.5	24.6	25.8	0	0.64	59.5	18.4	1.020	3.30	0.0206	3000	12.8
36[a]	22	25	23.9	27.0	0	1.80	65.2	28.1	1.000	1.85	0.0392	4950	18.3
37[a]	22	25	24.4	27.3	0	1.05	65.9	23.2	1.000	3.08	0.0280	4050	16.7
38[a]	22	24.5	24.6	25.9	0	0.42	59.4	18.3	1.000	5.90	0.0226	3300	14.6
39[a]	22	25	24.6	27.1	0	1.09	66.1	24.1	1.000	2.97	0.0300	4350	17.6
						Desorption of Ammonia from Aqueous Solution							
40[a]	21	23	24.7	20.4	10.50	8.35	0	58.5	1.010	2.03	0.0301	4250	16.3
41[a]	21	21	23.4	19.7	10.52	7.61	0	52.3	1.010	1.63	0.0372	5200	19.3
42[a]	21	23	24.6	21.6	10.45	9.55	0	68.8	1.010	4.35	0.0223	3200	14.7
43	22	22	24.5	20.6	8.55	6.18	0	42.2	1.000	1.33	0.0317	4500	16.0
44	23	23	24.7	22.5	8.70	7.82	0	47.4	1.000	3.13	0.0182	2600	10.5
						Absorption of Ammonia by 2 *N* Sulfuric Acid							
45	25	29	24.3	27.0	...	..	61.3	15.6	1.000	..	0.0328	4750	22.9
46	24	26	25.0	26.5	...	..	56.6	14.5	1.000	..	0.0197	2850	13.7
47	24	26	24.1	26.8	...	..	56.6	14.4	1.000	..	0.0238	3450	16.6
48	24	26	24.5	30.0	...	..	72.8	19.8	1.000	..	0.0168	2450	11.3
						Absorption of Sulfur Dioxide by 2 *N* Sodium Hydroxide							
49	24	26	25.0	29.5	...	..	29.3	11.3	0.995	..	0.0391	5800	30.7
50	23	27	25.0	29.5	...	..	40.8	14.7	0.995	..	0.0286	4350	24.3
51	24	27	25.2	29.5	...	..	37.1	13.5	0.995	..	0.0239	3600	20.0
52	24	27	25.3	29.3	...	..	38.7	14.4	0.995	..	0.0201	3050	16.3

[a] Inlet air humidified to more than 80% relative humidity.

$$\frac{\rho_L}{M_C}\frac{dy}{d\Theta} = \frac{PD_A}{RTyp_B}\left[2p_A + \frac{D_C}{D_A}p_c\right] \qquad (7)$$

On integration this gives:

$$y_2^2 - y_1^2 = \frac{2M_CPD_A\Theta}{\rho_LRTp_B}\left[2p_A + \frac{D_C}{D_A}p_c\right] \qquad (8)$$

The density of the liquid and the vapor pressure of the liquid dioxide were obtained from the International Critical Tables, and p_A and p_C were calculated from NO_2–N_2O_4 equilibrium data referred to above.

Since Equation 8 contains the two unknowns, D_A and D_C, it is not possible to obtain both diffusivities by means of a single experiment. The ratio D_C/D_A can be obtained from the kinetic theory, however, and the value of 1.43 for this ratio, obtained by either the theoretical equations of Maxwell or Jeans, or by the empirical equation of Gilliland, is doubtless quite reliable. Using this value, it is possible to calculate either D_A or D_C from the experimental data.

Two runs were made at 0° C. and one run at 10° C. The data and calculated values of D_A are shown in Table III, together with corresponding values of D_A calculated by the Gilliland equation. The agreement of the latter with the data was sufficiently good so that the empirical equation was used in all subsequent calculations.

Table III. Data on Diffusivity of N_2O_4 in Nitrogen

Temp. ° *C.*	y_1 *Cm.*	y_2 *Cm.*	Time *Hours*	D_A (Exptl.)	D_A (Gilliland)
0	4.43	9.01	88.45	0.084	0.081
0	5.20	9.44	88.45	0.085	0.081
10	12.10	16.70	91.92	0.090	0.086

Absorption of NO_2

The experimental results obtained in the wetted-wall tower and in the batch absorption vessel are given in Tables IV and V. Nitrogen dioxide was absorbed from a mixture in nitrogen using caustic solutions varying in strength from 2.7 to 34.1 per cent sodium hydroxide and acid solutions varying from 5.7 to 69.8 per cent nitric acid. In order to interpret the results, the effective film thickness x (or x_{NO_2}) was calculated by Equation 6 using values of D_A and D_C calculated from the Gilliland equation.

The effect of gas velocity is best illustrated by the data on the wetted-wall tower, a part of which is plotted as d/x vs. *Re* in Figure 5. It is evident that the values of d/x, calculated from Equation 6, vary approximately as the 0.8 power of *Re*, as is typical of processes in which the diffusional resistance of the gas film controls the rate. Comparison with Figure 4, however, shows that the values of d/x are considerably smaller than those obtained for ammonia absorption. It will be further observed that the points for 27.6 per cent nitric acid solutions fall approximately on the same line as those for 2.9 per cent sodium hydroxide solutions and that the points for 50.7 per cent nitric acid and for 18.0 per cent sodium hydroxide likewise agree.

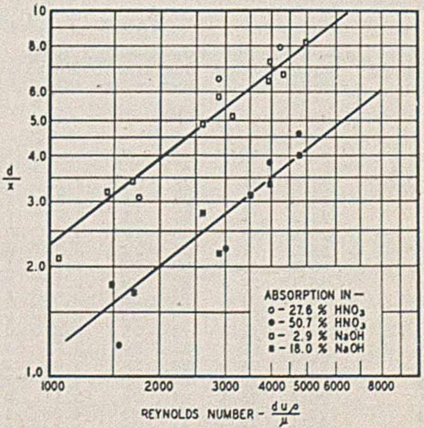

Figure 5. Effect of Gas Velocity on Absorption of NO_2 in Wetted-Wall Tower

The effect of acid or caustic concentration is illustrated by the two curves of Figure 6 for the tower and for the batch absorption vessel, respectively. The ordinate is the ratio of the effective film thickness for water vapor to that for nitrogen dioxide, and is essentially the same as the reciprocal ratio of the gas film absorption coefficients. A maximum is apparent in each curve, indicating the rate of absorption to be greatest in pure water. The decrease in rate with increase in acid strength is similar to that noted by Foerster and Koch (*10*). Because of the possible effect of solution viscosity, the values of x_{H_2O} for the caustic runs in the batch absorption vessel were determined experimentally by vaporizing water from caustic solutions of various strengths. The results varied only a few per cent from those for pure water but provided a sounder basis of comparison.

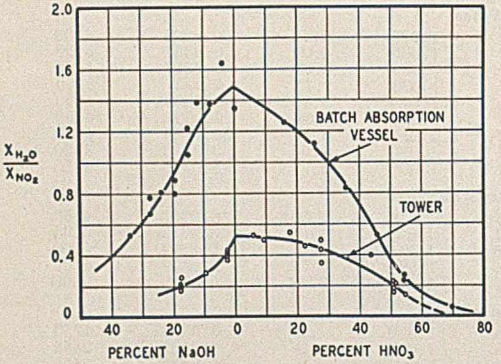

Figure 6. Effect of Solution Concentration on Relative Rate of Absorption of NO_2 from Nitrogen

The empirical equation of Gilliland and Sherwood, represented by the solid line of Figure 3, is

$$\frac{d}{x} = 0.023\,(Re)^{0.83}\left(\frac{\mu}{\rho D}\right)^{0.44} \tag{9}$$

As shown above, this equation is substantiated by the present results on vaporization of water and on absorption of ammonia and of sulfur dioxide. Since the effective film thickness, x, is proportional to the 0.44 power of the diffusivity, and diffusivities of both NO_2 and N_2O_4 are approximately half that for water vapor, it would be expected that x_{H_2O}/x_{NO_2} would be somewhat greater than unity. Figure 6 shows this ratio to be less than unity in every case except in the range from 20 per cent sodium hydroxide to 28 per cent nitric acid in the batch absorption vessel. In general, therefore, the effective film thicknesses are greater, and the rates of absorption less, than would be predicted from the data on water vaporization under similar conditions. The calculated values allow for no vapor pressure of NO_2 over the solutions since none would be expected except in strong acid.

Summarizing the results on NO_2 absorption, it is noted, first, that d/x (or the absorption coefficient) is proportional to the 0.8 power of the Reynolds number over a wide range of caustic and acid concentrations, and second, that the effective film thicknesses are larger, or the absorption coefficients smaller, than would be calculated from the data on water vaporization under the same conditions. The first point indicates strongly that the gas film resistance controls the absorption process, whereas the second point indicates that an added resistance has been placed in series with that of the gas film. This anomalous situation is explained on the assumption that interaction between NO_2 and water vapor occurs in the gas phase, with the formation of a moderately stable mist. Water vapor diffusing out into the gas from the liquid interface meets NO_2 diffusing toward the liquid and the two react to deposit a nitric acid–water mist in the

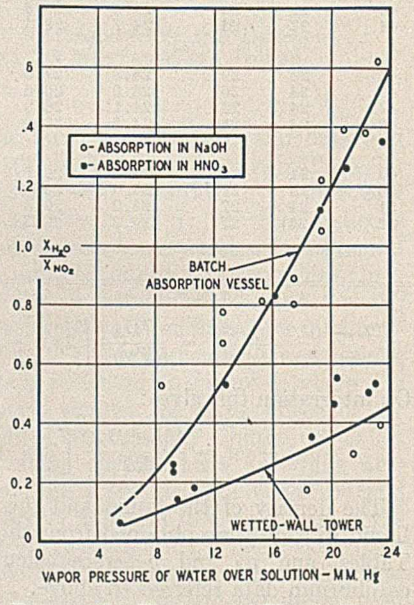

Figure 7. Effect of Vapor Pressure of Water over the Absorbing Solution on the Relative Rate of Absorption of NO_2 from Nitrogen

Table IV. Absorption of NO_2 in Wetted-Wall Tower

Run No.	Inlet Liquid Compn.	Temperature: Liquid inlet	Temperature: Liquid outlet	Temperature: Gas inlet	Temperature: Gas outlet	Inlet Gas Compn.: NO_2	Inlet Gas Compn.: N_2O_4	Inlet Gas Compn.: N_2	Outlet Gas Compn.: NO_2	Outlet Gas Compn.: N_2O_4	Outlet Gas Compn.: NO	Outlet Gas Compn.: N_2	Barometer	Nitrogen Flow	Reynolds No.	Absorption Rate	$\frac{x_{H_2O}}{x_{NO_2}}$
	%	° C.	° C.	° C.	° C.	Mole per cent			Mole per cent				Atm.	G. moles/sec.		$10^7 \times$ g. moles NO_2/(sec.)(sq. cm.)	
53	18.0 NaOH	25.2	24.1	22	28	3.72	0.97	95.3	3.22	0.79	0.17	95.8	0.995	0.0322	4700	7.7	0.21
54	18.0	24.6	24.7	22	28	4.52	1.46	94.2	4.13	1.18	0.04	94.7	1.000	0.0193	2900	5.5	0.17
55	18.0	25.2	24.5	23	28	3.78	1.00	95.2	3.32	0.82	0.17	95.7	1.000	0.0265	3920	6.3	0.20
56	2.97	25.3	24.0	23	29	3.75	0.98	95.3	2.92	0.64	0.06	96.3	1.010	0.0266	3950	11.3	0.39
57	2.97	25.3	24.5	23	29	3.63	0.94	95.4	2.99	0.64	0.09	96.2	1.015	0.0332	4900	11.8	0.40
58	2.97	25.3	25.0	23	29	4.17	1.24	94.6	3.23	0.72	0.17	95.8	1.010	0.0175	2550	9.7	0.41
59	2.97	25.1	24.9	23	29	3.70	0.97	95.4	2.86	0.58	0.12	96.4	1.010	0.0212	3100	10.0	0.36
60	2.97	25.3	24.5	23	28	3.53	0.94	95.4	2.74	0.52	0.14	96.5	1.010	0.0265	3850	12.1	0.44
61	17.8	24.8	24.6	23	28	2.70	0.55	96.5	2.21	0.34	0.14	97.4	1.000	0.0174	2520	3.9	0.26
62	17.8	24.9	24.4	23	28	3.57	0.91	95.7	3.16	0.70	0.14	95.8	1.000	0.0234	3460	5.5	0.20
63	2.86	25.4	24.5	23	29	3.72	1.00	95.3	2.99	0.67	0.09	96.3	1.000	0.0293	4300	11.6	0.36
64	2.86	25.0	24.5	23	29	4.04	1.15	95.0	3.07	0.64	0.17	96.2	1.000	0.0193	2860	11.1	0.44
65	2.75	25.2	25.1	24	28	4.17	1.27	94.7	3.26	0.76	0.12	95.9	0.995	0.0117	1700	6.8	0.40
66	2.75	25.4	25.4	24	28	3.41	0.84	95.7	2.50	0.43	0.11	96.7	0.995	0.0102	1450	5.0	0.43
67	2.70	25.7	25.3	24	29	4.36	1.37	94.2	2.80	0.58	0.17	96.7	0.995	0.0069	1000	3.9	0.36
68	17.9	25.5	25.2	24	27	3.54	0.91	95.6	2.99	0.64	0.14	96.3	0.995	0.0102	1450	3.2	0.24
69	17.9	25.4	25.4	24	28	4.07	1.18	94.7	3.60	0.88	0.12	95.7	0.995	0.0117	1750	3.7	0.20
70	10.3	25.4	24.7	24	28	3.78	1.00	95.2	3.11	0.67	0.23	96.0	1.000	0.0203	3000	7.4	0.29
71	27.6 HNO_3	25.1	25.1	24	27	4.10	1.21	94.7	3.23	0.76	0.32	95.7	0.995	0.0117	1750	5.8	0.35
72	27.6	25.4	25.2	23	28	4.14	1.24	94.7	3.10	0.67	0.32	96.0	1.000	0.0193	2860	12.1	0.50
73	27.6	25.4	24.1	23	27	3.44	0.84	95.5	2.62	0.52	0.37	96.4	1.000	0.0290	4200	11.8	0.44
74	54.5	26.0	25.1	24	26	3.78	1.00	95.2	3.48	0.85	0.15	95.6	1.000	0.0203	3000	3.4	0.14
75	43.7	25.6	25.2	24	26	3.63	0.94	95.4	2.80	0.58	0.49	96.3	1.005	0.0201	3000	8.7	0.40
76	17.5	25.8	25.0	24	28	3.75	0.98	95.3	2.59	0.49	0.49	96.5	1.015	0.0203	3000	11.8	0.55
77	9.2	25.4	25.0	24	28	3.78	1.00	95.2	2.75	0.55	0.29	96.5	1.015	0.0203	3000	11.0	0.50
78	5.7	25.5	24.7	24	28	3.78	1.00	95.2	2.74	0.52	0.29	96.5	1.015	0.0203	3000	11.6	0.53
79	22.3	24.9	24.5	24	28	3.86	1.09	95.2	2.95	0.61	0.38	95.8	1.015	0.0203	3000	10.8	0.46
80	50.7	25.7	25.2	24	26	3.60	0.92	95.6	3.20	0.70	0.12	95.8	1.005	0.0104	1550	2.4	0.18
81	50.7	25.3	24.9	24	26	3.63	0.94	95.4	3.20	0.73	0.14	96.0	1.000	0.0328	4850	7.9	0.23
82	50.7	25.6	25.3	24	26	3.82	1.05	95.2	3.55	0.87	0.19	95.3	0.995	0.0203	3000	4.2	0.16
83	50.7	25.6	25.3	24	26	3.63	0.94	95.4	3.20	0.73	0.26	96.0	0.995	0.0270	3950	6.6	0.22

Table V. Absorption of NO_2 in Batch Absorption Vessel

(All runs at 25° C.)

Run No.	Liquid Compn.	Inlet Gas Compn. NO_2	Inlet Gas Compn. N_2O_4	Inlet Gas Compn. N_2	Outlet Gas Compn. NO_2	Outlet Gas Compn. N_2O_4	Outlet Gas Compn. NO	Outlet Gas Compn. N_2	Barometer	Nitrogen Flow	Absorption Rate	$\frac{x_{H_2O}}{x_{NO_2}}$
	%	Mole per cent			Mole per cent				Atm.	$10^4 \times$ g. moles/sec.	$10^7 \times$ g. moles NO_2/(sec.)(sq. cm.)	
84	23.6 NaOH	5.46	2.14	92.4	3.98	0.82	0.25	95.0	1.015	7.72	4.96	0.81
85	15.2	4.76	1.65	93.5	2.62	0.49	0.37	96.5	1.005	7.72	5.08	1.22
86	27.2	5.46	2.14	92.4	3.93	1.13	0.12	94.8	1.010	7.72	4.30	0.67
87	27.2	5.27	1.97	92.8	3.60	0.94	0.17	95.3	1.010	7.74	4.50	0.78
88	19.5	5.38	2.09	92.5	3.63	0.95	0.21	95.2	1.000	7.74	4.85	0.80
89	19.5	5.24	1.96	92.8	3.39	0.82	0.26	95.5	1.000	7.72	4.92	0.89
90	12.0	5.29	2.01	92.7	2.81	0.58	0.44	96.2	1.000	7.72	6.35	1.39
91	7.9	5.16	1.90	92.9	2.72	0.53	0.29	96.5	1.000	7.70	6.16	1.38
92	34.1	5.32	1.98	92.7	4.08	1.19	0.06	94.7	1.000	7.74	3.45	0.53
93	15.4	5.26	1.98	92.8	3.20	0.72	0.25	95.8	1.000	7.74	5.46	1.05
94	4.1	5.30	2.02	92.7	2.58	0.47	0.31	96.6	1.000	7.70	6.92	1.64
95	54.4 HNO_3	5.04	1.77	93.2	4.26	1.30	0.18	94.3	0.995	7.66	2.05	0.26
96	54.4	5.32	1.99	92.7	4.62	1.49	0.33	93.5	1.005	7.66	2.05	0.24
97	45.5	5.28	2.06	92.7	4.00	1.09	0.79	94.2	1.000	7.66	3.84	0.53
98	35.1	5.27	2.00	92.7	3.38	0.81	0.99	94.8	1.010	7.66	5.04	0.83
99	25.7	5.32	1.99	92.7	3.06	0.68	0.99	95.2	1.010	7.66	5.88	1.12
100	69.8	5.32	1.99	92.7	5.14	1.83	0.00	92.8	1.005	7.66	0.59	0.06
101	15.7	5.59	2.19	92.3	3.10	0.64	1.13	95.3	1.005	7.66	6.38	1.26
102	H_2O	5.19	1.94	93.0	2.75	0.55	0.95	95.7	1.005	7.66	6.18	1.35

gas film. If the partial pressure of NO_2 in the gas is large and the vapor pressure of water over the solution is small, the mist is deposited in a layer very near the gas-liquid interface. Such a mist is difficult to dissipate, since this part of the gas film is quite stagnant. Consequently, the obstruction to NO_2 diffusion offered by the stagnant mist more than offsets the reduced distance the NO_2 must diffuse, and the rate of absorption is low. If the partial pressure of NO_2 in the gas is small and the vapor pressure of water over the solution is large, the mist is deposited in a layer further removed from the gas-liquid interface and is more easily dissipated. Under such conditions the rate of absorption may be larger than predicted for gas-film diffusion.

The hypothesis of mist formation in the gas film is supported in a number of ways. Although the film itself could not be observed, mist in the main body of the gas was evident in both types of experimental apparatus. At low gas velocities in the tower the stream lines in the exit gas could be followed visually because of the mist carried. At the critical gas velocity these broke into eddies, the break coming at a Reynolds number of 2000–2500. In the batch absorption vessel the mist made the gas space opaque, and some condensation occurred on the walls. The mist formation was always more noticeable when absorbing in water than when using strong acid or strong caustic.

The temperature of the solution passing through the wetted-wall tower showed a tendency to drop in nearly every run, although the liquid-phase reactions are exothermic, and the water in the surrounding jacket was within a fraction of a degree of the inlet solution. At the same time the gas temperature rose 2–6° C. in passing through the tower, and left several degrees above the temperature of the jacket water or of the inlet solution. These facts indicate evaporation of water from the solution and the occurrence of an exothermic reaction in the gas phase. Most of the heat effect noticed was probably due to the condensation of water in the mist formed.

The importance of the vapor pressure of water over the absorbing solution is indicated by Figure 7, which shows the ratio x_{H_2O}/x_{NO_2} plotted as ordinate with the vapor pressure of water over the solution as abscissa. Although the points scatter somewhat, a definite correlation is indicated, especially in the case of the data obtained in the batch absorption vessel.

The data of Table IV show that appreciable amounts of nitric oxide were found in the outlet gas. In the case of the sodium hydroxide solutions no nitric oxide could be liberated if the dioxide reacted in the liquid phase, and it must be concluded that any NO formed was the result of a gas-phase reaction of the dioxide and water vapor. With strong caustic the NO formed was 2 per cent of the dioxide disappearing from the gas phase, corresponding to the formation of an almost equal-molal mixture of nitrate and nitrite by reaction 1. Since the vapor pressure of water over the strong caustic is small, there was presumably little gas-phase reaction, and correspondingly little excess nitrate formed by direct reaction with the nitric acid mist. In the dilute caustic solutions the nitric oxide found was as high as 8 per cent of the dioxide disappearance, indicating a greater gas-phase reaction and proportionately greater excess of nitrate.

The total nitrogen in the exit solution was determined in the case of ten runs in the wetted-wall column using dilute caustic solutions. The ratio of NO_2 absorption as calculated from the liquor analyses (N_L) to the NO_2 disappearing from the gas phase (N_G) was less than unity in each case except for the run at the lowest gas velocity. The gas analysis does not include the mist, which presumably carried the unaccounted-for NO_2 as nitric acid. At the higher gas velocities the mist has less chance to settle out in the liquid on the tube walls, and the ratio N_L/N_G decreased progressively to approximately 0.6 at the highest Reynolds numbers.

It is seen that the hypothesis of mist formation near the liquid-gas interface can be used to explain the general failure to get equal-molal mixtures of nitrate and nitrite in the absorption of NO_2 by caustic, and the fact that nitrate as well as nitrite is formed when mixtures of NO and NO_2 are absorbed by caustic. In each case nitric acid mist deposited in the solution increases the ratio of nitrate to nitrite.

Perhaps the most difficult result to explain is the fact that the ratio x_{HO_2}/x_{NO_2} for the runs in the batch absorption vessel is considerably greater than for the wetted-wall tower, as shown by Figure 6. The liquid surface was horizontal in the first case and vertical in the tower; the time of contact of gas and liquid in the batch absorption vessel was of the order of three hundred times that in the tower. It may be supposed, therefore, that much less mist, as such, entered the solution in the tower than in the batch vessel and that the rates of disappearance of NO_2 in the former were relatively less when compared with water vapor diffusion in the calibration tests.

The importance of mist formation of NO_2 absorption as indicated by the results described will suggest a number of points of industrial interest. For example, it would appear that acid formation from NO_2 might be speeded up by encouraging the reaction in the gas phase, as by introducing water vapor into the gas, with the subsequent separation of the relatively unstable though possibly dilute mist formed.

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Nomenclature

d = tube diameter, cm.
D = gas diffusivity, sq. cm./sec.

D_A = diffusivity for N_2O_4–carrier gas system, sq. cm./sec.
D_c = diffusivity for NO_2–carrier gas system, sq. cm./sec.
M_c = molecular weight of liquid NO_2
N_G = absorption rate, gram moles NO_2/(sec.)(sq. cm.), as indicated by gas analyses
N_L = absorption rate, gram moles NO_2/(sec.)(sq. cm.) as indicated by liquor analyses
p_A = partial pressure N_2O_4 in main body of gas, atm.
p_B = mean partial pressure of nondiffusing or carrier gas in gas film, atm.
p_c = partial pressure of NO_2 in main body of gas, atm.
P = total pressure, atm.
R = gas constant, cc.-atm./(gram moles)(° K.)
Re = Reynolds number = $d\mu\rho/\mu$
T = absolute temperature, ° K.
x = effective film thickness, cm.
x_{H2O} = effective film thickness for evaporation of water, cm.
x_{N2O} = effective film thickness for absorption of NO_2, cm.
y = thickness of stagnant gas layer in diffusivity experiments, cm.
μ = gas viscosity, gram/(sec.)(cm.)
ρ = gas density, gram/(cc.)
ρ_L = liquid density, grams/(cc.)
Θ = time, sec.

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Effect of Humidity on Hygroscopic Properties of Sugars and Caramel[1]

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THE hygroscopicity has been investigated of saccharose, maltose, lactose, dextrose, levulose, galactose, and caramel made from saccharose and treacle with the addition of various sugars at relative humidities of 43, 62.7, 81.8, and 88.8 per cent. The experiments were made at 25° C. and lasted for 60–75 days. The temperature was held constant in the thermostat at 25° C. (±0.1°).

The sugar specimens were dried *in vacuo* until constant weight was obtained. Approximately 1-gram specimens of these anhydrous substances were placed in a weighed vessel and transferred to a desiccator over a saturated salt solution which created a constant relative humidity in the vacuum of the desiccator. The moisture-absorbing capacity of the specimens was obtained by weighing the vessels containing them at certain intervals, the difference in weight giving the amount of moisture absorbed. Specimens of caramel contained from 0.4 to 0.8 per cent moisture. The amount of moisture absorbed by the caramel under various conditions of relative humidity was found by the above method.

The data relating to the equilibrium conditions of supersaturated salt solutions with air are taken from the work of Adams and Merz.[2]

For the experiments the following saturated solutions were prepared: $K_2CO_3 \cdot 2H_2O$ corresponding at 25° C. to 43 per cent relative humidity, NH_4NO_3 corresponding to 62.7 per cent, $(NH_4)_2SO_4$ corresponding to 81.8 per cent, and K_2SO_4 corresponding to 98.8 per cent. The saturated solutions of these salts were placed at the bottom of the desiccator and over them were placed the vessels containing the sugar samples to be investigated. The desiccator was covered with a close-fitting lid at all times, and a vacuum was thus created in which a constant relative humidity was maintained.

When the sugar specimens were kept in the desiccator at a relative humidity of 62.7 per cent, the greatest absorbing capacity (9.93 per cent) was exhibited by maltose during the first 17 days. In the same period levulose absorbed 7.09 per cent of the moisture. The smallest quantity of moisture under the same conditions was absorbed by galactose, 0.03 per cent.

After 76 days under the same conditions, the greatest quantity of moisture was absorbed by levulose, 21.4 per cent. After 17 days the amount of moisture absorbed by maltose showed little variation. The smallest quantity of moisture was absorbed by galactose, 0.03 per cent. Levulose absorbed 15 per cent moisture, and then changed from the crystal to the liquid form.

When the different specimens of sugar were kept in the desiccator at a relative humidity of 81.8 per cent, during the

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[1] Browne [J. Ind. Eng. Chem., 14, 712–14 (1922)] carried out experiments on various pure sugars and commercial sugar products. Dittmar [*Ibid.*, 27, 333 (1935)] experimented with the hygroscopicity of certain sugars.

[2] Ind. Eng. Chem., 21, 305 (1929).

Table I. Moisture Absorption at Various Relative Humidities (25° C.)

Sugar	Per Cent Moisture Absorbed in: 1 day	3 days	7 days	17 days	30 days	50 days	60 days	76 days
			62.7 Per Cent Relative Humidity					
Saccharose	0.06	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Maltose (anhydrous)	4.51	8.14	9.77	9.93	9.85	9.9	10.01	9.95
Lactose	0.03	0.03	0.03	0.05	0.05	0.05	0.05	0.08
Dextrose	0.04	0.04	0.04	0.38	0.43	0.79	1.07	1.74
Levulose[a]	0.65	1.41	2.61	7.09	13.01	18.35	21.85	21.4
Galactose	0.05	0.03	0.03	0.03	0.03	0.03	0.03	0.03
			81.8 Per Cent Relative Humidity					
Saccharose	0.05	0.05	0.05	0.05	2.28	4.54	3.86	3.9
Maltose (anhydrous)[b]	8.52	9.2	9.8	9.95	10.77	...	...	..
Lactose	0.07	0.07	0.07	0.07	0.11	0.11	0.11	0.07
Dextrose	0.62	2.04	5.15	9.7	9.62	9.77	9.6	9.6
Levulose[c]	4.18	10.22	18.58	29.16	35.05	36.32	35.3	35.5
Galactose	0.06	0.06	0.06	0.06	0.07	0.13	0.16	0.11
			98.8 Per Cent Relative Humidity					
	1 day	3 days	7 days	11 days	20 days	26 days	40 days	60 days
Saccharose[d]	1.31	4.85	13.53	20.81	33.01	38.53	45.62	...
Lactose[e]	0.05	0.05	0.09	0.12	0.13	0.26	0.33	...
Dextrose[f]	4.68	8.61	15.02	20.78	28.43	33.95	42.82	...
Levulose[g]	11.09	18.43	30.74	37.61	45.95	49.41	54.99	59.14
Galactose	1.16	1.54	3.33	5.18	8.34	10.47	16.42	25.72

[a] All the levulose crystals liquefied.

[b] After 30 days mold began to form.

[c] After 6 days the levulose crystals began to liquefy; after 30 days a mobile liquid was formed.

[d] The saccharose crystals began to decompose and liquefy after having absorbed approximately 16–18% of the moisture; when they had absorbed approximately 36–38% all the crystals turned into a mobile liquid; when up to 45% of the moisture had been absorbed, a film of mold was formed.

[e] After the lactose had been kept for 25 days and had absorbed an insignificant amount of moisture, it was covered with mold.

[f] When the dextrose had absorbed 15–18% of the moisture, it began to dissolve; when it had absorbed 42%, it completely liquefied and was covered with mold.

[g] When the levulose had absorbed approximately 15% of the moisture, it began to dissolve. After having absorbed approximately 30%, it liquefied.

first 24 hours the greatest quantity of moisture was absorbed by maltose, 8.52 per cent; within the same period levulose absorbed 4.18 per cent moisture. The smallest amount under the same conditions was absorbed by lactose, 0.07 per cent.

After 76 days under the same conditions levulose absorbed the greatest percentage of moisture, 35.5; maltose absorbed the next largest amount, 10.77 per cent in 30 days, after which it became moldy and the experiment was stopped. Dextrose was third with 26 per cent moisture absorbed in 76 days and the smallest quantity was absorbed by lactose (0.07) and galactose (0.11 per cent).

When the sugar samples were kept in the desiccator with a relative humidity of 98.8 per cent, they absorbed large quantities of moisture, with the exception of lactose. In 40 days levulose absorbed the greatest quantity, 54.99 per cent; saccharose absorbed 45.62, dextrose 42.82, galactose 16.42, and lactose only 0.38 per cent. On the first day maltose became moldy and was not weighed. After having absorbed 15–18 per cent moisture, levulose, saccharose, and dextrose began to liquefy.

These experiments showed that, when the specimens were kept a certain length of time, the greatest hygroscopicity was exhibited by levulose and the least by lactose. After crystalline sugars absorbed 16–18 per cent moisture, they became liquids. Maltose absorbed a large quantity of moisture within the first few days, and became moldy at the same time.

Caramel Test

Absorption of moisture by caramel, made from saccharose with the addition of different sugars, was carried out at relative humidities of 43, 62.7, and 81.8 per cent.

Various kinds of caramel were prepared as follows:

Compn. No.	Saccharose Grams	Treacle (Dry) Grams	Other Ingredient Grams
1	100	+40	....
2	100	+35	5 dextrose
3	100	+30	10 dextrose
4	100	+35	5 maltose
5	100	+37.5	2.5 levulose
6	100	+35	5 dextrin
7	100	+37.5	2.5 starch

The caramels were prepared in the laboratory at 135° C. in a 740-mm. vacuum. The initial humidity of all the samples was between 0.4 and 0.8 per cent. The air temperature was 25° C. The samples were placed in dried and weighed vessels, which were then reweighed and placed in a desiccator with a close-fitting lid. The quantity of absorbed moisture was determined by weighing the samples at different intervals.

As shown in Table II, caramel is highly hygroscopic and attracts moisture even at a low relative humidity. The hygroscopicity of caramel is higher than that of its different ingredients. The composition of the caramel has little effect upon its hygroscopicity.

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Table II. Moisture Absorption by Caramel at Various Relative Humidities (25° C.)

Caramel No.	Per Cent Moisture Absorbed in: 1 day	3 days	5 days	11 days	20 days	26 days	32 days	40 days	50 days	60 days	75 days	Start of Crystallization Days
					Relative Humidity, 43 Per Cent							
1	0.15	0.28	0.34	0.56	0.66	0.81	0.87	0.9	1.06	1.18	1.2	20
2	0.29	0.35	0.46	0.65	0.75	0.88	0.93	1.01	1.13	1.14	1.18	26 (grew cloudy in 11 days)
3	0.25	0.31	0.41	0.56	0.63	0.74	0.76	0.78	0.85	0.86	0.96	3
4	0.21	0.32	0.40	0.67	0.84	0.91	0.99	1.07	1.37	1.4	1.4	20
5	0.33	0.34	0.41	0.56	0.66	0.7	0.73	0.81	0.92	0.97	0.98	3
6	0.32	0.36	0.45	0.72	0.84	1	1.08	1.13	1.41	1.41	1.48	3
7	0.25	0.32	0.36	0.52	0.61	0.64	0.69	0.73	0.82	0.82	0.88	3
					Relative Humidity, 62.7 Per Cent							
1	0.83	2.29	2.35	2.65	3.28	3.58	3.61	4.1	3.9	4.15	4.82	3
2	0.69	0.94	2.09	2.52	4.04	4.69	4.64	...	4.85	5	5.88	3 (started to liquefy in 5 days)
3	0.73	1.79	2.03	2.67	4.52	5.31	...	...	5.67	5.73	6.39	3 (started to liquefy in 3 days also)
4	0.06	1.73	1.92	2.2	2.83	3.17	3.1	3.58	3.48	3.61	4.3	3 (started to liquefy in 7 days)
5	0.66	1.27	1.39	1.73	3.28	3.73	3.37	3.67	3.78	3.92	4.6	3 (started to liquefy in 11 days)
6	0.61	1.53	1.6	2.06	2.91	3.22	3.28	3.83	3.63	3.92	4.46	5 (started to grow cloudy in 3 days)
7	0.66	1.43	1.45	1.74	2.42	2.73	2.79	3.81	3.42	3.47	3.93	3
					Relative Humidity, 81.8 Per Cent							
1	2.36	7.2	10.87	15.32	18.45	19.18	...	21.64	21.93	22.61	..	All the specimens began to crystallize in 8 to 12 hours; in 40 to 50 hours they began to liquefy; in 40 days they began to be covered with mold.
2	1.91	5.56	8.16	11.76	16.01	16.16	18.46	18.21	20.79	21.81	..	
3	1.77	5.04	7.81	12.12	15.97	17.04	20.27	19.99	19.89	21.08	..	
4	1.83	4.97	7.24	9.22	12.29	13.89	14.34	16.65	16.62	18.32	..	
5	1.44	3.83	5.92	8.57	11.33	12.34	14.5	14.59	15	15.05	..	
6	2	4.81	7.09	10.11	13.25	15.3	17.79	17.84	18.77	19.23	..	
7	1.71	3.59	4.64	6.97	8.85	11.15	12.81	13.52	15.68	15.62	..	

Heats of Formation of Simple Organic Molecules[1]

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Sufficiently accurate values are available for the normal paraffin hydrocarbons, one or two of the branched-chain paraffin hydrocarbons, the primary normal alkyl alcohols, the normal olefin (1-alkene) hydrocarbons, and those isomeric olefins for which accurate data on heats of hydrogenation have recently been obtained.

The existing values for the remaining simple organic compounds (branched-chain paraffin hydrocarbons, naphthene or cycloparaffin hydrocarbons, aromatic hydrocarbons, isoalkyl, secondary, and tertiary alcohols, ethers, ketones, aldehydes, acids, amines, cyanides or nitriles, sulfur compounds, and halogen compounds) depend, with a few exceptions, upon work done from 30 to 80 years ago. These values need to be redetermined on pure samples, with an accuracy commensurate with the possibilities of the calorimetric and analytical chemical apparatus available today.

The acquisition of these thermochemical data is desirable from the standpoint of their practical importance to industry and of their theoretical interest to science.

WITHIN the past fifteen years, the simpler organic molecules have assumed an importance of new magnitude in the chemical and petroleum industries. Organic molecules are being treated in many different types of reactions (such as addition, polymerization, oxidation, hydration or dehydration, hydrogenation or dehydrogenation, and decomposition) to produce, on a large scale, molecules hitherto available only in the laboratory. These industrial chemical syntheses are made economically possible because the substances produced have physical and chemical properties which permit them to fill with particular advantage the specialized services arising from the ever-expanding needs of our modern civilization. In the petroleum industry, especially, some of the above reactions are being carried out on a large scale to produce superior motor fuels for both land and air service in quantities which are increasing almost geometrically.

After the first rush of success in any virgin field of endeavor, the increase of competition makes necessary greater economy in operation and higher efficiency in processing methods. At this point inquiry must be made as to whether the chemical reactions involved in the given processes are being carried on under the optimum conditions of greatest economy and highest yield. Two important criteria in this respect are the rate and the free energy of the reaction. The rate of the reaction can usually be made sufficiently great by the selection of an appropriate catalyst and of a temperature compatible with the desired free energy. The question as to whether the reaction will proceed at all in the desired direction, and to what extent under given conditions of temperature and pressure, can be answered by the empirical and costly methods of trial and error or by simple calculation from the thermodynamic constants of the substances involved. One of the most important factors in this latter calculation is the heat of the given reaction; and an accurate value for this must be known to obtain a reliable thermodynamic analysis of the process.

The foregoing discussion gives some idea of the immediate technical importance of the heats of formation of organic molecules. Another value of such data lies in the more fundamental question of the energies of the atomic linkages in these molecules—the energy of binding which keeps atoms together in certain preferred structural relations. These bond energies are important in the calculation of energies of activation and rates of reaction, which yield information concerning the "mechanism" of given reactions. Although certain other data are also required in evaluating bond energies, the heat of formation is the keystone in the calculation.

The purpose of the present paper is to discuss the heats of formation of the simple organic molecules, to show how inadequate are the data from the standpoint of the needs of present-day science and technology, and to point out certain structural regularities that will simplify the acquisition of these much needed data.

Evaluation of Heats of Formation

In the assembly of a thermochemical table giving the heats of formation of the organic compounds from their elements, the values for the elements, carbon, hydrogen, oxygen, nitrogen, sulfur, fluorine, chlorine, bromine, iodine, etc., are arbitrarily assigned values of zero in their "standard" states at the "standard" temperature. A value for the heat of formation of a given organic molecule is then obtained from experimental data on the heat of a reaction in which all the reactants and products, except the given substance, are ones whose heats of formation from the elements are known. Appropriate addition and subtraction of values from the table will then give the value of the heat (ΔH) associated with a given reaction.

Because of its simplicity of execution, the reaction of combustion in oxygen has been the classical one employed to

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[1] Part of the Symposium on Characteristic Properties of Hydrocarbons and Their Derivatives as Related to Structure presented before the Division of Petroleum Chemistry at the 94th Meeting of the American Chemical Society, Rochester, N. Y., September 6 to 10, 1937.

determine heats of formation of organic compounds. For compounds containing only carbon, hydrogen, and oxygen, and in some cases nitrogen, the reaction of combustion is complete and clear-cut; but for compounds containing sulfur or a halogen, the simplicity of execution of the combustion reaction is misleading because of the complicated nature of the reaction and of the uncertainty as to the actual products of the reaction and their final states. Unless the identity and state of each of the products of the reaction can be established within the desired limits of accuracy, the experimentally measured heat of combustion has no thermodynamic significance. This latter point introduces a large chemical uncertainty, in addition to the calorimetric uncertainty, into many of the old thermochemical data.

Another point that must be emphasized in connection with evaluation of the heat of formation of a substance from data on its heat of combustion is that, in order that the uncertainty in the heat of formation shall be small, the heat of combustion must be measured with high accuracy. For example, the heat of combustion of gaseous *n*-hexane is twenty-five times the value of its heat of formation from solid carbon and gaseous hydrogen, so that an error of 0.1 per cent, or 1 kilocalorie per mole, in the heat of combustion contributes 1 kilocalorie per mole or 2.5 per cent uncertainty to the heat of formation.

It is sometimes possible and desirable to determine the difference in the heats of formation of two organic molecules directly—for example, by measurement of the heat of hydrogenation of an olefin hydrocarbon to the corresponding paraffin. Even in this case where the difference in the heats of formation is known, however, it is necessary to have the heat of formation of either the olefin or the paraffin hydrocarbon, from solid carbon and gaseous hydrogen, determined in separate sets of experiments, as by combustion.

In connection with the evaluation of heats of formation from data on heats of combustion, it is desirable to have accurate values for the heats of formation of gaseous carbon dioxide from gaseous oxygen and a reproducible form of solid carbon, and of liquid water from gaseous hydrogen and oxygen. The National Bureau of Standards (*77*, *87*) determined in 1930 a value for the heat of formation of water which has been selected as a standard by the International Committee on Thermochemistry (*106*), and is now carrying on an investigation on the heat of formation of carbon dioxide from diamond and several samples of artificial and natural graphite. The Coal Research Laboratory of the Carnegie Institute of Technology has recently completed measurements on the heats of combustion of four different samples of natural graphite and two samples of artificial graphite. When these new data are available, they should do much to clarify the thermochemistry of solid carbon and provide a reliable standard value for the heat of formation of carbon dioxide from a reproducible and known state of solid carbon (*23*, *81*).

Existing Thermochemical Data

Before examining the existing thermochemical data on the simple organic compounds, it may be well to consider to what extent errors in the heat (ΔH) of a given reaction affect the calculated value of the free energy (ΔF) or the equilibrium constant (K). At 380° C. (653° K.) an error of 3 kilocalories per mole makes an error of the same magnitude in the free energy change (ΔF) and causes the equilibrium constant to be in error by a factor of 10. It would seem, therefore, that for most reactions involving simple organic molecules an error of 2 or 3 kilocalories per mole would be very significant.

Until several years ago the great body of the thermochemical data on organic compounds was dependent upon experimental data obtained from 30 to 80 years ago in the European laboratories of Thomsen, Berthelot, Louguinine, Zubow, Stohmann, and others. References to these early investigations are given in the compilation by Kharasch (*43*), and, for molecules of 1 and 2 carbon atoms, by Bichowsky and Rossini (*23*). In connection with these old data two points must be emphasized: (*a*) These early investigators and their coworkers performed exceedingly well with the meager apparatus and the more or less impure materials available to them; (*b*) these old data fall short of meeting the present-day requirements of accuracy which have increased tenfold or more in the past half-century (*84*, *86*).

This latter point is exemplified by the following comparisons between the old values of the heats of combustion of some gases, taken from the International Critical Tables (*39*), and new values recently obtained at the National Bureau of Standards (*78–83*, *88–90*):

Gas	Heat of Combustion at 25° C., Kcal./Mole		
	Old value	New value	Difference
CH_4	210.6	212.79 ± 0.07	2.2
C_2H_6	368.2	372.81 ± 0.11	4.6
C_3H_8	526.0	530.57 ± 0.12	4.6
n-C_4H_{10}	No data	687.94 ± 0.15	...
Iso-C_4H_{10}	683.0	686.31 ± 0.13	3.3
n-C_5H_{12}	837.8	845.27 ± 0.21	7.5
C_2H_4	332	337.28 ± 0.07	5.3
C_3H_6	490.0	491.82 ± 0.15	1.8
CH_3OH	179.7	182.58 ± 0.05	2.8
C_2H_5OH	338	336.80 ± 0.10	−1.2

These differences are of such a magnitude that, if there are no compensating factors, the calculated equilibrium constant at 380° C. will be changed by factors ranging from 2.5 to 300.

From the above data on the simplest of all organic molecules, it may be concluded that practically none of the old data on organic compounds can be used in thermodynamic calculations where errors in ΔH of several kilocalories per mole are significant.

It is of interest to examine the extent of the existing data on the simple organic molecules, including only those with from 1 to 6 or 7 carbon atoms per molecule, from the following classes of compounds: paraffin (alkane) hydrocarbons, olefin (alkene) hydrocarbons, acetylene (alkine) hydrocarbons, naphthene or cycloparaffin hydrocarbons, aromatic hydrocarbons, alcohols, ethers, ketones, aldehydes, acids, amines, cyanides or nitriles, sulfur compounds, and halogen compounds.

Paraffin Hydrocarbons

Sufficiently accurate values are now known for all the normal or straight-chain paraffin hydrocarbons. Within the past seven years the heats of combustion of all the normal paraffins from methane to dodecane, inclusive, have been measured at the National Bureau of Standards (*41*, *78*, *80*, *81*). From the data on the normal paraffin hydrocarbons the writer recently deduced (*81*) the following generalization: In any organic molecule containing a normal alkyl group of more than 5 carbon atoms, the addition of a methylene group to the normal alkyl group to form the next higher normal alkyl group results in an increase in the heat of combustion of the organic molecule in the gaseous state, at 25° C. and a constant total pressure of 1 atmosphere, of 157.00 ± 0.08 kilocalories per mole.

There are seven branched-chain paraffin hydrocarbons with 6 or fewer carbon atoms per molecule—one butane, two pentanes, and four hexanes. No data have ever been reported for three of the isomeric hexanes—2-methylpentane, 3-methylpentane, and 2,2-dimethylbutane. In 1886 Thomsen (*105*) reported values for isobutane, tetramethylmethane, and 2,3-dimethylbutane. In 1923 Roth and Macheleidt (*95*) reported a value for 2-methylbutane which was later withdrawn (*91*). In 1936 Roth and Pahlke (*96*) reported another value for 2-methylbutane. In 1935 the writer reported a value for isobutane (*83*). Within the next several years the National Bureau of Standards plans to obtain new values for the two branched pentanes and the four branched hexanes. When these data become available, it is hoped that it will be possible to deduce, without measurement, values for all the higher branched-chain paraffins, at least for the gaseous state (*81*).

Olefin Hydrocarbons

Within the past several years data have been obtained which yield satisfactory values for the heats of formation of the normal olefin (1-alkene) hydrocarbons. The heats of combustion of ethylene and propylene were measured at the National Bureau of Standards (*89*), and the heats of hydrogenation of ethylene, propylene, *n*-butene-1, and *n*-heptene-1 were measured at Harvard University (*44, 45, 46*). Combination of the data on heats of combustion with values for the heats of formation of water and carbon dioxide yields values for the heats of formation. The data on heats of hydrogenation yield the difference in the heats of formation of the given olefin and its corresponding paraffin hydrocarbon, and, if a value for the heat of formation of the paraffin is available, then that for the olefin hydrocarbon becomes known. Utilizing the foregoing data, together with the previously reported values for the normal paraffin hydrocarbons and the rule regarding the increment in heat content per added methylene group for normal alkyl groups of more than 5 carbon atoms, Rossini and Knowlton (*90*) computed values for the heats of formation of all the normal olefin (1-alkene) hydrocarbons in the gaseous state.

With regard to the isomeric butenes, pentenes, and hexenes, the data existing prior to 1935 were meager, consisting of values reported for isobutene and trimethylethylene by Thomsen (*105*) in 1886, and a value for trimethylethylene by Zubow (*114*) in 1898. However, in 1935 and 1936 important and extensive data on heats of hydrogenation were reported by Kistiakowsky, Vaughan, and co-workers (*27, 44–47*) for the following molecules: *n*-butene-2 (*cis*), *n*-butene-2 (*trans*), isobutene, *unsym*-methylethylethylene, *n*-pentene-2 (mixture of *cis* and *trans*), *unsym*-methylisopropylethylene, trimethylethylene, tetramethylethylene, isopropylethylene, *tert*-butylethylene, neoamylethylene, 2,4,4-trimethylpentene-1, 2,4,4-trimethylpentene-2, 1,3-butadiene, 1,4-pentadiene, 1,3-pentadiene, 1,5-hexadiene, and 2,3-dimethylbutadiene-1,3. As pointed out above, these data on heats of hydrogenation will yield a value for the heat of formation of the olefin if that for the corresponding paraffin is known. Sufficiently reliable values for the branched-chain paraffins appear to be available only for isobutane and possibly 2-methylbutane. There is, therefore, a pressing need for values for the heats of formation of the branched-chain paraffin hydrocarbons, so that all the foregoing data on hydrogenation can be utilized to yield accurate values for the heats of formation of these olefin hydrocarbons.

Acetylene Hydrocarbons

With several exceptions the data on the simple alkines are those of Thomsen and Berthelot: acetylene, Berthelot (*5*) in 1881, Thomsen (*105*) in 1886, Berthelot and Matignon (*19*) in 1893, Mixter (*65*) in 1906; allylene, Thomsen (*105*) in 1886; dipropargyl (1,5-hexadiine), Berthelot (*6*) in 1881 and Thomsen (*105*) in 1886; dimethyldiacetylene (2,4-hexadiine), Louguinine (*60*) in 1888; 1-heptine, Moureu and André (*66*) in 1914.

Naphthene or Cycloparaffin Hydrocarbons

The data on the simple naphthene, cycloparaffin, or polymethylene hydrocarbons are meager. Values for cyclopropane were reported by Thomsen (*105*) in 1886 and by Berthelot and Matignon (*19*) in 1893, the difference in the two values being of the order of 7 kilocalories per mole. The heat of combustion of cyclobutane has never been measured. Zubow (*114–116*) reported values in 1898–1903 for methylcyclobutane, cyclopentane, methylcyclopentane, and cyclohexane. Data for cyclohexane were also reported in 1915 by Roth and von Auwers (*94*) and by Richards and Barry (*73*), but their values differ by over 3 kilocalories per mole.

Aromatic Hydrocarbons

Data on benzene and toluene were reported by Stohmann and co-workers (*102, 103*) in 1886–87, by Roth and von Auwers (*94*) in 1915, and by Richards and co-workers (*73, 74, 76*) from 1910 to 1917. The values from the latter two laboratories differ by over 1 kilocalorie per mole for benzene and by nearly 3 kilocalories per mole for toluene.

Alcohols

The data on the primary normal alkyl alcohols were recently reviewed by the writer (*82*). Data obtained on methyl and ethyl alcohols at the National Bureau of Standards (*79*) in 1932, on the primary normal alkyl alcohols from butanol to decanol, inclusive, by Verkade and Coops (*109*) in 1927, and on *n*-propanol-1 and *n*-butanol-1 by Richards and Davis (*74, 75*) in 1917–20 were utilized, in conjunction with the rule concerning the energy increment per added methylene group in a normal alkyl radical of more than 5 carbon atoms, to deduce fairly reliable values for the heats of formation of all the primary normal alkyl alcohols (*82*).

The data on the isoalkyl, secondary, and tertiary alcohols are far from satisfactory. With the exception of a value for isobutyl alcohol reported in 1917 by Richards and Davis (*74*), no thermochemical data on any of these monohydroxy alcohols have been obtained in the present century. Thomsen (*105*) reported a value for propargyl alcohol in 1886. Values for allyl alcohol and ethylvinylcarbinol were reported by Louguinine (*56*) in 1880. Data on isopropyl alcohol and trimethyl-, dimethylethyl-, and allyldimethylcarbinol were reported by Louguinine (*53, 54, 55*) in 1880–82 and by Zubow (*113–116*) in 1898–1903. In the same period Zubow (*113–116*) reported data on isobutyl, pinacolyl, and cyclobutyl alcohols and on methyldiethylcarbinol.

Ethers

No data on the simple ethers have been reported for half a century. In 1881 Berthelot (*5*) published values for dimethyl ether. In 1886 Thomsen (*105*) gave data for dimethyl, methyl ethyl, methyl propargyl, methyl allyl, and diallyl ethers. In 1887 Stohmann (*100*) reported a value for diethyl ether.

Ketones

With several exceptions the data on the simple ketones are also over 50 years old: allylacetone and ethyl allyl ketone, Roth (*93*) in 1911; acetone, Delépine (*26*) in 1900, and Emery and Benedict (*28*) in 1911; diethyl ketone and mesityl oxide, Louguinine (*57, 58*) in 1884–85; methyl propyl ketone, Thomsen (*105*) in 1886; methyl ethyl, diethyl, methyl propyl, methyl butyl, and *tert*-butyl methyl ketone, Zubow (*114*) in 1898.

Aldehydes

The data on the simple aldehydes are meager: formaldehyde, von Wartenberg and co-workers (*111*) in 1924; acet- and propionaldehyde, Berthelot and co-workers (*15, 22*) in 1881 and 1899, and Thomsen (*105*) in 1886; glyoxal, de Forcrand (*33*) in 1884; and acetaldehyde, Louguinine (*60*) in 1889.

Acids

Data on the simple organic acids were reported as follows: formic acid, Favre and Silbermann (*32*) in 1852, Berthelot (*1, 2*) in 1873–75, Thomsen (*105*) in 1886, Jahn (*40*) in 1889, Berthelot and Matignon (*17, 20*) in 1892; acetic acid, Thomsen (*105*) in 1886, Berthelot and Matignon (*16*) in 1892; propionic acid, Louguinine (*59*) in 1885, Stohmann and co-workers (*101*) in 1894; *n*-butyric acid, Stohmann and co-workers (*101*) in 1894, Guillemard (*35*) in 1908; isobutyric acid, Louguinine (*58*) in 1885. All of these data are from 30 to 50 years old. In 1927 Roth (*48, 92*) reported a value for acetic acid, and in 1935 Schjanberg (*97*) gave data for acetic and propionic acids. The newer values for acetic acid differ by about 2 kilocalories per mole (nearly 1 per cent of the measured value).

Amines

With the exception of values for trimethylamine and ethylamine reported by Berthelot (*8*) in 1881, all of the existing data on the simple primary, secondary, and tertiary amines were reported by three investigators: Thomsen in 1886, Muller in 1885 and 1910, and Lemoult in 1907. Thomsen (*105*) reported values for methyl-, ethyl-, *n*-propyl-, allyl-, dimethyl-, diethyl-, trimethyl-, and triethylamine; Muller (*67, 68*) on methyl-, dimethyl-, diethyl-, trimethyl-, and triethylamine; Lemoult (*51*) on methyl-, ethyl-, *n*-propyl-, *n*-butyl-, isobutyl-, *sec*-butyl-, *tert*-butyl-, allyl-, dimethyl-, diethyl-, trimethyl-, and triethylamine.

Cyanides or Nitriles

The existing data on the simple nitriles are neither plentiful nor new. Thomsen (*105*) reported data on acetonitrile in 1886 and Lemoult (*52*) on aceto- and propionitrile in 1909. For hydrogen cyanide, only two determinations were reported: Berthelot (*9*) in 1881 and Thomsen (*105*) in 1886. For cyanogen, values were reported in 1879 by Berthelot (*3*), in 1886 by Thomsen (*105*), and in 1933 by von Wartenberg and Schütza (*112*) and by McMorris and Badger (*62*). Unfortunately the two latter modern determinations yield values which differ by 10 kilocalories per mole (about 4 per cent of the measured value).

Sulfur Compounds

On the simple sulfur compounds, data have been reported only by Thomsen and Berthelot. Thomsen (*105*) in 1886 reported values for carbonyl sulfide, carbon disulfide, methyl and ethyl mercaptans, and dimethyl sulfide. Berthelot gave data on carbon disulfide (*7, 10*) in 1881 and 1893, and on ethyl mercaptan (*13, 14*) in 1901.

Halogen Compounds

With several exceptions, data on the simple chloro-, bromo-, and iodo-methanes, ethanes, and ethylenes were reported only from the laboratories of Thomsen and Berthelot. In 1886 Thomsen (*105*) reported values for CH_3Cl, $CHCl_3$, C_2H_5Cl, CH_2ClCH_2Cl, CH_3CHCl_2, CCl_4, CH_3Br, C_2H_5Br, CH_3I, and C_2H_5I. From 1881 to 1900 Berthelot and his co-workers (*4, 10, 11, 12, 18, 21, 22*) gave data on CH_3Cl, CH_2Cl_2, $CHCl_3$, CCl_4, C_2H_5Cl, CH_3CHCl_2, CH_3Br, C_2I_4, CH_3I, CH_2I_2, CHI_3, and CH_2ICH_2I. In 1930 Kablukow and Perelman (*42*) reported values for $CHCl_3$, $CHBr_3$, and CH_2BrCH_2Br, and in 1933 Popoff and Schirokich (*72*) reported a value for CH_2Br-CH_2Br. Unfortunately the uncertainties in these new values range from 7 to 20 kilocalories per mole. In 1926 Bodenstein and co-workers (*24*) reported data on the reaction of CCl_4 with hydrogen to form solid carbon and gaseous hydrogen chloride.

New Data Needed

The foregoing résumé shows that accurate values are greatly needed for the heats of formation of the following compounds:

Paraffin hydrocarbons: the branched-chain pentanes and hexanes.
Olefin hydrocarbons: the branched-chain olefins. (Values for the corresponding branched-chain paraffins will suffice, since data on the heats of hydrogenation are already available.)
Naphthene or cycloparaffin hydrocarbons: cyclopropane, cyclobutane, cyclopentane, cyclohexane, cycloheptane, and their simple alkyl derivatives.
Aromatic hydrocarbons: benzene and its simple alkyl derivatives.
Alcohols: all the simple isoalkyl, secondary, and tertiary alcohols.
Ethers: all the simple aliphatic ethers.
Ketones: all the simple aliphatic ketones.
Aldehydes: all the simple aliphatic aldehydes.
Acids: all the simple aliphatic acids.
Amines: all the simple primary, secondary, and tertiary aliphatic amines.
Cyanides or nitriles: hydrogen cyanide, cyanogen, and the simple aliphatic nitriles.
Sulfur compounds: carbonyl sulfide, carbon disulfide, and the simple alkyl mercaptans.
Halogen compounds: all the simple chloro-, bromo-, and iodomethanes, ethanes, and ethylenes.

Bond Energies

As has been known for many years (*30, 31, 34, 63, 69, 99*), it is possible to express, to a more or less rough approximation, the energy of formation of a molecule from its constituent atoms, each in the normal gaseous state, as the sum of constant terms representing the energies of the various atomic linkages in the molecule. For example, in the formation of ethane from gaseous carbon and hydrogen atoms,

$$2C\ (\text{gas}) + 6H\ (\text{gas}) = C_2H_6\ (\text{gas}) \tag{1}$$

the energy of formation can, to this rough approximation, be written as

$$-\Delta E = 6a + b \tag{2}$$

where a and b are numbers assigned to represent, respectively, the energies of the carbon-hydrogen and carbon-carbon bonds. As recently as 1933 the existing data on the paraffin hydrocarbons appeared to indicate a linearity in the heat of formation with the number of carbon atoms in the molecule (*70, 99*), which linearity leads to agreement with the relation of the additivity of bond energies as given by Equation 2. However, it was also observed at that time (*99*) that, when an atom other than carbon or hydrogen (such as a halogen atom) was introduced into each member of the series of homologous molecules, the simple additivity relation was apparently thrown out of line.

Within the past several years it has been demonstrated both experimentally and theoretically that for accurate values the energy of formation of a molecule is not capable of such a simple expression as that given by Equation 2. From the new experimental data on the normal paraffin hydrocarbons, it was shown (*81*) that the atomic energy of formation cannot be expressed accurately as a linear function of the number of carbon atoms, or by the simple addition of constant values of the carbon-carbon and carbon-hydrogen bond energies. Furthermore, the new data indicated that the energies of formation of the simple isomeric paraffin hydrocarbons are significantly different; the difference between *n*-butane and isobutane was found by measurement to be 1.6 kilocalories (*83*), and that between *n*-pentane and tetramethylmethane was estimated to be about 5 kilocalories per mole (*85*). From these data, it was concluded (*81*) that even in these simple hydrocarbons each atom has a measurable sphere of influence that includes the atoms twice removed from it, so that there is a specific interaction between atoms, either carbon or hydrogen, which are not directly linked to one another but which are attached to the same carbon atom.

It has also been pointed out (*36, 64, 69, 107, 110*) that, in evaluating the true energy of the atomic linkages in molecules, due cognizance must be taken of the fact that some of the atoms in combination in the molecule may not be in their normal state but will be in an excited valence state. If all the atoms of one kind—the carbon atoms, for example—are in the same state in the molecule, the inclusion of this excitation energy term will not change the linear relation given by Equation 2, but will change only the values of the constants giving the energies of the links of which the particular kind of atom is a member. For example, if the energy state of the carbon atom in combination in the paraffin hydrocarbons is q calories per mole above the normal state of the atom, then the conventional value assigned to the carbon-hydrogen and carbon-carbon links will be increased, respectively, by $q/4$ and $q/2$ calories per mole.

In making calculations leading to bond energies, it is desirable to correct the experimental values of the energies of formation down to the absolute zero of temperature, where the atoms and molecules will possess no energy of translation, rotation, or vibration, with the exception, for the molecules, of the zero-point vibrational energy of one-half quantum. In making assignments of true bond energies, it is necessary to take account of this zero-point energy. If for the 2 molecules, X_2 and Y_2, the true energies of binding are identical, then the values of ΔE at 0° K. for the energies of the reactions

$$X_2 = 2X \text{ and } Y_2 = 2Y$$

will differ by an amount equal to the difference in the zero-point energies, which is essentially $\frac{1}{2}\, h\, (\nu_{X_2} - \nu_{Y_2})$, where h is Planck's constant and ν_{X_2} and ν_{Y_2} are, respectively, the fundamental frequencies of vibration of the molecules X_2 and Y_2.

It appears, then, that any accurate representation of the energies of the atomic linkages in organic molecules must consider the following points, either individually or in certain combinations which may make a workable resultant: (*a*) the simple and direct energy of binding of the directly attached atoms; (*b*) the various interaction energies between all atoms twice removed from one another; (*c*) the energy of excitation of the carbon atoms to the appropriate valence state; (*d*) the correction to the absolute zero of temperature to eliminate translational, rotational, and ordinary vibrational energy; and (*e*) the zero-point energy.

It does not seem possible at present to reproduce, within the narrow experimental error, the heats of formation of those compounds for which accurate data exist, by means of considerations of bond energies including the points outlined above. However, progress is being made in this direction by theoretical chemists and physicists (*25, 29, 61, 70, 71, 98, 104, 107, 108, 110*).

It is not possible at this time to evaluate accurately the atomic energies of formation of organic molecules, because an indisputable value for the energy of formation of gaseous monatomic carbon has not yet been established.

The energy of the reaction

$$\mathrm{C\ (gas) + 4H\ (gas) = CH_4\ (gas)} \qquad (3)$$

is derivable from two series of reactions. The first series is:

$$\mathrm{CH_4\ (gas) + 2O_2\ (gas) = CO_2\ (gas) + 2H_2O\ (liquid)} \qquad (4)$$
$$\mathrm{2H_2\ (gas) + O_2\ (gas) = 2H_2O\ (liquid)} \qquad (5)$$
$$\mathrm{CO\ (gas) + {}^1\!/_2O_2\ (gas) = CO_2\ (gas)} \qquad (6)$$
$$\mathrm{2H_2\ (gas) = 4H\ (gas)} \qquad (7)$$
$$\mathrm{{}^1\!/_2O_2\ (gas) = O\ (gas)} \qquad (8)$$
$$\mathrm{CO\ (gas) = C\ (gas) + O\ (gas)} \qquad (9)$$

Addition of reactions 5, 6, and 8, and subtraction of 4, 7, and 9 yield the desired reaction 3. In this series accurate values are known for the heats of reactions 4, 5, and 6 from calorimetric data, and for 7 and 8 from spectroscopic data. The value for the energy change for reaction 9, in principle derivable directly from spectroscopic data, has never been ac-

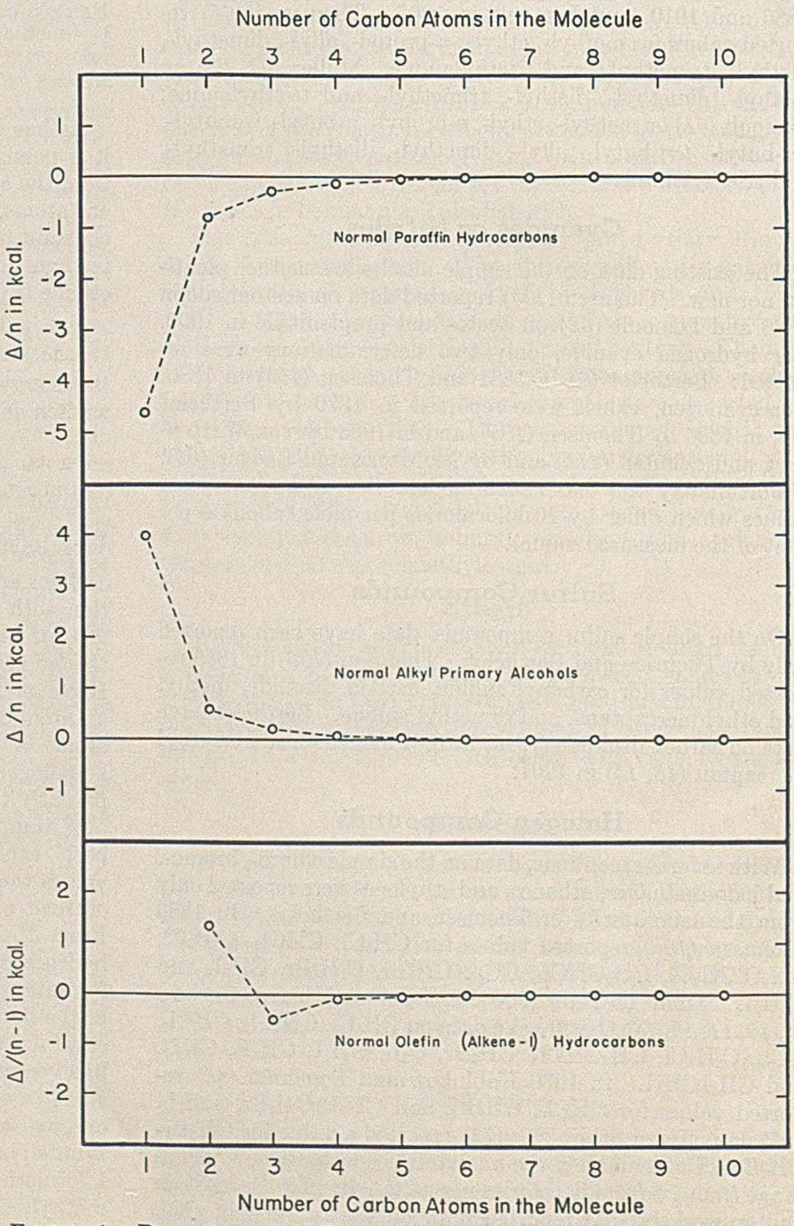

FIGURE 1. DEVIATION FROM LINEARITY IN THE RELATION BETWEEN THE NUMBER OF CARBON ATOMS IN THE MOLECULE AND ITS HEAT OF FORMATION IN THE GASEOUS STATE AT 25° C.

curately established. The published values range from about 270 to 160 kilocalories per mole and yield, for reaction 3, values ranging from about 290 to 400 kilocalories. The value most favored at this time for the energy of dissociation of carbon monoxide according to reaction 9 is near 210 kilocalories per mole (*23*, *37*).

The second series of reactions is

$$\text{CH}_4\ (\text{gas}) + 2\text{O}_2\ (\text{gas}) = \text{CO}_2\ (\text{gas}) + 2\text{H}_2\text{O}\ (\text{liquid}) \tag{10}$$

$$2\text{H}_2\ (\text{gas}) + \text{O}_2\ (\text{gas}) = 2\text{H}_2\text{O}\ (\text{liquid}) \tag{11}$$

$$\text{C}\ (\text{crystal}) + \text{O}_2\ (\text{gas}) = \text{CO}_2\ (\text{gas}) \tag{12}$$

$$2\text{H}_2\ (\text{gas}) = 4\text{H}\ (\text{gas}) \tag{13}$$

$$\text{C}\ (\text{crystal}) = \text{C}\ (\text{gas}) \tag{14}$$

Addition of reactions 11 and 12 and subtraction of 10, 13, and 14 yield the desired reaction 3. In this series accurate values are known for the heats of reactions 10 and 11, and a fairly accurate value is known for reaction 12, from calorimetric data; an accurate value for reaction 13 is known from spectroscopic data. Unfortunately an indisputable value for the heat of sublimation of solid carbon to gaseous monatomic carbon has not yet been established (*23*, *37*, *38*). The published values range from about 130 to 210 kilocalories per mole, and these yield values ranging from about 350 to 430 kilocalories per mole for the energy of reaction 3.

It is hoped that the recent theoretical work of Herzberg et al. (*37*, *38*) and the new experimental work on the vapor pressure of carbon, carried on by Johnston and Marshall in the laboratories of the General Electric Company, will soon resolve the existing discord among the various data involving the energy of formation of gaseous monatomic carbon, so that accurate values for the atomic energies of formation of organic molecules may be calculated.

Regularities in Heats of Formation

Since it has been definitely established that the heats of formation of organic compounds cannot be reproduced accurately by means of simple equations, it is desirable to see just what regularities do exist, and whether these regularities will not make it possible to deduce, without actual measurement, values for some of the molecules.

The data on the gaseous normal paraffin hydrocarbons show that the energy content of the members of this simple homologous series is a linear function of the number of carbon atoms for those molecules above *n*-pentane, but not linear below; and that the deviations from linearity are in the direction of lesser energy content, or greater stability, and increase to a maximum of nearly 5 kilocalories per mole for methane. These data make it possible to say exactly how much the energy content of a gaseous molecule containing a normal alkyl group of 5 or more carbon atoms will be increased on the addition of a methylene group to form the next longer normal alkyl group. For any homologous series of gaseous molecules Y—R (where Y is any atom, radical, or combination of atoms and R is a normal alkyl group) a knowledge of the heat of formation of the molecule having R equal to C_6H_{13} or, possibly with slightly more uncertainty, C_5H_{11}, immediately gives a knowledge of the heat of formation for all the members of the series with normal alkyl groups above pentyl. This means, then, that, in order to know the heats of formation for all the members of a homologous series of gaseous molecules, Y—R, it is necessary to determine experimentally values for not more than six of them—namely, Y—CH_3, Y—C_2H_5, Y—C_3H_7, Y—C_4H_9, Y—C_5H_{11}, and Y—C_6H_{13}. The deviations of the fourth and fifth members are so small that the value for Y—C_5H_{11} can be interpolated as accurately as it can be measured, and that for Y—C_4H_9 nearly so.

Figure 1 shows the values recently obtained for all the normal alkyl members of three homologous series of gaseous molecules: normal paraffin hydrocarbons, normal olefin (1-alkene) hydrocarbons, and primary normal alkyl alcohols. In Figure 1 the deviation from linearity of the heat of formation is plotted against the number of carbon atoms in the molecule. The heat of formation (ΔH) of the molecule Y—R can be represented as

$$\Delta H = A + Bn + \Delta \tag{15}$$

where A is a constant characteristic of the end group Y of the given homologous series, B is a universal constant for all series, and n is the number of carbon atoms in the normal alkyl radical R. Δ, the deviation from linearity, is zero for $n > 5$. For the three homologous series considered in Figure 1, the end group or radical, Y—, is H—, HO—, and $H_2C{=}CH$—, respectively. When the end group Y contains one or more carbon atoms, n in Equation 15 may, if desirable, be taken as the number of carbon atoms in the entire molecule by appropriately changing the value of constant A. Values of A for each of the above three homologous series of molecules, of constant B common to all series, and of Δ for each of the molecules with $n < 5$, have already been obtained (*81*, *82*, *90*).

In the case of the normal paraffin hydrocarbons, the deviations are uniformly in the direction of lesser energy content or greater stability. For the primary normal alkyl alcohols, the deviations are uniformly in the opposite direction of greater energy content or lesser stability. For the normal olefin (1-alkene) hydrocarbons the deviation for ethylene is in the direction of greater energy content or lesser stability; for the others it is in the direction of lesser energy content or greater stability.

The magnitude and sign of the deviation from linearity for the lower members of the series is determined by the specific interactions of the "near neighbor" atoms not directly attached to each other and by the deviation from linearity in the zero-point energies for the various members of the series. These contributions to the net deviation will be expected to be greatest for the first member of the series, and they may be of such sign and magnitude as to produce the irregular trend observed for the normal olefin (1-alkene) hydrocarbons.

Sufficiently accurate data for determining the effect of branching in the alkyl radical on the energy content of a given molecule are as yet available only for *n*-butane and isobutane (*83*). The data show that in this case branching results in a decrease (toward greater stability) in the energy content of the gaseous molecule of 1.63 ± 0.15 kilocalories per mole at 25° C., or of 1.55 ± 0.16 kilocalories at absolute zero temperature. By utilizing the experimental value for methane, ethane (monomethylmethane), propane (dimethylmethane), and isobutane (trimethylmethane), and extrapolating to tetramethylmethane, the writer estimated a value for the latter (*85*). This estimate indicates that the energy content of gaseous tetramethylmethane is less than that of gaseous *n*-pentane by 4.9 ± 1.0 kilocalories per mole. (It is expected that an experimental determination of the difference in the energies of these two isomers will soon be made.) Because of the paucity of the data, it is hardly safe to make any generalizations concerning the effect of branching except to say that branching appears to yield a lower energy content (toward greater stability).

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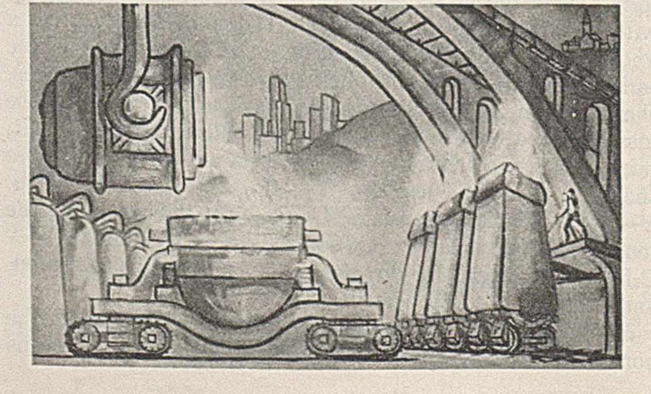

THE COOKING PROCESS

X. Pulping Wood with Alcoholic Nitric Acid Solutions[1]

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A series of cooks was made on aspen and jack pine sawdust and chips by refluxing with aqueous and alcoholic (ethyl and *n*-butyl) solutions of nitric acid, followed by boiling the acid-treated wood with dilute sodium hydroxide solutions. The concentrations of the acid and alkali as well as the duration of the treatment were varied. A number of cooks were also run with mixtures of aqueous and alcoholic nitric acid and with alcoholic solutions of sulfur dioxide and lithium bisulfite. The alcoholic nitric acid solutions gave much higher yields of good pulp than were obtained with the aqueous acid under similar pulping conditions. Increasing the concentration of the acid resulted in lower total yields but gave larger yields of screened pulp. Dilution of the alcoholic solutions with water had but little effect on the yields of pulp. Jack pine did not pulp as readily as the aspen. Soda ash was not as efficient as sodium hydroxide in removing the compounds formed by the action of nitric acid on wood. Sulfur dioxide and bisulfites in alcohol were not efficient pulping agents.

THE use of nitric acid as a pulping agent has received considerable attention in recent years. Although the pulping qualities of this acid were known as early as 1861 (*2*) and possibly earlier, its high cost prevented it from competing with the common cheap pulping agents used in the sulfite, soda, and kraft processes. The present relatively low cost of nitric acid and the search for an efficient, economical method of pulping fibrous plant material other than wood are probably the main reasons for the revival of this pulping method.

Brief reviews of recent research and patent literature on this process were given by Klein (*6*) and Krais (*8*). Hachihama, Onishi, and Takemura (*3*, *4*), Lynch and Goss (*10*), and Payne (*11*) showed that yields of 35–40 per cent of high α-cellulose pulp, with low copper numbers and ash contents, could be obtained from sugar cane bagasse by the nitric acid process. Relatively high yields of good pulp were obtained from cornstalks by Horváth and Éber (*5*) and Suida, Sadler, and Noss (*18*, *19*). Suida and Sadler (*17*) and Shimoda (*15*) obtained good pulp by cooking cereal straws with nitric acid. The effects of this acid on woods were studied by Routala and Sevón (*12*), Schaarschmidt and Nowak (*13*), Shimoda (*14*), Solechnik (*16*), and Suida and Sadler (*17*). They obtained 40–50 per cent yields of pulps with low copper numbers and ash contents and high α-cellulose contents. These pulping experiments were carried out by steeping the raw material in aqueous nitric acid solutions of various concentrations and temperatures for definite time intervals, and then heating the resultant product in hot alkalies.

An analytical method for the determination of the cellulose content of fibrous plant material was recently given by Kürschner and Hoffer (*9*). This method consists of repeated extraction of the plant material with a solution of nitric acid in ethanol. Aronovsky and Gortner (*1*) and Kleinert and Tayenthal (*7*) showed that fairly high yields of good pulp could be obtained by using alcohols as the pulping agents. It was therefore thought that high yields of pulp with desirable properties might be obtained by using a combination of these methods—i. e., treatment of the fibrous raw material with alcoholic nitric acid followed by extraction with dilute alkalies.

Experimental Procedure

Aspen and jack pine wood, both in chip and sawdust form, were used in these experiments. Ethyl and *n*-butyl alcohols and c. p. nitric acid and sodium hydroxide were used as the pulping agents. A number of cooks were made on jack pine wood in which sulfur dioxide and lithium bisulfite were used in place of the nitric acid as pulping agents. The procedure was as follows:

The wood (50 grams) and the liquor were placed in a 1-liter Erlenmeyer flask and boiled gently under reflux. The concentration of acid, volume of liquor, and time of refluxing were varied. After the desired boiling period had elapsed, the contents of the flask were poured into a large Büchner funnel fitted with a filter paper, and the excess liquor was removed by suction. The residue in the funnel was washed three or four times with 800-cc. portions of water and then replaced in the flask, covered with water, and allowed to stand overnight. The water was then decanted from the residual wood, a dilute solution of sodium hydroxide was added, and the mixture was again boiled under reflux, varying the volume and concentration of the sodium hydroxide solution and the time of boiling. The contents of the flask were then poured into a set of laboratory screens (top screen, 0.065-inch or 1.65-mm. openings; bottom screen, Four-

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[1] Previous papers in this series appeared in INDUSTRIAL AND ENGINEERING CHEMISTRY in 1930, 1933, 1934, 1935, and 1936.

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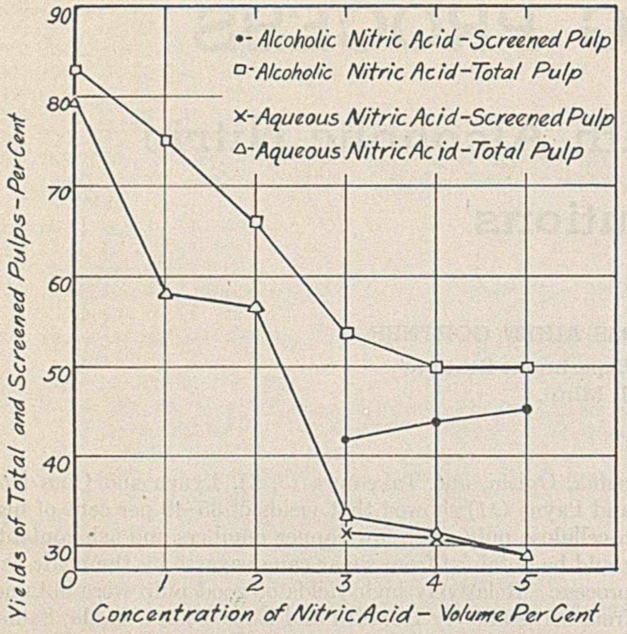

FIGURE 1. EFFECT OF NITRIC ACID CONCENTRATION ON YIELDS OF TOTAL AND SCREENED PULP

drinier wire) where the residue was washed and screened, if possible, to separate the pulp from the unpulped portion. The pulps and unpulped portions were then dried to constant weight in order to determine the yields obtained under the various experimental conditions.

The data obtained are given in Tables I and II and Figures 1 to 4.

Aspen

The first striking feature of the results on aspen (Table I) can be seen by comparing the yields obtained with ethanol and water, the other conditions remaining constant. This is shown particularly by cooks 154 and 156. The yield obtained by using alcoholic nitric acid was 1.7 times that produced by the aqueous nitric acid liquor. This result may be due to the action of the alcohol in hindering the hydrolytic effects of the acid upon the cellulosic constituents of the wood. When water was used in these cooks, the brown fumes of nitric oxide were given off from the top of the reflux condenser, indicating decomposition of the nitric acid. This effect was not noticed when alcoholic nitric acid was used as the cooking agent.

As shown in Figure 1 and by cooks 159 and 163 (Table I), the concentration of nitric acid in the liquor, whether water or ethanol, should be greater than 2 volume per cent in order to obtain pulped material. This may not hold true under conditions of cooking other than those employed here.

In the experiments conducted on aspen sawdust, the concentration of nitric acid was kept constant at 3 volume per cent. The total volume of liquor used was varied in cooks 170 to 177 (Table I), thus varying the actual quantities of nitric acid present in these cooks. The results show that the yields of screened pulp decreased and the screenings and total yields increased with the decrease in quantities of nitric acid and the ratios of total liquor to wood. This effect was more noticeable with alcohol than with water (Figure 2). Apparently the nitric acid delignifies the wood more readily in aqueous than in alcoholic solution, but the degradation of cellulose also takes place to a greater extent in water. Considerably lower yields were obtained with sawdust than with chips. This may have been due to the greater ease of impregnation and consequently more drastic cooking of the sawdust, under similar cooking conditions.

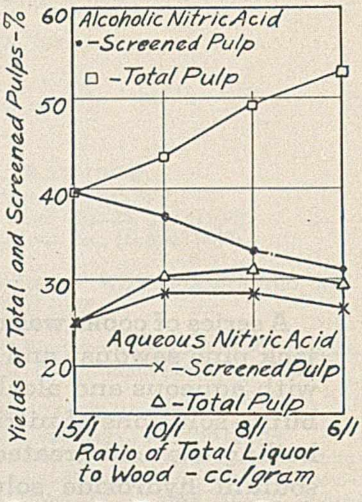

FIGURE 2. EFFECT OF RATIO OF TOTAL LIQUOR TO WOOD ON YIELDS OF TOTAL AND SCREENED PULP

The use of mixtures of water and ethanol gave results intermediate between those obtained with aqueous and with alcoholic nitric acid solutions, as shown in Table I and Figure 3. Eighty per cent ethanol and 20 per cent water gave nearly the same yield as was obtained with 100 per cent alcohol (cook 170). The substitution of 20 per cent of the water by ethanol (cook 181) gave a considerably larger yield than was obtained with 100 per cent water (cook 174), thus indicating that a relatively small amount of alcohol tends to inhibit the degrading effect of nitric acid on the cellulose. It was also noticed in these four cooks that no nitric oxide fumes were formed during the refluxing.

Using aqueous nitric acid solutions, varying the time of refluxing with these liquors, and keeping the other cooking conditions constant, the yields tended to decrease with increas-

TABLE I. COOKING DATA AND YIELDS OF PULP OBTAINED FROM ASPEN

		Acid Treatment			Alkaline Treatment		Pulp Yields[a]		
Cook No.	Liquor	Vol. HNO_3	Total vol.	Time of boiling	Vol. 2% NaOH	Time of boiling	Screened pulp	Unpulped wood or screenings	Total
		Vol. %	*Cc.*	*Hr.*	*Cc.*	*Hr.*	%	%	%
				Aspen Chips					
155	H_2O	None	750	7	750	6	..	79.2	79.2
158	H_2O	1	750	7	750	6	..	58.1	58.1
159	H_2O	2	750	7	750	6	..	56.6	56.6
160	H_2O	3	750	7	750	6	31.4	2.2	33.6
161	H_2O	4	750	7	750	6	30.8	0.7	31.5
156	H_2O	5	750	7	750	6	28.9	..	28.9
157	Undiluted spent liquor from cook 156			7	750	6	21.7	19.7	41.4
153	Ethanol	None	750	7	750	6	..	82.0	82.0
162	Ethanol	1	750	7	750	6	..	75.3	75.3
163	Ethanol	2	750	7	750	6	..	66.2	66.2
164	Ethanol	3	750	7	750	6	41.6	12.0	53.6
165	Ethanol	4	750	7	750	6	43.8	6.1	49.9
154	Ethanol	5	750	7	750	6	45.1	4.8	49.9
				Aspen Sawdust					
170	Ethanol	3	750	7	600	6	39.6	..	39.6
171	Ethanol	3	500	7	600	6	37.0	6.6	43.6
172	Ethanol	3	400	7	600	6	33.0	16.4	49.4
173	Ethanol	3	300	7	600	6	30.8	22.0	52.8
174	H_2O	3	750	7	600	6	25.0	..	25.0
175	H_2O	3	500	7	600	6	28.6	1.6	30.2
176	H_2O	3	400	7	600	6	28.6	2.4	31.0
177	H_2O	3	300	7	600	6	26.6	2.8	29.4
178	8A-2W[b]	3	750	7	600	6	38.2	0.6	38.8
179	6A-4W	3	750	7	600	6	34.0	0.6	34.6
180	4A-6W	3	750	7	600	6	36.0	0.4	36.4
181	2A-8W	3	750	7	600	6	31.6	1.0	32.6
184	H_2O	3	750	1	600	6	28.6	1.2	29.8
185	H_2O	3	750	2	600	6	27.6	0.4	28.0
186	H_2O	3	750	4	600	6	28.4	0.4	28.8
187	H_2O	3	750	6	600	6	26.8	..	26.8
188	H_2O	3	750	2	600	1	32.0	0.4	32.4
189	H_2O	3	750	2	600	2	30.0	0.4	30.4
190	H_2O	3	750	2	600	3	27.8	0.4	28.2
191	H_2O	3	750	2	600	4	30.2	0.4	30.6

[a] On basis of oven-dried wood.
[b] A = parts alcohol; W = parts water.

Table II. Cooking Data and Yields of Pulp Obtained from Jack Pine

Cook No.	Acid Treatment: Liquor	Acid Treatment: HNO_3	Acid Treatment: Total vol.	Acid Treatment: Time of boiling	Alkaline Treatment: Alkali	Alkaline Treatment: Concn.	Alkaline Treatment: Volume	Alkaline Treatment: Time of boiling	Pulp Yields[a]: Screened pulp	Pulp Yields[a]: Unpulped wood or screenings	Pulp Yields[a]: Total
		Vol. %	Cc.	Hr.		%	Cc.	Hr.	%	%	%
					Jack Pine Chips						
301	H_2O	4	500	2	NaOH	4	500	2	25.6	15.2	40.8
302	H_2O	4	500	4	NaOH	2	500	2	16.8	23.8	40.6
303	Ethanol	4	500	2	NaOH	4	500	2	..	73.2	73.2
304	Ethanol	4	500	4	NaOH	2	500	2	3.0	64.8	67.8
305	*n*-Butanol	4	500	2	NaOH	2	500	2	5.8	66.0	71.8
306	*n*-Butanol	4	500	2	NaOH	2	500	2	4.4	67.6	72.0
307	Ethanol	3	500	6	NaOH	2	500	5	2.4	68.2	70.6
308	Ethanol	4	500	6	NaOH	2	500	5	5.6	59.6	65.2
309	Ethanol	5	500	6	NaOH	2	500	5	29.6	26.2	55.8
310	Ethanol	6	500	6	NaOH	2	500	5	38.6	11.4	50.0
329	Ethanol	3	750	7	NaOH	2	750	6	6.4	58.2	64.6
330	Ethanol	3	750	7	Na_2CO_3	2.65	750	6	2.8	71.4	74.2
331	Ethanol	6	750	6	NaOH	2	750	5	34.0	19.2	53.2
332	Ethanol	6	750	6	Na_2CO_3	2.65	750	5	33.2	29.0	62.2
					Jack Pine Sawdust						
323	Ethanol	3	500	6	NaOH	2	500	5	..	65.0	65.0
324	Ethanol	4	500	6	NaOH	2	500	5	..	58.4	58.4
325	Ethanol	5	500	6	NaOH	2	500	5	44.4	3.8	48.2
326	Ethanol	6	500	6	NaOH	2	500	5	43.4	0.8	44.2
327	Ethanol	3	750	7	NaOH	2	600	6	..	58.2	58.2
328	Ethanol	3	750	7	Na_2CO_3	2.65	600	6	..	69.4	69.4

[a] On basis of oven-dried wood.

ing time of boiling but the differences so obtained were very slight. These data are given by cooks 184 to 187 (Table I) and Figure 4. In cooks 188 to 191 the conditions of acid treatment were held constant while the time of boiling with alkali was varied. The results showed that there was a slight decrease in yield with increasing time of alkali treatment (Figure 4). These data seem to show that, under the conditions used in these experiments, it is possible to obtain a good pulp of fair yield by refluxing for 1 to 2 hours with 3 volume per cent aqueous nitric acid solution, followed by a 1-hour treatment with 1.5 to 2 per cent sodium hydroxide solution.

The pulps obtained with aqueous nitric acid solutions were very light in color, approximating that of sulfite pulp; the alcohol-treated woods yielded pulps which were only slightly darker. After the acid treatment the residual woods were orange to orange-red in color; the residual liquors were orange-red to red. The residual alkali liquors were black in bulk. The screenings were dark brown and generally fairly soft, although some hard cores were found occasionally. It was noticed, in boiling with the alkali solution, that the liquor foamed profusely.

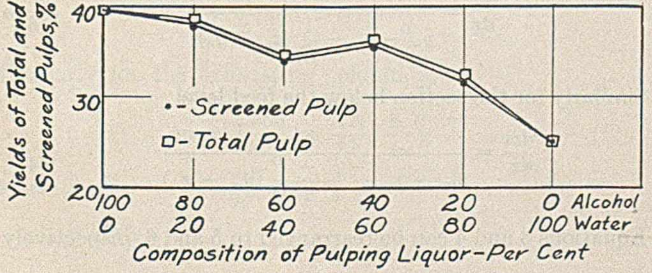

Figure 3. Effect of Diluting Alcoholic Nitric Acid with Water on Yields of Total and Screened Pulp

That the nitric acid is not completely used up in this cooking process is shown in the case of cook 157, in which the undiluted residual liquor of cook 156 was used as the cooking agent. A check on the nitric acid consumption, based on the oven-dry weight of the original wood, was attempted in cooks 184 to 187:

Cook No.	HNO_3 Added	HNO_3 Recovered	HNO_3 Consumed
	%	%	%
184	42.4	33.4	9.0
185	42.4	29.6	12.8
186	42.4	27.0	15.4
187	42.4	23.6	18.8

The amounts of nitric acid recovered, on the basis of the original nitric acid used, were approximately 79, 70, 64, and 57 per cent for cooks 184, 185, 186, and 187, respectively, decreasing with the increased duration of the cooking period. Although the percentage recovery of acid in cook 184 can be considered fairly good, it must be pointed out that these results were obtained by titration of the residual liquors and wash liquors with standard alkali; and any other acids, such as acetic, formic, and oxalic, formed by the oxidizing action of the nitric acid on the wood, would be calculated in this manner as nitric acid.

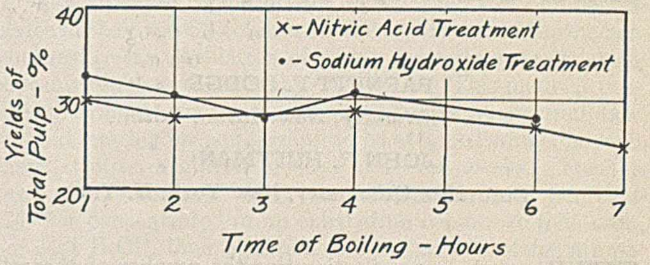

Figure 4. Effect of Duration of Acid and Alkaline Treatments on Yields of Total and Screened Pulp

Jack Pine

The data on pulping jack pine wood are given in Table II. These results indicate that, in order to obtain a pulp from jack pine under the conditions used in these experiments, the concentration of nitric acid, whether in alcoholic or aqueous solution, should be at least 6 volume per cent. Increasing the concentration of the acid resulted in increased yields of screened pulp and decreased total yields, similar to the results obtained with aspen. *n*-Butanol–nitric acid mixtures and ethanol–nitric acid solutions had approximately equal effects on the yields of pulp. Lower total yields but higher yields of screened pulp were obtained from jack pine sawdust than from the chips. It is apparent from these data that jack pine is not pulped as readily as is aspen by the nitric acid process.

The substitution of sodium carbonate for the sodium hydroxide in the alkaline treatment had a deleterious effect on the resultant pulps, as shown in Table II. Apparently the reaction products from the action of alcoholic nitric acid on wood are not as soluble in sodium carbonate as in the sodium hydroxide solution.

When sulfur dioxide and lithium bisulfite were substituted for the nitric acid in both ethyl and *n*-butyl alcohols, no pulped residues were obtained after the sodium hydroxide treatment. This indicates that the nitric acid acts as an oxidizing rather than as a hydrolyzing agent.

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Calculation of the Number of Theoretical Plates for a Rectifying Column

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THE usual means of estimating the number of theoretical plates for a given separation of two liquids is the McCabe-Thiele graphical method. When the number of plates is very large, as is the case with certain hydrocarbon separations and especially with isotopes, this method is tedious and apt to be inaccurate if carried out with the usual, small-scale diagram. The purpose of this paper is to call attention to the method proposed by Lewis (*3*) some years ago which has been completely supplanted by the later method of McCabe and Thiele (*4*), but which has distinct advantages in the case of a large number of plates. This method was given in the first edition of Walker, Lewis, and McAdams' book (*7*) but was omitted from the second.

The usual material balance on a rectifying column, coupled with the assumption of constant heat content of the vapor and liquid streams throughout the column, leads to the following equation for rectification above the feed level:

$$y_n = x_{n+1} + \frac{1}{R}(x_c - y_n) \qquad (1)$$

Subtracting x_n from both sides,

$$x_{n+1} - x_n = y_n - x_n - \frac{1}{R}(x_c - y_n) \qquad (2)$$

$x_{n+1} - x_n$ is the enrichment per plate and may be written $\Delta x/\Delta n$. When the number of steps is large, $\Delta x/\Delta n = dx/dn$ very closely. Finally we may write:

$$\frac{dn}{dx} = \frac{1}{y_n - x_n - \frac{1}{R}(x_c - y_n)} \qquad (3)$$

Similarly for the section below the feed level:

$$\frac{dm}{dx} = \frac{1}{y_m - x_m - \frac{F-P}{F+O}(y_m - x_w)} \qquad (4)$$

Equations 3 and 4 can be rearranged to 5 and 6, respectively:

$$\Delta n = \int_{x_f}^{x_c} \frac{dx}{y_n - x_n - \frac{1}{R}(x_c - y_n)} \qquad (5)$$

$$\Delta m = \int_{x_w}^{x_f} \frac{dx}{y_m - x_m - \frac{F-P}{F+O}(y_m - x_w)} \qquad (6)$$

In the original application of these equations, as given by Lewis (*3*), and in the text by Walker, Lewis, and McAdams (*7*), they were integrated graphically; but in the case of an

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ideal solution, which would be a valid assumption in many cases of hydrocarbon separation and certainly in all cases of isotope separation, the algebraic integration is relatively simple. Thus for an ideal solution at constant temperature,

$$y = \frac{\alpha x}{1 - x + \alpha x} \tag{7}$$

and for the constant-pressure distillation of an ideal solution, α, which is the ratio of the vapor pressures of the two pure components, is substantially constant and an average value may be used.

Substitution of Equation 7 in 5 and rearrangement (with the subscripts dropped for simplicity) leads to:

$$\Delta n = R \int_{x_f}^{x_c} \frac{dx}{Ax^2 + Bx + C} - A \int_{x_f}^{x_c} \frac{xdx}{Ax^2 + Bx + C} \tag{8}$$

where $A = R(1 - \alpha)$
$B = R(\alpha - 1) - x_c(\alpha - 1) + \alpha$
$C = -x_c$

Integrating and substituting limits:

$$\Delta n = 2.303 \left[\frac{2R + B}{2\sqrt{B^2 - 4AC}} \left\{ \log \frac{2Ax_c + B - \sqrt{B^2 - 4AC}}{2Ax_f + B - \sqrt{B^2 - 4AC}} \cdot \frac{2Ax_f + B + \sqrt{B^2 - 4AC}}{2Ax_c + B + \sqrt{B^2 - 4AC}} \right\} + {}^1/_2 \log \frac{Ax_f^2 + Bx_f + C}{Ax_c^2 + Bx_c + C} \right] \tag{9}$$

The equation for plates below the feed level is exactly the same in form but, in place of R we have $R' = (F + O)/(F - P)$ (in the case of an exhausting column alone, $R' = F/W$) and the limits are x_f (in place of x_c) and x_w (in place of x_f). Also, $A = R'(1 - \alpha)$; $B = R'(\alpha - 1) + x_w(\alpha - 1) - \alpha$; $C = x_w$.

In the special case of a rectifying column where x_f approaches 1.0 (or x_w approaches 1.0 in an exhausting column), Equation 9 is not satisfactory because the log term involves a small difference of large numbers. This can be avoided and the equation greatly simplified by using the equilibrium relation in the form:

$$y' = \alpha' x' \tag{10}$$

This equation holds only where y' and x' are approaching zero.

Substituting Equation 10 in 5 and integrating,

$$\Delta n = \frac{2.303}{A} \log \frac{Ax_c' + B}{Ax_f' + B} \tag{11}$$

where $A = \alpha' - 1 + \frac{\alpha'}{R}$ and $B = -\frac{x_c'}{R}$

Similarly for the exhausting column,

$$\Delta n = \frac{2.303}{A} \log \frac{Ax_f' + B}{Ax_w' + B} \tag{12}$$

where $A = \alpha' - 1 - \frac{\alpha'}{R'}$

$B = \frac{x_w'}{R'}$

The Δn equations are readily solved for any given case where R (or R'), x_c (or x_w), x_f, and α would be known. There is a minimum value of R which can readily be found by the usual equations. It may be assumed that the minimum overflow for the rectifying section will supply more than the minimum requirement for the exhausting section.

The minimum possible number of plates for separation is found by letting R (or R') $= \infty$ in Equations 5 and 6 and integrating. This gives the equation,

$$\Delta n \text{ (min.)} = \frac{2.303}{\alpha - 1} \left[\log \frac{x_c}{x_f} + \alpha \log \frac{1 - x_f}{1 - x_c} \right] \tag{13}$$

For the analogous equation applying below the feed level, replace x_c by x_f and x_f by x_w. Adding the two Δn equations would give the following for the number of plates in the entire column:

$$\Delta n \text{ (min.)} = \frac{2.303}{\alpha - 1} \left[\log \frac{x_c}{x_w} + \alpha \log \frac{1 - x_w}{1 - x_c} \right] \tag{14}$$

Peters (*5*) developed equations which appear to be the same in general form as those of the writers, but there are evidently some differences in detail because they do not give results in agreement with the McCabe-Thiele method as do the writers'. Furthermore Peters' derivation considers a packed column and makes the assumption (stated to be based on experiment) that the ratio between the enrichment and the height of the column is a constant. This does not appear to be a good assumption, and, although it leads to the same differential equation as the Lewis derivation given above, the latter is to be preferred.

Underwood (*6*) gives equations for analytical (as distinct from graphical) calculation of the number of plates which are not the same as Equations 9 and 13 but give approximately the same results in many cases. His equations were obtained by series summation of finite steps rather than by integration and hence should be more accurate when the number of plates is relatively small. Underwood also states that his equations for finite reflux are restricted to the case where both products of the column are nearly pure. The equations given here should not be subject to this limitation.

The second log term in Equation 9 is usually negligible. More than sixty different cases were calculated with it, and in none was this term more than 2 per cent of the whole.

The use of the equations will be illustrated by a few examples. One of the most interesting applications is to the separation of isotopes by distillation. Huffman and Urey (*2*) developed an equation for calculating the number of plates in their special column for the separation of the oxygen isotopes by the distillation of water, from the rate at which concentrations were changing with time. This made it possible to estimate the number of plates from experimental data without waiting for equilibrium to be attained which, in such cases, is often a matter of days and even weeks. For the case where ordinary water containing 0.2 mole per cent H_2O^{18} is concentrated in an exhausting column to 0.85 mole per cent H_2O^{18}, their equation shows that 428 plates are required with total reflux. Using Underwood's formula, they calculated that if equilibrium were attained, the tail product should contain 2.54 mole per cent H_2O^{18}. α for this case is 1.006, based on concentration of H_2O^{16}. Using Equation 13, the minimum number of plates to produce this separation with total reflux is 427, which checks the result obtained from the Underwood equation.

The minimum reflux ratio (F/W in this case) is estimated to be 1960. Assuming a reflux ratio of double the minimum is used, how many plates would be required for this separation? Equation 12 should be used since 9 is unsatisfactory owing to the small differences of large numbers that are encountered. The result obtained is 520 plates. Obviously the calculation of such a large number of plates by the equations is far simpler than the usual graphical method.

Fenske and co-workers (*1*) state that 98 theoretical plates are required to rectify a *n*-heptane–methylcyclohexane solution ($\alpha = 1.07$) containing 3.3 mole per cent *n*-heptane to produce a distillate containing 96 mole per cent, under total reflux. This same figure is obtained from Equation 13. The minimum reflux ratio for this separation is 415. Assuming a reflux ratio of 1000, Equation 9 calls for 105 plates for the given separation. As a check the same calculation was made by the McCabe-Thiele method, and the same result was obtained.

Nomenclature

x = mole fraction of more volatile component in liquid
y = mole fraction of more volatile component in vapor
x' = mole fraction of less volatile component in liquid
y' = mole fraction of less volatile component in vapor
O = overflow or reflux in section of column above feed level, moles
P = overhead product, moles
W = tail product, moles
R = reflux ratio for the rectifying section = O/P
R' = reflux ratio for the stripping section = $(F + O)/(F - P)$ or F/W for a stripping column alone
F = feed, moles
n = number of plates
α = ratio of vapor pressure of the more volatile component of a binary solution to that of the less volatile component, at the same temperature
α' = reciprocal of α

Subscripts:
$n, n + 1$ = plates above feed level
$m, m + 1$ = plates below feed level
c = overhead product
w = bottoms or tail product
f = feed

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Production of Starch from Water Caltrop

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A method has been worked out for the preparation of water caltrop starch (sangara). Its preparation in northern India would imply a more extensive utilization of an economic crop than at present. The determination of its physical properties and actual factory tests seem to show that the starch can be used with advantage for sizing cotton and rayon yarns, for finishing and printing cotton cloth, and for preparing ice cream and milk powders.

WATER caltrop or water chestnut (*Trapa bispinosa*) is an aquatic plant which has been grown in India from the most ancient times. It yields a nut whose kernel is used locally in bilious troubles and diarrhea, as a general article of food, and in the preparation of poultices (*1*). No statistics are available as to the total production of the nut, but it has been roughly estimated to be more than 10,000 tons a year at present and is gradually decreasing (*5*). Economic utilization of this crop would be important to areas of the country where it is grown extensively and is available at a low cost.

The caltrop nut is triangular in shape and about 0.75 inch long (*3*). It is covered with a tough brown skin whose thickness varies with the species of plant. In certain cases the shell is very thick and has long projected horns. The kernel is white and of a fine fibrous texture. Usually a thin-skinned nut is composed of two-thirds kernel and one-third shell. The nut is collected from underneath the surface of the water where it grows, and the skin is removed by specially designed knives. The kernel is spread in the open for drying.

Production of Starch

For the preparation of starch the sun-dried broken kernel was used. The percentage composition of the dried kernel was as follows:

Moisture	7.65	Oil	0.07
Protein	7.56	Gums, sugar, etc.	7.92
Ash	1.93	Starch	72.55
Crude fiber	2.32		

The following practical procedure was developed for starch production:

The dried kernels were washed with water to remove dust and dirt. They were then steeped in 0.25 per cent sodium hydroxide solution for 24 hours, preferably at a temperature of 40° to 45° C. This removes most of the coloring matter and softens the kernel for further treatment. The kernels were washed to remove as much of the alkali as possible and were finally immersed in a 0.25 per cent hydrochloric acid solution to neutralize the re-

Table I. Gelatinization Temperature from $^1/_5$-Second Viscosity Measurements

3% Starch Paste	60°C.	62°C.	64°C.	66°C.	68°C.	70°C.	72°C.	74°C.	76°C.	78°C.	80°C.	82°C.	84°C.	86°C.	88°C.	90°C.	92°C.	94°C.	96°C.
Sangara	33	33	33	33	33	33	33	(34)	35	36	38	38	39	40	42	42	44	45	46
Farina	33	33	(37)	41	45	50	56	59	62	72	81	90	97	109	120	138	150	186	225
Maize	33	33	33	33	33	33	33	(36)	37	41	44	48	52	54	54	52	50	50	49
Wheat	33	33	33	33	33	33	33	33	33	33	33	33	(34)	35	35	36	36	37	39

Table II. Effect of Continued Heating at 90° C. on Change in Viscosity (in $^1/_5$ Seconds)

3% Starch Paste	10 Min.	15 Min.	20 Min.	25 Min.	30 Min.	60 Min.	120 Min.	180 Min.	240 Min.	360 Min.
Sangara	48	51	52	50	50	47	45	43	41	40
Farina	265	305	421	374	358	226	116	78	53	46
Maize	57	52	51	51	51	49	45	41	39	37
Wheat	45	46	46	43	43	39	37	36	35	34

Table III. Viscosity of Constantly Agitated Starch Pastes (in $^1/_5$ Seconds)

3% Starch Paste	5 Min.	10 Min.	15 Min.	20 Min.	25 Min.	30 Min.	60 Min.	90 Min.	120 Min.	180 Min.	240 Min.	300 Min.	360 Min.
Sangara	72	82	82	73	72	70	55	51	45	43	40	...	39
Potato	1800	750	514	454	290	243	158	81	60	47	..	...	..
Maize	58	55	51	50	49	49	47	45	43	41	..	...	..
Wheat	45	46	47	44	45	45	43	43	41	38	36	...	35

maining alkali. The washed and softened kernels were pulped in a coconut shredder under a regulated constant stream of water, the pulp was strained through a sieve (120 mesh per inch), and the residue was ground in an edge runner, washed, and passed through a series of shaking sieves. The residue which did not pass through the sieves was thoroughly stirred with water and again passed through sieves to remove all possible starch. The washings were collected and again passed through a finer sieve (200 mesh per inch). The liquors passing through the sieve were concentrated to the desired consistency by deposition and then allowed to settle in a series of tanks or a set of tables where the starch was deposited. The liquor containing fibrous suspended matter was allowed to flow away.

The starch was further purified by washing with slightly dilute sodium hydroxide and retabling. It was dried in the open or in an air oven at a temperature not exceeding 30° C. (86° F.). The starch obtained was white and had the following percentage composition:

Moisture	9.83	Nitrogen	Trace
Starch	89.92	Fatty matter	None
Ash	0.13		

By-Products of Water Caltrop Starch Process

The waste material from the production of water caltrop starch consists of the residual pulp (36 per cent) and the water from the various starch operations and purifications. The approximate percentage composition of the suspended air-dried pulp was as follows:

Water	6.75	Ash	3.44
Starch	54.48	Protein	1.52
Crude fiber	33.60		

It can be satisfactorily used as a cattle feed.

Properties of Water Caltrop Starch

Water caltrop starch (sangara) granules are of medium size. One hundred twenty granules were measured and found to range in size from 10 to 48μ. The average diameter was 20μ. To measure the starch granule, the micrometer ocular (× 10) was used on the microscope, together with a 0.65-mm. (× 40) objective. The microscopic examination showed that the starch consisted of simple oval or round granules. On the whole, the granule resembled that of potato starch in shape.

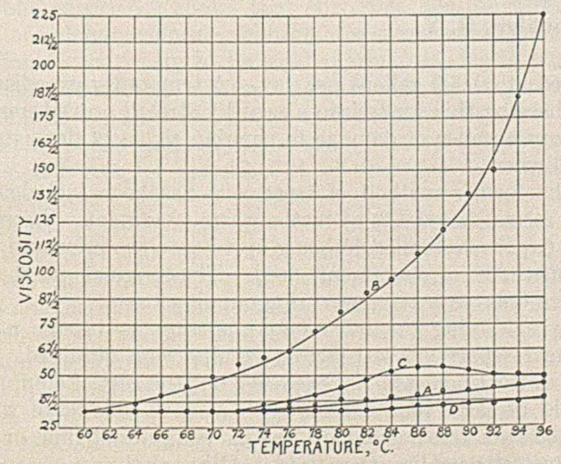

Figure 1. Gelatinization Temperature from $^1/_5$-Second Viscosity Measurements

A. Sangara *B.* Farina *C.* Maize *D.* Wheat

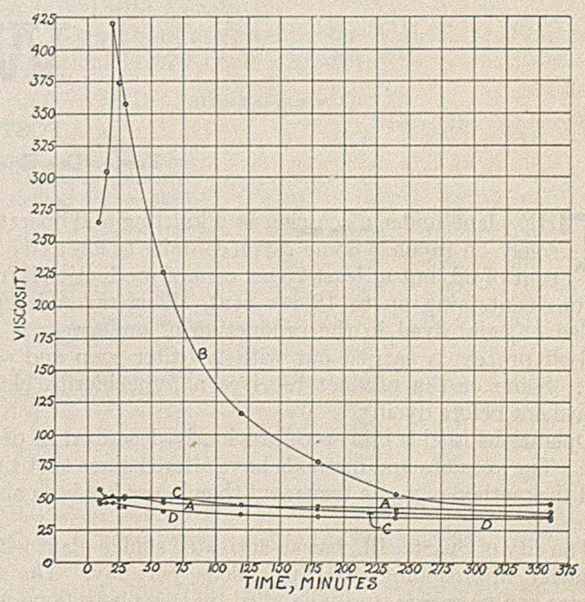

Figure 2. Effect of Continued Heating at 90° C. on Viscosity Changes (in $^1/_5$ Seconds)

A. Sangara *B.* Farina *C.* Maize *D.* Wheat

For viscosity determinations, a 3 per cent starch paste was prepared. The required amount of starch was first suspended in 10 cc. of cold water, and then the remaining water was added from a pipet, allowance being made for the moisture content of the starch. For all measurements this water was maintained at 99° C., except for the determination of gelatinization temperature when it was held at 50° C. Paste uniformity was ensured by agitating with a stream of water from the pipet. A Stormer viscometer was used for all viscosity determinations (*4*).

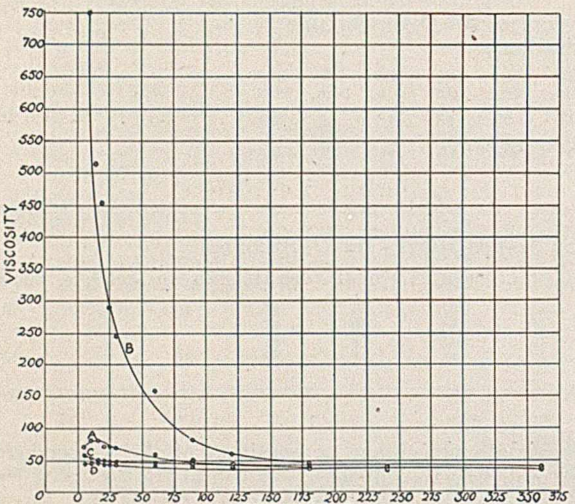

FIGURE 3. VISCOSITY OF CONSTANTLY AGITATED STARCH PASTES (IN $^1/_5$ SECONDS)

A. Sangara *B.* Potato *C.* Maize *D.* Wheat

A series of measurements was made of the temperature at which the starch begins to swell for gelatinization. The maximum viscosity was determined by continuous heating and this also served as a measure of the point at which complete gelatinization occurs. Readings were taken at 2° C. intervals. The effect of continuous heating with and without constant agitation was also investigated. For comparison, determinations of viscosity were also made of potato, maize, and wheat starches. The results are given in Tables I, II, and III and in Figures 1, 2, and 3. Water caltrop starch behaves similarly to maize and wheat starches.

Proposed Uses

Sangara starch can apparently be used for textile sizing, since its viscosity varies little over a wide temperature range. Its suitability as a sizing and finishing material can be judged when the experimental work on the chemical properties and penetrating and coating power of the starch on cotton yarn is finished. Actual sizing and finishing tests carried out in the Government Finishing and Dyeing Factory, Shahdara, show that the water caltrop starch possesses satisfactory coating and penetrating qualities and is suitable for sizing cotton and rayon yarns, for finishing cloth, and as a thickening material in calico printing.

Another use appears to be in the manufacture of ice cream "improvers" and powders (intended for boiling milk and sugar mixes) and as a constituent of dried milk powders. Analysis of a number of ice cream powders showed that they contain an appreciable percentage of cornstarch (*2*). When water caltrop starch was substituted for cornstarch in these powders, it gave better results in making the ice cream more creamy and in improving and smoothing its texture and body.

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Treatment of Rayon Boil-off Waste

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THE plant under discussion is a knitting mill operating solely on rayon. Some rayon contains as low as 6.5 per cent of oil, but at least 25 per cent of production is from rayons containing up to 18 per cent. This rayon is knit, boiled off, and dyed in the production of underwear. The boil-off process is carried out with low-titer soap and soda ash. Some of the product receives a hypochlorite bleach treatment before dyeing.

Operations in this mill were previously described in detail (*2*). The volumes and methods have altered since that time, and the method of waste treatment then in use has been abandoned.

The city of Sparta, Ill., has an activated sludge plant with a capacity approaching 400,000 gallons per day. The dye wastes can be satisfactorily handled by this plant along with the normal sewage. The problem is therefore only the treatment of the minor amount of boil-off waste. This has been as low as 15,000 gallons per day and is at present estimated at 60,000 gallons per day. A temporary expedient of discharging this waste into a near-by stream proved unsatisfactory because of damage to riparian rights of downstream landowners.

The former method of treatment has been included (*1*) in a recent survey (*2*) of textile waste treatment. Therefore this paper is intended to bring up to date the information as to methods of treatment used. The original plant now serves only as a temporary impounding basin.

By acidifying the boil-off and putting it through a centrifugal separator, satisfactory results were obtained. The cost of treatment was not excessive but the cost of equipment would be large for handling such a small volume of waste. Methods of treatment with ferrous sulfate and lime or aluminum salts and lime were tried. Although the waste could be clarified, the cost was substantial and the finished effluent was strongly alkaline. Precipitation by lime was tried and was even more objectionable because of alkalinity.

The ingredients of the waste are mainly sodium carbonate, alkali metal soaps, and emulsified mineral oil. Such an emulsion would be decomposed by conversion of the soap to an insoluble form. Experimental work indicated that addition of calcium chloride will convert the soap to insoluble calcium soaps which will entrain all of the emulsified oil to give it a clear and colorless effluent.

In laboratory experiments 2 and 4 cc. of 12 per cent calcium chloride solution per 100 cc. of boil-off gave the finished effluents shown in Table I. These factor weights correspond to treatment with 2 and 4 pounds of calcium chloride per 100 gallons, respectively, the calcium chloride being the commercial 75 per cent grade. For practical use a solution of calcium chloride containing about 3 pounds to the gallon would be suitable.

TABLE I. RESULTS OF TRADE WASTE TREATMENT (IN PARTS PER 100,000)

Treatment	Raw Liquor	2 Lb. $CaCl_2$ per 100 Gal.	4 Lb. $CaCl_2$ per 100 Gal.	Filtered through Bed of Ashes
pH	10.6	7.6	7.2	7.0
Total solids at 110° C.	668	394	739	241
Inorganic solids (by loss on ignition)	308	333	509	216
Organic solids (by difference)	360	61	130	25
O_2 consumed (permanganate method)	376	[a]	[a]	66

[a] Not significant because chlorides are present.

The amount of calcium chloride required is substantial because the sodium carbonate must be converted to sodium chloride and calcium carbonate as well as the alkali soaps to calcium soaps. The pH of the finished effluents indicates that the reaction takes place smoothly since they are nearly neutral. Laboratory results such as these are only an indication, and for practical results it is highly probable that further reduction could be made. The process was tried out on a plant scale and operated satisfactorily with a pilot plant. The development of a simpler process rendered its complete installation unnecessary.

The removal of such sludge in a relatively concentrated condition is satisfactorily carried out by filtration on a light cotton fabric. The rate of filtration is about 1 gallon per 90 square inches of filtering area per minute so that commercially about 1.25 square feet of filter area would be required per 1000 gallons per day. The sludge is curdy in nature. If it stands for several hours, it becomes oily. It was expected that the sludge would need to be filtered before it became oily but experience shows that such was not the case. A tank of calcium chloride solution was expected to feed the solution to the waste to be treated while passing through a suitable calender for mixing. As indicated by the analyses of Table I, the finished effluent is clear and transparent and harmless to fish and vegetable life. Pilot plant operation indicated a cost for materials of 20 cents per 1000 gallons. The indicated labor cost is low.

The use of ashes as a filter bed was developed with the coöperation of the State of Illinois Sanitary Water Board and proved to be simpler and less expensive. The effluent was found acceptable, and analysis of a representative sample is included in Table I. The results reported with addition of calcium chloride cannot be directly compared because of the increase in solids due to the salts resulting from treatment. The effluent from the ashes contains considerable suspended matter at times but is much clarified from the original condition.

The ashes can be expected to contain substantial amounts of soluble heavy metal compounds, mainly lime. Probably the reaction of these with the soap is similar to the reaction of calcium chloride. Since the stabilizing agent is destroyed by this treatment, the emulsion is broken and precipitation of the oil results.

In practice the bed used is 3 feet deep and contains 1440 cubic feet or 30 tons of ashes. It is roughly divided into three sections, and the oldest section is replaced each week. The used ashes are hauled away by local people because their oily condition makes them excellent material for building secondary roads. Each charge of 30 tons of ashes treats about 1,000,000 gallons of boil-off. It is estimated that this volume of boil-off contains 6500 pounds of oils and 1500 pounds of soap, soda ash, etc. Although this treatment has been in use for only about a year, satisfactory results have been obtained.

Acknowledgment

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Life of Shellacs after Heating

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TESTS were made to determine how long various samples of shellac would stand heating without losing their tackiness. The samples were aged in an electric oven for varying periods and tested on an electric hot plate maintained at 275° F. The table gives the time in seconds, after the shellac had melted, necessary for the samples to lose all tackiness when tested with a spatula.

The specifications are given in the A. S. T. M. Standards (Designations D237-33 and D207-55):

After Heating at 140° F.

		Time of Heating				
	Shellac	0	1 hr.	2 hr.	3 hr.	4 hr.
A.	Refined dry bleached	0	0	0	0	0
	Regular dry bleached	94	50	0	0	0
B.	Refined dry bleached	183	104	88	87	0
		512	340	270	255	115
	Grade A, orange shellac	1636	1282	1238	1216	925
		1153	1237	995	895	561
		866	688	638	575	530
C.	Regular dry bleached	137	36	30	0	0
	Refined dry bleached	570	462	394	365	17
D.	Grade A, orange shellac	1415	1395	1365	1137	1047
	After Heating at 180° F.					
A.	Refined dry bleached	0	0	0	0	0
	Regular dry bleached	94	0	0	0	0
B.	Refined dry bleached	183	0	0	0	0
		512	290	217	0	0
	Grade A, orange shellac	1636	891	836	122	0
		1153	708	633	0	0
		866	470	355	90	0
C.	Regular dry bleached	137	0	0	0	0
	Refined dry bleached	570	206	174	0	0
D.	Grade A, orange shellac	1415	984	930	0	0

Each group represents a product of a different manufacturer. The samples were furnished through the courtesy of George Lawson.

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Oils from Resins by Distillation with Phosphoric Acid

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WHILE studying the cause of spoilage of beer in wooden kegs whose interior walls had been coated with a certain rosin, it was found that this rosin yielded a larger percentage of oil than other and satisfactory rosins. Also it was found that, when distilled directly, "common rosin I" gave only 17 per cent oil. However, when it was distilled with phosphoric acid in accordance with the method described here, 80 per cent oil was obtained. Certain industrial and natural resins were then distilled by the latter method. A study of the data thus obtained showed no correlations of percentages of oil with melting points, acid numbers, or class of resin.

When compared with methods of destructive distillation and of distillation with sulfuric acid the phosphoric acid method showed certain advantages. For example, Schultze (*6*) obtained 60 per cent oil by dry distillation of American rosin. From kauri resin by dry distillation Rennie (*5*) obtained 10 per cent oil; Andés (*1*), 24 per cent; Wallace (*7*), 40 per cent. Easterfield and McClelland (*3*) obtained 40 gallons of oil per ton of kauri resin. Guedras (*4*) obtained oils from copals by dry distillation. Von Buyen (*2*) described a process of heating rosin with sirupy phosphoric acid to 260° C. until effervescence ceases. Since the present method yields a preponderance of oils boiling above this temperature, after being carried over by steam, the composition of the oils from the two processes differs. Owing to the fact that phosphoric acid can easily be recovered for reprocessing, this method can be applied industrially. The method for total oil is as follows:

In a 0.5-liter distilling flask are placed 50 grams of the powdered resin and a few cubic centimeters of water. The flask is connected with a dropping funnel and a condenser. A separatory funnel is used as a receiver. The flask is heated until some water distills, then 50 cc. of 85 per cent phosphoric acid are dropped in slowly while continuing to heat strongly. Oil and water distill into the receiver and, as the heating is continued, white fumes begin to form. After all of the acid has been added, water is dropped in at such a rate as to avoid the evolution of copious white fumes. The addition of water, and distillation to the point of evolution of fumes are continued until no more oil is carried over by the steam. Advantageously the water collected in the separatory funnel is dropped into the distilling flask to carry over the oil. The oil is extracted with ether, poured into a weighed beaker, and concentrated by evaporation of ether on the water bath.

In Table I the weight of the oil is reported as percentage of the weight of the original material used.

TABLE I

Name	Class[a]	M. p.[b] ° C.	Acid No.	Oil[c] as % of Resin	Oil Fractions							
					Below 200° C.		200–275° C.		275–350° C.		Over 350° C.	
					%	Color[d]	%	Color	%	Color	%	Color
Common (wood) rosin I	I	69	156	80	..	..	8	Y	73	Y/V	19	B
Common rosin II	I	56–74	155	67	1	Y	20	Br	71	G/Br	8	B
Kauri	I	101–125	...	61	13	Y	24	A	38	Br/G	25	B/G(S)
Dammar	I	93–110	33	56	..	..	21	A	34	Br/V	45	B/G(S)
Mastic	I	77–94	57	65	2	A	16	A	28	Br/G	54	B/G(S)
Copal	I	97–117	128	66	2	Y	15	A	48	Br/G	35	B/G(S)
White shellac	I	Decomposed	50	55	12	Br	15	B	45	Br/G	28	Br(S)
Jalap	I	128–132	21	18	36	A	27	A	29	Br/G	8	B(S)
Sandarac	I	130–145	132	70	6	A	25	A	45	Br/G	23	B/G(S)
Guaiacum	I	67–81	57	11	26	A	38	B	36[e]	B	..	....
Tolu	II	80–90	121	20[f]	21	Y	30	Y	44	B	5	....
Storax	II	.....	60	66	21	Y	15	Br	39	B/G	25	B(S)
Gum rosin F	III	82–98	158	56	2	A	10	Br	58	Br/G	30	B(S)
Gum rosin G	III	80–98	158	70	..	..	16	Br	71	Br/G	13	B(S)
Gum rosin Z	III	71–89	155	81	5	Y	13	Y	67	Br/G	13	B(S)
Ammoniac	III	125–149	...	27	11	Br	39	Br	32	Br/G	18	B(S)
Benzoin	I	74–76	76	3			(After 42% benzoic acid had distilled)					
Gambier	...	88–110	...	0.4								
Myrrh	III	.....	...	0.0								

[a] I = resin; II = oleoresin; III = gum resin.
[b] Determined in sealed capillary tubes.
[c] After 3-year exposure to atmospheric oxygen, these oils showed little or no resinification.
[d] A = amber; B = black; G = green; S = solid or semisolid; V = violet; W = colorless; Y = yellow; / = fluorescent.
[e] Because of decomposition these fractions were not distilled above 275° C.
[f] Benzoic acid (18%) distilled before oil appeared.

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