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The Editor's Point of View

ALUMINUM IN FOOD. Being under the impression that the question of toxicity in foods because of their preparation in aluminum vessels had long since been settled, we have been surprised on several occasions to have some one in an audience ask whether or not it is true that aluminum is unsuitable for cooking untensils. The first time the question was asked we took the trouble to check again with authorities on foodstuffs and, finding nothing against this useful metal, we wondered where the source of agitation might be. There is a certain editor of an eastern publication, with exact support unknown, and a midwestern dentist who appears to spend on this crusade more than his visible income would justify, who are the two leaders in this unfair movement. They falsely point to many things which they assert can happen to anyone who apparently has done no more than eat one meal in which the majority of dishes were prepared in aluminum.

We know of people who have some pet crusade and who pursue it honestly, and at times at great personal sacrifice, merely because they are sure they are right. Facts and the results of careful examinations which show data contrary to their point of view are of no interest to them, and they strive on, too blind in their enthusiasm, or shall we say fanaticism, to see, let alone consider, the other side. Perhaps the individuals in the case under discussion are of this class.

The widespread use of aluminum cooking ware, which is sanctioned by the best-known medical journals of this and other countries, could scarcely be permitted by public health officials of municipalities, states, and the Nation if the situation were as has been incorrectly represented. A number of authorities have looked into the matter and have given the results of their investigations that show aluminum is safe.

We are pleased to print in this issue two papers which have a bearing on this question. They have to do with the occurrence and determination of aluminum in organic materials. They come with the authority of a research organization widely and well known for its achievements. With this information before our readers it should be easy for those interested, not only to make check determinations, but to go as far beyond as they may wish in the examination of all sorts of materials for the occurrence of aluminum. Not being pharmacologists, nor physiologists, nor physicians, we make no comment upon the importance of such mere traces of those forms of aluminum as may occur in foods. We can observe, however, that most of the people we know have numerous pieces of aluminum ware in their culinary equipment and that, fortunately, the health of the Nation is surprisingly good.

* * *

"TOO MANY CHEMISTS." This seems to be the erroneous conclusion of some in the chemical profession at this particular time. Observing the surplus of labor among coal miners and other classes of manual workers, they apparently apply similar reasoning to their own profession and believe a surplus of men to be a contributing cause or the sole reason for their difficulty in getting jobs.

It is very important to distinguish clearly between those types of manual work for which there is only a limited demand, and brain work, of which humanity always can use more. The professional activity of chemists falls in the latter class. And the public always wants more of the service of worth-while chemists. This is a fact to be remembered, especially when employment conditions are decidedly discouraging for the individual. He should not lose faith in his profession. He should understand that he is suffering from a period of readjustment and not a real shortage of demand.

Another distinction can properly be made under present conditions—that between true chemists and those who merely use this *nom de plume*. In many cases those who claim such a title do not represent thorough scientific grounding and that professional attitude toward their science which is essential to real chemical service. This very lack lies at the root of much of the difficulty encountered now, more than in other times, by certain individuals. But, of course, there is another class of well-trained, professionally sound, able chemists who, through no fault of their own, are temporarily without employment. Every scientist is anxious to assist this latter group into con-

structive service that will compensate the individuals according to their worth. The fact that unquestionably a few such men are finding serious difficulty in locating employment does not disprove the generalization that society needs all and more than the present supply of really able chemists.

PATENT HEARINGS. On February 17 the Patent Committee of the House of Representatives concluded its hearings on the general subject of patents. A few weeks ago the chairman announced that the committee would hear all and sundry on any phase of our patent system, following which legislation would be drafted for presentation to Congress. The idea was that, from time to time, amendments and changes have been made piecemeal in the patent laws. It was felt that the whole situation should be surveyed and, if it seemed necessary, a real renovation undertaken.

There is pretty wide agreement that the patent laws are just about as important as any to commerce, and that in the past they have been invaluable in the development of the American industrial system. They are quite as essential from many points of view as are the banking laws or the tariff. While the value of the hearings is recognized, it seems unfortunate that the plans of the committee could not have been such as to allow more time for carefully considered criticisms and constructive recommendations to be presented by several industrial groups. It would obviously take months to review the patent laws as a whole and then develop procedure for the future, setting that course from the line of sights marking past experience.

However, some comments of great value were made before the committee. One of the principal defects stressed is the issuance of patents without sufficient examination of the prior art. This results in a failure to maintain a high standard in our inventions, which in every case should be required to show conclusively the discovery of a new principle or technical effect. Another defect is the long pendency for patent applications. It was brought out that there are 18,000 applications which have been kept in the office five years and impressive numbers which have been kept alive longer, a few as long as fifteen years. One of the sometimes tragic results of this abuse of the patent system is that a concern may bring out a fully developed commercial article of value, only to find some application musty with age lying in the Patent Office waiting to spring forth as a patent and demand its royalty. One famous instance has to do with wire wheels used on automobiles. But this is only one of a long and well-recognized series of abuses that have arisen.

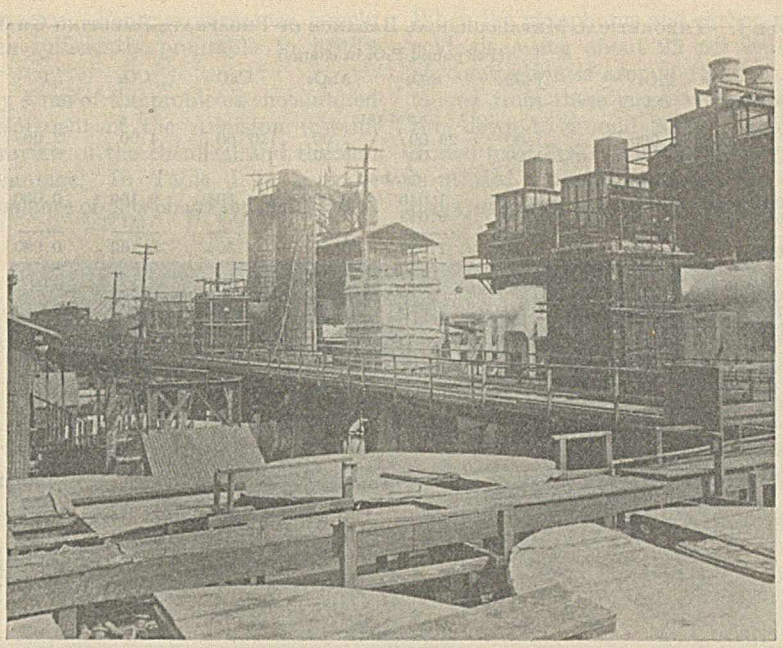
Industry is primarily interested in the validity of patents and expedition in their issuance. Adequate examination of prior art before the granting of a patent is essential. It should be possible to maintain a very high standard for inventions and prevent many types of patents which, under present laws, have had to be granted, but which either have nothing more than a nuisance value or are downright ludicrous. While the life of a patent might be seventeen years, it should not run in any case beyond a definite period from the date of the application. It should also be possible for an assignee to file divisional, continuation, renewal, or reissue applications without having to go back to the original inventor or his heirs, as is now required.

The patent laws are so important and have served us so well that their alteration should be undertaken with the greatest care. Nevertheless, it is doubtful whether these laws or their administration have kept pace with the rapid development in the sciences and the arts, especially where those industries resting upon research are concerned. The chemical industries, the electrical developments, the great strides made in communication, transportation, and aviation, have introduced new problems for which in many cases there are no precedents. It should be possible to cure those defects which the patent system may have developed, without weakening the valuable aspects of the patent laws. It is a question of great complexity upon which the attorneys are far from agreement, but that is to be expected. Industry should take the leadership.

WE EXPORT NITROGEN. From an importer of fixed nitrogen for generations, the United States has now become an exporter of this commodity in tonnages sufficiently large to be impressive. In 1931, 450,000 tons of ammonium sulfate left our shores for other countries, there to be used for fertilizer purposes. In 1932, in addition to whatever ammonium sulfate may find its way abroad, 25,000 tons of synthetic sodium nitrate are to be exported to France. That is indeed a unique development.

It will be recalled that, having predicted the impossibility of directly fixing the nitrogen of the air, experts next prophesied that sodium nitrate could never be made synthetically to compete with the Chilean product. As we all know, that has been done on a large scale, and now the exportation of this nitrate would seem to mark the final stage in this competition.

All of this does not look much like a dearth of low-priced fixed nitrogen in the United States, and yet in the face of this condition there are still those who soberly argue for the use of the old plants at Muscle Shoals in the manufacture of fertilizers, specifying fixed nitrogen. They even talk seriously of cheap fertilizer, whatever that term may mean, and assure us that the operation of a plant by the Government, if no one is so unwise as to accept the proffered lease, will mean a reduction in fertilizer costs throughout the country. Is there anything more absurd?



HYDRATORS AND PRECIPITATORS AT FEDERAL PHOSPHORUS COMPANY PLANT OF SWANN CORPORATION

Thermal Production of Phosphoric Acid

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SUBSTANTIALLY every application of thermal methods in production of phosphoric acid involves the step of reduction of elemental phosphorus from natural phosphates. Whether the source of heat be fuel or electricity, or whether the reduction and reoxidation of the phosphorus be separate or connected operating steps, the same fundamental thermal principles are involved in the smelting operation. The practice of reducing, volatilizing, and collecting phosphorus in the elemental state has been carried out along the same basic lines for a quarter of a century. The modern electric furnace practice, with all of its refinements and secrecy of details, involves the same principles as, and is the outgrowth of the old externally heated retort. The smelting mixture consists of phosphate rock, carbonaceous reducing agent, and silica.

The function of the carbon is well understood as being for the sole purpose of reduction of the P_2O_5 to phosphorus. That of the silica is not so well known. Reduction of the P_2O_5 can be effected without any silica, with a wide ratio of silica to lime, or by substitution with alumina. In a normal smelting operation, the silica-lime ratio of the mixture is controlled more with a view to convenience feature of obtaining a free-flowing slag and for ease in removal of the residue in a molten state, than that of a factor in the reactions. In this, and in many other features, lies an interesting field of research.

FUNCTION OF CARBON

It is generally conceded that the reduction of the phosphorus from the natural oxide combination is solely by solid carbon. Carbon monoxide gas and hydrocarbons have substantially no influence under the conditions of temperature and pressure prevailing where the normal P_2O_5 reduction operations obtain. This reduction being only by solid carbon, and actual contact of any two bodies being necessary for reaction therebetween, a state of fusion supplies most effective conditions for complete reduction of the P_2O_5. The records of a number of cases of highly creditable laboratory research (*1–4*) in thermal phosphate reactions would indicate upon casual interpretation that the reduction of the P_2O_5 to phosphorus had been effected by reaction with carbon monoxide or other reducing gases. However, it appears more likely that the essential molecular contact was effected through a partial reduction to extent of actual contact of the solid carbon and solid phosphate compound, followed by intimate carbon deposition contact through dissociation of the evolved carbon monoxide, cyclically recurring in the mass. It will be noted that, in all cases of laboratory work where substantial reduction of the P_2O_5 is attained with the mass in unfused state, a large excess of carbon over the theoretical requirements was employed. This provides a combination of conditions favoring cyclic carbon deposition through carbon monoxide decomposition. The reaction between the P_2O_5 and carbon must be in molecular proportion. Comminution of the two solids to molecular proportion is practically impossible. Therefore complete reduction, on a practical scale, demands that the reaction be finished in the liquid phase. The P_2O_5 in combination, being in solution can, through motion, provide molecular contact with the requisite carbon for complete reduction. The fluxing function then appears more physical than chemical.

It is further generally conceded that substantially no reduction of P_2O_5 by carbon takes place below 1200° C.

It is known that a portion of the total P_2O_5 content of the $(CaO)_3P_2O_5$ can be reduced and volatilized from the solid state, provided the contact between the two constituents has a great degree of intimacy through fine state of division and compactness. Since, however, there can be no further reaction after that of the contacting particles is completed, the degree of complete reduction would not be in-

TABLE I. THEORETICAL METALLURGICAL BALANCE OF PHOSPHATE-SMELTING CHARGE

(Per pound P_2O_5 in charge)

	Pounds	P_2O_5	Fe_2O_3	SiO_2	Al_2O_3	CaO	CO_2	F	H_2O	C	V. C. M.[a]
ANALYSIS											
Phosphate rock + silica	...	25.00	1.00	26.00	2.00	37.60	4.00	2.00	2.40	...	...
Coke	...	...	1.00	7.00	5.50	...	...	...	...	85.00	1.50
CHARGE											
Phosphate rock + silica	4.000	1.000	0.040	1.040	0.080	1.504	0.160	0.080	0.096	...	...
Coke	0.616	...	0.006	0.043	0.034	...	...	...	...	0.524	0.009
Total	4.616	1.000	0.046	1.083	0.114	1.504	0.160	0.080	0.096	0.524	0.009
PRODUCTS											
Metal	0.043	(P) 0.011	(Fe) 0.032	...	...	...	...	...	...	...	...
Slag	2.735	0.026	...	1.039	0.114	1.504	...	0.052	...	...	...
Gases + C loss	1.838	...	...	...	...	...	...	...	...	...	...
Carbon loss	0.048	...	...	...	...	...	...	...	...	0.048	...
P_2	0.414	0.414	...	...	...	...	...	...	...	...	...
C + O	1.199	(O) 0.549	(O) 0.014	...	...	...	0.160	...	...	0.476	...
SiF_4	0.072	...	...	0.044	...	...	...	0.028	...	...	...
H_2O	0.096	...	...	...	...	...	...	...	0.096	...	...
V. C. M.	0.009	...	...	...	...	...	...	...	...	...	0.009

CARBON REQUIREMENT

$P_2O_5 + 5C = P_2 + 5CO$	$1.000 \times 0.423 =$	0.423
$Fe_2O_3 + 3C = Fe_2 + 3CO$	$0.040 \times 0.225 =$	0.009
$CO_2 + C = 2CO$	$0.160 \times 0.273 =$	0.044
Total C required		0.476
10% for losses		0.048
Total C for charge		0.524
Coke $\frac{0.524}{0.85}$		0.616

SLAG ANALYSIS

	%
P_2O_5	0.95
SiO_2	38.00
Al_2O_3	4.15
CaO	55.00
F	1.90
	100.00

P_2O_5 BALANCE

	%
In metal	2.50
In slag	2.60
In gases	94.90
Assume loss in gases	3.00
Recovery in acid	91.90
Recovery in acid and metal	94.40

[a] Volatile combustible matter.

creased by increase of temperature until such increase effects a state of physical change by bringing the other particles of P_2O_5 and carbon into further contact. This usually requires bringing the temperature up to the fusion point, whereby the liquid phase provides ample means of contact of the reacting particles.

The reaction occurring in the phosphorus-reduction operation is usually written

$$(CaO)_3P_2O_5 + 5C + 2SiO_2 = P_2 + 5CO + 3CaO - 2SiO_2$$

The CaO–SiO_2 ratio may vary considerably from the 3 to 2, as shown, but this combination is known to result in satisfactory operation. As above stated, this reaction is involved in substantially every thermal process that has had any degree of successful employment. Where phosphoric acid is the desired final product, there must be subsequent operations of reoxidation and hydration. The oxidation function is usually written

$$P_2 + 5CO + 10\,(O) = P_2O_5 + 5CO_2$$

The hydration is understood as

$$P_2O_5 + 3H_2O = 2H_3PO_4$$

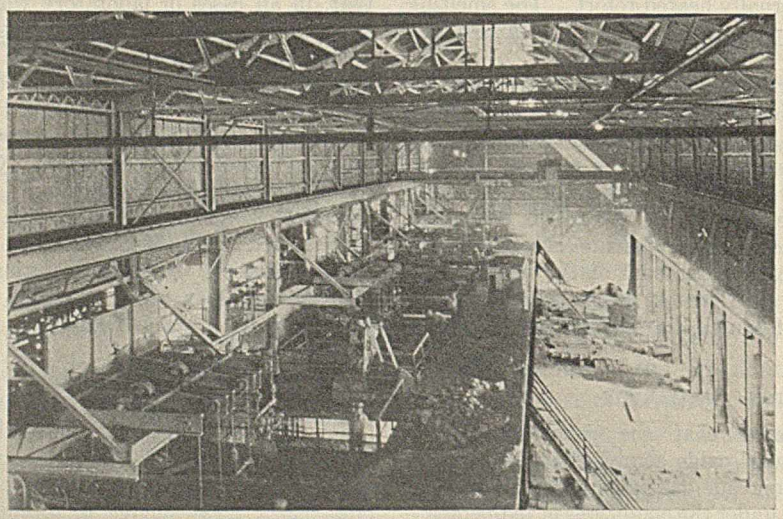
The steps shown in the three foregoing reactions may be, and are in different instances, conducted separately or in continuity:

(1) All three may be conducted as a continuous operation.

(2) All three may be conducted separately—that is, the phosphorus reduced, volatilized, and collected, then oxidized with separate collection of the P_2O_5 which is then hydrated to H_3PO_4.

(3) The phosphorus may be collected in elemental state, followed by a step in which the oxidation and hydration are performed in continuity.

All three of the above general procedures have been actually practiced on commercial scale. Procedures 2 and 3 are the logical outgrowth of production operations of elemental phosphorus, in which it was desired to extend such operations to phosphoric acid production. Naturally, separation of the functional steps of any process provides greater ease of control, since the synchronizing of several steps for continuous operation demands more careful design in the solution of problems arising than in control of the individual step functions. However, the disconnected processes involve greater attendant costs and processing losses than connected or continuous processes. The conversion of a process from separated or intermittent stage operation to one of continuity usually involves overcoming many difficulties in design, construction, and operation before successful outcome results.



PHOSPHORIC ACID FURNACES, LOOKING DOWN ON CHARGING PLATFORM FROM CRANE

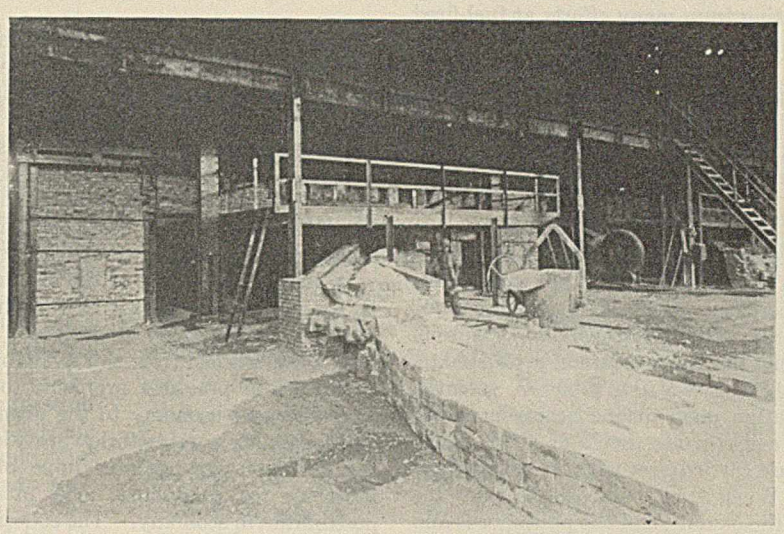
All furnaces are operating under full load.

ELECTROTHERMAL PROCESS

The electrothermal phosphoric acid process in use at Anniston, Ala., was conceived upon the above principle of greater economies from process continuity. Its development to a commercial success required solution of many problems not foreseen in the disconnected step process. There had been several previous attempts at production of phosphoric acid through reduction of phosphorus, with immediate reoxidation and

hydration in continuous process. For various reasons, largely technical, none had been sufficiently profitable to justify continuance in the field.

To explain more clearly some of the problems encountered and solved in the development of the Anniston (Swann Corporation) process, a review of the chemical and thermal fundamentals is of advantage. In Table I is given a theoretical metallurgical balance of phosphate-smelting, based upon typical materials. From this is constructed the thermal balance shown in Table II. These tables show only the process for the stage of phosphorus production. Table I shows the distribution of the various constituents as they reappear in the three classes of products. The results shown are about as found in normal practice. The thermal balance figures in Table II indicate the theoretical requirements of energy for the physical and chemical reactions involved in the production of phosphorus by thermal means. Where no combustion of the phosphorus and carbon monoxide occurs in contact with the charge within the furnace, the temperature of the escaping gases from the furnace is, as shown, about 200° C. However, if the gases are burned in contact with the top surface of the charge, a portion of the heat evolved from such combustion will raise the temperature of the incoming and descending charge; hence, it will cause the gases escaping through the charge to attain a higher temperature.



Front of Phosphoric Acid Furnace at Tap Hole, Showing Slag Runner

Table II. Theoretical Thermal Balance of Smelting of Phosphate Rock

(Per pound P_2O_5 charged)

Reaction	Phosphate Rock	Factor	Endothermic	Exothermic
	Pounds	*P. C. U.*[a]	*P. C. U.*	*P. C. U.*
Decomposition of $3CaO\text{-}P_2O_5$	2.183	514	1122	..
Reduction P_2O_5	0.973	2672	2502	..
Reduction Fe_2O_3	0.046	1223	56	..
Decomposition $CaO\text{-}CO_2$	0.365	451	165	..
CaF_2 to SiF_4 (net)	0.053	895	47	..
CO_2 to CO (net)	0.160	883	141	..
Heat in slag at 1450° C.	2.735	525	1436	..
Heat in metal at 1450° C.	0.043	308	13	..
Heat in carbon at 1450° C.	0.048	610	29	..
Heat in gases at 200° C.:				
P_2	0.414	60	25	..
CO	1.199	50	60	..
SiF_4	0.072	40	3	..
V. C. M.	0.009	136	2	..
H_2O	0.096	610	59	..
C to CO	0.432	2430	..	1050
Slag formation ($3CaO\text{-}2SiO_2$)	2.543	150	..	381
	Total		5660	1431
	Net		4229	..
	Equivalent in kw-hr.		2.225	..

[a] Pound Centigrade units.

The combustion of the phosphorus and carbon monoxide evolved in the above typical example will develop heat as follows:

P_2 to P_2O_5: $0.414 \times 5895 = 2440$ P. C. U. (pound Centigrade units)

CO to CO_2: $1.199 \times 2430 = \underline{2913}$ P. C. U.

Total heat evolved 5353 P. C. U.

Then $\frac{5353}{4229} = 1.263$ times energy theoretically required for reactions within furnace

When the phosphorus and carbon monoxide are burned with cold air, using about 25 per cent excess, the temperature of combustion is around 1800° C. This heat must be removed from these gases sufficiently to bring the temperature down to around 200° C. before the P_2O_5 may be hydrated to H_3PO_4. Whether this available heat in the gases is utilized by transference to the incoming cold charge or other useful purposes, or is wasted in such cooling, there is a serious problem of handling such gases. P_2O_5 and fluorine compounds at this temperature exert a very strong corrosive influence on all refractories in common practice. This was one of the most serious problems encountered in the early stages of development of this continuous process.

The solution was found in design rather than in materials of construction. The construction of all hot-gas conduits, in such manner that the conducted heat through the walls provided a sufficient cooling rate to make a protective coating from the corrosion products themselves, produced a satisfactory solution.

Electric Furnace as Phosphate-Reduction Vehicle

The electric furnace as a phosphate-reduction vehicle has its advantages, not so much in the usually assumed purpose of high-temperature producing capacity, as in its reserve quantitative heat capacity, which is essential for the thermal reduction of phosphorus from natural phosphate. To illustrate this essential point, note the thermochemistry of the principal reaction,

$$\frac{(CaO)_3P_2O_5}{919200} + 5C + \frac{2SiO_2}{392000} = P_2 + \frac{5CO}{145600} + \frac{3CaO - 2SiO_2}{832650}$$

Molecular heat requirement = 323950 P. C. U.

or, per pound of P_2O_5 = 2280 P. C. U.

The exothermic reactions of formation of carbon monoxide from the reducing carbon and that of the combination of lime and silica involved in the fusion, above mentioned, to provide the feature of the liquid phase for complete reduction of the P_2O_5, occur simultaneously with the reduction per se; hence, they reduce the requirement by that amount. It must, however, be borne in mind that the 2280 P. C. U., which is about 54 per cent of the total heat required per unit of P_2O_5, involved, must be supplied at a temperature of around 1300° to 1400° C. in order to perform any work in the required reduction. In practical furnacing operations, this fundamental requirement demands a reservoir of heat energy available at temperatures above 1300° C. When such heat energy is derived from fuel combustion, with the difficulty of maintaining such a reserve supply with requisite thermal head, it is necessary to carry such reserve at the risk of heavy conduction and radiation losses, especially if conventional types of furnaces are employed. With the heat transfer from combustion gases, the temperature of the source falls rapidly with effective transfer, so that, unless the reser-

voir contains available energy far in excess of that required for the reactions, the temperature of the gases from which the reaction demand is supplied may drop to the point at which such reaction stops. The heat useful in raising the temperature of the charge consumes only about 40 per cent of the total required energy in phosphorus reduction. This may all be supplied up to 1300° C. After such raise in temperature of the charge is effected, no additional heat supply is of any value unless it be kept available at above 1300° C. This probably explains the failures resulting from many efforts at fuel-fired methods of phosphate smelting, or the low thermal economy attained in many cases.

In the electric furnace the reservoir of available heat at the required thermal head lies in the power source, since the transformation from electrical energy to heat energy may be had instantly and without temperature limitation.

Disadvantages of Electrical Method

With the above described specific advantage in the electrical method also lies a possible disadvantage, not discernible except through actual experience. This consists in the disastrous practical effects resulting from excessive temperature in phosphate smelting. When the temperature of a phosphate-smelting charge appreciably exceeds the 1400° C. essential for reduction, a volatilization phenomenon occurs in which the usually nonvolatile constituents, such as lime, silica, alumina, magnesia, etc., are carried over with the phosphorus and carbon monoxide. When such constituents take the fume state in presence of the oxidation of the phosphorus and carbon monoxide in the gas phase, there results a series of complex compounds of P_2O_5 with the silica, lime, etc., that renders collection and especially purification of the resulting acid practically impossible, thus defeating the purpose of the operation. This difficulty asserted itself in the early stages of the Anniston operations to such an extent as to threaten defeat of the entire project. This was overcome through the accumulative effect of a number of governing factors being maintained under exact control. These include sizing; proportioning and proper mixing of the materials; maintaining of exact depth of charge; especially avoiding accumulation of carbon in the reducing zone beyond that necessary for reduction, as well as preventing arcing at any local points; and regulating relative aggregates of the various materials according to resistivity necessary.

The above-noted fact, that the heat of combustion of the evolved gases is around one and a quarter times that necessary for the net smelting-energy requirement, naturally accelerates efforts toward utilization of this heat through returning it to the charge. By use of preheated combustion air, the initial temperature of combustion of the gases bearing P_2O_5 may be had over 2000° C., thus giving a thermal head adequate to transfer a considerable portion of the energy to the charge in the reduction range.

In addition to the difficulties of finding refractories to withstand such temperatures, there is one outstanding feature that has defeated the greater number of efforts at practical application of heat transfer in this case. This lies in the avidity of the nascent P_2O_5 for the compounds in the charge $(CaO)_3P_2O_5$ and silica, probably according to the reactions

$$P_2O_5 + SiO_2 = SiP_2O_7$$
$$2P_2O_5 + 4(CaO)_3P_2O_5 = 6Ca_2P_2O_7$$

These compounds and analogs have lower melting points than other constituents of the charge; hence, when formed on the surface of aggregates thereof, they produce a cohesion of the mass of the charge which bodily prevents further descent into the fusion zone and effectively stops operation. Wherever the heat transfer from the combustion gases bearing P_2O_5 is attempted by convection through contact, with the entering charge, these reactions will defeat the object. It is therefore necessary that the transfer be made without actual physical contact of the nascent P_2O_5 with the $(CaO)_3$-P_2O_5 and silica materials of the charge, in order that the available benefits may be derived. Partial heat transfer has been accomplished from this available source. There are yet a number of practical problems to be solved to carry the available heat economy to the ultimate degree. The newer developments in refractories provide means for approaching the problem with greater hope of success. The thermal processes for phosphoric acid production have yet great possibilities in economy. The concentration and purity of the product offer distinct advantages in production of phosphate salts demanded in the impending developments in the chemical fertilizer industry.

The relative fertilizing value of plant food compounds can only be known with scientific exactness when substantially pure compounds are available. Nitrogen and potassium compounds are being offered in the fertilizing field relatively pure and free from minor elements, the influence of which is still subject to question. P_2O_5 compounds in any degree of purity are available only to a very limited degree for this field. When such are available in unlimited quantities, there will probably result some beneficial discoveries and results in agricultural chemistry. Development of the obvious possibilities in the thermal phosphoric acid processes carry contributing potentialities of great importance in agricultural economics.

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Received February 3, 1932.

Sulfur in the United States in 1931. Production, shipments, and exports of sulfur in 1931 showed marked decreases in comparison with 1930, according to the United States Bureau of Mines. Sulfur production amounted to 2,128,930 long tons, a decrease of 17 per cent from the record output of 2,558,981 tons in 1930. Shipments declined from 1,989,917 tons, valued at about $35,800,000, in 1930, to 1,376,526 tons, valued at $24,800,000, in 1931, or 31 per cent both in quantity and in value, and were the smallest recorded since 1922. Stocks of sulfur at the mines increased steadily and amounted to 3,250,000 tons on December 31, 1931, a net gain of 753,000 tons for the year. These stocks were approximately 250,000 tons higher than the previous record stocks on hand at the mines at the end of 1923.

As in 1930, Texas was the only sulfur-producing state. The properties that contributed to this production were those of the Duval Texas Sulphur Co. at Palangana Dome, Benavides, Duval County; Freeport Sulfur Co. at Bryan and Hoskins Mounds, Freeport, Brazoria County; and the Texas Gulf Sulphur Co. at Long Point Dome, Long Point, Ft. Bend County, Big Hill Dome, Gulf, Matagorda County, and at Boling Dome, Newgulf, Wharton County.

The average quoted price for sulfur was unchanged at $18 a ton f. o. b. mines throughout the year. Open prices were $1 to $3 a ton higher and prices for sulfur exported were given as $22 a ton f. a. s. Atlantic ports.

No imports of sulfur or sulfur ore were recorded for the year 1931. Exports of sulfur or brimstone in 1931 totaled 407,586 long tons, compared with 593,312 tons in 1930, a decrease of 31 per cent. Exports to all the countries that receive important quantities of American sulfur, with the exception of those to France, showed large decreases.

Manufacture of Calcium Gluconate by Electrolytic Oxidation of Dextrose

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In a previous paper the authors (2) described a simple method for the preparation of the calcium salts of the aldonic acids by electrolytic oxidation of the aldose sugars in the presence of a bromide and calcium carbonate. This method has been applied on a larger scale and has proved to be very satisfactory for the manufacture of calcium gluconate in considerable quantity. The principal products of the reaction are calcium gluconate, carbon dioxide, and hydrogen. The calcium gluconate which crystallizes from the electrolyte is collected upon a filter, and the mother liquors containing the bromide are returned to the cell after the addition of more dextrose and calcium carbonate. Since the process is continuous, the raw material and electrical energy are readily available and cheap, and the product is obtained without any expensive evaporation or difficult steps, it is now possible to prepare calcium gluconate at a very reasonable cost.

Among the many sugar derivatives which hold promise for future development and industrial application are the monobasic sugar acids which are obtained by mild oxidation of the aldose sugars. Although these compounds have been known for a long time and have been of great importance in acquiring our present knowledge of the molecular structures of the various sugars, until recently they have received little attention from those interested in applied chemistry. Gluconic acid in particular should find many uses because it may now be prepared at low cost. The calcium salt of the acid has already found some application in the medicinal field, while the free acid offers many possibilities for the future. The sugar acids and their salts resemble the sugars, in that they form soluble complex compounds with numerous substances. Hence they are able to hold in solution many difficultly soluble substances, as, for example, certain amphoteric hydroxides. The sugar acids are also unique in that they form two anhydrides or lactones (*4*). One of these is formed by condensation of the carboxyl group in gluconic acid with the hydroxyl on the fourth or gamma carbon, and the other by condensation with the hydroxyl on the fifth or delta carbon. These lactones are crystalline substances which should prove valuable additions to our supply of organic acids. Many uses for these weak organic acids or their lactones will undoubtedly be found when they are more readily available.

The older methods for the preparation of calcium gluconate by the oxidation of aldoses with chlorine (*5*) or bromine (*3*) are not satisfactory because two molecules of calcium bromide or chloride are formed for each molecule of sugar which is converted into the acid. This large quantity of the halogen salt seriously interferes with the separation of the product. As may be seen from the following equation, this objectionable feature has been overcome in the new electrolytic process which the authors have developed:

$$\underset{\text{Dextrose}}{2C_6H_{12}O_6} + CaCO_3 + \underset{\text{Catalyst}}{CaBr_2} + \underset{\text{Electrolysis}^1}{H_2O} \longrightarrow \underset{\text{Catalyst}}{Ca(C_6H_{11}O_7)_2 + CaBr_2} + CO_2 + 2H_2$$

The bromide solution on electrolysis gives free bromine at the anode and hydrogen at the cathode. The bromine thus freed reacts with the sugar to give gluconic and hydrobromic acids. The calcium carbonate reacts with the acids as fast as they are formed and thus maintains a nearly neutral solution (about pH 6.2) in which the bromine combines as fast as it is liberated. The bromide is continuously regenerated; hence a small amount of it acts catalytically to facilitate the oxidation of a large quantity of the sugar. As was shown in the previous publication (*2*), the amount of oxidation produced by a given quantity of current is close to the theoretical, and the reaction proceeds smoothly without the production of large quantities of objectionable degradation products. The sugar is converted into the calcium salt of the sugar acid, and the principal by-products are hydrogen and carbon dioxide which escape from the solution as gases.

[1] The oxidation of 2 molecules of dextrose requires 4 Faradays of electricity.

Semi-Commercial Preparation of Calcium Gluconate

The adaptation of the electrolytic method for the production of calcium gluconate to a semi-commercial scale[2] was accompanied by very little difficulty such as is usually experienced in extending a laboratory method to a larger scale. This is due to the following facts: The process is unusually free from side reactions; the method does not necessitate careful control and can be applied efficiently under considerable variation of conditions; and the equipment is simple and easily constructed. The apparatus used in these studies is illustrated in Figure 1.

The outer jar is an ordinary 5-gallon water cooler. The solution is stirred with the mechanical stirrer shown in the center. There are four anodes and four cathodes, which are graphite rods 12 inches long and 1 inch in diameter. The cell was run at 10 amperes on an e. m. f. of 6 volts, and the temperature under these conditions was 55° C. On continuous operation at 20 amperes the temperature rose to 65° C. Although the cell ran satisfactorily at the higher rate, it was usually run at 10 amperes; the current density was about 1.7 amperes per square decimeter of anode surface.

The cell was charged with 15 liters of water containing 2.7 kg. of crystalline anhydrous dextrose, 0.75 kg. of calcium carbonate, and 375 grams of bromine.[3] The bromine reacts with the sugar and calcium carbonate to give calcium bromide and calcium gluconate. After oxidation had proceeded for 3 days at 10 amperes, considerable calcium gluconate crystallized from the electrolyte. A 5-liter portion was withdrawn

[2] An application filed by one of the authors (H. S. I.) for a public-service patent covering this process has been placed in interference with applications filed by other parties. Those desiring to use the process are advised to await the outcome of the interference proceedings.

[3] The bromine reclaimed by one of the methods suggested below in the section on Recovery of Bromine may be used. If the method yielding free bromine is employed, the bromine may be collected directly in the sugar solution. The resulting solution contains practically no free bromine and hence is easily handled.

and the calcium gluconate separated by filtration. The mother liquor and wash water were returned to the cell, together with 806 grams of dextrose and 225 grams of calcium carbonate. The oxidation was continued for 30 days with daily withdrawal of calcium gluconate and addition of dextrose and calcium carbonate in the amounts mentioned above. Each day's crop of calcium gluconate was recrystallized; the mother liquors from this recrystallization were used to wash the crude product obtained the following day, and were ultimately returned to the cell. A small amount of calcium carbonate reclaimed in the recrystallization was likewise returned. The volume of the electrolyte was kept at 15 liters,

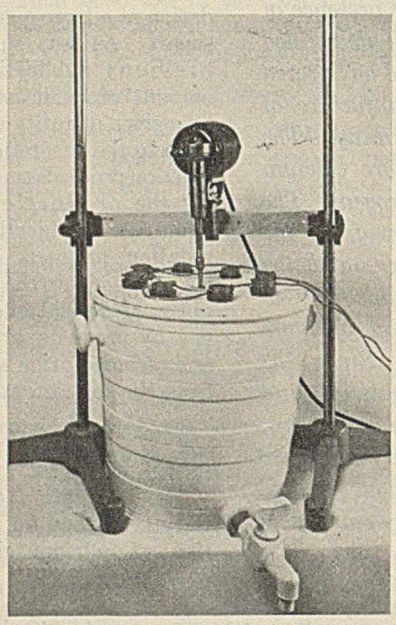

FIGURE 1. ELECTROLYTIC OXIDATION CELL

and occasionally the wash waters were concentrated in order to maintain this volume. At the end of the 30-day run, the entire electrolyte was filtered, and a sugar determination made upon the filtrate showed that 1.88 kg. of sugar remained. The electrolyte was then returned to the cell, the required calcium carbonate added, and the amount of electricity (560 ampere hours) theoretically necessary to complete the oxidation of the remaining sugar was passed through. The calcium gluconate which crystallized was separated, and an additional yield was obtained on concentrating the mother liquors. After one recrystallization, these crops were combined with the previously recrystallized salt to give a total of 27.63 kg.

A quantity of calcium gluconate remained in the mother liquors and would not crystallize from the solution containing calcium bromide. This was reclaimed in part through precipitation as a basic calcium gluconate[4] by adding 1.5 kg. of hydrated lime and heating to 70° C. The basic salt was washed with lime water and then converted into the normal salt by removing the excess lime with carbon dioxide. The normal salt thus obtained after one recrystallization weighed 2.21 kg. The total yield of nearly pure calcium gluconate was 29.84 kg. or about 85 per cent of the theoretical.

At the end of the run the electrolyte was light colored and still in condition for continuing the process. In commercial operation it would be necessary to renew the electrolyte occasionally. The frequency of renewal would depend upon the impurities in the raw materials and upon the operating conditions. Recovery of the bromide from the mother liquors will be discussed below.

As previously shown, under favorable conditions the sugar is nearly quantitatively oxidized. The experimental conditions in this case were not ideal, and there were relatively larger losses in handling and recrystallizing the material and in over-oxidation than would occur in actual plant operation. Excess calcium gluconate caused the electrolyte to become thick enough to prevent thorough stirring, and some local over-oxidation resulted. This difficulty would be overcome in a plant through continuous removal of the calcium gluconate by a suitable filter. After one recrystallization the product usually contains a small quantity of calcium bromide. Although calcium gluconate is easily recrystallized from hot water, and calcium bromide is much more soluble than calcium gluconate, still the bulky nature of the calcium gluconate makes the removal of the last traces of the bromide difficult. This is the most troublesome step in the process; but, with proper facilities for crystallizing and washing the salt in large quantity, it would be less burdensome.

In larger units, cooling coils would be necessary. In the experiments reported in this paper, no cooling device was used, but cooling is necessary when the described cell is run at its maximum capacity.

A small amount of foaming occurs during the reaction, but this does not cause any trouble provided the cell is not too full. The foaming may be reduced by the addition of a few drops of an antifoam compound, such as caprylic alcohol, although this is not necessary.

TABLE I. SEMI-COMMERCIAL MANUFACTURE OF CALCIUM GLUCONATE

	Chemicals		
	Actually used in exptl. run		Required to produce 100 lb. calcium gluconate
	Lb.	*Kg.*	*Lb.*
Dextrose	59.3	26.9	90 at $0.05 = $4.50
Calcium carbonate	16.1	7.3	25 at 0.01 = 0.25
Bromine	0.83	0.375	1.25 at 0.36 = 0.45
Electricity (for electrolysis only)	51 kw-hr.		80 kw-hr. at 0.01 = 0.80
			Estimated cost of above items $6.00

Experimental run gave 29.84 kg. (65.78 lb.) of calcium gluconate, $Ca(C_6H_{11}O_7)_2.2H_2O$, which is about 85% of the theoretical yield as calculated from the dextrose used.

Costs for the production of calcium gluconate by this process depend largely upon the volume of production. Reliable figures cannot be determined from the operation of a unit of the size outlined in this paper, but some idea of their magnitude may be obtained. A comparatively small initial investment is necessary, as the equipment is simple and easily constructed. As shown in Table I, the cost of the raw materials may be conservatively estimated at about $6.00 per 100 pounds. This estimate is based on current prices and the results obtained in the experimental run. The cost for electricity will depend largely on the location and operating conditions. The cell used in the run under discussion requires about 6 volts for a current of 10 amperes, and produces about 2 pounds of calcium gluconate per day; if the capacity is doubled by increasing the voltage to 12, more energy is lost as heat. The most economical operating conditions as well as the cost for electrodes, maintenance, operation, depreciation, etc., cannot be determined at this time, but it is evident that calcium gluconate may be made by the new process at a very reasonable figure.

POLARIZATION AND CRACKING OF ELECTRODES

In the course of the electrolytic oxidation, the cathodes occasionally become coated with a calcareous deposit. The composition of this deposit varies considerably, but it always

[4] The crude basic calcium gluconate obtained from the impure electrolyte after a washing with lime water may be used in a subsequent run in place of some of the calcium carbonate. The calcium gluconate is then recovered along with the crude oxidation product. However, in the event that the basic salt is very impure, it is probably better to prepare the normal salt by decomposition with carbon dioxide in the usual manner.

contains calcium carbonate, calcium hydroxide, calcium gluconate, and a small amount of material which reduces Fehling's solution. The coating is generally formed when dilute solutions are employed and is seldom found when the electrolyte contains considerable sugar or calcium gluconate. Presumably the sugar derivatives, by their solvent action, prevent the deposit of calcium hydroxide in the alkaline region immediately surrounding the cathode.

A typical cathode coating obtained with a dilute solution is illustrated in Figure 2. This deposit may be removed by reversing the current. The previously coated cathode then becomes the anode, and the hydrobromic acid formed in its vicinity quickly dissolves the deposit.

Table II. Effect of Reversing Direction of Current on Current Efficiency

Time between Changes in Direction of Current	Current Density	Current Efficiency[a]
Minutes	*Amp./dm.*^{2}	%
1	1.6	39.4
1	3.2	53.5
25	1.6	80.1
400 (approx.)[b]	1.6	95.5
∞ [c]	1.6	94.7

[a] Current efficiency is the percentage of the sample found to have been oxidized after 13.4 ampere hours. The quantity of electricity theoretically required for complete oxidation of the sample is 13.4 ampere hours.
[b] The current was reversed whenever it was believed necessary to prevent the formation of a heavy deposit.
[c] The current was not reversed, and consequently considerable deposit formed on the cathode.

A number of experiments were made to determine the effect of reversing the direction of current upon the efficiency of the oxidation. The determinations were made on solutions containing 45 grams of dextrose, 8 grams of calcium bromide, and 25 grams of calcium carbonate in 1 liter of water. The solution was electrolyzed in a flask fitted with graphite electrodes and a mechanical stirrer. A timing device was included in the circuit so that the direction of the current could be reversed at definite intervals. As shown in Table II, reversing the current lowered the efficiency. With an alternating (60-cycle) current, practically no oxidation occurred.

It is apparent from the results given in Table II that the current should not be reversed except when it is necessary to clean the electrodes. If the proper conditions are maintained, this is seldom required. In the continuous oxidation reported, the current was reversed three or four times at the beginning of the run.

Frequently, with concentrated solutions and high current densities the anodes split longitudinally, but the cathodes are unaffected. The effect seems to be mechanical, for the graphite is not corroded. The cracks usually are filled with crystalline material, and the difficulty occurs only during long-continued oxidation. This suggests the explanation that the electrodes originally contained minute cracks in which calcium gluconate or some other substance collected, producing fractures in a manner analogous to the fracture of rocks by the freezing of water. This difficulty may be largely overcome by impregnating the electrodes with paraffin to fill up the minute cracks and thus prevent penetration by the electrolyte.

Recovery of Bromide

In a plant it would be necessary to recover the bromide from mother liquors which become contaminated by long-continued use. The simplest method consists in evaporating the residues to dryness and igniting to remove the organic matter. The ash which remains is largely calcium carbonate, oxide, and bromide, and hence it may be used in a subsequent electrolytic oxidation as a source of bromide. Frequently it contains objectionable impurities, in which case it requires further purification. The ash or residue may be extracted with water, and the aqueous solution used directly; or the bromine may be liberated by electrolysis of the extract after acidification with sulfuric acid. In the latter case the free bromine is distilled into a dextrose solution containing calcium carbonate in suspension.

In the semi-commercial experiment described in a previous section, the residues were ignited and the ash extracted with 2 liters of boiling water. The extract was acidified with sulfuric acid, and the bromine liberated by electrolysis. Platinum electrodes were used. Air was bubbled through the solution to aid in removing the bromine, and the vapors were led into a solution containing 2.7 kg. of dextrose, and 750 grams of calcium carbonate in suspension. After all the bromine had been collected in the sugar solution, it was transferred to the cell and used directly for the preparation of more calcium gluconate in manner analogous to that described above. The bromine recovered (and determined by bromide analysis upon the fresh electrolyte) was about 53 per cent of that originally used. This figure is not indicative of the efficiency of the method of recovery because of preventable losses in handling, and retention of the bromide in the calcium gluconate. In this connection it should be recalled that the cost of the bromine is only a small fraction of the total cost.

Basic Calcium Gluconate

Although Fischer (*1*) reported in 1890 that gluconic acid forms a basic calcium salt, the compound has not been studied further nor its composition determined. The writers have found that the difficultly soluble basic salt obtained from calcium gluconate by the addition of hydrated lime may be used to advantage for the separation of calcium gluconate from impure solutions which will not yield the crystalline normal salt. As stated in a previous paragraph, it was used for this purpose in reclaiming calcium gluconate from the residual mother liquors. The product obtained was impure and contained an excess of lime. It is not necessary to prepare the pure salt when it is to be used for separating calcium gluconate, since the excess lime is removed later as the carbonate. However, in order to determine the composition of the substance, it is necessary to obtain it pure. This may be accomplished by taking advantage of the fact that basic salts of this type are less soluble in hot water than in cold. The following procedure was used for preparing the basic salt of gluconic acid:

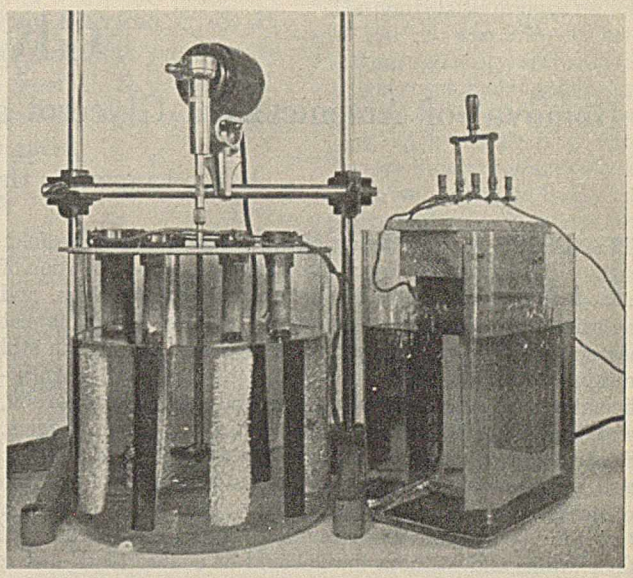

Figure 2. Cell Showing Calcareous Deposit on Cathodes

To a solution of 100 grams of pure calcium gluconate in 1400 ml. of water were added 600 ml. of milk of lime prepared from 27 grams of calcium oxide. Both solutions were kept ice-cold. The resulting mixture was filtered quickly on a large Büchner funnel with a coarse filter paper. After the addition of a small quantity of decolorizing carbon, the solution was filtered again. The basic salt was precipitated by warming the clear filtrate on the steam bath. It was separated by filtration while hot, washed thoroughly with hot lime water and finally with a small quantity of hot water, and then dried to constant weight at 80° C. *in vacuo* (about 24 hours).

During its preparation, it was protected as much as possible from the carbon dioxide of the air, and when dried was kept in small air-tight bottles until used. The crude basic calcium gluconate may be prepared with good yield, but the quantity of the pure salt obtainable by the above procedure varies considerably with the technic. As much as 40 grams of the pure dry salt have been obtained; but, in case the solution of calcium gluconate and the milk of lime are not cold, or an excess of lime is added, the basic salt may precipitate before the mixture can be filtered, and the yield from the filtrate is then very small.

Several preparations by the above procedure, dried to constant weight *in vacuo* at 80° C., gave consistent analyses corresponding to the formula $Ca(C_6H_{11}O_7)_2 \cdot 2CaO$. However, when dried at lower temperatures, the salt appears to hold varying amounts of water. The calcium oxide content usually ran a little low and the carbon somewhat high; this is probably caused by the absorption of a small amount of carbon dioxide during the preparation of the sample.

Analyses of $Ca\ (C_6H_{11}O_6)_2 \cdot 2CaO$ are as follows:

	Calcd. %	Found %
Carbon	26.55	27.09 27.09
Hydrogen	4.09	4.03 4.07
Calcium	22.16	22.10
Calcium oxide	20.68	20.30

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Losses in Distillation of Crude and Refined Glycerol

Removal of Arsenic from Glycerol and Its Purification by Crystallization

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Losses in the refining of crude glycerol are threefold: (1) mechanical losses, due to imperfect condensation of the vapor during distillation and concentration, and entrainment losses in the evaporation of dilute glycerol (sweet water). To this may be added unrecovered glycerol in still residues (foots) if these are washed into the sewer. Insufficient washing of filter-press cakes and decolorizing carbon, and losses due to spillage or overflow are other dangers. Sewer connections should be very few in a glycerol refinery; and a preliminary discharge of wastes to a safety tank, the contents of which can be dumped to the sewer only after a test for glycerol has been made, is highly advisable. All floor drains and washout lines should be connected to such a tank. (2) Losses in sweet water or spent lye due to the fermentation of the glycerol with the production of gas, acids, or trimethylene glycol. (3) Chemical losses in distillation due to the destruction of the glycerol by its reaction at the temperature of the still with the impurities ordinarily present in crude glycerol.

Distillation Method for Determination of Recoverable Glycerol

A study of chemical losses was undertaken by means of an experimental still (Figures 1 and 2) built on the lines of a glycerol-refining plant but permitting a much more rapid distillation. This still was based on a vacuum distilling apparatus obtained from Eimer and Amend, New York, and illustrated in their catalog (*3*).

A vacuum of 28.0 to 28.5 inches was obtained by a water aspirator pump, the discharge from which cooled the copper condenser and its block tin coil. The receiver for the condensed steam used in distillation with its charge of glycerol was connected at the top to a Woulfe bottle connected in its turn to a vacuum gage and the aspirator pump. The glass dome in the Eimer and Amend illustration and the glass tube to the condenser were replaced by a removable brass still top and a brass pipe connection to the condenser, provided with a short piece of glass tubing to detect foaming. The brass dome carried two sight glasses and was insulated with 85 per cent magnesia covering. The steam jacket was filled with a mixture of equal parts of technical aniline and *o*-toluidine, boiling at 364° and 391° F. (184.4° and 199.7° C.), respectively. The contents of the jacket were heated to boiling by four Bunsen burners. The vapor was condensed in an air-cooled iron pipe and returned to the jacket. A large air-cooled brass condenser was placed between the still and the water-cooled condenser. Superheated steam at 350° F. (176.7° C.) was supplied by a steam jet at the bottom of the still just above the jacket. Steam may be taken from any convenient source but must be dry. The presence of water in the steam causes foaming and bumping just as it does on a large scale. (Doubtless some unexplained explosions of glycerol stills during operation have been caused by the sudden addition of water in the steam to the hot glycerol at 350° F. (176.7° C.).

Operation of Experimental Still. Refer to Figures 1 and 2. Rinse out both condensers *C*1 and *C*2 with steam and wash out the still, *A*, with hot water. Place a weighed quantity, 450 to 500 grams, of crude glycerol in the still. Clamp on the dome, *B*, and connect with the condenser, *C*1, by means of the glass tube, *D*, and rubber connection, *E*. Start the vacuum pump, *F*, and open the valves, *V*1, *V*2, and *V*4. *V*4 is connected with the bottle, *M*1, by means of a rubber tube. Keep the valves *V*3, *V*6, *V*7, and *V*8 closed. Start the gas burners, *G*1, under the still jacket which is filled with a mixture of half and half aniline and toluidine. Should the glycerol show a tendency to shoot, when examined through the eyeglass in *B*, break the vacuum by opening valve *V*8 on the vacuum breaker, *P*. By the time the vacuum has reached 28 inches, the water will have been removed from the glycerol and the steam may be turned on. It is most important that the steam be dry. The superheaters cannot be relied upon to prevent water reaching

the hot glycerol unless all steam lines are well lagged. If the steam supply is at some distance from the boilers and there is much condensed steam present, special separators must be installed to remove all entrainment. Any convenient steam pressure may be used. After opening the connection to the main steam line, open valve *V*7 on the separator to remove the drip. Start the gas burner, *G*2, under the superheater. Then open cautiously the valve *V*6. The temperature of the steam entering the still should be about 350° F. (176.7° C.) as shown by the thermometer, *K*, which dips into a tube containing Wood's metal.

Glycerol will be seen passing through the glass tube, *D*, and at the end of 20 minutes the glycerol will be practically all over, provided the vacuum is good and the steam is dry. Foaming will seldom be troublesome on crudes of fair quality unless water reaches the hot glycerol, when foaming is bound to take place. About 75 per cent of the glycerol is caught in the bottle, *M*1, and the balance with the condensed steam in the receiver, *M*2. The steam should be kept on until the receiver is full to the top of the gage glass, *L*. Shut off the gas, steam, and vacuum pump. Break the vacuum by opening the valve *V*8. Remove the heavy glycerol at *M*1 and set aside. Run out the dilute glycerol at *V*3 and boil it down in a large dish or copper kettle. The time up to this point will be about 1.5 to 2 hours. After the still has cooled, put on the vacuum and draw into the still through *P* about 800 cc. of water. Shut the valve at *V*8 and also the valve *V*2, while still allowing the water to flow through the pump, *F*, and condenser, *C*2. Start the burner at *G*1 and boil off the water in the still without vacuum to wash down the sides of the still and dome. The steam that escapes condensation in the still will condense in *C*1 and *C*2 and will rinse out the two condensers and receiver. The rinsings are caught in *M*1 and through the open valve at *V*3. These rinsings are added to the dilute glycerol already boiling down. When the water is all boiled out of the still, the residue will lie around the bottom of the still and may contain 1 to 2 per cent glycerol, based on the original charge. This must be removed by a second distillation. Put on the vacuum, and, when everything is hot and dry, distil as before until *M*2 is nearly full. Nothing will collect in *M*1 this time. Combine this distillate with that already boiling down. In accurate work it is necessary with some crudes to distil a third time to recover 0.25 to 0.50 per cent held in the residue. The combined thin distillates are concentrated until the temperature of the liquid is 218–220° F. (103.3–104.4° C.). No glycerol will be volatilized. Then combine with the heavy glycerol collected in *M*1, and filter and wash the whole into a weighed liter flask. Make up to approximately 1000 cc. and determine the specific gravity by a pycnometer. Reference to a glycerol table will give the equivalent per cent of glycerol for the computation of the anhydrous glycerol in the distillate. The difference between this figure and the anhydrous glycerol present in the crude, as determined by chemical analysis, is the distilling loss. The method of analysis is the acetin process (International Standard Method, 1911). In the United States, but not in England, the straight acetin percentage is always corrected for the acetyl value of the nonvolatile organic residue at 160° C.

If the dry residue (foots) is scraped out of the still and burned off in a platinum dish, the ash will usually run about 72 per cent. It is instructive to compare this figure with the ash on the dry foots from the large-scale plant. The difference will be a measure of the amount of nonvolatile polyglycerols produced by distillation of the crude on a large scale in comparison with that formed by the distillation in the experimental still.

An experimental still for distilling 500 grams of crude or refined glycerol with steam in vacuo is described. With this still a study is made of the losses incurred when glycerol containing various common impurities is distilled. Carbonate of soda (2.0 per cent) causes a loss of 2.2 per cent glycerol; 2.0 per cent aluminum sulfate gives a loss of 10.6 per cent; 5.0 per cent of soap, a 14.8 per cent loss. The losses are materially reduced in the presence of sodium chloride and sulfate. Good soap-lye crudes can be distilled with a loss of 0.50 to 1.00 per cent, bad crudes will show 3.50 to 5.00 per cent, and exceptional ones up to 13.0 per cent. Sodium chloride and sulfate cause no loss. Refined glycerol may be distilled without loss.

The Wood process of multiple-effect distillation is briefly described.

Arsenic may be removed from distilled glycerol at 20 to 25 per cent strength by the action of powdered cast iron and air. Potassium permanganate in amounts as low as 0.05 per cent will remove arsenic at concentrations of 65 to 70 per cent.

Detailed analyses of eleven American U. S. P. glycerols are given. Glycerol of high purity may be made by crystallization from U. S. P. glycerol. A specific-gravity table based on twice-crystallized chemically pure glycerol is given.

Losses in Distilling Glycerol

The percentage of glycerol lost when distilling in the experimental still described above ranged from 0.25 to 0.50 per cent on high-grade saponification crudes, and 0.50 to 1.00 per cent on high-grade soap-lye crudes. Bad crudes of both varieties may run up to a 13 per cent loss. Losses of 3.50 to 5.00 per cent are quite common.

An average sample representing 2.5 million pounds of rather good crudes showed by the straight acetin (I. S. M., 1911) 81.86 per cent glycerol. The nonvolatile organic residue at 160° C. was 2.71 per cent and gave an acetyl correction of 1.10 per cent, making the actual glycerol by analysis 80.76 per cent. Ash was 7.91 per cent. Twelve hundred grams of this crude were distilled in the experimental still as above described, except that the distillate was treated for the removal of arsenic with 0.06 per cent potassium permanganate and 0.3 per cent sodium hydroxide, filtered, and redistilled. The loss with this double distillation and treatment was 1.60 per cent. The ash on the dry foots from the crude or first distillation was 74.4 per cent.

Eleven other average samples, representing receipts of 1 to 3 million pounds of crude, showed losses on double distillation and treatment to remove impurities, as is done in the manufacture of C. P. glycerol, of 1.73 to 2.87 per cent (average 2.34 per cent). The ash of the still residues on these crudes was 70.75 to 73.62 per cent (average 71.92 per cent).

An analysis of the distillation losses was undertaken by still tests using C. P. glycerol to which had been added varying amounts of impurities commonly present in crudes. The term "chemically pure" in this article is synonymous with U. S. P. X.

There is no loss in evaporating dilute glycerol at temperatures below 220° F. (104.4° C.), equivalent to approximately 70 per cent glycerol. Four hundred twenty-five and four-tenths grams of C. P. glycerol were diluted to the mark in a liter flask at 29.25° C. The weight was 1188.5 grams. The contents of the flask were rinsed out, diluted to 5 liters, and evaporated until the temperature reached 220° F. (104.4° C.), when they were retransferred to the liter flask at the same temperature (29.25° C.), made up to the mark, and weighed. The weight was the same—1188.5 grams.

There is no loss in the distillation of pure glycerol with steam *in vacuo*. Four hundred and fifty-one grams of C. P. glycerol were diluted and made up to the mark in a liter flask

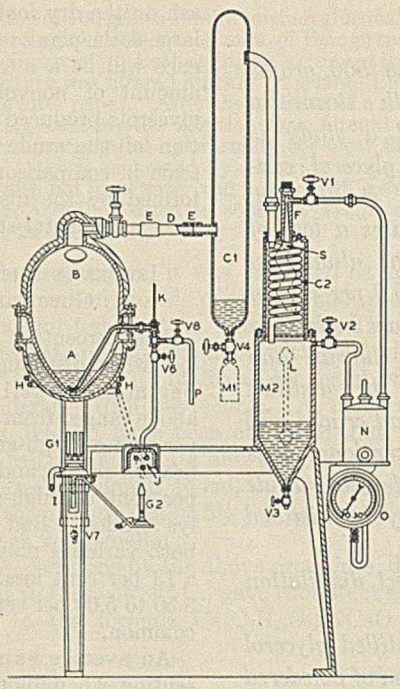

FIGURE 1. DIAGRAM OF GLYCEROL EXPERIMENTAL STILL

A.	Aniline-jacketed still	*I.*	Steam separator
B.	Dome with sight glasses, front and rear	*K.*	Thermometer
		L.	Gage glass
C1.	Hot condenser	*M1.*	Receiver of hot condenser
C2.	Cold condenser	*M2.*	Receiver of cold condenser
D.	Glass connections	*N.*	Woulfe bottle and catchall
E.	Rubber joints	*O.*	Vacuum gage
F.	Filter pump	*P.*	Vacuum breaker
G1, G2.	Gas burners	*S.*	Overflow from cold condenser
H, J.	Steam superheaters	*V1–V8.*	Valves

at 60° F. (15.6° C.). The net weight was 1101.6 grams. The diluted glycerol was transferred to the experimental still, concentrated, distilled, and evaporated for transfer back to the flask. It was made up to the mark at 60° F. (15.6° C.) and showed a weight of 1101.0 grams, a negligible loss.

The loss is dependent on the time of the distillation. An 81.1 per cent soap-lye crude was slowly distilled at a 25.0-inch vacuum showing a loss of 5.0 per cent. The same crude, rapidly distilled at 28.5-inch vacuum, lost only 3.9 per cent.

Mixtures of 450 grams C. P. glycerol with the commonly occurring impurities in crudes were distilled rapidly in 20 to 25 minutes with steam at a vacuum of 28.75 inches in the experimental still. Chemically pure glycerol, to which 2.0 per cent sodium carbonate (dry) were added, showed a distilling loss of 2.2 per cent; sodium acetate, equivalent to 2.0 per cent sodium carbonate, destroyed 1.5 per cent glycerol; sodium butyrate, 1.1 per cent; sodium caproate, 0.8 per cent; and sodium hydroxide, 1.7 per cent. The addition of 5.0 per cent sodium carbonate gave a loss of 6.0 per cent.

Technical aluminum sulfate (alum), when distilled with C. P. glycerol, showed a 2.3 per cent loss with 0.5 per cent alum; 10.6 per cent loss with 2.0 per cent alum; and 62.7 per cent loss with 10.0 per cent alum. As aluminum sulfate has often been used as a purifier for spent lye, any excess left in the lye after filtration may cause serious losses. Alum in the presence of acid is even more prejudicial. Thus 1.0 per cent of sulfuric acid and 2.0 per cent of alum gave a loss of 66.0 per cent. Persulfate of iron, another spent lye purifier, is less destructive, a 10 per cent addition reducing the yield by 7.7 per cent.

These losses are materially reduced by the presence of sodium chloride and sulfate commonly contained in soap-lye crudes. Thus, an admixture of 7.0 per cent sodium chloride and 3.0 per cent sulfate brought the loss with 2.0 per cent alum to 0.5 per cent, and with 5.0 per cent sodium carbonate to 1.4 per cent. The addition of 5.0 per cent of a soap made from half stearic and half oleic acids caused a 14.8 per cent glycerol loss. When 10.0 per cent sodium chloride was added to this 5.0 per cent soap, the loss dropped to 2.7 per cent.

Borax, present in some soap-lye crudes, may cause heavy losses in distillation unless first neutralized with acid. A mixture of 80.0 per cent anhydrous glycerol, 4.0 per cent borax, 8.0 per cent salt, and 8.0 per cent water, heated in a ventilated oven at 160° C. to determine nonvolatile organic residue (I. S. M., 1911), showed 5.94 per cent, whereas there was no nonvolatile organic matter in the original mixture, this amount being produced by the action of the borax in polymerizing the glycerol.

Distilling experiments with sodium chloride and sodium sulfate showed no losses.

These results show that, during the process of distillation, a destructive reaction occurs between the glycerol and certain impurities present. The loss will depend upon the time, concentration of the impurities, and temperature in particular, the speed of a reaction being approximately doubled for each 10° C. rise in temperature.

Time can be reduced by raising the temperature or increasing the vacuum or the steam supply. The choice of all these factors will be determined by the quality of distillate required; the cost of steam, labor, and plant; the price of glycerol; and the output desired at times to take advantage of market conditions. If anhydrous distilled glycerol is worth 12 cents per pound, a distilling loss of 2.0 per cent is equivalent to a quarter of a cent per pound, about a third of the factory manufacturing cost.

Crude soap-lye glycerol is commonly alkaline to a degree which will cause distilling losses. This excess alkalinity can be reduced by neutralization with acid along the lines suggested by the method for the determination of nonvolatile organic residue at 160° C. (I. S. M., 1911) (*5*). If too much acid is added, however, the fatty acids in the glycerol distillate may exceed the limits set by buyers of dynamite glycerol, who have fatty-acid specifications.

WOOD DISTILLATION PROCESS

Varying requirements of plant operation are most easily met by the Wood multiple-effect stills, with their preheaters, uniform vacuum, forced circulation, and boiling-water condensers with a definite temperature control. This process was described by Wood and Langmuir (*10*) and is covered by four patents (*9*) all of which have expired. Lawrie (*6*) discusses the method in considerable detail with illustrations. Young (*11*) also describes the process using a different illustration. Webb (*8*), referring to its success in England says, "This system is extremely efficient in practice, and the author's opinion that it seems to be the system of the future is certainly borne out as far as practical experience is concerned." He also states (*7*) that the process will distil crude at 25 to 30 per cent of the fuel cost of the Van Ruymbeke process.

The Wood process was in use at the glycerol-refining plant of Marx and Rawolle, Inc., Brooklyn, N. Y., from 1909 up to the discontinuance of the business in 1926. It has also been in use in England from 1910, and in Montreal, Canada, from 1910 to 1926. During the writer's connection with the Brooklyn plant up to 1920, about 135 million pounds of U. S. P. and dynamite glycerol were produced which compared very favorably with other glycerols in quality and were sold in open and sometimes cutthroat competition with other makes, and usually at a good profit. When the old type single-

effect stills were connected in series of six (two sets of six each) and four (one set including two foots stills), the output was doubled and the coal consumption reduced 60 per cent.

Considering the losses on the experimental still during only a 20-minute distillation of 3.50 to 5.00 per cent on bad crudes running up to 13.00 per cent in exceptional cases, it is difficult to understand the claims often made of 99.00 per cent yields unless the crudes worked were of excellent quality. Some refiners consider their dynamite glycerol as 100 per cent, whereas it contains 1.0 per cent water. Others have used faulty specific-gravity tables for the estimation of the glycerol in the distillate.

A refiner on a large scale, purchasing crude in the open market, must take good and bad crudes as they come, in order to obtain a large supply at a fair price. On a 14 million pound run of average American and foreign crudes (about 80 per cent soap lye and 20 per cent saponification), the loss was 3.14 per cent. The output was 70 per cent chemically pure (second distillation from crude) and 30 per cent dynamite glycerol (one distillation from crude). The distilling temperature in the crude stills was 340° F. (171.1° C.); and in the C. P. stills, 350° F. (176.7° C.) The average vacuum was 28.5 inches. The crude soap lye was mixed with 20° muriatic acid in the proportion of one carboy to ten drums. The contents of the C. P. stills were rendered alkaline with 0.3 per cent sodium hydroxide. The stills were operated in two sets of six each, the C. P. stills being the first units in each series. There was a third set of four stills, the first and second stills of the series being foots stills and the last two being crude stills. The stills for foots were each provided with double nests of high-pressure steam coils (175 pounds) to supply ample heating surface. The alkalinity of the foots should be reduced by acid. The foots were distilled to dryness, a hydrometer test showing only water in the steam flowing to the third effect (a portion of the vapor is condensed for this purpose). The salty residue was then dissolved in hot water and discharged to the sewer. While somewhat better yields are obtainable by purification of the foots before distillation, the author has never found it economical in a glycerol refinery not attached to a soap plant.

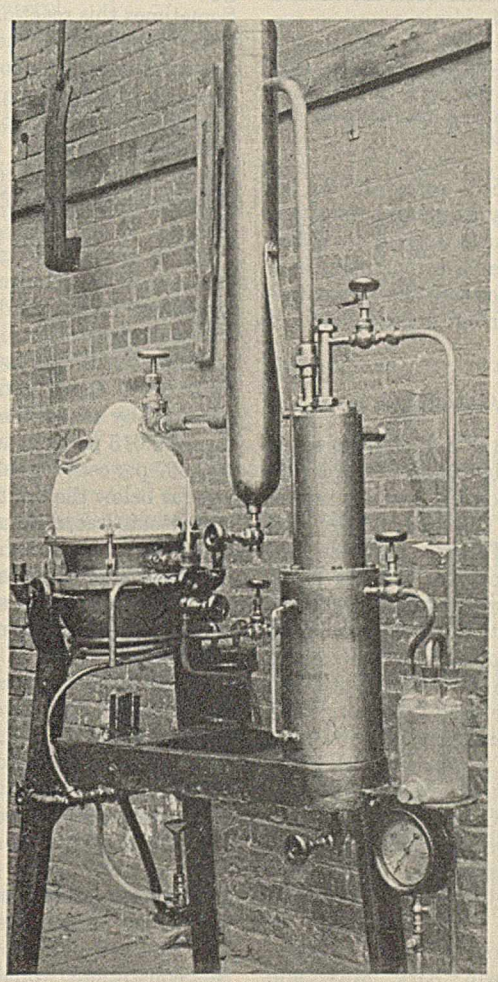

Figure 2. Photograph of Glycerol Experimental Still

Removal of Arsenic from Glycerol

When a sufficient quantity of crude or refined glycerol is examined by a delicate test, such as the Gutzeit or Marsh, arsenic will always be found. This has been the writer's experience with some hundreds of samples from all over the world. Even high-grade saponification (candle) crudes manufactured from clean fats by the autoclave process with a small percentage of lime will inevitably show distinct traces. It is quite possible that the fats themselves from which these crudes are made carry very small amounts of arsenic. Such crudes will run up to 0.00100 per cent arsenious oxide. Soap-lye crudes which have been neutralized with arsenical acid will occasionally carry 0.05000 per cent. The limit of the United States Pharmacopeia is 1 part in 100,000, or 0.00100 per cent. The limit of the Royal Commission on Arsenical Poisoning, London, 1903, was placed at 0.01 of a grain of arsenious oxide per pound of 7000 grains on food ingredients. This is equivalent to 0.00014 per cent as an upper limit. It is desirable to reduce the arsenic in C. P. glycerol below this figure.

When the refiner's raw material is his own spent lye, which may be treated with crude ferric sulfate and may be filter-pressed, the great bulk of any arsenic present is held by the precipitated ferric hydrate. Purchasers of 80 per cent soap lye or 88 per cent saponification crudes cannot afford to dilute these glycerols to a spent-lye concentration of 4 to 5 per cent in order to apply this purification. The removal of arsenic must be effected in the once-distilled glycerol to be used for chemically pure manufacture, which is already of a high degree of purity. The method must be cheap, it must not destroy glycerol in appreciable amount, and it must not introduce impurities difficult to eliminate in the distillation for chemically pure. Such limitations bar out such reagents as hydrogen sulfide or the addition of ferric chloride to the diluted glycerol, followed by precipitation with ammonia and filtration of the ferric hydrate.

It was found that storage of chemically pure for several months in galvanized-iron drums reduced the arsenic somewhat. Filtration through bone black was also effective, but the black soon became poisoned. Agitation of the diluted glycerol with powdered limonite or pyrolusite removed a little arsenic. Magnesium oxide, free from carbonate, was very effective. Calcined magnesite was tried on a large scale, but the method had to be abandoned because of the slimy precipitate produced after agitation with 20 per cent glycerol, which clogged the filter presses.

Stirring of the 20 to 25 per cent glycerol with powdered cast-iron borings removed most of the arsenic but was not serviceable a second time. If the glycerol was agitated, however, by a jet of air instead of a stirrer, the iron could be used indefinitely. It became at once evident that it was the oxidation of the iron in contact with the glycerol which produced a form of oxide extremely effective in combining with the arsenic present. This process was successful on a large scale in cutting the arsenic below the Royal Commission limit. The once-distilled, hot, 20 to 25 per cent glycerol was treated in a 14 foot diameter, iron, brewer's mash tube. The bottom of the tank was covered with 4 inches of pulverized cast-iron borings which were brought up into the glycerol by the iron

shovels of the revolving arm. At the same time, air was introduced from an air compressor. A little iron went into solution owing to the presence of a little fatty acid. This was precipitated with sodium carbonate while air was being injected and then filter-pressed. The iron process entirely met the requirement of cheapness. It destroyed no glycerol and introduced nothing which would later make trouble. The process is, however, effective only with glycerol diluted to 20 to 25 per cent.

Following up the clue afforded by the behavior of pyrolusite, permanganate of potash suggested itself as affording an active variety of manganese oxide, the glycerol acting as a reducing agent. Heated with dilute or concentrated glycerol, a brown to black oxide is separated in a form readily filtered and which carries with it nearly the last traces of arsenic, bringing it well below the limit of 0.01 grain per pound. The permanganate process does not work well with dilute glycerol of 20 per cent concentration, but is most effective with 65 to 70 per cent glycerol. It destroys about its own weight of glycerol by oxidation, but only very small amounts are needed—from 0.05 to 0.10 per cent potassium permanganate figured on the anhydrous glycerol present. The glycerol, as it runs from the boiling-water condensers of the Wood apparatus, is collected and mixed with the requisite quantity of permanganate dissolved in sufficient water to lower the concentration of the glycerol to 65 per cent. The mixture is heated to 195° F. (90.6° C.), made alkaline with 0.3 per cent sodium hydroxide, and filter-pressed. The arsenic will be well below 0.00014 per cent. The excess sodium hydroxide in the filtrate serves to hold back the volatile fatty acids during the C. P. distillation.

Warning. If concentrated glycerol comes in contact with dry permanganate of potash, even in the cold, the mixture ignites spontaneously with the production of an intensely hot violet-colored flame and a red-hot residue.

The successful use of permanganate of potash in the removal of traces of arsenic from glycerol suggests its application for a similar purpose with organic products, such as citric and tartaric acids or salts, and with inorganic compounds, such as sodium phosphate, etc. In the latter case the permanganate would be combined with a convenient organic reducing agent.

Impurities in "Chemically Pure" Glycerols, U. S. P.

The tests below were made on eleven U. S. P. glycerols purchased on the open market in the original 50-pound boxed tins in the year 1911 from the following manufacturers: Armour, Cudahy, Colgate, Jobbins, Harshaw, Fuller and Goodwin, Kirk, Larkin, Marx and Rawolle, Procter and Gamble, Swift, and Wrisley. The analyses are not listed in the same order. Specific gravities were taken at 60/60° F. (15.6/15.6° C.) with a 50-cc. pycnometer. Sodium chloride was determined on the water extract of the charred residue after burning off 25 grams of glycerol and titration with 0.01 *N* silver nitrate and potassium chromate as an indicator. The other tests were in conformity with the details given in both Revisions IX and X of the United States Pharmacopeia under the heading "Glycerinum." These tests were the result of a conference held at Atlantic City between the Revision Committee and representatives of leading glycerol refiners prior to the issue of the Revision IX. These tests still govern the purity of U. S. P. glycerol in the United States.

In 1910 samples were obtained from Armour, Colgate, Cudahy, Harshaw, Fuller and Goodwin, Kirk, Marx and Rawolle, Peet, Procter and Gamble, and Wrisley for an examination of the nature of the ash in U. S. P. glycerols. Portions of 1000 grams each were burned off, and the residue analyzed by the customary methods of mineral analysis.

Table I. Analyses of Eleven American U. S. P. Glycerols

	Net Weight Glycerol	Sp. Gr.[a]	Sodium Chloride	Fatty Acids	Arsenious Oxide	Carbonaceous Residue	Ash
	Pounds		%	*Cc.*	%	%	%
A	51	1.2612	0.00046	0.5	0.00020	0.0100	0.0030
B	50	1.2575	0.00081	1.4	0.00005	0.0130	0.0046
C	50.5	1.2524	0.00131	0.5	0.00008	0.0060	0.0022
D	45.5	1.2567	0.00023	0.2	0.00002	0.0070	0.0020
E	50	1.2526	0.00140	0.4	0.00004	0.0060	0.0030
F	50	1.2591	0.00023	1.8	0.00005	0.0092	0.0054
G	50	1.2533	0.00046	0.6	0.00003	0.0074	0.0044
H	50	1.2593	0.00040	0.3	0.00001	0.0660	0.0200
I	50	1.2520	0.00120	0.45	0.00005	0.0170	0.0060
J	50.5	1.2589	0.01566	0.7	0.00003	0.0760	0.0410
K	50	1.2530	0.00046	0.6	0.00008	0.0080	0.0040

[a] At 60/60° F. (15.56/15.56° C.).

Table II. Detailed Ash Analyses of U. S. P. Glycerols

Glycerol	Ferric Oxide	Lime	Silica	Glycerol	Ferric Oxide	Lime	Silica
	%	%	%		%	%	%
L	0.0051	0.0062	0.0010	Q	0.0019	0.0050	0.0004
M	0.0028	0.0035	0.0005	R	0.0020	0.0051	0.0005
N	0.0035	0.0025	0.0003	S	0.0031	0.0020	0.0006
O	0.0055	0.0130	0.0008	T	0.0036	0.0022	0.0005
P	0.0020	0.0007	0.0003				

The presence of silica is surprising. It was determined by volatilization with hydrofluoric acid.

If crudes contain ammonia or amines, traces of copper may be taken up from the copper condensers or evaporators used in C. P. manufacture. If this copper gets by the decolorizing carbon, it may make trouble in the storage tanks if the glycerol stays hot, owing to the formation of cuprous oxide. Sometimes this reaction does not take place until the glycerol is in the hands of the customer. It is characterized by a beautiful light pink color, seen best in direct sunlight. The presence of copper may also cause discoloration in hydriodic preparations, owing to the slow separation of cuprous iodide darkened by iodine. On the other hand, glycerol suppositories with stearic acid require the presence of a trace of sodium chloride in the glycerol (U. S. P.) to give the requisite consistency.

All of the U. S. P. glycerols whose analyses are tabulated above met the requirements on specific gravity except one, which was only a shade too low. All contained therefore 95 per cent glycerol, or over, as specified. One of the samples contained 98.37 per cent glycerol. The fatty acid and ester limit of 1.0 cc. of normal sodium hydroxide on 100 cc. was exceeded by two of the lots. The limit on carbonaceous residue of 0.015 per cent was exceeded in three cases. The limit of 0.007 per cent for ash was passed by two samples. Arsenic was far below the limit of 1 part in 100,000. Not one sample was arsenic free, although all except one were below the Royal Commission maximum of 0.00014 per cent.

While these samples were representative only of glycerols of 1911, the U. S. P. standards of purity are the same today and there has been no material change in processes of glycerol refining.

The presence of trimethylene glycol is quite possible in the 95 per cent U. S. P. glycerol in considerable amount. No test is given in the U. S. P. for its detection. It is a common impurity in crude glycerols and in distilled glycerols made from such crudes. It may also occur because of fermentation of sweet waters in the refining plant. The specific gravity of trimethylene glycol is very low (1.053), and it has a marked effect in lowering the gravity. The high specific-gravity requirements of the dynamite-glycerol users, 1.2620 at 60/60° F. (15.6/15.6° C.), in itself necessitates the absence of glycol. The best safeguard for the freedom of U. S. P. glycerol from this constituent would be the requirement that the specific gravity should be 1.2600 at 60/60° F. (15.6/15.6° C.) or higher.

U. S. P. Requirements of Glycerol

Both in England and Canada the Pharmacopeia standards call for 98 per cent glycerol (1.26 specific gravity). Since, in refining processes, the glycerol runs from the condensers at 98 per cent or over, no additional expense would be incurred in removing water as would be the case with 95 per cent alcohol. The U. S. P., of course, permits the delivery of 98 per cent glycerol on a 95 per cent requirement, but competition compels the dilution of the 98 per cent glycerol to 95 per cent by the addition of distilled water. The shipment of this needlessly dilute glycerol to the trade imposes a 3 per cent tax on the consumers for freight and container. Another disadvantage is that manufacturers have to stock two grades if they do a foreign business.

In 1922 the advisability of petitioning the U. S. P. X Revision Committee to raise the gravity of the U. S. P. glycerol to 1.26 (98 per cent) in conformity with the practice of Canada and Great Britain was suggested to a group of chemists representing American glycerol refiners. The project was dropped because only two of the refiners approved of the plan. Revision XI of the U. S. P. is now under way.

Purification of U. S. P. Glycerol by Crystallization

Volatile fatty acids and reducing impurities are the most difficult things to remove in glycerol distillation. Fatty acids tend to volatilize in the regular course of distillation and are condensed in part in the air or water-cooled condensers with the refined glycerol. These fatty acids are undoubtedly combined as esters in the U. S. P. glycerol, as they have been in solution with a huge excess of hot glycerol.

They may be liberated, however, in such a test as the following:

Add 10 cc. water and 1 cc. of 10 per cent sulfuric acid to 10 cc. glycerol; mix and stand in a closed bottle for 30 minutes on a hot-water bath. Shake the bottle and open; no disagreeable odor should be perceptible. Many U. S. P. glycerols fail on this test. Another test is as follows: add 30 cc. of a 10 per cent hydriodic acid solution to 90 cc. of glycerol, shake well, and allow to stand several hours. The solution should remain colorless, and there should be no unpleasant smell.

Fatty acids are most effectively removed by crystallization. During an experience of twenty years when refined glycerol was shipped in winter from Brooklyn, N. Y., all over the United States, complaints due to freezing of the glycerol could be counted on the fingers of one hand in spite of the fact that the freezing point of glycerol is 63° F. (17.0° C.). One customer in Providence, R. I., wrote one January that he was unable to remove any part of the contents of a drum of U. S. P. glycerol and demanded an "honest explanation" of this unprecedented occurrence. To thaw out frozen glycerol, the entire contents of the drum must be heated above the melting point of 17° C., and this is not easy in winter with a viscous liquid like glycerol. While the freezing of glycerol in small containers up to 1100 pounds was almost unknown even when stored for months in unheated rooms in winter, yet, when two 150,000-pound outdoor storage tanks for U. S. P. glycerol were put into use, the glycerol froze almost every winter and heating coils had to be provided. The particular configuration of glycerol molecules favoring the formation of a crystal is evidently extremely rare. The likelihood of such an occurrence as the formation of a crystal is much greater in a very large bulk.

Glycerol cooled below 17° C. may be easily crystallized by seeding with an already formed crystal from a supply kept in a refrigerator at a temperature below 63° F. (17.0° C.). In one case known to the writer, a 100-drum delivery of dynamite glycerol was being sampled in winter outdoors by means of a glass tube. One of the first drums opened happened to be frozen and the tube which was used for the remaining liquid drums inoculated almost the entire lot which had to be kept until the following summer before they melted. There is always the possibility of the solidification of the tanks and pipe lines carrying concentrated glycerol when the refining plant is shut down in winter, although the author has never seen this happen.

Gibson and Giauque (*4*) were able to obtain glycerol crystals at will by chilling not less than 100 grams of concentrated glycerol to liquid-air temperatures and allowing the temperature to rise very slowly over a period of a day.

Crystallization induced by inoculation with a few crystals proceeds very slowly if the glycerol is of high concentration and the temperature low, due to the high viscosity of the liquid. It is fairly rapid with ordinary U. S. P. glycerol of 95 per cent. U. S. P. glycerol of 95.25 per cent was crystallized to a 33 per cent crop of crystals which were centrifuged in a laboratory centrifuge. When melted these crystals showed 99.8 per cent glycerol.

The optimum conditions for the crystallization of glycerol are at a concentration of 95 to 98 per cent and at temperatures of 35° to 40° F. (1.7° to 4.4° C.). If the crystals so obtained from U. S .P. glycerol are centrifuged in a high-speed centrifugal and then melted, a glycerol of very high gravity and exceptional purity is obtained. Such a glycerol may be boiled freely at atmospheric pressure in an open test tube without discoloration. Fatty acid esters can be barely detected on a 100-gram portion when saponified with normal alkali and titrated back. The glycerol stands all fatty-acid odor tests and the ammoniacal silver nitrate tests which have been ruled out as impracticable for U. S. P. glycerols. Should there be a demand for a glycerol of superior quality, it can be met by the process described.

Table III. Specific-Gravity Data

Glycerol	Sp. Gr. in Air[a]	Glycerol	Sp. Gr. in Air[a]	Glycerol	Sp. Gr. in Air[a]
%		%		%	
100	1.26533	75	1.19882	40	1.10238
95	1.25245	70	1.18508	30	1.07565
90	1.23920	60	1.15742	20	1.04937
85	1.22608	50	1.12970	10	1.02426
80	1.21238				

[a] At 60/60° F. (15.56/15.56° C.).

Specific-Gravity Table Based on Crystallized Glycerol

A U. S. P. glycerol of good quality was seeded and crystallized to a 25 per cent crop. These crystals were centrifuged, melted, and recrystallized to a 50 per cent crop at 30° F. (−1.1° C.). After centrifuging, this second batch of crystals was melted. It tested 1.2648 specific gravity at 60/60° F. (15.6/15.6° C.). The melted crystals (1.2648) were then heated under a vacuum of 29.25 inches until the liquid was boiling freely. There was no discoloration. The final product, free from all traces of water, was then mixed with varying quantities of cold, previously boiled, distilled water for the preparation of the specific-gravity data (Table III), based on twice-crystallized C. P. glycerol. A 50-cc. pycnometer, with side capillary tube, ground-in thermometer, and cap ground to fit the capillary, was used. The cap was fused at the end and drawn out to a capillary which was broken to permit the expansion of the glycerol while weighing without being forced down the capillary on its exterior. The thermometer and weights were compared with the Bureau of Standards. The methods in general were those recommended by Bosart and Snoddy (*1*) and Comey and Backus (*2*). The results have not been reduced to *vacuo*, which are about 0.0003 lower in the high concentrations. The temperature is the standard of the dynamite-glycerol trade, 60/60° F. or 15.56/15.56° C.

ACKNOWLEDGMENT

The data given in this paper were obtained mainly before 1920 at the factory of Marx and Rawolle, glycerol refiners, at Brooklyn, N. Y. The literature to date has been carefully searched and, as far as the author is aware, the matter presented has not previously been published. The author's thanks are due to F. J. Wood, F. S. White, and R. Stansfield for much valuable work and many suggestions.

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Dewaxing Lubricating Oils with Methylene Chloride

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Methylene chloride (dichloromethane) satisfies to an unusual extent the requirements for an ideal dewaxing solvent. Its selective solubility at low temperatures is high, giving an oil with nearly the same pour point as chilling temperature. At room temperatures methylene chloride is miscible with oil containing 27 per cent wax. It is only slightly soluble in water; the amount of water dissolving in methylene chloride is negligible. It is one of the most stable of all chlorohydrocarbons.

Precipitated wax may be separated readily from the oil–methylene chloride solution either by filtration or centrifuging, giving a crystalline wax nearly free from oil. The methylene chloride may be stripped from the oil or wax by distillation with steam or by passing air through the mixture heated to 80° C. (176° F.). The solvent can be recovered by condensation or by scrubbing the air-solvent mixture with oil to be dewaxed, or by both condensation and scrubbing.

Methylene chloride can be used simultaneously as a dewaxing solvent and refrigerant.

THE use of solvents for the separation of oil and wax in order to produce superior wax-free lubricating oils from paraffin-base crudes has been discussed by a number of investigators. Poole (*12*) has reviewed the work done in the use of solvents for dewaxing and has listed the important requirements that a solvent must possess in order to be of practical value. Poole and his collaborators (*13*) have also determined the solubility of oils and paraffin wax in a number of solvents. Sullivan, McGill, and French (*15*) have determined the solubility of paraffin waxes in petroleum ether and in Midcontinent oils of varying viscosities. Weber and Dunlap (*18*) have investigated the solubility of wax in *n*-pentane, *n*-hexane, *n*-heptane, *n*-octane, and isodecane, and suggested the use of close-cut kerosene or heavy naphtha as selective dewaxing solvents. Wyant and Marsh (*20*) have determined the solubility of paraffin wax and oils in acetone. Henderson and Ferris (*8*) have supplied data on the solubility of wax and oil in acetone and nitrobenzene. Smith (*14*) has determined the solubility of wax and oil in acetone, isopropyl alcohol, normal and secondary butyl alcohols, and their mixtures.

A number of patents have been granted to various investigators for the use of solvents in dewaxing lubricating oils. Wagner (*16*, *17*) has patented the use of methyl ethyl ketone, and butyl alcohol and naphtha. Wilson (*19*) holds a patent on the use of isopropyl alcohol. Greenspar (*7*) uses kerosene while Lane (*9*) uses benzene to effect the crystallization of paraffin wax from lubricating oils. Lane and Montgomery (*10*) found a diluent, comprising 35 to 60 per cent naphtha 15 to 30 per cent butyl alcohol, and 18 to 35 per cent benzene, satisfactory for removing petrolatum from oils. Trichloroethylene and "other liquids" (*11*) have been found suitable to add to the oil before filtering or centrifuging.

The requirements for a satisfactory or ideal dewaxing solvent are given by Poole (*12*) as follows:

1. High selective solubility at low temperatures.
2. High solvent capacity for both oil and wax at moderately elevated temperatures.
3. The solvent must be readily recovered from the wax or oil, resulting in pure solvent, oil, and wax.
4. The solvent must establish sufficient physical differences between the portions of the mixture so that the two may be easily separated.
5. The solvent must have no damaging effect on the wax or oil.
6. Cost of solvent and necessary equipment should be moderate.
7. The solvent should be insoluble in water.

Methylene chloride fulfils to an unusual extent the requirements of an ideal dewaxing solvent, as will be shown in subsequent paragraphs.

SELECTIVE SOLUBILITY OF METHYLENE CHLORIDE

The solubility of paraffin wax, melting at 50.5° C. (122.9° F.), in methylene chloride, together with other common dewaxing solvents—acetone, butyl alcohol, ethylene dichloride, isopropyl ether, and naphtha—is given in Figure 1.

The solubility of wax in methylene chloride decreases rapidly with temperature. At −10° C. (+14° F.) only 0.025 gram of wax dissolves in 100 grams of solvent.

The method used in determining the solubility was essentially that of Sullivan et al (*15*), which consists of determining the cloud temperatures for known mixtures of wax and solvent. The results are correct if the solid constituent is a pure compound. Since the wax used in this work was a commercial

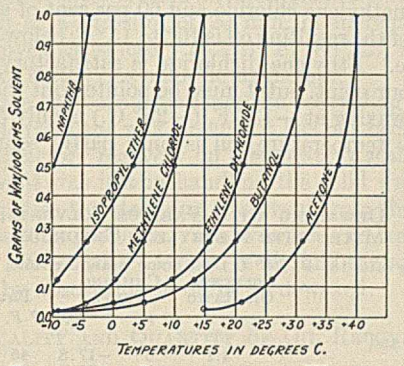

FIGURE 1. SOLUBILITY OF WAX IN VARIOUS SOLVENTS

product, the data represent the solubility of the least soluble components. The values are consequently lower than those obtained when an excess of wax is extracted with a solvent at a given temperature and an aliquot removed and evaporated. Such procedure gives the solubility of the most soluble constituent. For the purpose of evaluating the relative solubility of wax in different solvents, either method would give satisfactory results.

Lubricating oils are miscible with methylene chloride in all proportions and at all temperatures encountered in commercial dewaxing operations (−50° C. or −58° F. to room temperatures). Lubricating oils are only partially soluble in the solvents to the right of methylene chloride in Figure 1 with solubility increasing in the order: acetone, butyl alcohol, and ethylene dichloride. Lubricating oils are completely soluble in ethylene dichloride at ordinary temperatures. At lower temperatures, high-viscosity oils are only partly soluble in ethylene dichloride. Hence, to dewax with acetone, butyl alcohol, or ethylene dichloride, suitable oil solvents must be added, such as naphtha or benzene, to prevent the oil from precipitating with the wax.

The solvents to the left of methylene chloride in Figure 1—naphtha and isopropyl ether—are excellent oil solvents. Paraffin wax is moderately soluble in these solvents, and consequently lower temperatures must be used to obtain a given degree of dewaxing.

DEWAXING OILS WITH METHYLENE CHLORIDE

MATERIALS. Paraffin-base oils were used throughout this investigation. Two types of oil were investigated, a 60–80″ at 100° F. viscosity wax distillate and a 70–75″ at 210° F. viscosity long residuum kindly furnished by the Vacuum Oil Company. Characteristics for these oils are given in Table I.

The methylene chloride was a regular commercial grade, the specifications and properties of which have already been published (*5*). The naphtha used had a boiling range from 154.4° to 200° C. (310° to 392° F.) and a flash point of 46.1° C. (115° F.) The acetone, butyl alcohol, and the other solvents were commercial-grade materials.

DEWAXING PROCEDURE. The apparatus consisted of an iron container of 5.5 liters capacity surrounded by a jacket for cooling, and equipped with a filter as illustrated in Figure 2.

The general procedure for dewaxing was to add 3 liters of solvent-oil mixture of a given ratio, agitate with a mechanical stirrer, and chill at a predetermined rate, usually 18° F. per hour, by adding solid carbon dioxide to methanol contained in the outside jacket until the temperature of the methylene chloride–oil mixture was 1° F. below the desired chilling temperature. The chilled solvent and oil were then transferred to the filter maintained at the same temperature, and pressure was applied if necessary by admitting an inert gas under pressure. The filtrate was transferred to a distilling apparatus and freed from methylene chloride by distillation at 80° C. (176° F.) in a current of air. The wax was washed with methylene chloride at the chilling temperature, and then removed from the filter and freed from the last traces of solvent by distillation.

TABLE I. CHARACTERISTICS OF ORIGINAL AND DEWAXED OILS

	Wax Distillate		Long Residuum	
	Before dewaxing	After dewaxing at −13° F.	Before dewaxing	After dewaxing at −25° F.
Pour point (*3*), ° F. (° C.)	70 (21.1)	−5 (−20.6)	90 (32.2)	−15 (−26.1)
Viscosity (*2*), sec.	80 at 100° F. (37.8° C.)	83 at 100° F. (37.8° C.)	98 at 210° F. (98.9° C.)	98 at 210° F. (98.9° C.)
Wax (*20*), %	27	3.2	...	...
Oil, %	73	96.8	...	...
Flash point (*1*), ° F. (° C.)	330 (165.6)	330 (165.6)	425 (218.3)	450 (232.2)
Fire point (*1*), ° F. (° C.)	380 (193.3)	370 (187.8)	540 (282.2)	540 (282.2)
Specific gravity	0.852	0.862	...	...
Gravity A. P. I. at 60° F.	...	...	29.5	29.3
Color N. P. A. (*6*)	2.5	3	6	6
Neutralization number (*4*)	0.0	0.0	0.02	0.03
Chlorides	None	None	None	None

The effect of a number of variables on the pour point of the oils was determined, and the results are given in Table II.

TABLE II. EFFECT OF VARIABLES ON POUR POINT OF WAX DISTILLATE AND LONG RESIDUUM DEWAXED WITH METHYLENE CHLORIDE

EFFECT OF SOLVENT-OIL RATIO

(Chilling temp., −13° F. (−25° C.); chilling rate, 18° F. (10° C.)/hour; standing time, 1 hour)

Solvent-Oil Ratio (Vol.)	Pour Point: Wax distillate ° F.	Wax distillate ° C.	Long residuum ° F.	Long residuum ° C.
1:1	−5	−20.6	.	..
2:1	−5	−20.6	0	−17.8
4:1	0	−17.8	0	−17.8
6:1	5	−15.0	0	−17.8

EFFECT OF CHILLING TEMPERATURE

(Chilling rate, 18° F. (10° C.)/hour; standing time, 1 hour)

Chilling Temperature ° F.	Chilling Temperature ° C.	Pour Point: Wax distillate (2:1 solvent-oil ratio) ° F.	Wax distillate ° C.	Long residuum (4:1 ratio) ° F.	Long residuum ° C.
32	0	55	+12.8	..	....
0	−17.8	20	− 6.7	..	....
−13	−25.0	− 5	−20.6	0	−17.8
−25	−31.7	−15	−26.1	−15	−26.1
−40	−40.0	−40	−40.0	−15	−26.1

EFFECT OF CHILLING RATE

(Chilling temp., −13° F. (−25° C.); standing time, 1 hour)

Chilling Rate ° F.	Chilling Rate (° C.)/hour	Pour Point ° F.	Pour Point (° C.)	Solvent-Oil Ratio
18	(10)	−5	(−20.6)	1:1
72	(40)	−5	(−20.6)	2:1

EFFECT OF STANDING AFTER REACHING CHILLING TEMPERATURE

(Chilling temp., −13° F. (−25° C.); solvent-oil ratio, 2:1; chilling rate 18° F. (10° C.)/hour)

Time Hours	Pour Point: Wax distillate ° F.	Wax distillate ° C.	Long residuum ° F.	Long residuum ° C.
0	5	−15.0	0	−17.8
14	0	−17.8	5	−15.0
21	−5	−20.6	.	....

DISCUSSION. The ratio of solvent to oil has only a slight effect on the pour point of the resulting oil. A 1:1 ratio for solvent to wax distillate gave an oil with pour point from 5° to 10° F. above the chilling temperature. At greater dilutions the pour point was slightly higher, owing to larger quantities of wax dissolved in the methylene chloride–oil mixture. With a 1:1 ratio for methylene chloride to wax distillate, the crystallized wax was filtered without applying any pressure. A 1:1 mixture of methylene chloride and long residuum gave an oil with pour point about 10° F. above the chilling temperature.

Slight pressure had to be applied in order to filter off the crystallized wax. No pressure was required with a 2:1 ratio. With the other solvents some difficulty was encountered in the filtering, owing to the amorphous nature of the wax. From methylene chloride, on the other hand, the wax precipitates in crystalline form and consequently can be filtered and washed readily. The nature of the wax will be discussed in a subsequent section.

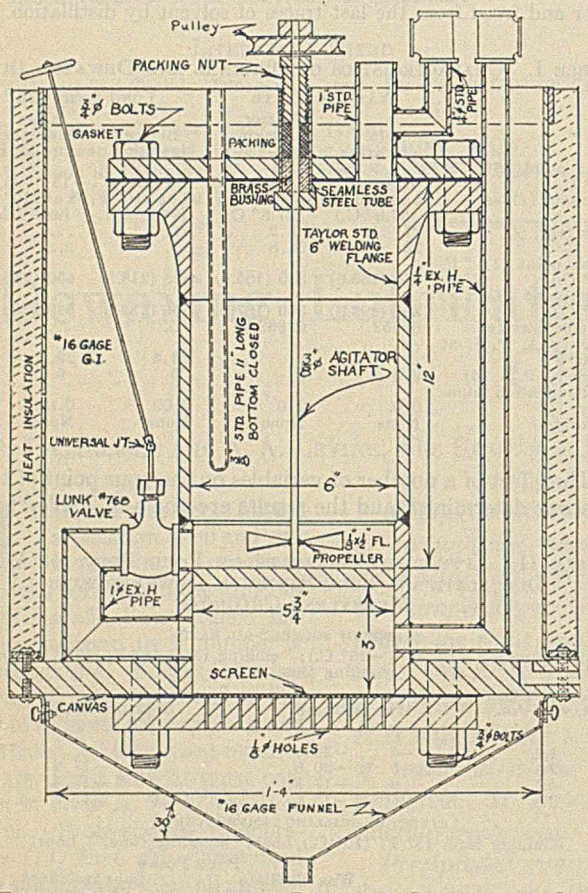

FIGURE 2. APPARATUS FOR DEWAXING LUBRICATING OILS

The chilling temperature is the only factor of importance in dewaxing oils with methylene chloride. It will be noted from Table II that for wax distillate the pour point is the same as the chilling temperature at −40° F. (−40° C.), while at −13° F. (−25° C.) it is 5° to 10° F. above the chilling temperature. With long residuum, the pour point is 10° to 15° F. above the chilling temperature if the latter is −13° F., and 25° F. above if the chilling temperature is −40° F. The relatively high pour point in the case of long residuum is apparently associated with the rather high viscosity of the oil.

The rate of chilling is an important factor in dewaxing with naphtha, since at high rates the wax precipitates in an amorphous condition and consequently is difficult to filter. In dewaxing with methylene chloride, the rate of chilling is of no consequence. The same pour point was obtained with chilling rates of 72° and 18° F. per hour. The rate of cooling appears to have little effect on the ease of filtering the crystallized wax. At the rate of 72° F. per hour and 2:1 ratio of methylene chloride to wax distillate, the crystallized wax was filtered without applying any pressure.

Standing of the oil after the chilling temperature has been reached has relatively little effect on the pour point of the oil or the rate of filtration. Hence, a process using methylene chloride can be operated continuously. Satisfactory dewaxing is possible with a rapid rate of cooling.

DEWAXING WITH OTHER SOLVENTS

In Table III, results are tabulated for dewaxing the same wax distillate and long residuum with other solvents and with mixtures containing methylene chloride. It will be noted that methylene chloride together with a concentration of acetone, which does not precipitate the oil at the chilling temperature, is slightly superior in dewaxing effect to methylene chloride alone. With a mixture containing 40 per cent by volume of methylene chloride and 60 per cent of acetone, the pour point of the resulting oil is 10° to 15° F. below the chilling temperature. Ethylene dichloride is satisfactory, giving an oil of low pour point, but it must be pointed out that the yield of oil on dewaxing at −13° F. (−25° C.) is only 52 per cent. At this low temperature, oil is only partly soluble in this solvent.

TABLE III. DEWAXING WITH VARIOUS SOLVENTS, ALONE OR MIXED WITH METHYLENE CHLORIDE

(Chilling rate, 18° F. (10° C.) per hour; standing time, 1 hour)

	Solvent-Oil Ratio	Chilling Temp. °F.	Chilling Temp. °C.	Pour Point °F.	Pour Point °C.
Wax distillate and					
Naphtha	4:1	0	−17.8	45	7.2
Naphtha	4:1	−13	−25.0	25	− 3.9
Ethylene dichloride	2:1	0	−17.8	25	− 3.9
Ethylene dichloride	2:1	−13	−25.0	−10	−23.3
Acetone 60% by vol. Benzene 40%	4:1	5	−15.0	10	−12.2
Methylene chloride 60% Acetone 40%	4:1	5	−15.0	20	− 6.7
Methylene chloride 60% Acetone 40%	4:1	−13	−25.0	−10	−23.3
Methylene chloride 40% Acetone 60%	4:1	5	−15.0	5	−15.0
Methylene chloride 40% Acetone 60%	4:1	−13	−25.0	−25	−31.7
Methylene chloride 50% Acetone 50%	1:1	8	−13.3	15	− 9.4
Long residuum and					
Naphtha	2:1	−13	−25.0	85	29.4
Methylene chloride 80% Acetone 20%	2:1	−13	−25.0	−15	−26.1
Acetone 20% Benzene 80%	2:1	−13	−25.0	35	+ 1.7

NATURE OF RECOVERED WAX

With methylene chloride as a dewaxing solvent, the wax crystallizes in well-defined plates, and these may be separated readily by filtration or centrifuging. A ratio of solvent to oil of 1:1 permits filtration at −13° F. (−25° C.) without difficulty.

The filter cake from the wax distillate and long residuum are substantially free from oil, the last traces of which may be removed by washing with fresh solvent at the chilling temperature.

The melting point of the recovered wax before washing was 108° F. (42.2° C.). The sample on washing twice with methylene chloride at 0° F. (−17.8° C.) gave a product melting at 113° F. (45° C.). Thus a commercially usable wax is prepared directly without resorting to fractional melting and "sweating" operations now in use. The fact that a crystalline wax is produced in dewaxing with methylene chloride will simplify commercial dewaxing operations. No filter aid is required.

RECOVERY OF OIL AND SOLVENT

The low boiling point of methylene chloride, 39.8° C. (103.6° F.), permits complete recovery of the solvent at relatively low temperatures either by direct distillation in a current of air or by steam distillation. Since lubricating oils are excellent solvents for methylene chloride, it is difficult to remove the last traces of methylene chloride by simple distillation unless a temperature higher than 100° C. (212° F.) is used. The last traces may be removed by steam or a stream of air. In the laboratory, 99.5 per cent of the methylene chloride has been recovered by distilling the greater portion of the solvent and then by passing a slow stream of air through

the oil heated to 176° F. (80° C.), using water and a carbon dioxide–methanol mixture to condense the solvent or scrubbing the air-vapor mixture with oil to be dewaxed.

In commercial dewaxing processes it should be possible to recover methylene chloride completely by simply carrying out all the operations in a closed system and recirculating the air used for sweeping out the solvent.

By steam distillation, 99.6 per cent of the methylene chloride has been recovered from oil–methylene chloride mixtures. Distillation at a pressure of 20 mm. of mercury, absolute, has not proved satisfactory at 176° F. (80° C.) owing to the solubility of methylene chloride in the oil.

No trouble has been experienced in recovering the methylene chloride from the wax, though it has not been possible to obtain satisfactory recovery on a laboratory scale since some of the solvent was lost in handling the solid wax. In commercial practice the stripping of solvent from the wax would not be a serious problem. The wax may be freed from the solvent at 176° F. with a stream of air, and the solvent can be recovered by absorption in oil to be dewaxed.

Quality and Quantity of Oil Recovered

In a series of experiments on the quantitative separation of solvent, oil, and wax, an oil was recovered after dewaxing the wax distillate at −13° F. (−25° C.) which contained an average of 3.2 per cent wax. The recovery of the oil was quantitative; that is, there was no separation of oil at the chilling temperature. The characteristics of the oils are given in Table I. There was no change in the properties of the oil except in pour point in the dewaxing process, and except for some slight changes due to removal of the wax.

The recovered oil was free from methylene chloride or halogens. Determinations by the method of Carius of the halogen content of the oil, stripped by steam distillation or distillation in a stream of air, showed complete absence of halogens. This is important since small quantities of methylene chloride, if remaining in the oil, might decompose at the high temperature reached in an internal-combustion engine to give hydrochloric acid and lead to corrosion.

Methylene chloride is exceptionally stable (*5*) so that no decomposition was anticipated. The test for halogens shows that no decomposition of the methylene chloride occurred in separating the solvent from the oil.

Poole has reported that oils dewaxed with chlorohydrocarbons darken on standing. If the solution of methylene chloride and oil is exposed to light, darkening may occur after exposure for several hours. In the absence of direct light no discoloration has been observed. The oil stripped of solvent has not changed in color after standing in darkness or in diffused light for 60 days. Darkening of the oil is not a problem with methylene chloride.

Methylene Chloride as a Dewaxing Solvent and Refrigerant

Methylene chloride with a boiling point of 39.77° C. (103.6° F.) may serve as a refrigerant and dewaxing solvent at the same time. By adding an excess of methylene chloride to the oil which is to be dewaxed, and reducing the pressure by suitable means, the methylene chloride evaporates and can thus be made to lower the temperature of the remaining mixture. The methylene chloride vapor can be condensed and absorbed in a second tank, containing oil to be dewaxed and cooled with water, or by the dewaxed oil–methylene chloride solution from which the wax has been removed. Laboratory experiments have been carried out showing that the desired chilling temperature may be attained.

Conclusions

It will be seen from the above discussion that methylene chloride fulfils to an unusual extent the seven requirements of an ideal dewaxing solvent. As outlined by Poole more specifically:

1. Methylene chloride dissolves oil in all proportions at temperatures down to −45.6° C. (−50° F.), while at usual chilling temperatures paraffin wax is only slightly soluble. Hence, an oil may be produced with a pour point of 5° to 10° F. above the chilling temperature.
2. Methylene chloride satisfies Poole's second requirement that the dewaxing solvent should dissolve the components of the crude oil at moderate temperatures. This requirement does not appear essential; if the dewaxing solvent should dissolve only one component at ordinary temperatures, dewaxing might be accomplished without refrigeration.
3. Methylene chloride may be readily removed from wax and solvent, leaving an essentially pure solvent (wax and oil), by simple steam distillation or distillation in a stream of air.
4. The wax crystallizing out from methylene chloride–oil mixture may be removed readily by filtration or centrifuging. The precipitated wax is crystalline.
5. Methylene chloride has no damaging effect on wax or oil.
6. The cost of solvent and equipment need not be prohibitive.
7. Methylene chloride is only slightly soluble in water, and water is not soluble in methylene chloride.

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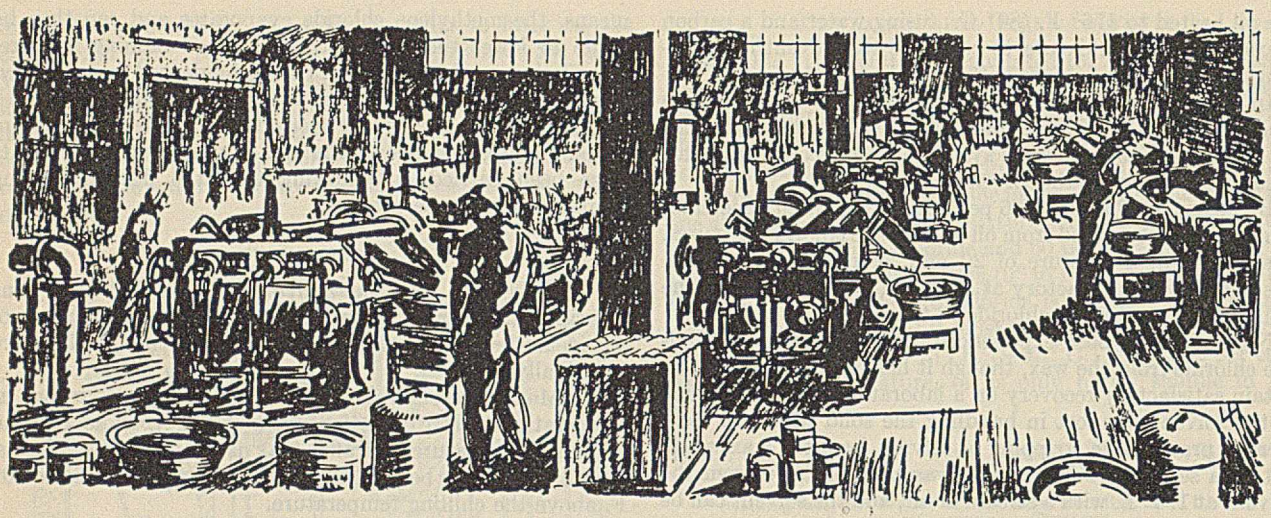
Chemical Industry of Australia. Generally speaking, the Australian chemical trade, in common with other lines of business, suffered from depression in 1931, according to the Department of Commerce. At no time was any briskness really evident. Toward the end of the year, with the abandonment of the gold standard by Great Britain, the position of American chemicals was even further affected, and a larger part of the trade in more or less standard lines went to Great Britain than formerly.

The oil, paint, and color trade had a quiet year, the only improvement noticeable being a slight seasonal gain in the spring of the year because of general painting. Demand for solvents, lithopone, turpentine, and rosin was at a low ebb and the year ended on an extremely quiet basis. The low price of tallow has caused Australian soap manufacturers to employ less rosin in their finished products. Manufacturers also are turning to sources other than America for lithopone.



Our Greatest Decade in Chemical Manufacture

Otto Wilson, National Press Club, Washington, D. C.

As everyone knows, the World War and the prosperous era that followed it almost recreated the American chemical industry. War demands and the economic dislocations of the times gave an immense stimulus to chemical manufacture, and, when the war period was followed by such favoring circumstances as high tariffs, technical advances in chemistry, and an unprecedented foreign and domestic demand, such manufacture enjoyed by far its greatest decade. We now have an official measure of the enormous expansion in the war and post-war periods. The Government has just released the final detailed figures of the census of 1929 covering the manufacture of chemicals in this country in that year. The totals show not only the swift progress made in most lines of production but also the amount of such production at its peak, the year 1929 being the greatest of all years for the industry as a whole. The depression that has ruled since that time has drastically reduced most activities, but the solid character of the previous expansion is shown by the fact that the chemical industry has suffered less than most other major industries.

Before taking up the detailed returns for the various branches of this industry, it will be interesting to glance at the position to which chemical manufacture in its broadest sense has attained. In blocking out the general field of manufacture in the United States, the Bureau of the Census recognizes sixteen great groups. One of these is Chemicals and Allied Products, including "not only the industries whose products are chemicals in the ordinary sense, but also those which employ to a large extent chemical processes in their manufacturing operations. The group is complex in character, and its several products differ widely, both in kind and in the uses to which they are put." It is divided into thirty-one subgroups, which include, besides commercial chemicals (listed under Chemicals Not Elsewhere Classified), such lines of manufacture as paints and varnishes, perfumes, cosmetics and toilet preparations, rayon, compressed and liquefied gases, explosives, soap, tanning and dyeing materials, etc. The final 1929 returns for only a few of these subgroups have been published, but all of them should be available early in the present year.

In point of total value of its products the great group, Chemicals and Allied Products, ranked sixth among the broad classes of American industries in 1929, an advance from seventh position in 1927. It stood eighth in 1925, seventh in 1923, eighth in 1921, and sixth in 1919, the higher ranking in the latter year being partly due to the inclusion of nearly $500,000,000 worth of alcoholic liquors, an item reduced to a low figure in later years by prohibition. Table I shows the total value of the products of chemical and allied industries in 1927 and 1929 compared with those of other great groups.

Table I. Value of Manufactures in U. S.

Industrial Group	1927	1929
Food and kindred products	$11,016,000,000	$12,024,000,000
Textiles and their products	8,950,000,000	9,243,000,000
Forest products	3,457,000,000	3,592,000,000
Paper and paper products	1,800,000,000	1,892,000,000
Printing, publishing, and allied industries	2,846,000,000	3,170,000,000
Chemicals and allied products	3,352,000,000	3,759,000,000
Products of petroleum and coal	3,060,000,000	3,648,000,000
Rubber products	1,225,000,000	1,117,000,000
Leather and its manufacture	1,869,000,000	1,906,000,000
Stone, clay, and glass products	1,613,000,000	1,561,000,000
Iron and steel and their products, not including machinery	6,199,000,000	7,138,000,000
Nonferrous metals and their products	2,669,000,000	3,597,000,000
Machinery, not including transportation equipment	5,368,000,000	7,043,000,000
Transportation equipment—air, land, and water	4,694,000,000	6,047,000,000
Railroad repair shops	1,290,000,000	1,270,000,000
Miscellaneous industries	3,310,000,000	3,428,000,000
Total	62,718,000,000	70,435,000,000

In comparing these returns with those for earlier years of the post-war decade, it is to be remembered that the 1919 figures represent a carry-over from the abnormally high prices of the war and hence afford no proper basis of comparison. That and the inclusion of the alcoholic liquors mentioned put the total value of the products of the group, Chemicals and Allied Products, at a higher figure than has since been attained, although the 1929 total almost reached it. Since 1921 this group has shown a rapid climb in output, increasing about 70 per cent in eight years, as compared with 60 per cent for the combined industries of the country.

This gain was due very largely to increased plant capacity, as is shown by the fact that the number of establishments in the industry in 1927 (the latest available figures) was only 7541 as compared with 7348 in 1921 and 10,732 in 1919. The horsepower used in these plants totaled about the same as

in 1919. These and other data of interest relating to this group are given in Table II.

Progress of the chemical and allied industries since prewar years cannot be measured accurately from the census returns, since the group included coal and petroleum products (manufactured gas, coke, etc.) in the earlier census years, these items comprising nearly half the total. There have also been other minor changes in the composition of the group. Deducting these products and making other necessary adjustments, it is found that the value of the products of chemical and allied industries in 1914, comprising roughly the same subgroups as those in the present list, was about $1,307,000,000. In a decade and a half the group has thus almost trebled the value of its contribution to the economic life of the nation.

Of more practical significance to chemists are the figures showing the manufacture of commercial chemicals in 1929. These, as explained, are comprised in one of the thirty-one subgroups of Chemicals and Allied Products, and it is with these detailed figures that the present review is chiefly concerned. They make up about one-fifth of the total value of products of Chemicals and Allied Products, and in value of output lead the whole list of the thirty-one subgroups.

The subgroup, Chemicals Not Elsewhere Classified, includes nine classes of manufacture as follows: I, Acids; II, Nitrogen and Fixed Nitrogen Compounds; III, Sodium Compounds; IV, Potassium Compounds; V, Alums and Other Aluminum Compounds; VI, Bleaching Compounds; VII, Coal-Tar Products; VIII, Plastics; and IX, Chemicals, Miscellaneous. Before 1927 it also included compressed and liquefied gases, and before 1925, rayon. But the rise of these commodities in industrial importance was so marked that in censuses of the years mentioned and in later censuses they have been classified as separate industries. Figures for 1929 and 1927 for the classification, Chemicals Not Elsewhere Specified, are therefore not strictly comparable with those for earlier years. Table III, however, giving the returns for each census year since 1899, will in general show the growth of American manufacture of chemicals within the past generation and some of the features of this expansion.

The value of the products of the compressed- and liquefied-gases industry in 1929 was $52,190,000 and in 1927, $50,547,000; the value of the products of the rayon industry in the last three census years was: 1929, $149,546,000; 1927, $109,888,000; 1925, $88,061,000. If these amounts should be added to the totals for all chemical industries in the years named, the aggregate value of the products of these industries would be: 1929, $939,784,000; 1927, $732,526,000; 1925, $658,371,000. The output for 1929 would thus be more than twice that of 1921 and would surpass that of 1914 by nearly 450 per cent.

Disregarding these two industries, which enjoyed their great growth since the war, it will be seen from the table that the remarkable expansion of our chemical industries has come from enlargement of existing factories and progressive increase of the use of machinery rather than a multiplication of plants or a geographical spread. In twenty years the number of establishments manufacturing these chemicals rose from 401 to 551, or only 37 per cent, while the value of

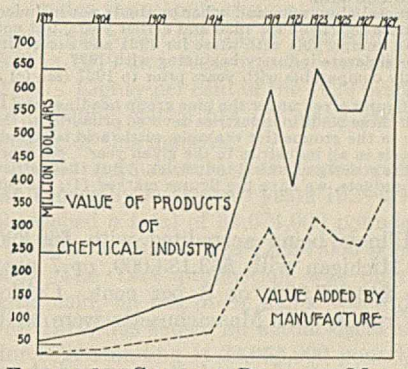


FIGURE 1. CHEMICAL PRODUCTS MADE IN U. S. AND VALUE ADDED BY MANUFACTURE

output was increasing nearly 500 per cent, and the total horsepower used, 300 per cent. The number of wage earners employed was greater by 140 per cent in 1929 than in 1909, while total wages paid were 500 per cent larger.

The high concentration of manufacture to which these figures point is further evidenced by other census returns for 1929, showing the distribution by states. From the beginning, chemical manufacture was markedly an eastern industry, and, in spite of encouraging growth in other sections, it continues to remain so. Out of the total production in 1929, valued at $738,048,000, New York, the leading state, accounted for $168,729,000, or 23 per cent; New Jersey, $155,783,000, or 21 per cent; and Pennsylvania, $48,111,000, or nearly 7 per cent. This area thus produced more than half the total for the whole country. The middle west

TABLE II. STATISTICS ON MANUFACTURE OF CHEMICALS AND ALLIED PRODUCTS SINCE THE WAR

	1919	1921	1923	1925	1927	1929
No. of establishments	10,732	7,348	7,197	7,282	7,541	[a]
Wage earners (av. for year)	329,053	199,596	246,527	244,812	253,436	[a]
Wages (thousands of dollars)	$364,884	$224,333	$288,834	$296,526	$317,908	[a]
Cost of materials, supplies, containers for products, fuel, and power (thousands of dollars)	$2,269,000	$1,353,000	$1,703,000	$1,831,000	$1,803,000	[a]
Value of products (thousands of dollars)	$3,804,000	$2,226,000	$2,934,000	$3,211,000	$3,352,000	$3,759,000
Value added by manufacture (thousands of dollars)	$1,534,000	$873,000	$1,231,000	$1,381,000	$1,549,000	[a]
Horsepower	1,721,000	[b]	1,654,000	1,748,000	1,848,000	[a]

[a] Data not yet available. [b] No returns.

TABLE III. MANUFACTURE OF CHEMICALS

Year	No. of Establishments	Wage Earners (Av. for Year)	Wages	Cost of Materials, Containers, Fuel, and Purchased Electrical Energy	Value of Products	Value Added by Manufacture	Horsepower
1899	350	17,519	$8,717,000	$31,126,000	$56,755,000	$25,629,000	[a]
1904	329	22,294	12,319,000	47,071,000	84,410,000	37,339,000	94,000
1909	401	25,981	15,591,000	69,531,000	127,625,000	58,094,000	214,000
1914	427	35,375	24,279,000	96,185,000	173,269,000	77,084,000	289,000
1919	836	76,918	105,062,000	301,519,000	614,279,000	312,760,000	480,000
1921	728	49,138	62,161,000	200,273,000	412,231,000	211,959,000	[a]
1923	773	77,254	103,301,000	328,597,000	655,275,000	326,678,000	592,000
1925	751	57,890	83,537,000	282,712,000	570,310,000	287,598,000	547,000
1927	492	52,347	78,275,000	296,677,000	572,091,000	275,414,000	576,000
1929	551	62,199	94,680,000	363,577,000	738,048,000	374,472,000	854,000

[a] No data.

TABLE IV. CHEMICAL MANUFACTURE BY GROUPS

(In thousands of dollars)

	Chemical Group	1914	1919	1921	1923	1925	1927	1929
I	Acids	$32,837	$86,086	$59,538	$79,006	$79,274	$88,176	$98,620
II	Nitrogen and fixed nitrogen compounds	9,870	27,154	21,060	30,436	29,660	26,086	38,337
III	Sodium compounds	32,626	99,690	83,698	111,848	109,522	113,880	137,655
IV	Potassium compounds	7,906	18,407	4,935	6,319	6,071	9,306	9,998
V	Alums and other aluminum compounds	[a]	43,433[b]	23,244[b]	11,607	11,581	13,563	15,949
VI	Bleaching compounds	5,302	12,393	13,900	16,729	17,167	18,674	19,871
VII	Coal-tar products	13,492	133,500	75,918	121,893	112,201	106,057	130,652
VIII	Plastics[c]	13,896	77,477	58,837	102,230	48,732	28,203	40,531
IX	Chemicals, miscellaneous	52,898[d]	156,673[d]	99,950	188,682	190,970	234,435	307,873
	Compressed and liquefied gases	10,415	43,264	40,421	53,384	55,533	[e]	[e]
(1)	Gross total	[a]	[a]	481,501	721,594	660,711	638,380[f]	799,486[f]
	Intergroup duplication	[a]	[a]	38,336	34,063	49,398	21,559	33,558
(2)	Net total, showing total production of chemicals in U. S.	191,895	643,993	443,165	687,530	611,313	616,821[f]	765,928[f]
	Amt. mfd. as by-products in nonchemical industries	26,927	79,657	42,143	53,097	66,662	83,229	87,048
(3)	Total production chemicals in chemical industries	164,968	564,336	401,023	634,433	544,651	533,593[f]	678,880[f]
	Other products of chemical industries	8,300	41,275	11,208	20,842	25,659	38,498	59,168
(4)	Total value of all products of chemical industries	173,269	605,612	412,231	655,275	570,310	572,091[f]	738,048[f]

[a] No comparable data.
[b] Includes metal aluminum and other products not included after 1921.
[c] Includes data for rayon for 1923 and earlier years, but not for years subsequent to 1923; and for pyroxylin plastics for 1925 and earlier years.
[d] Figures not comparable with those for 1921 and succeeding years.
[e] Treated as separate industry beginning with 1927.
[f] Not strictly comparable with years prior to 1927 (see (c) and (e) above).

Note: The figures given under the nine group headings and Compressed and Liquefied Gases cover the total output of such chemicals in the United States, including both these made in industries devoted primarily to their manufacture and those made in other industries as by-products. There is a certain amount of duplication in the groups (for example, nitric acid is included in both I and II). Eliminating this we have the amounts marked (2), the actual production of chemicals in all industries in the given year. Subtracting the output of nonchemical industries, we have the figures marked (3), the production of chemicals in the strictly chemical industries. But these strictly chemical industries often produce other articles besides chemicals, and, adding these nonchemical by-products, we have the figures marked (4), the total value of all products of the chemical industries.

followed, Illinois being accredited with $60,396,000, or 8 per cent; Michigan with $53,183,000, or 7 per cent; and Ohio with $46,287,000, or 6 per cent. California, West Virginia, Virginia, and Massachusetts were well up in the list.

Of the nine classes of manufacture named above, the most important in point of value of commercial products is that of compounds of sodium, followed by coal-tar products and acids. The record of manufacture of the various classes since the war, and comparative figures for 1914, are shown in Table IV. These figures cover production of chemicals not only in the industries primarily devoted to their manufacture but also in the industries in which they are turned out as by-products.

GROUP I, ACIDS

The manufacture of acids in this country showed a gain in total value of about 12 per cent in 1929 over 1927. The increase was more notable in organic than inorganic, the former registering about a 30 per cent and the latter a 6 per cent advance. As compared with 1914, the output of acids has more than trebled, organic acids showing a somewhat larger gain than inorganic because of the large 1929 increase. Since 1921 the output has almost doubled. Total value of production since 1914 is shown in Table V.

TABLE V. PRODUCTION OF ACIDS SINCE 1914

Acids	1914	1919	1921	1923	1925	1927	1929
Inorganic	$25,083	$59,876	$46,880	$59,436	$58,958	$66,027	$70,085
Organic	7,754	26,318	12,658	19,569	20,315	22,148	28,535
Total	32,837	86,194	59,538	79,005	79,273	88,175	98,620

Far in the lead of all other items in this group is sulfuric acid, the value of which made up nearly half the total for the whole group. Manufacture of sulfuric acid for sale reached a total of 5,816,165 tons (basis, 50° Baumé) in 1929 with a value of $45,573,000. This, however, was only a part of the amount actually produced, as 2,675,000 tons were consumed in the same establishments as those in which they were made. On the same basis of valuation as that sold, this added amount would be worth $20,945,000, making a total value of production for the year of $66,518,000.

Graded according to strength, production of sulfuric acid in 1929 is shown in Table VI.

There is a wide fluctuation from year to year in amounts produced with a given strength; the 1927 production of 50° Baumé, for example, was 2,565,000 tons, about one-fourth larger than in 1929. In 1914 production of this grade was 1,701,000 tons, almost as much as fifteen years later; of 60° Baumé, it was 795,000 tons; of 66° Baumé, 828,000 tons; and of other grades (mostly 100 per cent), it was 78,000 tons.

The greater part of the 1929 output of sulfuric acid was turned out in plants in which it was a primary product, the census returns for which were included in the group, Chemicals Not Elsewhere Classified. These accounted for 5,157,835 tons (all quantities on basis 50° Baumé unless otherwise specified), of which about four-fifths, having a value of $32,736,000, was made for sale and the rest for consumption within the manufacturing plants. Of the rest, 2,002,105 tons were credited to the fertilizer industry, of which only 629,000 tons were made for sale; 133,656 tons to the explosives industry, of which 45,287 tons were sold; and 1,197,518 tons to petroleum refining, zinc and copper smelting, etc., of which 1,000,993 tons valued at $7,418,000 were made for sale. From the smelting and roasting of zinc ores, twelve establishments reported that 639,432 tons (60° Baumé) of sulfuric acid valued at $6,311,000 were obtained; and from copper ores, 588,325 tons (60° Baumé) valued at $3,333,000.

Of the total production of sulfuric acid, 5,415,000 tons, or almost two-thirds, were obtained by the chamber process in 1929 as compared with 3,076,000 tons by the contact process. Since 1921 the proportion obtained by the contact process has been steadily increasing, returns for the census years showing the following: 1921, contact process, 25.2 per cent; 1923, 27.6 per cent; 1925, 29.2 per cent; 1927, 30.2 per cent; 1929, 36.2 per cent. No earlier figures are available for comparison.

Geographically the manufacture of sulfuric acid is fairly well distributed over the country. To avoid disclosing the details of private businesses, the Census Bureau must restrict publication of separate returns for 1929 to only thirteen states. Of these New Jersey leads in volume of total production (for sale and for factory consumption together) with 1,165,000 tons; Pennsylvania is second with 984,000 tons. Other leading states include Illinois, 802,000 tons; Tennessee, 757,000 tons; Maryland, 757,000 tons; and Ohio, 621,000 tons. The four states Connecticut, Delaware, Massachusetts, and New York report a production of 801,000 tons; and the western group, including Arizona, California, Montana, Utah, and Washington, 539,000 tons. In point of value of sulfuric

acid made for sale, Pennsylvania leads all other states with $6,804,000; followed by Illinois with $5,892,000; New Jersey, $4,779,000; and Ohio, $3,914,000. The New York group mentioned is credited with $5,054,000.

Comparing 1929 returns with those for earlier years, we find that total production of sulfuric acid has increased by about 108 per cent since 1914, chiefly in the amounts made for sale. Production for plant consumption and for sale in the various census years since 1914 has been as shown in Table VII (basis 50° Baumé).

That this manufacture has followed the general tendency of chemical manufacture in the United States of expansion in plant capacity rather than in number of plants, is shown by the fact that the number of establishments making sulfuric acid in 1914 was greater than in 1929 (194 as compared with 171).

In addition to direct manufacture, a considerable amount of sulfuric acid has been obtained by reclaiming processes. In 1929 sixty-nine plants reported a total thus reclaimed of 981,000 tons, of which 599,000 tons were for plant consumption, and 381,000 tons (valued at $1,389,000) for sale. Texas, with 290,000 tons, was by far the most important of the separate states mentioned. This industry has had largely a post-war development. Total production in 1919 was 474,000 tons, and in 1921, 201,000 tons.

Mixed sulfuric-nitric acid to the extent of 184,000 tons was made by thirty-six establishments in 1929, compared with 112,000 tons by thirty-seven establishments in 1914. The 1921 production was only 90,000 tons. About two-thirds of this production is made and consumed in the manufacture of explosives, which accounted for 120,000 tons in 1929. The value of the output marketed was $4,214,000, slightly less than in 1919. New Jersey is the leading state in the manufacture of these acids, being credited with 87,000 tons in 1929, or nearly 50 per cent of the total.

Nitric acid manufacture shows much the same features as that of sulfuric-nitric. The explosives industry accounted for 106,000 tons of the total 160,000 tons produced in 1929, of which only 35,000 tons (valued at $3,495,000) were made for sale. Fifteen years before, production was 79,000 tons, of which less than one-fifth was made for sale. A marked change in the output, graded according to strength, was registered in 1929 when almost three-fourths of the total, or 115,000 tons, was 100 per cent strength. In 1927 about 60 per cent and in 1925, 80 per cent were graded 40° Baumé; much the same proportions had been in evidence in previous years. New Jersey likewise leads all other states mentioned separately in this manufacture, being accredited with 66,000 tons, or 40 per cent of the total, in 1929.

Of the other inorganic acids, carbonic ranks first in value of output, the 1929 total being $6,932,000. This is three times the total of fifteen years before, which stood at $2,321,000, but it is only slightly larger than the 1919 figure of $6,574,000. Since 1923, however, there has been a steady advance. Returns for volume of manufacture show that the 1929 value would have been much larger had the prices of earlier years prevailed, as production reached 136,930,000 pounds, whereas in 1927 it was only 74,344,000 pounds; in 1919, 59,771,000 pounds; and in 1914, 50,446,000 pounds.

The advance in the manufacture of hydrochloric acid in the last fifteen years has not been as marked as that in many other lines, but it has been steady; the 1929 output exceeded that of 1914 by 50 per cent in quantity (258,000 tons as against 169,000). About three-fourths of the 1929 production was made for sale and had a value of $3,195,000. In general this proportion has held since the war, but in 1914 almost one-half was consumed in the manufacturing establishments themselves. The average value per ton of that sold, which went as high as $29 in 1919 and 1921, was $16 in 1929, the same value as in 1914. Eighty per cent of the 1929 production was graded at 20° Baumé, which has for many years been the favorite strength for this material.

Phosphoric acid manufacture has shown notable gains since the war, especially in the two years 1928–29. Production in 1929 reached a total of 34,674,000 pounds valued at $2,073,000, whereas in 1927 it was 22,397,000 pounds valued at $1,682,000. The 1921 production was only 8,943,000 pounds. Boric acid, on the other hand, while doubling in quantity since 1919, has shown an actual decrease in value, the figures for 1929 standing at 26,055,000 pounds valued at $1,541,000 as against 13,454,000 pounds valued at $1,755,000 in 1919 and approximately the same figures for 1921. Since 1914 production has increased both in quantity and value nearly 200 per cent. Chromic acid has appeared separately in the returns only since 1927, in which year production stood at 898,000 pounds valued at $242,000. In 1929 these figures jumped to 4,212,000 pounds valued at $710,000.

Among the organic acids, acetic easily stands in the lead in total value, with $6,890,000 in 1929. This valuation covered only that made for sale, which amounted to 52,915,000 pounds valued at $5,487,000 for dilute and 13,449,000 pounds valued at $1,403,000 for glacial. In addition to these amounts, 19,823,000 pounds of dilute acid were made for consumption within the industry, a total production of dilute (basis of 100 per cent) of 72,738,000 pounds. This compares with 41,400,000 pounds in 1927. The manufacture of this product has shown wide fluctuation since 1914. Census Bureau statistics for 1927 and 1929, because of a revised method of compiling and stating returns, are not comparable with those for earlier years, but the total values of amounts made for sale are approximately comparable and will indicate roughly the variations in the industry. In 1929 this total value was $6,890,000 and in 1927, $5,049,000 (a gain in the two years of 36 per cent). In 1914 products valued at $1,272,000

Table VI. Production of Sulfuric Acid in 1929

	50° Baumé	60° Baumé	66° Baumé	100 Per Cent	Other
Made and consumed, tons	1,469,366	130,179	95,196	554,680	4,119
Made for sale:					
Tons	409,782	1,397,208	258,371	1,852,146	177,705
Value	$3,203,000	$11,725,000	$3,720,000	$24,690,000	$2,234,000
Total, tons	1,879,148	1,527,387	353,567	2,406,826	181,824

Table VII. Manufacture of Sulfuric Acid

(In thousands of tons and thousands of dollars)

	1914	1919	1921	1923	1925	1927	1929
Made and consumed in same establishments, tons	1,734	2,222	1,766	2,211	2,304	2,364	2,675
Made for sale:							
Tons	2,338	3,331	2,604	4,345	4,700	4,972	5,816
Value	$15,395	$35,933	$27,418	$38,275	$38,230	$42,886	$45,573
Total, tons	4,072	5,553	4,370	6,556	7,004	7,336	8,491

were made for sale, this figure jumping to $4,264,000 in 1919 and then dropping sharply to $1,791,000 in 1921. In 1923 there was a rise to $4,155,000 and in 1925 to $4,438,000. The number of establishments has increased but slightly, being thirteen in 1914 and seventeen in 1929.

Stearic, oleic, and citric acids are the chief other organic acids for 1929. All of them show very large gains over pre-war output. Stearic acid sold in 1929 was more than four times that of 1914 in value ($5,488,000 as compared with $1,242,000), and almost three times as much in quantity (39,154,000 pounds as compared with 14,351,000). The 1929 output was 5 per cent larger in quantity than in 1927 but 43 per cent larger in value. Oleic acid, produced to the extent of 56,948,000 pounds valued at $5,375,000 in 1929, showed no marked gain over 1927. As compared with 1914, however, it was far ahead, the pre-war output being 21,933,000 pounds valued at $1,301,000. Five manufacturing establishments were making citric acid in 1929, reporting a production of 10,756,000 pounds having a value of $4,833,000, a gain of about 50 per cent in both quantity and value over 1927. As compared with 1914, the increase was about 300 per cent in quantity and 200 per cent in value, the average value per pound having fallen from 57 to 45 cents in that time. Tartaric acid (with a 1929 output of 4,906,000 pounds valued at $2,060,000) and tannic acid (1,449,000 pounds valued at $504,000) showed much smaller gains as compared with earlier years, the value of the former, in fact, being less than half that of 1919.

Group II, Nitrogen and Fixed Nitrogen Compounds

This group consists chiefly of ammonia and ammonia compounds, cyanogen compounds, nitric acid (already covered under group I), and nitrous oxide.

The ammonia group of products is derived from three general lines of manufacture—the coke industry, the manufacture of chemicals, and the manufactured-gas industry.[1] The value (for sale) of the output from these three sources since the war has been as shown in Table VIII.

Table VIII. Manufacture of Ammonia Products

(In thousands of dollars)

Industry	1919	1921	1923	1925	1927	1929
Coke	$26,752	$16,143	$31,094	$26,850	$26,240	$26,862
Chemicals	16,192	10,526	12,546	15,068	11,597	15,964
Manufactured-gas	2,030	1,668	1,926	1,816	1,753	2,173
Total	44,974	28,337	45,566	43,734	39,590	44,999

Curiously, the manufacture of these products was thus practically the same in 1929 as ten years before, not only in aggregate value but in the value of the contributions from each of the three sources. There are no comparable statistics for 1914 except for the chemicals industry, which reported ammonia products made for sale in that year at $5,532,000.

[1] Of these three, only the output of chemical establishments is included in the group Chemicals Not Elsewhere Classified, or in the great group Chemicals and Allied Products. The statistics of output of ammonia and compounds from the coke and manufactured-gas industries are included under Coal and Petroleum Products, but are given here in order to cover the subject completely.

In the coke industry, despite the even valuation reported in the post-war decade, the actual quantity has shown a rapid and consistent advance since 1921. In terms of NH_3 equivalent of all forms, total ammonia production for sale in 1919 was 191,020,000 pounds; 1921, 162,493,000 pounds; 1923, 287,682,000 pounds; 1925, 310,745,000 pounds; 1927, 349,619,000 pounds; and 1929, 401,441,000 pounds. In 1929 this output came from sixty-seven establishments. By far the greater part was ammonium sulfate, production of which in the United States is so largely a function of the coke industry. The biennial output of this important chemical in the three industries mentioned above since the war is given in Table IX.

Thus, while production and sales have for the most part mounted steadily upward, prices and total values have fluctuated widely but have trended downward. In the coke industry, for example, the average value of ammonium sulfate in 1919 was about $80 per ton, whereas in 1929 it was less than $36.

The only other ammonia product from coke manufacture is ammonia liquor, sales of which in 1929 amounted to $2,687,000. This is slightly larger than in 1927 but is less than half the 1919 value ($5,693,000). The quantity sold, however, (25,881 tons, NH_3 equivalent), compares with 25,823 tons in 1919.

In the gas industry, besides the ammonium sulfate, liquor and other ammonia forms valued at $446,000 were reported in 1929, with an NH_3 equivalent of 13,010,000 pounds. This was about one-fourth the value of these products in 1919.

In the chemicals industry the chief ammonia form is anhydrous, of which 173,349,000 pounds valued at $10,673,000 were made for sale in 1929. This is far above the figure for any previous year in point of value and especially of quantity. The 1927 output was 45,115,000 pounds with a value of $4,011,000, while that of 1919 was 25,684,000 pounds valued at $7,074,000. Along with mounting production in late years there has come a drastic reduction in average valuation per pound. For 1919, 1921, and 1923 it stood at 27 cents. In 1925 it dropped to 21 cents, in 1927 to 9 cents, and in 1929 to 6 cents. For aqua ammonia and ammonia liquor the 1929 returns were much the same as those of ten years before: 30,200,000 pounds (NH_3 content) valued at $1,784,000, as compared with 30,918,000 pounds valued at $2,241,000 in 1919.

Manufacture of cyanogen compounds, including the metal and other cyanides, hydrocyanic acid, etc., has remained fairly steady since the war, but the value of the present output is three times as large as before the war. Prussian blue (ferric ferrocyanide) stood at 4,803,000 pounds valued at $1,446,000 in 1929, about 30 per cent higher in quantity and value than in 1921, the earliest year for which separate returns were published. For all cyanogen compounds, including Prussian blue, the total value of manufacture in 1929 was $7,783,000, which compares with $6,311,000 in 1927, $7,115,000 in 1919, and $2,399,000 in 1914.

Aside from nitric acid (group I), the only other nitrogen product for which separate returns are available is nitrous

Table IX. Production of Ammonium Sulfate

	1919	1921	1923	1925	1927	1929
Coke industry:						
Total production, tons	272,152	264,274	457,963	506,639	586,322	698,276
Sales:						
Tons	278,746	264,966	442,476	493,090	612,812	675,077
Value	$21,059,000	$13,091,000	$25,954,000	$22,465,000	$23,905,000	$24,174,000
Chemicals industry, sales:						
Tons	13,899	1,101	712	2,854	6,191	5,926
Value	$1,390,000	$65,000	$70,000	$153,000	$266,000	$240,000
Manufactured-gas industry, sales:						
Tons	2,537	1,951	4,025	6,720	28,029	46,413
Value	$205,000	$101,000	$278,000	$351,000	$1,256,000	$1,728,000

TABLE X. MANUFACTURE OF SODA ASH AND CAUSTIC SODA

	1914	1919	1921	1923	1925	1927	1929
SODA ASH							
No. of establishments	10	18	19	14	12	12	14
Total production, thousand tons	[a]	1507	960	1708	1908	2038	2682
Made and consumed, thousand tons	[a]	474	184	449	539	571	868
For sale:							
Thousand tons	935	1033	776	1259	1369	1466	1814
Thousand dollars	$10,938	$31,195	$29,347	$32,427	$32,244	$29,939	$34,649
CAUSTIC SODA[b]							
Total production, thousand tons	[a]	313	239	437	497	573	762
Made and consumed, thousand tons	[a]	11	8	6	10	26	37
For sale:							
Thousand tons	292	302	231	431	487	547	725
Thousand dollars	$9,105	$18,691	$16,628	$25,057	$27,392	$29,193	$36,089

[a] No data.
[b] Primary production, not including repacked; also not including caustic soda made and consumed in wood pulp and textile industries.

TABLE XI. PRODUCTION OF SODIUM PHOSPHATES

PHOSPHATE	1914	1919	1921	1923	1925	1927	1929
Tribasic:							
Tons	[a]	[a]	[a]	26,224	48,783	63,531	82,045
Value	[a]	[a]	[a]	$1,956,000	$3,288,000	$4,525,000	$5,009,000
Monobasic, dibasic, and not specified:							
Tons	[a]	[a]	[a]	10,375	30,561	32,950	64,134
Value	[a]	[a]	[a]	$1,216,000	$2,467,000	$2,461,000	$3,956,000
Total:							
Tons	15,397	22,351	26,214	36,599	79,344	96,481	146,179
Value	$854,000	$2,439,000	$3,053,000	$3,172,000	$5,755,000	$6,986,000	$8,965,000

[a] Not separately stated.

oxide, or laughing gas. Manufacture of this commodity has increased enormously in the last fifteen years, the 1929 production standing at 109,812,000 gallons valued at $1,196,000, as against 17,838,000 gallons valued at $213,000 in 1914, a sixfold gain. The number of producing establishments, however, was only nine in 1929 and seven in 1914. As compared with 1927, the 1929 output showed a 65 per cent gain in quantity. The manufacture of Other Nitrogen Compounds and Gaseous Nitrogen, a basket clause which includes sodium nitrate, silver nitrate, sodium nitrite, etc., has made rapid strides, the total value of these products in 1929 being $9,899,000 as against $3,809,000 in 1927 and $2,678,000 in 1921.

GROUP III, SODIUM COMPOUNDS

This group, the largest among the groups of chemicals in value of products made for sale, has shown the marked advance since pre-war days that has characterized other chemical industries, and its progress since the war has also kept pace with them. In 1929 the total value of its commercial production was 38 per cent above that of 1919 and 320 per cent above that of 1914, the totals for these and other census years being as follows:

YEAR	VALUE	YEAR	VALUE
1914	$32,626,000	1925	$109,522,000
1919	99,690,000	1927	113,880,000
1921	83,698,000	1929	137,655,000
1923	111,848,000		

All but a very small proportion of this manufacture is made up of inorganic compounds. Sodium cyanide, acetate, benzoate, citrate, and other organic compounds accounted in 1929 for an aggregate value of only $6,624,000.

Until 1929 the leading product of this sodium group, comprising more than one-fourth the total sales, was soda ash. But the manufacture of caustic soda (sodium hydroxide) has been steadily mounting year by year, and in 1929 it assumed the position of first importance in the list. The record of manufacture of these two commodities, accounting together for more than half the commercial production of sodium compounds, for fifteen years (1914–29) is shown in Table X.

It will be noted that the value of commercial soda ash has been remarkably even since the war, the 1929 production being only slightly above the ten-year average as disclosed by census figures. This average is about three times that of 1914. But the gain over pre-war manufacture was due chiefly to much higher prices, as indicated by the fact that the 1914 quantity made for sale was little below the average post-war quantity up to 1929. Average valuation, which stood at $12 per ton in 1914, was $19 in 1929, $20 in 1927, and $30 in 1919.

Ninety-five per cent of this soda ash is made by the ammonia-soda process in six establishments. In 1929 their production for commercial purposes was 1,718,000 tons valued at $32,541,000, and their production for their own uses was 868,000 tons. Using processes producing natural and electrolytic soda, eight establishments in 1929 turned out 96,000 tons valued at $2,108,000. The relative proportion of production by these different processes has been practically the same, at least as far back as 1921 when separate returns were first made.

Modified sodas to the extent of 59,154 tons valued at $1,783,000 were produced in 1929, consisting of 49,219 tons of soda ash and bicarbonate valued at $1,151,000 and 9935 tons of soda ash and caustic valued at $632,000. This represents a 32 per cent gain over 1923, the earliest year for which figures are available.

Caustic soda production has doubled in value since 1919 and quadrupled since 1914. This expansion seems to have been

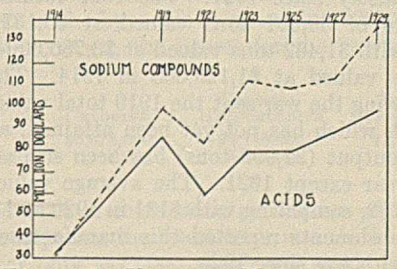


FIGURE 2. VALUE OF MANUFACTURE OF ACIDS AND OF SODIUM COMPOUNDS IN U. S.

induced by other factors besides prices. While the reported average valuation has sloped downward since the war 1929 average per ton was still some 60 per cent higher than the pre-war figure, the average for each of the last seven census years being as follows: 1914, $31; 1919, $62; 1921, $72; 1923, $58; 1925, $56; 1927, $53; 1929, $50. With regard to the process of manufacture followed, the six establishments

employing the lime-soda process have, since the war, consistently turned out about 70 per cent of the total, the rest being the product of sixteen to twenty firms using the electrolytic process. For 1929 a total of 524,985 tons was manufactured by the former process and 236,807 tons by the latter.

In addition to the primary production, a considerable amount of repacked caustic soda appears in the returns. Since 1921 both the amount and total value of this manufacture has been declining, but it is still a large item. Production in 1929 stood at 17,474 tons valued at $3,612,000, as compared with 33,228 tons valued at $5,305,000 in 1921 (a drop of 32 per cent), and 20,625 tons valued at $2,102,000 in 1919. There are no data for earlier years.

Of all the commodities listed in the sodium group, none has made such striking advance in the war and post-war periods as the phosphates. In 1914 the total production was reported as 15,397 tons, and the total value as $854,000. By 1929 these figures had mounted to 146,000 tons with a valuation of $8,965,000, almost a tenfold gain in quantity and more than a tenfold gain in value. The tribasic phosphates have comprised the larger part of the output from one year to another, and their value was increased two and a half times between 1923 and 1929. In the same period, however, the output of monobasic, dibasic, and other phosphates was trebling in value and increasing sixfold in quantity.

Table XI shows the steps of this rapid rise.

Less pronounced but still very notable has been the growth in sodium silicate manufacture, which in the fifteen years 1914–29 registered a fourfold increase in value. Whereas eight producing firms in 1914 were turning out commercial silicate valued at $1,649,000, twenty-three firms in 1929 were producing an output valued at $7,179,000. In quantity this 1929 manufacture aggregated 590,277 tons (basis 40°), or nearly three times as much as in 1921. As compared with 1927, the 1929 production showed a gain of 17 per cent in quantity and 5 per cent in value. Besides the production for sale, a considerable quantity, amounting to 10 to 20 per cent of the total manufacture, was formerly reported as being made for other than commercial purposes, but in later years no returns have been made for such production.

Bichromate and chromate, while showing the usual immense advance as compared with 1914, have maintained a fairly steady level since the war in the value of output, though the quantity manufactured has increased each census year since 1921. In 1929 a marked gain of about 40 per cent in value and 25 per cent in quantity was registered over the 1927 figures, which in point of value represented a fair average for the industry since 1921. The 1929 returns showed a manufacture of 39,301 tons valued at $5,137,000, which compared with 31,462 tons valued at $3,780,000 in 1927 and 11,824 tons valued at $1,125,000 in 1914. The abnormal prices following the war sent the 1919 total value to $5,337,000, a mark which has not yet been attained, although the volume of output (22,992 tons) has been surpassed in each following year except 1921. The average value per ton in 1919 was $232, comparing with $131 in 1929 and $95 in 1914. Eight establishments reported this manufacture in 1929 as compared with five since 1923.

Besides soda ash the carbonates of soda include two other chemicals of commercial importance—refined bicarbonate and sal soda. The 1929 production of the former (140,234 tons valued at $4,062,000), while well above the average for post-war activity, showed a comparatively smaller gain than many other major products, the figures representing an advance over 1914 of 55 per cent in quantity and 180 per cent in value. The 1919 output (141,556 tons) was still somewhat higher than that of 1929, although the value was about 10 per cent less. These figures of production cover only that made for commercial purposes, and do not include a very considerable tonnage used in the plants. Sal soda is one of the few important chemicals whose recent production is less in quantity than that before or immediately after the war. In nineteen establishments a total of 57,850 tons valued at $1,523,000 were manufactured in 1929. This compares with a 1914 production of 106,591 tons valued at $1,510,000 and made in fifty establishments; and a 1919 production of 82,992 tons valued at $2,273,000, the contribution of forty-one manufacturing concerns. The average value per ton was $14 in 1914, as compared with $27 in 1919, and $26 in 1929.

Production of borax has fluctuated very widely in the census years since 1914, as shown in Table XII.

Table XII. Production of Borax

Year	No. of Establishments	Tons	Value
1914	7	26,500	$2,072,000
1919	8	29,635	4,622,000
1921	6	18,499	2,745,000
1923	6	53,092	5,102,000
1925	7	49,967	4,083,000
1927	7	64,864	5,079,000
1929	8	92,250	3,280,000

It will be noted that the 1929 output, while far higher in quantity than for any previous census year since 1914, was valued at a total only 60 per cent greater than in 1914 and less than for any other year except 1921. The average valuation in 1929 was only about $36 per ton, whereas in 1914 it stood at $78, in 1919 at $156, and in 1927 at $78.

Four sulfates are listed among the sulfur compounds, niter cake (bisulfate), salt cake, Glauber's salt, and thiosulfate (hyposulfite). Three of these show decreases in 1929 as compared with earlier years, but the fourth (niter cake) registered a gain in value which was nothing less than extraordinary. While the amount manufactured for sale (82,683 tons) was only about two-thirds that of 1927, the value ($1,023,000) exceeded that of two years before by about 64 per cent. The average value in 1929 was $12 per ton and in 1927 it was $5, the latter figure being a fair average for many preceding years. As compared with 1914, the recent output in this field is such as to make it seem almost a new industry, created in the last fifteen years. The value of the 24,129 tons made for sale in 1914 was only $32,000, and the average value $1.31 per ton. Besides the commercial output, there is a large production each year for consumption within the manufacturing plant. In 1929 this amounted to 28,839 tons, or about one-fourth of the total made.

Salt cake, with a production in 1929 of 170,176 tons valued at $2,015,000, has doubled in commercial production since 1914, but the total value is less than for any census year since 1919. The tonnage output is slightly less than in 1927 but is well ahead of that of other years, and the lowered value is due to a smaller ton valuation (about $11 as against nearly $16 in 1927 and as much as $20 in earlier years). Glauber's salt, of which 61,953 tons with a value of $1,112,000 were made for sale in 1929, was above the average since the war in quantity but below it in total value, but was nearly three times the value and twice the quantity turned out in 1914. Hyposulfite has shown a steady decrease in the total value of its production since 1919, the 1929 figure of $906,000 being the lowest since the war. But this was evidently due entirely to lower prices, since the 25,020 tons of the latest census were exceeded only in 1919. There are no data for pre-war manufacture.

Hypochlorite of sodium almost doubled its contributions to American commerce between 1927 and 1929. The number of producing concerns grew from eleven to twenty, the tonnage output from 14,697 to 26,772, and the value of the

product from $1,141,000 to $2,016,000. Sulfide production, for sale (33,032 tons valued at $1,407,000), was rather below the average in the after-war decade.

Group IV, Potassium Compounds

Cream of tartar (potassium bitartrate) is one of the few important chemicals whose manufacture was markedly heavier before than after the war. In 1914 the eight reporting concerns engaged in its manufacture enjoyed an aggregate output of 12,696,000 pounds which sold for $3,125,000. Those figures have not been attained in any later census year. In 1919 the quantity produced was a little more than one-third the pre-war figure; and, while there has been a steady increase since, production in 1929 had reached only 7,853,000 pounds or about 60 per cent of that of fifteen years before. The value ($1,931,000) represented about the same proportion.

For iodide of potassium, no separate returns were made before the war; since the war, production has been fairly even. The 1929 returns (444,000 pounds with a value of $1,487,000) were a fair average of output over the decade so far as quantity was concerned, but the value was lower than for any year since 1921. Potassium hydroxide was first reported separately in 1929, 7191 tons yielding a revenue in that year of $638,000. Potassium citrate reached its highest mark in 1929 (in point of quantity produced) with 151,000 pounds, but the total value ($80,700) was still 20 per cent under that of 1919.

Besides manufactured potassium compounds, potash mined from original sources in 1929, as reported by the Bureau of Mines, amounted to the respectable total of 108,000 tons, the potassium oxide content of which was 61,500 tons. It is interesting to note that this figure approaches that of 1919 (116,634 tons) which reflected the war-time exploitation of our own resources when the normal trade with Europe was cut off. The year-by-year advance since 1921 illustrates the progressive development of our own latent resources: 1921, 25,485 tons; 1923, 39,029 tons; 1925, 51,565 tons; 1927, 76,819 tons; 1929, 107,820 tons.

Group V, Alums and Other Aluminum Compounds

As compared with the pre-war total, the value of alums produced in this country in 1929 maintained well the general ratio of gain evidenced by the whole chemical industry, approaching a figure three times as great as that of 1914. Except for a slight falling-off as compared with 1927, this total of $9,388,000 for 1929 represented a step in a continued advance since 1921 and stood about 40 per cent higher than the mark reached in that year. While the progress made in the industry has thus not been so rapid as in some other lines of manufacture, it has been of very substantial proportions. About 85 per cent of this value in recent years has consisted of aluminum sulfate, or concentrated alum, whose production in 1929 was almost five times as great in value as in 1914, although but little more than half that of 1919, when prices were enormously enhanced by the abnormal conditions following the war. Since 1919 the value of this manufacture has been increasing each census year. The 1929 total of $8,039,000 compares with $1,729,000 in 1914 and $15,666,000 in 1919. In point of quantity the 1929 output of 345,000 tons (manufactured in twenty-seven establishments) is the highest record in the statistics, comparing with 93,000 tons in 1914, 313,000 tons in 1919, and 314,000 tons in 1927.

Of the other three alums for which separate returns were made (beginning in 1925), ammonia alum and soda alum recorded smaller total values in 1929 than in either of the two preceding census years, but that for potash and chrome alums was considerably increased. The value of the 1929 production of ammonia alum ($287,000) was 13 per cent below that of four years before; that of soda alum ($848,000) was 9 per cent less; and that of potash and chrome alums ($215,000) was greater than in 1925 by nearly 200 per cent.

Aluminous abrasives took a large stride forward in 1929, attaining a production of 33,000 tons which were valued at $3,446,000. Prior to that year, post-war output had been fairly steady, the 1927 total of 20,000 tons valued at $1,970,000 being approximated in each of the other census years. The 1929 figures exceeded these by about 70 per cent and may be considered as representing an advance of that size over the average production in the preceding period following the war. There are no data for 1914. Of the aluminum chloride manufactured in recent years, only a small part has been diverted to commercial channels. In 1929 a total of 1521 tons (crystals, and solutions calculated on a 100 per cent basis) with a value of $225,000 was reported as made for sale, whereas, according to the United States Bureau of Mines, the whole manufacture in that year was 16,551 tons with an estimated value of $1,601,000. For 1927 entire production was placed at 17,130 tons and for 1925, 12,830 tons, the respective totals of value being $4,054,000 and $4,013,000. Aluminum stearite returns for 1929 showed a manufacture of 1066 tons with a value of $440,000, about three times the output in 1925 when figures were first compiled separately for the product.

Group VI, Bleaching Compounds

The growth in the manufacture of bleaching compounds over the last fifteen years has fully kept pace with that of chemical industry in general. By 1929 this manufacture enjoyed an output with a value nearly four times that of 1914 ($19,871,000 as against $5,302,000). Since the war the growth has been steady and continuous, each census year seeing a substantial gain over the one preceding (Table IV).

Of the three classes of compounds making up this group—chlorine, peroxide, and sulfur bleaches—the first named is the most important in point of total value of goods made for sale. In 1929 chlorine bleaches were made commercially to a value of $12,479,000, or more than 60 per cent of the value for the whole group. Substantially this proportion has held for many years, and the advance in the value of bleaching compounds as a whole has thus been paralleled by that of the chlorine compounds.

In the manufacture of these bleaches there has been in late years a marked growth in the production for sale of pure chlorine, while the hypochlorites of calcium and of sodium have remained stationary or receded. In 1927 for the first time the value of chlorine made in this country for the market exceeded that of the hypochlorites, and in 1929 the lead was considerably increased, the figures for the two years being:

Year	Chlorine	Calcium Hypochlorite	Sodium Hypochlorite
1927	$6,678,000	$4,148,000	$1,141,000
1929	7,113,000	3,351,000	2,016,000

The swift advance in commercial production of chlorine can be seen by comparing the latest returns with those for 1914, in which year only $473,000 worth was made for sale, this figure contrasting with $2,916,000 for the two hypochlorites combined.

It should be noted that in all the above figures for chlorine the amounts made and consumed in the wood pulp industry are not included. The values given also cover only the amounts of chlorine made for sale, which in 1929 totaled 289,855,000 pounds. In that year 109,089,000 pounds were consumed in the industry, making a total chlorine production of 398,944,000 pounds, a striking advance from the 234,979,000 pounds of 1927. New York is by far the leading state,

accounting for 134,099,000 pounds, or 46 per cent, of the total made for sale in 1929. That state also reported 36,390 tons of calcium hypochlorite (almost 40 per cent of the total in 1929) and 8693 tons of sodium hypochlorite (about one-third of the total).

Of the other bleaches, hydrogen peroxide, with a 1929 output of 8,509,000 pounds (basis of 100 volumes) valued at $2,372,000, was the leading one in point of value. Production has fluctuated considerably in the last decade. The total 1929 value was somewhat higher than that of 1919, and, as compared with 1914, represented an increase of about 80 per cent. New York, with a production of 6,438,000 pounds, was credited with three-fourths of the total. Other peroxide bleaches reached a value of $1,139,000 in 1929, somewhat below the post-war average. Of the sulfur bleaches, sulfur dioxide has shown a steady upward climb in recent years; in 1929 its value ($974,000) was almost tenfold that of ten years before, while its quantity (17,601,000 pounds) was more than twenty times that of 1919. However, it still represents but a minor part of the total manufacture of sulfur bleaches, as others (including sulfurous acid, sulfhydrates, etc.) totaled $2,907,000 in 1929 and practically the same value in 1927.

Group VII, Coal-Tar Products

Since 1917 the United States Tariff Commission has taken a yearly census of the production of coal-tar dyes and other coal-tar products in this country, and detailed figures are published annually in the Commission's reports under the title "Census of Dyes and of Other Synthetic Organic Chemicals." The Census Bureau accordingly does not collect detailed returns, and its published figures cover only the totals for the value of crudes, intermediates, and finished products.

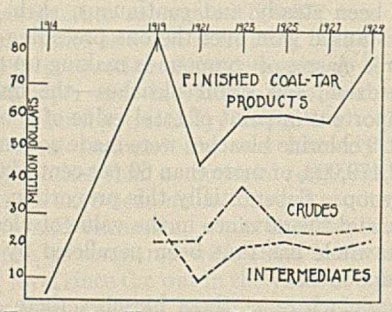


Figure 3. Value of Manufactures of Crudes, Intermediates, and Finished Coal-Tar Products in U. S.

Although the coal-tar group is second only to sodium compounds in the total value of its products and represents one-sixth of the aggregate value of chemical manufactures, it will be unnecessary here to review production in detail, since the Tariff Commission reports are widely circulated and are familiarly known to the trade.

The Aladdin-like creation of an American coal-tar industry through stress of sheer necessity brought on by the war in Europe makes it unique among American industries. In the five years of the war period (1914–19) the value of its production increased ten times. The value of finished products manufactured increased more than fifteen-fold. This swift ascent established the industry permanently in this country, but the heights to which it was carried by war prices and other abnormal factors have never been quite equaled since, so far as aggregate values are concerned. At the peak of the period of hectic prosperity in 1929, the total value of output almost reached the 1919 level, but not quite, although production of crudes for several years had surpassed that of 1919. Census Bureau figures for the last fifteen years show how the war-born activities have held up through a decade of peace (Table XIII).

Table XIII. Value of Coal-Tar Products

Year	Crudes[a]	Intermediates	Dyes and Other Finished Products	Total
1914	b	b	$5,427,000	$13,492,000
1919	$21,149,000	$28,240,000	84,111,000	133,500,000
1921	21,633,000	8,998,000	45,287,000	75,918,000
1923	38,297,000	23,280,000	60,317,000	121,894,000
1925	25,403,000	25,324,000	61,474,000	112,201,000
1927	24,862,000	22,845,000	58,350,000	106,057,000
1929	26,370,000	25,594,000	78,688,000	130,652,000

[a] Does not include by-product crudes of by-product coke plants and gas works.
[b] Crudes and intermediates together totaled $8,065,000 in 1914.

Because of certain differences in compilation, these Census Bureau figures do not quite check with those published by the Tariff Commission, although the two sets of returns are not far apart.

Of the finished products, dyes comprise 60 to 70 per cent of the total value. While they have occupied first place in output and in public attention, other products such as synthetic resins have enjoyed an amazing growth. Production and sales of the leading finished coal-tar products in 1929 and 1930 with production figures for 1918 are given by the Tariff Commission in Table XIV.

Group VIII, Plastics

Articles reported under this heading are largely pyroxylin products. Because of several changes in classification, the output of recent years cannot be compared with that of earlier census years, but it is evident that the decade prior to 1929 was a highly prosperous one, with considerable fluctuations in production and value. In 1929 ten establishments turned out a total of 25,283,000 pounds of pyroxylin plastics, which represented a gain of 30 per cent over 1927 but was more than 2,000,000 pounds under the 1923 figure. Four-fifths of the 1929 production (20,427,000 pounds) was made for sale in a form suitable for further manufacture, the value of this commercial product being $18,063,000. This

Table XIV. Production and Sales of Finished Coal-Tar Products

(In thousands)

Products	1918 Production		1929 Production	1929 Sales		1930 Production	1930 Sales	
	Pounds	*Value*	*Pounds*	*Pounds*	*Value*	*Pounds*	*Pounds*	*Value*
Dyes	58,464	$62,026	111,422	106,071	$45,842	86,480	89,972	$38,622
Color lakes	9,591	5,020	13,245	12,908	7,263	9,563	9,590	5,692
Medicinals	3,623	7,793	5,000	4,745	8,359	7,508	5,450	7,880
Flavors	458	4,926	2,292	2,253	3,517	2,010	2,031	2,739
Perfumes	116	585	1,599	1,480	1,083	1,042	1,019	745
Photographic chemicals	317	824	581	580	791	625	606	761
Synthetic resins	4,233	2,642	33,036	30,661	10,393	30,868	24,014	7,324
Synthetic tanning materials			a	a	a	a	a	a
Research chemicals	....	.....	a	a	a	2,968	2,378	1,772
Miscellaneous	....	.....	a	a	a			
Total	76,802	83,816	167,176[b]	158,698[b]	77,247[b]	141,065[b]	135,059[b]	65,535[b]

[a] Figures could not be given without disclosing details of private business. [b] Totals for 1929 do not include synthetic tanning materials, research chemicals, and miscellaneous chemicals; those for 1930 do not include synthetic tanning materials.

TABLE XV. PRODUCTION OF MISCELLANEOUS CHEMICALS

ARTICLE	1919	1927	1929
Alcohols (butyl, synthetic, methanol, etc.), value[a]	$1,051,000	$9,944,000	$11,841,000
Arsenate of calcium:[b]			
Pounds	1,192,000	27,282,000	33,064,000
Value	$248,000	$1,665,000	$1,860,000
Arsenate of lead:[b]			
Pounds	11,466,000	21,528,000	30,682,000
Value	$2,090,000	$3,190,000	$3,523,000
Butyl acetate:			
Total production, gallons	[e]	4,220,000	5,963,000
Made and consumed, gallons	[e]	1,878,000	1,439,000
For sale			
Gallons	[e]	2,342,000	4,524,000
Value	[e]	$3,613,000	$5,680,000
Calcium acetate:			
Tons	76,955	69,017	58,163
Value	$2,682,000	$4,021,000	$4,695,000
Calcium chloride:			
Tons	74,699	191,123	277,010
Value	$1,043,000	$4,443,000	$5,947,000
Calcium phosphates:			
Tons	22,135	34,003	38,139
Value	$4,727,000	$4,914,000	$5,557,000
Calcium hypochlorite:			
Tons	[e]	110,524	93,116
Value	[e]	$4,148,000	$3,351,000
Carbon disulfide:			
Pounds	11,606,000	44,972,000	71,010,000
Value	$640,000	$2,160,000	$2,860.000
Carbon tetrachloride:			
Pounds	9,812,000	17,026,000	32,713,000
Value	$804,000	$1,036,000	$1,728,000
Copper sulfate (blue vitriol):			
Pounds	35,288,000	56,667,000	78,669,000
Value	$3,165,000	$2,774,000	$4,345,000
Ether:			
Total production, pounds	4,898,000	8,068,000	7,026,000
Made and consumed, pounds	765,000	1,933,000	562,000
For sale:			
Pounds	4,133,000	6,135,000	6,464,000
Value	$1,126,000	$1,720,000	$1,897,000
Ethyl acetate:			
Total production, gallons	771,000	6,638,000	14,100,000
Made and consumed, gallons	416,000	2,031,000	3,168,000
For sale:			
Gallons	354,000	4,607,000	10,932,000
Value	$340,000	$3,701,000	$9,007,000
Glycerol, crude:[c]			
Pounds	21,403,000	27,000,000	28,790,000
Value	$2,962,000	$3,943,000	$2,358,000
Glycerol, refined:			
Total production, pounds	69,464,000	95,353,000	138,487,000
Made and consumed, pounds	2,121,000	5,768,000	25,347,000
For sale:			
Pounds	67,343,000	89,585,000	113,140,000
Value	$20,724,000	$19,185,000	$12,716,000
Ferro-alloys (electric furnace only):			
Tons	[e]	197,425	246,859
Value	[e]	$17,049,000	$28,655,000
Magnesium sulfate (Epsom salt):			
Tons	29,348	27,665	36,983
Value	$1,497,000	$1,142,000	$1,405,000
Nickel salts and compounds, value	$642,000	$836,000	$1,218,000
Silver nitrate:			
Ounces	3,018,000	4,897,000	5,647,000
Value	$2,184,000	$1,957,000	$2,016,000
Sulfur, refined:			
Tons	52,099	43,508	78,119
Value	$2,713,000	$1,799,000	$3,066,000
Sulfur-lime solution:			
Gallons	[e]	7,653,000	11,974,000
Value	[e]	$1,056,000	$1,446,000
Tin salts and compounds, value	$3,887,000	$10,583,000	$13,112,000
Vanillin:			
Pounds	135,000	300,000	317,000
Value	$1,366,000	$1,923,000	$1,858,000
Vitreous enamels, value[d]	[e]	[e]	$4,512,000
Zinc chloride:			
Pounds	74,089,000	58,268,000	77,232,000
Value	$4,349,000	$1,921,000	$1,619,000

[a] Not including glycerol, ethyl alcohol, or methanol from wood distillation.
[b] In 1927 and 1929 (but not in 1919) includes by-products of patent and proprietary medicine manufacture.
[c] Production for sale by chemical and soap-manufacturing establishments only. Total production of crude glycerol (80 per cent basis) was: 1927, 128,209,000 pounds; 1929, 140,080,000 pounds.
[d] In addition to this figure, 90,933,000 pounds valued at $5,684,000 were made and consumed in further manufacturing operations in industries producing stamped ware, enameled ware, etc., and plumbers' supplies.
[e] No data.

was more than for any other year in which these returns were made separately.

Articles of pyroxylin made in the pyroxylin-manufacturing establishments (such as blanks for toothbrushes, toys, novelties, fancy articles, handles for cutlery and umbrellas, etc.) were valued at $10,522,000 in 1929, $6,801,000 in 1927, $10,984,000 in 1925, and $11,300,000 in 1923.

Of plastics other than pyroxylin, the only one for which separate returns were compiled in 1929 was rubber substitutes, of which eight establishments reported a total output of 9,923,000 pounds with a value of $1,003,000. In point of value this is hardly more than one-third the output of 1923, and is some 25 per cent under that of 1919. Other plastics, including phenolic resins, cellulose plastics, casein plastics, etc., for which separate returns were not made, were manufactured to a value of $10,943,000 in 1929. Rayon, which was formerly classed under plastics, is now treated as a separate industry; pyroxylin solutions in the last two census years have been included under Paints and Varnishes.

GROUP IX, MISCELLANEOUS

Under this heading there are included some sixty different chemicals, such as alcohols, ether, glycerol, and various compounds and salts of metals, etc. All separate items for which the 1929 returns showed a total production valued at $1,000,000 or more are shown in Table XV, with comparative figures for 1927 and 1919. It should be noted again that 1919 values are abnormal because of war-inflated prices. Comparison of recent output with pre-war production is impossible with most of these articles because of lack of separate returns in 1914 and earlier years.

RECEIVED February 24, 1932.

The German Chemical Industry

According to the Department of Commerce, in 1931 Germany had the highest favorable trade balance in the history of the country, notwithstanding the depression. Chemicals contributed nearly 800,000,000 marks to this balance, being preceded by metals and metal goods, 1,500,000,000 marks, and machinery, 1,700,000,000 marks.

As interpreted in Germany, the chemical industry is hampered by two outstanding recent international developments—the rapid expansion of the chemical industries of the principal producing countries with increasing international competition and prohibitive tariffs and import restrictions. Consequently, many countries formerly regarded as markets for chemicals, not only have made themselves independent in many lines but have appeared as competitors in international trade, Germany's chemicals exports having declined 18 per cent in value.

Competition in world chemical markets in 1931 was more drastic than ever before. Toward the end of 1931 a dumping scare developed, which called forth immediate governmental counteractions in the countries which thought themselves jeopardized. High tariffs no longer were regarded as sufficient protection and embargoes and import restrictions were introduced as an additional safeguard.

The German Government inaugurated a series of tariff rate increases and import restrictions during 1931. Among important measures enacted was the imposition of formidable import duties on fertilizers, which was strengthened by a decree of the Minister of National Economy, effective August 18, 1931, containing a virtual prohibition of imports of the principal nitrogen, and some mixed, fertilizers except under special permits.

On January 18, 1932, an emergency decree was issued authorizing the government to impose higher rates of duty on products of those nations which have depreciated currencies, as well as those with which Germany has no treaty relations or which discriminate against German goods.

Intermittent Chlorination of Condenser Water

C. S. Boruff, State Water Survey, Urbana, Ill., and K. E. Stoll, Super-Power Company of Illinois, Pekin, Ill.

Continuous chlorination of condenser waters in order to keep cooling equipment free of biological growth dates back to about 1922. Intermittent chlorination, however, has recently been proposed and put into use (*3, 5*), and hence the experience at Powerton should be of interest.

The Powerton Station of the Super-Power Company of Illinois is located on the Illinois River not far below the City of Pekin. At present the station consists of three units and has a capacity of 215,000 kilowatts. The condenser cooling water is drawn from the heavily polluted Illinois River.

Cause of Accumulated Slime Deposits

During the summers of 1928 and 1929 considerable trouble was had in keeping the Super-Power Company's condensers clean. This was due to the abundant growth and accumulation of slime deposits in the cooling equipment.

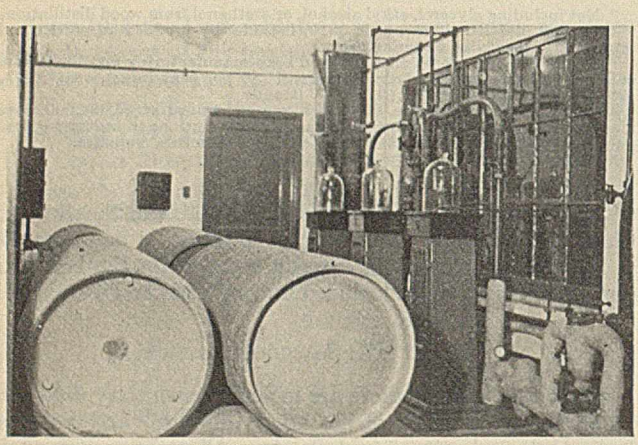


Figure 1. One-Ton Chlorine Tanks and Chlorinators, Powerton, Ill.

Reversing the flow would not remove this slime. During the periods of one- and two-unit operation, it became necessary to introduce sand once or twice daily into the water boxes of the condensers in order to remove the slime. Cleaning of the condensers with rubber plugs during outage of the unit was also necessary.

In October, 1928, samples of the slime and river water were sent to the State Water Survey and were examined. The slime was identified as being composed mainly of the sewage fungus, *sphaerotilus*. Others have reported algae as the causitive agent (*3, 5*), but this seems improbable in highly polluted waters. The water submitted for analysis was found to be highly polluted with organic wastes.

Sphaerotilus natans, the organism causing the trouble in this case, grows best in polluted waters, especially waters in which only a few blue-green algae can survive. It forms short rods which are held together by a gelatinous sheath, thus forming long threads. Under the microscope these threads may appear as a single filament or as a tuft of interlaced filaments (*6*). It is nonmotile, Gram positive, and forms spores (1.5 to 2.0 microns) which resist boiling in water for 5 minutes. These spores also guarantee its survival over the winter months when conditions are not favorable to its growth. Its growth is favored by moderate ammonia or peptone concentrations, carbohydrates (*4*), and a temperature of about 25° C. (77° F.). It is always found in domestic sewage.

Sanitary chemical and bacteriological studies carried on during this and other investigations have shown the Illinois River at Powerton to be highly polluted (*1, 2*). The following data may serve to characterize this water: five-day biochemical oxygen demand, 6.0 to 8.0 p. p. m.; dissolved oxygen, 3.5 to 5.0 p. p. m.; ammonia nitrogen, 0.7 to 1.6 p. p. m.; organic nitrogen, 0.8 to 1.6 p. p. m.; nitrate nitrogen, 0.6 to 0.7 p. p. m.; alkalinity 130 to 180 p. p. m.; pH, 7.0 to 7.8 p. p. m. The authors have no evidence that these conditions are optimum for *sphaerotilus* growth, but they at least represent conditions under which it grows luxuriantly. These data, along with those given elsewhere (*3, 5*), may be of value to others who are already using or anticipate using such waters in their condensers.

Advantages of Intermittent Chlorination

After due consideration of all factors and the various methods of treatment, it was deemed advisable to try chlorination. On the basis of a yearly average chlorine requirement of 1.5 p. p. m., a flow of 287 million gallons per day (two condensers), and chlorine at 2 cents a pound, it would cost $71.75 a day for the chlorine for continuous chlorination. Although it is probable that this would be worth while, the cost seemed considerable. The idea of intermittent chlorination had been proposed and was being tried at a few plants (*3, 5*); hence the advisability of this method was considered, and finally it was adopted. The main attractive feature of intermittent

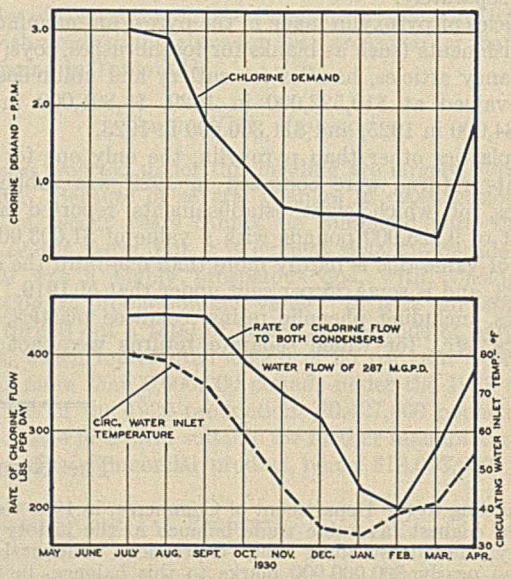


Figure 2. Characteristic Circulating-Water Data and Corresponding Rate of Chlorine Flow (Monthly Averages)

chlorination (intermittent disinfection) is that it takes less chlorine to periodically clean condensers of growth than it does to keep all the water chlorinated to the extent that *sphaerotilus* cannot grow or live in it. A chlorine dosage of from 1.9 p. p. m. in winter to 4.2 p. p. m. in summer (16 to 35 pounds per million gallons) during a period of 4 minutes out of every 90 was found most effective and satisfactory.

The present chlorine installation went into operation in February, 1931. It was designed to have sufficient capacity for four units or a total of 540,000 g. p. m. of cooling water. The installation consists of four 1-ton chlorine tanks; three chlorinators, each having a capacity of feeding 450 pounds of chlorine gas per day on a continuous basis (Figure 1); two solution tanks, 14 feet high and 7.3 feet in diameter, and having a solution capacity, after being filled with limestone, of 730 gallons; and six 200 g. p. m. rubber-lined solution pumps. The object of the limestone is to react with the free chlorine

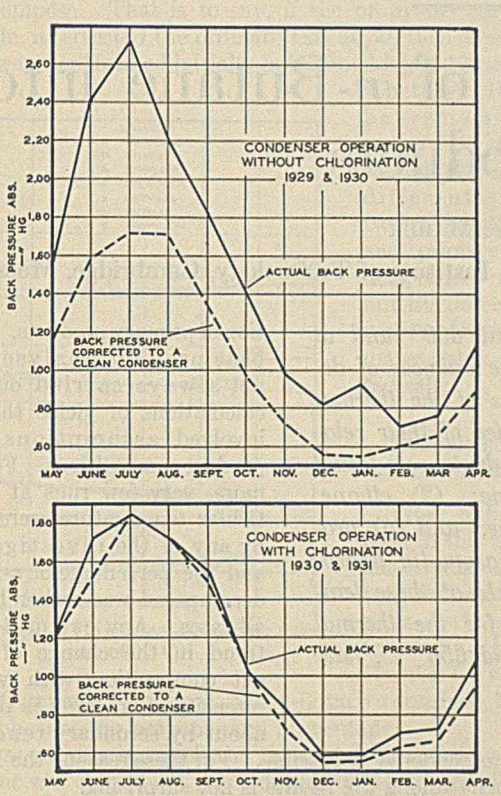


FIGURE 3. CONDENSER OPERATION WITH AND WITHOUT CHLORINATION

in the solution tanks and thus form a chlorine-hypochlorite solution. This makes it possible to carry higher active chlorine concentrations to the condensers. The available chlorine content of this solution, as delivered to the condenser water pumps, is about 0.3 per cent or 3000 p. p. m. This procedure also decreases the possibility of gas fumes escaping from the solution tanks. Limestone is added to these tanks periodically to keep them full. The operation of the rest of the equipment is similar to other Wallace and Tiernan installations. Chlorine is fed continuously to the solution tanks from which the chlorine-hypochlorite solution is periodically (4 minutes out of every 90) and automatically pumped to the suction side of the circulating pumps. As an insurance for continued operation of the electrical generating equipment during any unexpected but highly improbable breakdown of the chlorine storage or dosing apparatus, the entire equipment (including the chlorine dosage pumps which deliver the chlorine-hypochlorite solution to the condenser water pumps) was located in the crib house which is a little distance from the main building. As an added safety measure, the chlorinator and gas tanks were enclosed in a separate mechanically ventilated room.

Figure 2 graphically represents monthly averages of the chlorine demand and temperature of the raw inlet condenser water as drawn from the canal and lagoon from May, 1930, to April, 1931. The main significant fact is that the chlorine demand and hence the amount of chlorine added to the condenser varies directly with change in water temperature. As the water temperatures approach that of optimum growth for the *sphaerotilus*, more chlorine is necessary. During the summer months, as much as 0.19 p. p. m. (1.56 pounds per million gallons) of chlorine was necessary, while during the cooler winter months only 0.08 p. p. m. (0.70 pound per mlilion gallons) was necessary. The average chlorine dosage for the one-year period discussed in this paper was 0.16 p. p. m. (1.3 pounds per million gallons of water circulated). This chlorine was all added during intermittent and short intervals. The dosage during these periods (4 minutes out of every 90) was from 4.2 to 1.9 p. p. m. (35 to 15.6 pounds per million gallons). This dosage program was found to be the most effective. The average residual chlorine in the effluent from the condensers at the end of these 4-minute treatments was 0.4 p. p. m.

The above data bear out the fact that condensers can be kept clean with much less chlorine per day if it is introduced intermittently, rather than continuously. Dosages of 0.4 to 0.8 p. p. m. are not uncommon in plants using (or trying) continuous chlorination (*5*).

The curves in Figure 3 are self-explanatory. They compare the condenser performance with chlorination (1930–31) and without chlorination (1929–30) for a period of a year, and show a decided decrease in the absolute back pressure on the condenser. Figure 4 shows the comparison of losses in heat consumption due to a dirty condenser and also shows the percentage saved in B. t. u. per kilowatt hour because of chlorine treatment.

Particular observation has been given the condenser tubes for corrosion and for other detrimental effects, but nothing harmful has been observed. A piece of condenser tubing was weighed and placed in the condenser water box for over a year with no loss in weight and no indication of corrosion.

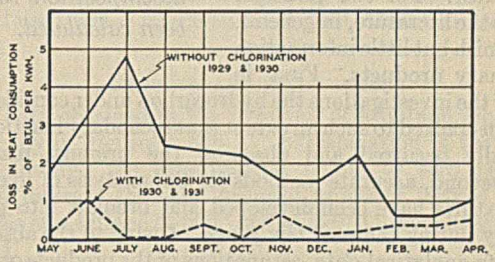


FIGURE 4. AVERAGE MONTHLY LOSSES IN HEAT CONSUMPTION CORRECTED TO A ZERO LOSS OF A CLEAN CONDENSER

Careful consideration of operating-cost data, that is, the cost of chlorine, limestone, and maintenance to the equipment for a period of a year, indicate that a gain in vacuum of 1.5 mm. (0.06 inch) of mercury will pay for the cost of operation and maintenance. The actual gain in vacuum being several times this—namely, an average of about 6.1 mm. (0.24 inch) of mercury—makes the treatment desirable economically as well as from an operating point of view.

SUMMARY

In summarizing the performance and results of intermittent chlorination of polluted river condenser water at the Powerton Station, the following conclusions may be drawn:

1. Intermittent chlorination is a successful method of removing biological growths from condensers.
2. A decided gain in vacuum conditions is indicated for the year period.
3. The greatest increase in vacuum is obtained during the summer months.
4. Chlorine consumption parallels raw water temperatures.

5. Intermittent chlorination is economically desirable and requires much less chlorine than continuous chlorination.

6. No detrimental effects, such as corrosion, have been encountered.

7. Manual cleaning of condensers has been considerably reduced.

8. With proper design and location of the chlorine equipment, the potential danger which accompanies the handling of chlorine gas may be kept at a minimum.

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Thermal Decomposition of *n*-Butane into Primary Products

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The pyrolysis of n-butane at 600° and at 650° C. was investigated for the purpose of determining the primary products of the thermal dissociation. Listed in the order of their relative importance, the reaction products were found to be: (1) methane, propylene; (2) ethane, ethylene; (3) hydrogen, butylene; and (4) propane. Neither butadiene nor aromatic hydrocarbons were formed as products at these temperatures. Velocity constants for the thermal decomposition rates at 600° and 650° C. have been calculated.

Owing to the necessity for the most profitable utilization of waste gases from petroleum refineries and from the fields, as well as to the importance of obtaining a knowledge of the reaction mechanism through which the paraffin hydrocarbons dissociate, accurate determinations of the primary products of their decomposition are of both practical and theoretical interest. For two principal reasons the literature, in general, can furnish but little information on primary products. First, in most of the investigations the hydrocarbon under consideration has been cracked to such an extent that secondary reactions undoubtedly occurred and obscured the primary reactions. Then, second, accurate methods for the analysis of hydrocarbon mixtures have been developed and brought into general use only during the past few years. Owing to the absence of complete analytical data, estimations of the products obtained on pyrolysis have actually involved a priori assumptions as to the nature of the dissociation reactions. The recent work of Schneider and Frolich (*10*) has involved the thermal dissociation of propane, propylene, ethylene, and butadiene. The use of low-temperature fractionation as an aid in carrying out the product analyses in this work, and the cracking of the several hydrocarbons to various extents permitted satisfactory estimation of the primary products.

Previous Work

Pease (*7*), Pease and Durgan (*8*), Hague and Wheeler (*4*), and Hurd and Spence (*5*) have investigated the pyrolysis of *n*-butane. The primary decomposition reactions suggested in the above contributions were:

$$CH_3CH_2CH_2CH_3 = CH_3CH{:}CH_2 + CH_4 \quad (1)$$
$$CH_3CH_2CH_2CH_3 = CH_2{:}CH_2 + CH_3CH_3 \quad (2)$$
$$CH_3CH_2CH_2CH_3 = CH_3CH_2CH{:}CH_2 + H_2 \quad (3)$$
$$CH_3CH_2CH_2CH_3 = CH_2{:}CHCH{:}CH_2 + 2H_2 \quad (4)$$

A summary of the yields obtained by the various investigators is given in the table which follows.

This table includes all data available on the pyrolysis of *n*-butane over the temperature range 600–700° C. Only Hurd and Spence (*5*) were directly concerned with the determination of primary products. Complete product analyses were not always carried out, and calculations of yields therefore involved assumptions as to product compositions. Furthermore, very few runs at a particular temperature were made by any of the investigators, and the percentage of *n*-butane decomposed was rather high in all cases. Any estimation of trend in the change of product composition with varying intensity of cracking as brought about by secondary reactions was thus rendered impossible. For these reasons the lack of agreement among the results is not surprising.

Summary of Yields Obtained by Various Investigators

Reaction	Product	Variations Obtained in Each Product per 100 Moles of *n*-Butane Reacting
		Moles
1	Methane and propylene	36 to 87
2	Ethane and ethylene	22 to 46
3	Hydrogen and butylene	5 to 20
4	Hydrogen and butadiene	0 to 4

Method of Attack

In order to determine the primary products formed in the pyrolysis of hydrocarbon, it is necessary either to eliminate secondary reactions entirely, or to determine in some manner the effect of secondary reactions on the relative proportions of the products formed. The complete elimination of secondary reactions could possibly be brought about by cracking the hydrocarbon to only a very small extent. However, the difficulty of separating very small quantities of products from the original hydrocarbon and the inherent chances of error involved in the quantitative estimation of such small quantities serve to render this method rather impractical. The effects of the secondary reactions in the pyrolysis may be determined quite simply, however, by cracking the hydrocarbon in varying degree and then by plotting the results in such a manner that extrapolation of the curves to zero per cent reacting is easily carried out. In this way the analytical difficulties involved in accurately determining very small amounts of a given constituent are eliminated.

POLITECHNI... ŚLĄSKI

The latter method employed by Schneider and Frolich (*10*) was also used in carrying out this work. The data were plotted as moles of each product formed per 100 moles of *n*-butane reacting *vs.* percentage of *n*-butane reacting, the curves so obtained being extrapolated to zero per cent cracked. A clear distinction between secondary and primary products was hereby obtained, in that the curves for the secondary products passed definitely through the origin, while those for primary products cut the ordinate axis at points representing the proportions of the products formed when the butane just began to decompose. That is to say, if the propylene curve, for example, intersected the ordinate axis at 50, then 50 moles of propylene were formed initially in the cracking of 100 moles of *n*-butane. It must be remembered, however, that although this method differentiates between secondary and primary products, it does not permit the detection of unstable intermediates, such as free radicals.

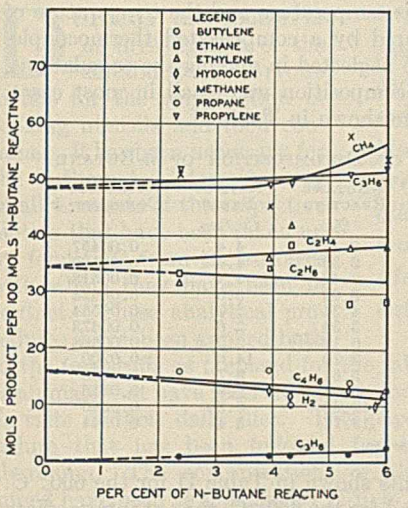

FIGURE 1. CRACKING OF *n*-BUTANE AT 600° C.

EXPERIMENTAL PROCEDURE

The *n*-butane used in this investigation was obtained by refractionation of a butane cut furnished by the Humble Oil and Refining Company. As used, the *n*-butane contained 1.6 per cent isobutane, no propane, and no pentane.

The apparatus in which the thermal decomposition of the *n*-butane was carried out was a duplicate of that described by Schneider and Frolich (*10*).

In making a run, the *n*-butane was passed through a flowmeter, scrubbed with concentrated sulfuric acid, and dried over calcium chloride. The gas was then passed through a 24 × 1 inch (61 × 2.5 cm.) fused silica preheater maintained at a temperature of 540° C., and from the preheater it entered directly into a 24 × 0.5 inch (61 × 1.25 cm.) fused silica reactor which was held at the desired cracking temperature. The true temperature of the gas leaving the reactor was measured by means of a compensated thermocouple. Upon leaving the reactor, the decomposition products and the remaining *n*-butane then passed into a cold trap immersed in a mixture of solid carbon dioxide and acetone. The gas not condensing in the cold trap was collected in a calibrated gas bottle by displacement of saturated zinc sulfate solution. This gas contained methane, ethane, ethylene, propylene, and *n*-butane, as well as all the hydrogen formed in the pyrolysis. The liquid condensing in the cold trap contained most of the undecomposed *n*-butane, propylene, propane, ethylene, ethane, and methane. The quantity of propane formed was never so great as to cause an appreciable amount of it to be present in the noncondensed gas.

Upon completion of a run, the liquid which had collected in the cold trap was fractionated in a Davis column (*2*). The various fractions were collected over saturated zinc sulfate solution in displacement burets. With the exception of those fractions in which the percentage of olefins was inordinately low, analyses were carried out in a Williams gas-analysis apparatus, in which the usual absorbents were employed. Hydrogen was determined by combustion over copper oxide at 300° C., and saturated hydrocarbons were estimated by explosion with oxygen. Explosions were carried out with small gas samples with oxygen present in excess.

From three to six explosions were made in each case in order that accurate average values for the ratio of contraction to carbon dioxide could be obtained. The explosion data sufficed for those fractions which contained only two saturated hydrocarbons, but the presence of a third prevented the determination of the composition of the mixture from the explosion data alone. It was possible, however, to determine the concentration of the third saturated hydrocarbon in some independent manner whenever this condition arose. For example, the propane-propylene fraction was always found to contain small amounts of *n*-butane and ethane, as well as propane. The amount of butane present was estimated from the fractionation curve obtained in making the cut, and the quantities of the other components present were then calculated from the explosion data. As the noncondensed gas also contained three saturated hydrocarbons, the explosion data alone did not serve to fix its composition. Since no fractionation of this gas could be carried out with the equipment available, it was necessary to find some other method of estimating the third hydrocarbon. It was seen that the ratio of moles of ethane to moles of ethylene in the liquid could be calculated from the analyses of the Davis-column fractions. As the concentration of the ethylene in the noncondensed gas was already known from absorption data, it seemed possible that the percentage of ethane in the gas could be calculated by simple proportion, provided that the relative volatility, in butane solution, of ethane with respect to ethylene could be obtained. The data compiled by Copson and Frolich (*1*) provided vapor pressures for the two compounds; and, by assuming a Raoult's law deviation of −10 per cent for the ethylene, the relative volatility was calculated to be 0.525. Estimation of the ethane by this method and calculation of the percentages of methane and butane from the explosion data were found to yield consistent results.

In those fractions in which the olefin concentration was small, titration of the gas samples with 0.02 *N* potassium bromide–potassium bromate solution was employed. The method used was a modification of that described by Francis (*3*).

RESULTS AND DISCUSSION

The data obtained in the pyrolysis of *n*-butane are shown graphically in Figures 1 and 2. Extrapolation of the curves drawn through the experimental points to zero per cent cracked indicate that the primary products formed in the pyrolysis of *n*-butane at 600° and at 650° C. were as shown in Table I.

TABLE I. DISTRIBUTION OF PRIMARY PRODUCTS FROM THERMAL DISSOCIATION OF *n*-BUTANE

PRODUCT	AMOUNT FORMED PER 100 MOLES *n*-BUTANE REACTING	
	At 600° C.	At 650° C.
	Moles	*Moles*
Methane	48.5	48.0
Propylene	48.5	48.0
Ethane	34.5	36.7
Ethylene	34.5	38.7
Hydrogen	16.0	12.3
Butylenes	16.0	12.3
Propane	0	1.0 (?)

As the weighing of the cold-trap condensate obtained in these runs could well have brought about loss of methane (the most volatile component present in the liquid, particularly in those cases in which the degree of cracking was high), the propylene curve was given full weight in the estimation of primary products at 650° C. The propane determinations were probably not as accurate as were the determinations of the other constituents, because of the fact that only very small quantities of propane were formed in the pyrolysis. At 600° C. the propane curve seems to pass definitely through the origin, indicating that propane is a secondary product at this temperature. At 650° C., however, the indications are that approximately 1 mole of propane is primarily formed per 100 moles of *n*-butane reacting. It is not believed, however, that

the determinations of propane in such small amounts were sufficiently accurate to warrant a positive statement as to whether or not propane was formed as a primary product. The rather rapid decrease in the relative amount of ethane found in the products as a degree of cracking increased is worthy of note.

In order to determine the nature of the butylenes formed in the pyrolysis, a long-time run was made at 650° C. The butane-butylene fraction was brominated at 0° C., the bromination temperature being kept low in order to prevent substitution reactions. The fractionation of the bromides and the refractive indices of the fractions so obtained indicated that approximately 20 per cent of the butylene formed in the pyrolysis was 1-butene, while the remainder was 2-butene. The absence of butadienetetrabromide in the brominated product indicated that no butadiene had been formed.

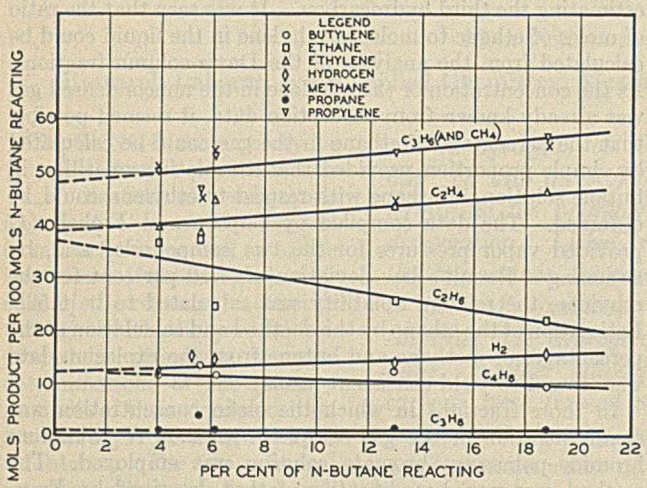

FIGURE 2. CRACKING OF *n*-BUTANE AT 650° C.

Neither tars nor aromatic hydrocarbons were formed in appreciable amounts in any of these runs. The fractionation data, as well as analyses of the gases remaining in the still and column at the end of the distillation, failed to indicate the presence of any hydrocarbon having a molecular weight greater than that of *n*-butane.

This latter fact seems to indicate that propane is not formed in the pyrolysis through a bimolecular reaction of the type found by Schneider and Frolich (*10*) to take place in the thermal dissociation of propane, in which ethane and butane were formed. A similar reaction in the case of *n*-butane would yield propane and pentane. Because of the relative thermal instability of pentane, the proportions of pentane in the product, if it were formed by such a reaction, would decrease as the extent of reaction increased. It is probable that the analytical methods employed would not permit detection of the small amounts of pentane that could form in this way.

It is interesting to note that the cracking mechanism proposed by Rice (*9*) on the basis of free-radical formation gives a ratio of the extent of occurrence of the two major reactions (1 and 2) which approximates very closely that obtained in the present work:

	Ethane + Ethylene (Reaction 2) / Methane + Propylene (Reaction 1)	
Temp., ° C.	Predicted by Rice	Experimentally determined
600	0.75	0.71
650	0.79	0.79

However, the primary formation of butylenes and hydrogen in the pyrolysis of *n*-butane is not accounted for by this proposed mechanism.

Although the principal object of this work was to determine the distribution of the primary thermal-decomposition products of *n*-butane, the velocity constants for the over-all decomposition have been calculated from the present data for their practical and theoretical interest. The general first-order rate equation was used:

$$2.303 \log (1/1 - x) = kt$$

where x = fraction of *n*-butane undergoing thermal dissociation
t = av. time of contact, seconds
k = velocity constant

In calculating the rate constants, it was assumed that no cracking took place in the preheater. It was assumed further that, for the purpose of calculating the time of contact for each run, the temperature of the gas entering the reactor was 540° C., the temperature of the preheater wall. The gas temperature used in calculating time of contact was the arithmetic mean of this temperature and the temperature of the exit gas as measured by a compensated thermocouple. Reverse reactions were neglected in making the calculations, since the extent of decomposition was small in most cases. The calculated data are shown in Table II.

TABLE II. RATE OF DECOMPOSITION OF *n*-BUTANE

Temp. of Exit Gas	Calcd. Av. Temp.	*n*-Butane Reacting	Rate of Feed[a]	Velocity Constant k
° C.	° C.	%	Cc./sec.	
600	570	2.14	4.4	0.00457
...	...	2.39	4.4	0.00500
...	...	2.42	4.4	0.00518
...	...	3.92	3.3	0.00624
...	...	4.31	2.7	0.00564
...	...	5.34	2.6	0.00673
...	...	6.12	2.2	0.00668
650	595	3.79	14.6	0.0200
...	...	5.51	9.7	0.0268
...	...	6.08	6.8	0.0215
...	...	12.60	5.3	0.0346
...	...	18.77	3.4	0.0344

[a] At 0° C. and 1 atm. pressure.

The velocity constants shown in Table II for the 600° C. runs at low feed rate and for the 650° C. runs at intermediate feed rates approximate those obtained for *n*-butane at 570° and 595° C., respectively, in a separate, unpublished investigation. The thermal-decomposition rates of the lower members of the paraffin hydrocarbon series are being investigated in a special apparatus (*6*) designed to give an accurate knowledge of temperature and time of contact.

CONCLUSIONS

The primary products of the thermal decomposition of *n*-butane at 600° and 650° C. were found to be as follows:

Product	Amount Formed per 100 Moles *n*-Butane Reacting: At 600° C.	At 650° C.
	Moles	*Moles*
Methane and propylene	48.5	48.0
Ethane and ethylene	34.5	37.7
Hydrogen and butylene	16.0	12.3
Propane	0	1.0 (?)

Over the temperature range investigated and with the times of contact used, neither butadiene nor aromatic hydrocarbons were formed. No hydrocarbons of molecular weight higher than that of butane were detected in the reaction products.

ACKNOWLEDGMENT

The authors wish to acknowledge the assistance given by the Humble Oil and Refining Company toward this work.

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Occurrence and Determination of Aluminum in Foods

I. Determination of Aluminum in Organic Materials

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Aluminum in organic tissues is determined colorimetrically as a lake with aurin tricarboxylic acid. Exact details of ashing procedure and conditions for lake formation are given. Simplification of technic and increased precision over previously described methods are attained by use of a permanent color standard and a combined reagent for lake development. Mercaptoacetic (thioglycolic) acid is used as a test for iron.

DURING the course of an investigation of the suitability of various metals for the construction of cooking utensils and food containers, it has been necessary for the authors to determine very small amounts of the respective metals that have been taken up by foodstuffs from the surfaces with which they have been in contact. These analytical procedures have been applied both to the foodstuffs as prepared for the table and to the tissues of animals that have received known concentrations of metallic salts in their daily diet. This paper describes the procedure that has been followed for the determination of aluminum. The concentrations of aluminum thus determined have been as small as 0.1 p. p. m.

A colorimetric method for aluminum, based on the procedures of Myers, Mull, and Morrison (*2*), and of Winter and his associates (*7, 8, 9*), has been used. The method, in brief, consists of ashing the material at as low a temperature as possible, solution of the ash, precipitation of aluminum as the phosphate adsorbed on an excess of ferric phosphate, removal of iron, development of a color by means of the aurin tricarboxylic acid lake, and determination of the aluminum by comparison with a fixed color standard.

PROCEDURE

Fresh washed tissue (5 to 150 grams) is dried overnight in a platinum dish at 110° C. It is then placed on a nichrome-triangle in a cold electrically heated muffle, and the temperature is gradually raised during the day to a faint red heat. The ashing process is completed overnight while a slow current of oxygen is passed into the muffle to hasten the combustion.

The ash is treated with 10 cc. of concentrated hydrochloric acid and 25 cc. of water. The resulting solution is evaporated to dryness to dehydrate silica. To the residue are added 10 cc. of 3 *M* hydrochloric acid and 25 cc. of water, and the solution is boiled for 5 to 10 minutes. The solution is centrifuged at 1800 r.p.m. for 5 minutes and decanted into a 100-cc. Erlenmeyer flask. The residue, if any, is washed and discarded; but if carbon remains in the residue, the latter is transferred to a platinum crucible and dried. The silica is volatilized with hydrofluoric acid and sulfuric acid, followed by gentle ignition. The residue is then fused in a small amount of equal parts of sodium and potassium carbonates and dissolved in the main solution.

To the solution of the ash are added 1 cc. of concentrated nitric acid (specific gravity, 1.42) and 1 cc. of 0.1 *M* ferric sulfate. The solution is evaporated to about 10 cc. and diluted with water to approximately 60 cc. Five cc. of 1 *M* monosodium phosphate and 2 cc. of 0.04 per cent bromophenol blue are added and then 7 *M* ammonium hydroxide until a permanent precipitate is formed. Next the pH is brought to 4.2 by the addition of 3 *M* sodium acetate. The mixture is centrifuged for 5 minutes at 1800 r. p. m., and the liquor is discarded.

The precipitate of ferric and aluminum phosphate is dissolved in 0.5 cc. of 6 *M* hydrochloric acid and 1.25 cc. of glacial acetic acid, and approximately 15 cc. of hot water are added. Five cc. of 6 *M* sodium hydroxide are stirred in with a glass rod, and the mixture allowed to stand for an hour with frequent stirring. The glass rod is washed, and the ferric hydroxide thrown down by centrifuging for 5 minutes at 1800 r. p. m. The solution is decanted through two 9-cm. filter papers prepared by washing with warm 1.2 *M* sodium hydroxide, followed by hot water until practically all alkali is removed. The filtration is made into a 100-cc. volumetric flask containing 1 cc. of 6 *M* hydrochloric acid. The precipitate remaining in the centrifuge tube is washed once by stirring with 20 cc. of hot water and centrifuging. The washings are decanted through the filter. The ferric hydroxide is not transferred to the paper. The filter paper is thoroughly washed with water, the solution cooled, made faintly acid to litmus, and diluted to 100 cc.

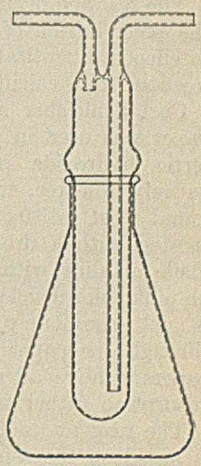

FIGURE 1. FLASK AND CONDENSER FOR LAKE DEVELOPMENT

Twenty cubic centimeters of the solution are measured into a dry 250-cc. glass-stoppered Erlenmeyer flask. Then there are added 25 cc. of a solution containing, in 1 liter, 1 mole of ammonium acetate, 1 mole of ammonium chloride, 80 cc. of 0.1 per cent ammonium aurin tricarboxylate (aluminon), and 60 cc. of 6 *M* hydrochloric acid. The pH at this point must be between 4.5 and 5.5. A snugly fitting test-tube condenser (Figure 1) is placed in the neck of the flask, and the solution is boiled for 1 minute, timed from the first appearance of steam bubbles. The solution is cooled for 1 minute under the condenser and then to room temperature in running water.

Enough 1.6 *M* ammonium carbonate (4.8 to 5 cc.) is added with gentle shaking to give a final pH of 7.1. The flask is stoppered and shaken up and down twenty times. Carbon dioxide is released by cautiously removing the stopper, and

the flask is allowed to stand for 20 minutes, with the stopper loosened, for the excess dye to be decolorized. The pH should now be within the limits 7.0 and 7.3, but preferably at 7.1.

The concentration of the aluminum is determined immediately in a Duboscq colorimeter by comparison of the intensity of the lake color with a standard containing 5 cc. of 0.04 per cent thymol blue and 8 cc. of 6 *M* hydrochloric acid in 500 cc. of solution. The aluminum lake solution is set at a constant depth of 30 mm., and the depth of the standard is varied for the color matching.

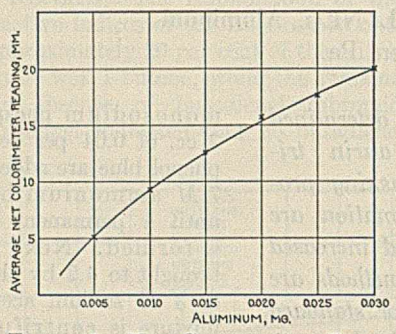

FIGURE 2. NET COLORIMETER READINGS OBTAINED WITH ADDED ALUMINUM

The amount of aluminum present in the aliquot is determined by reference to a curve plotted from the colorimeter readings obtained when varying amounts of aluminum are subjected to the entire scheme of analysis beginning with the ash (Figure 2).

DISCUSSION OF TECHNIC AND REAGENTS

In the initial solution of the ash of heavy carcasses it is necessary to use 25 cc. of concentrated hydrochloric acid and 25 cc. of water and to aid the process by trituration of bone ash with a flattened glass rod. The second solution is effected by 20 cc. of concentrated hydrochloric acid and 150 cc. of water. An aliquot, usually one-fifth, is taken for the rest of the procedure. No addition of monosodium phosphate is necessary in the analysis of carcasses.

The reaction of pH 4.2 should be very closely controlled in the precipitation of the phosphates of iron and aluminum, to effect a quantitative removal of aluminum and insure its freedom from calcium phosphate.

Carl Schleicher and Schüll No. 589 white ribbon filter paper was used in preparing the iron-free filtrate from the ferric hydroxide precipitation. These filtrates must be entirely iron-free, and the mercaptoacetic acid test has been found most satisfactory. When 10 cc. of the solution are treated with a drop of mercaptoacetic acid (*1*) and then made alkaline with ammonium hydroxide, there should be no pink color developed. The writers have found that iron is not completely removed by centrifuging. Filtration through one paper removes part of the residual iron; two papers remove all of it. The process seems to be one of adsorption rather than of filtration.

The reagent used for development of the aluminum lake is based on the separate solutions used by Winter, Thrun, and Bird (*9*).

The combined reagent obviously reduces the manipulations and insures more uniform conditions during the lake development.

Because of variations in the escape of carbon dioxide in the decolorization of the excess dye after lake development, the given procedure for shaking must be rigidly adhered to in order to insure a final pH of 7.1. If the solution is not shaken enough, the pH will be too low for complete change of the dye to the yellow form; if the shaking is too vigorous or prolonged, the pH will be high enough to result in appreciable fading of the lake color.

The thymol blue permanent standard used by Thrun (*5*) in the study of the stability of aluminum lakes is very convenient and preferable to standards prepared from aluminum solutions. The pink color is stable over periods of at least 6 months. The color match is not perfect, but readings are readily duplicated to give thoroughly reliable analyses. The precision of the readings is such that the probable error of sixteen random observations at about 30 mm. is ±0.10 mm. A random selection of some early readings, made by another trained observer, of aluminum lake against aluminum lake shows the probable error of ±0.25.

All reagents were made up from large stocks of chemicals of the same lot number in order to maintain a uniform blank in all analyses. Mallinckrodt's C. P. quality sodium hydroxide crystals ($NaOH + H_2O$) have been found to be practically aluminum-free. Its use obviates the tedious preparation of the alkali solution from aluminum-free sodium. The 6 *M* solution was prepared by direct weighing without subsequent standardization. The 6 *M* hydrochloric acid was prepared by distilling an approximately 6 *M* solution and collecting the last three-fourths of the distillate. The aluminon of the Fales Chemical Company was used.

The empirical curve employed is an inverse curve compared with that of Winter, Thrun, and Bird (*9*), as the depth of the standard in the colorimeter was varied rather than that of the unknown. The curve automatically corrects for the blank of the reagents, as it is a record of the colorimeter readings obtained when definitely known amounts of aluminum enter the analytical system. The curve shown in Figure 2 represents the net colorimeter readings obtained in a series of observations of the intensity of color produced by known amounts of pure aluminum salts added at the beginning of the procedure. The reagents used produced color equivalent to 12.5 to 14 mm. of the thymol blue standard. In routine analyses a blank control was invariably carried through to secure the net reading of the colorimeter, a reading which is obviously altered by the size of the aliquot required. The curve shown in Figure 2 is not reproduced for use, as its form and position depend on the quality of all reagents. It is necessary to prepare a curve for each set of reagents, a process that is simply a matter of "blanking" the reagents.

In a system which involves the use of standards prepared from known amounts of aluminum, the reagents involved in the preparation of those standards always introduce an additional unknown amount of aluminum. An inherent property of an empirical curve based on the use of a permanent standard and the values of aluminum entering the system is that it corrects for the entire blank of the procedure.

At the beginning of this investigation two general methods were available—the chemical and the spectrographic procedures. The latter presented the advantage of speed and the complete absence of contamination of the ash by the addition of reagents, but at that time was only roughly quantitative and required the installation and maintenance of expensive equipment. The advances made by Myers, Mull, and Morrison (*2*), and, during the period of the present studies, by Winter and associates (*5, 7, 8, 9*) and by Underhill and Peterman (*6*), have influenced the choice of the chemical method here used.

After an exhaustive investigation of ashing by the wet method—i. e., by sulfuric acid digestion with the addition of perchloric acid or nitric acid—and of the alternative ashing by ignition, the latter was chosen. In the wet-ashing procedure, some aluminum was introduced by the reagents, and containers were etched to give insoluble residues which were difficult to handle. These objectional features were absent

from the dry-ashing procedure. The authors were not able to demonstrate a loss of added aluminum in smoke evolved in ignition of various materials.

An investigation was made of the removal of iron, which interferes in the colorimetry, by means of cupferron. The removal effected was very complete, but the method was cumbersome and required an ashing procedure to remove the excess of cupferron. Iron is not removed completely by centrifuging, but, by adsorptive filtration through two filter papers, the mercaptoacetic acid test becomes uniformly negative.

A study of the interference of silica in colorimetry reveals that it is sufficiently removed by dehydration so that hydrofluoric acid treatment is unnecessary.

The absolute quantity of aluminum present in a given tissue, of course, cannot be determined by any method. Recourse must therefore be had to experiments on the recovery of added aluminum to prove the accuracy of a method. A well-mixed sample of ground beef liver showed, after the manipulations of grinding and mixing, 5.0 p.p.m. of aluminum. When 0.05 mg. of aluminum was added to 25 grams of the beef liver (yielding 0.125 mg. of aluminum), making a total apparent aluminum content of 0.175 mg. before ashing, 0.1785 and 0.1725 mg. were recovered. When the aluminum was added to the ash, 0.1725 and 0.1715 mg. were recovered.

The reader is referred to the articles cited (*2*, *5*, *6*, *9*) for other details of technic and for the underlying principles of the method. Other articles in this series (*3*, *4*) have been published, and further contributions will follow. Copies may be obtained by addressing the senior author.

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II. Aluminum Content of Foodstuffs Cooked in Glass and in Aluminum

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Foods cooked in glass and in aluminum have been analyzed for aluminum, and the average increase has been calculated. The taking up of aluminum by neutral foods is negligible: acid and alkaline foods are relatively more corrosive. In no case, however, is sufficient aluminum dissolved from utensils to interfere seriously with phosphorus absorption. An average daily intake of aluminum in case all foods are cooked in aluminum is estimated at 12 mg., of which about 5 mg. is derived from the utensils.

A NECESSARY qualification of all materials that come into contact with food during its production, distribution, cooking, or service is that they must not in any way depreciate the quality of the food. Primarily, it is not permissible that any essential constituent of the food be removed or any harmful substance added. Of secondary importance is the requirement that a specific undesirable taste or odor should not be imparted and that a discoloration should not be produced in foods by containers during any of the operations mentioned. It is, of course, also of importance that the utensil be inert to corrosion by foods in order that it survive use in cooking.

Aluminum is today the most popular of all materials for the construction of cooking utensils because of its light weight, bright attractive appearance, durability, high heat conductivity, and ease of cleaning and maintenance for constant use.

This wide popularity of aluminum after about thirty years of employment is convincing evidence that it is satisfactorily resistant to food attack, and that no harm results from eating foods customarily prepared in aluminum vessels. It has been shown elsewhere (*14*) that only barely detectable amounts of aluminum appear in the tissues, following diets containing large amounts of aluminum; the results to be expected (phosphorus starvation) when overwhelming doses of soluble aluminum salts are fed have also been described (*3*). In the present paper a study of the amounts of aluminum which enter foods by contact with aluminum in a variety of culinary practices will be recorded. In every case the amount of aluminum added to foods by utensils made of it has been found to be small and far below that necessary to produce phosphorus starvation and its sequelae, the only abnormal conditions which the authors were able to cause by administering to experimental animals excessively large doses of aluminum.

PREVIOUS STUDIES OF ALUMINUM CORROSION

A few quantitative and many qualitative studies of the corrosion of aluminum by foods have been made, especially in European laboratories. The latter have consisted of observations of pitting, polishing, or staining of aluminum surfaces exposed to foods; of precipitates in water and clear liquids; of discoloration of foods; and of alleged changes in taste. Occasionally, chemical demonstrations of the presence of aluminum in the food have been mentioned. Most of these reported findings, both qualitative and quantitative, are of little value now, as they were obtained by the use of articles constructed of various grades of early commercial aluminum

TABLE I. ALUMINUM CONTENT OF FOODSTUFFS COOKED IN GLASS AND IN ALUMINUM

Foodstuff	Duration of Cooking	Aluminum Content: Cooked in glass	Aluminum Content: Cooked in aluminum	Av. Increase in Aluminum	Remarks
	Min.	*P. p. m.*	*P. p. m.*	*P. p. m.*	
Fried bacon	5	0.25	0.68		.....
		0.26	0.68	0.43	.....
Boiled ham	120	0.78	2.1		Meat only
		0.78	2.1	1.32	
Beef pot roast	120	0.64	0.87		Meat and proportional part of gravy
		0.64	0.86	0.23	
Creamed chicken	120	0.95	2.43		.....
		0.98	2.28	1.39	.....
Beef soup stock	150	0.16	0.39		.....
		0.16	0.39	0.23	.....
Drip coffee	5	0.097	0.38		5 minutes dripping time
		0.097	0.38	0.28	
Percolated coffee	15	0.25	1.03		.....
		0.25	1.03	0.78	.....
Boiled potatoes, whole	30	0.26	0.25		.....
		0.25	0.27	0	.....
Boiled potatoes, skin removed	30	0.55	1.10		.....
		0.54	1.10	0.55	.....
Oatmeal	150	1.51	9.13		.....
		1.43	8.28	7.24	.....
Stewed tomatoes	20	0.12	4.36		Bright pan
		0.12	4.20	4.16	
Stewed tomatoes	20	0.14	15.3		Dark pan
			15.6	15.3	
Sauerkraut	45	0.83	16.4		.....
		0.83	16.4	15.6	.....
Green beans	90	0.91	2.28		.....
		0.91	2.28	1.37	.....
Navy beans	180	1.44	3.60		.....
		1.44	3.60	2.16	.....
Beets	150	0.57	0.74		.....
		0.58	0.74	0.16	.....
Creamed onions	30	0.50	1.10		.....
			1.11	0.61	.....
Creamed celery	20	1.00	1.57		.....
		1.00	1.57	0.57	.....
Creamed cabbage	45	0.37	2.76		Cooked without $NaHCO_3$
		0.37	2.80	2.41	
Creamed cabbage	45	0.34	90.8		Cooked with $NaHCO_3$
		0.34	90.8	90.5	
Creamed cauliflower	20	0.64	2.10		.....
		0.64	2.12	1.47	.....
Cranberry sauce	10	0.53	7.90		Bright pan without sugar
		0.54	7.90	7.36	
Cranberry sauce	10	0.62	3.12		Bright pan with sugar
		0.63	3.20	2.54	
Cranberry sauce	10	0.52	28.0		Dark pan without sugar
		0.53	28.0	27.5	
Cranberry sauce	10	0.75	3.40		Dark pan with sugar
		0.75	3.50	2.70	
Rhubarb	5	0.95	13.45		Bright pan
		0.95	13.35	12.5	
Rhubarb	5	0.94	41.8		Dark pan
		0.94	41.8	40.9	
Apricots	40	24.6	73.3		.....
		24.6	73.3	48.7	.....
Prunes	40	4.60	7.10		.....
		4.60	7.10	2.50	.....
Apple sauce	10	0.28	1.40		.....
		0.28	1.40	1.12	.....
Apple butter	390	5.28	118		Includes time to concentrate cider
		5.28	118	113	
Orange marmalade	90	0.30	3.06		.....
		0.30	3.06	2.76	.....
Lemon-pie filling	2	0.31	2.24		.....
		0.31	2.24	1.93	.....

which, because of impurities and methods of fabrication, were more susceptible to corrosion than the high-grade metal used in modern cooking utensils.

Two types of quantitative procedure have been employed in performing observations of corrosion of aluminum. One of the methods most frequently used has been the determination of the loss of weight of strips of metal or of utensils per se after exposure to foods. The other experimentation has been based upon analysis of the foods for increase of aluminum due to contact with the metal surfaces.

The work of Lunge and Schmid (*8*) is an example of the earlier investigations. Lunge and Schmid found that aluminum strips exposed to various food acids in concentrations from 1 to 5 per cent for a period of 6 days lost from 1.08 to 4.77 mg. per 100 sq. cm. They ascertained that coffee caused a loss of 0.5 mg., but could not detect loss of weight in the case of plates exposed to tea or beer. Smith (*16*) has cited similar investigations showing that corrosion of aluminum by foods is insignificant.

Studies that have been described since the appearance of Smith's book, give confirmation to the findings of the older investigators. Quam (*13*) has shown that aluminum is very inactive to corrosion by milk. Up to 70° C. no change in weight was detectable in aluminum plates immersed in milk; above 70° C. an increase in weight of 0.12 to 0.18 mg. per 100 sq. cm. occurred. Chiaria (*1*), using the same method, has verified Quam's results on the relation of temperature and extent of corrosion of aluminum by milk. Mrak and Cruess (*10*) have found small and varied degrees of corrosion of aluminum strips by various fruit juices. Colobraro (*2*) has analyzed various materials for aluminum after 1000 cc. were boiled in an aluminum vessel of 1400 cc. capacity for 1 hour. He has reported 1.69 mg. of aluminum in milk, 5 mg. in olive oil, 2 mg. in a sugar solution, 9.54 mg. in compote, 45.6 mg. in tomato preserves, 1.2 mg. in broth, and 1.83 mg. in white wine.

Plagge and Lebbin (*12*) were the first to examine foods to show indirectly the extent of corrosion of aluminum utensils. They included whole meals and compared the analytical results thereon with those of meals cooked in iron; but their data are of little value, owing to the inadequacies of their analytical methods.

The Lancet in 1913 reported in an editorial (*6*) on the corrosion of aluminum by a variety of foods. Not only were the utensils examined for the appearance of corrosion, but the foods were ashed and examined qualitatively for aluminum. Later *The Lancet* presented, also editorially (*7*), an account of a similar series of experiments by Glaister and Allison. In this latter report it was stated that the maximum amount of aluminum was observed in orange and lemon marmalade. The 1.018 grains of aluminum hydroxide that were found in 2.5 pounds of marmalade are equivalent to 20 p. p. m. of aluminum. No other quantitative data were given.

Schwartze, Murphy, and Cox (*15*), in one of the present series of investigations, have accorded attention to a fresh milk whose aluminum content was 0.07 p. p. m.; after pasteurization in aluminum for 30 minutes at 60° C., it was 0.67 p. p. m. It is of interest, in studying the quantity of aluminum introduced into foods by utensils and observing the effects of dietary aluminum, to know the amounts of aluminum that occur in raw foods in common use. The analyses of the tissues of various animals by several investigators (*9, 11*) show how little aluminum is to be expected in fresh meats. Winter and Bird (*18*) have analyzed a large

variety of plant and animal materials by practically the same method that has been employed here. Underhill, Peterman, Gross, and Krause (*17*) have also analyzed numerous common foods by a modern method of the same order of sensitivity as that of the present authors.

Experimental Work

As the purpose of this investigation has been to determine the amount of aluminum that enters food during cooking, attention has been directed to the food rather than to the utensil. Furthermore, analysis of the food gives the final data directly and without those assumptions of distribution that must always be made when weight losses of metallic strips or utensils are determined. Incidental to the main purpose, analysis of foods cooked in Pyrex glass has established what is probably the minimum practical aluminum content of cooked foods. Certain other observations have likewise been made, such as the relative rates of corrosion of bright and stained utensils, and the effects of sugar and of baking soda on aluminum. In a few cases a slightly perceptible difference of taste has been noted between foods cooked in glass and those cooked in aluminum.

In Table I are given the data of analyses of various foodstuffs. The foods were cooked in exact simultaneous duplicate in appropriate Pyrex glass and aluminum utensils according to standard recipes (*5*). Duplicate samples, ranging from 35 to 150 grams, were taken and analyzed for aluminum by a colorimetric method (*4*). From the average of the analyses the increase of aluminum derived from the metal utensil has been determined on the assumption that the glass contributed no aluminum.

In all cases Pittsburgh tap water was used, and no correction was made for its aluminum content. Excepting as noted in the table, proportionate parts of liquid and solid parts of foods were analyzed. In the case of the "boiled potatoes, whole," the potatoes were cooked *in toto*, but were analyzed after removing the skins. The juices arising in cooking the vegetables that were creamed were discarded; i. e., these vegetables were analyzed as creamed.

Discussion of Results

In general, the data in Table I demonstrate that clean aluminum utensils are attacked to an insignificant degree by foods of neutral reaction. Acid foods or foods to which baking soda has been added dissolve small amounts of aluminum from utensils. Dark utensils yield more aluminum to foods than bright ones, but probably only in proportion to the quantity of stain. The few experiments with and without sugar indicate that sugar decreases corrosion of aluminum utensils. The largest amount of aluminum that the authors have found in any food was 118 p. p. m. in apple butter, which had been cooked in aluminum for 6.5 hours. Even this apparently large amount of aluminum (0.118 per cent) is far less than the 1400 p. p. m. that have been found necessary to produce symptoms of phosphorus starvation in animals on a low phosphorus diet (*3*). Obviously the aluminum content of the general run of aluminum-cooked foods is so far below the phosphorus content that it may be regarded as of no significance.

The data in the table enable the calculation of the daily ingestion of aluminum in foods. In a balanced ration planned from the foods listed therein, it has been estimated that about 12 mg. of aluminum would be consumed if all the foods were cooked in aluminum. This amount is equivalent to approximately 4.9 p. p. m. in the ration chosen, of which 2.1 p. p. m. came from the utensil.

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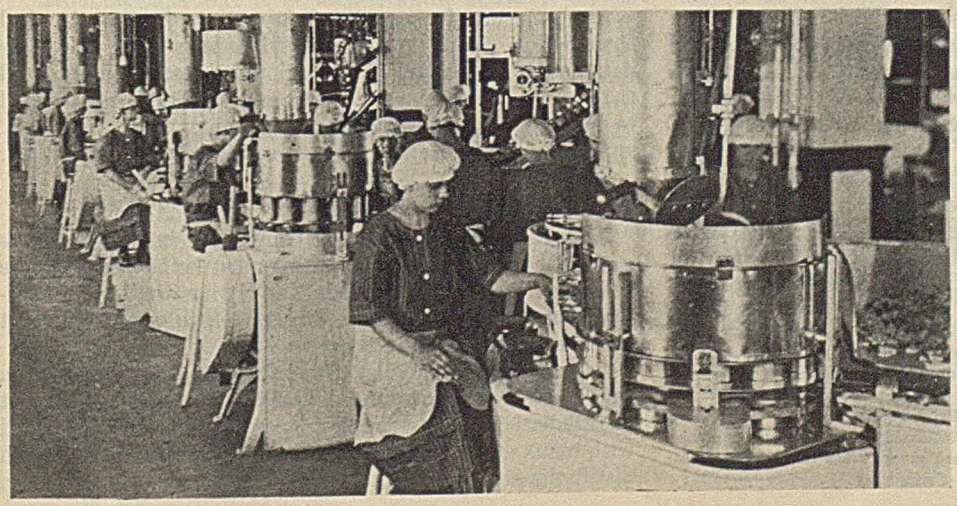

Bean-Filling Rig in H. J. Heinz Company Plant

Here oven-baked beans are placed in tins and sealed, some with special tomato sauce and pork, and others strictly vegetarian. The tins come directly from the can factory on mechanical conveyors, being washed and sterilized on the way.

Composition of Straight-Run Pennsylvania Gasoline

I. Design of Fractionating Equipment

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For the purpose of studying the composition and knock properties of straight-run Pennsylvania gasoline, two packed fractionating columns were constructed of metal, one being 27 feet long and 3 inches in diameter with a capacity of 13 gallons, the other, 52 feet long and $^3/_4$ inch in diameter with a capacity of 1.5 gallons.

The essential features in the design of these columns were adiabatic operation, controlled reflux, and high efficiency with a large throughput and a minimum of liquid holdup in the column. Operation was very simple.

To test the efficiency of these columns, diisobutylene, which was known to consist of two isomeric olefins, was fractionated. No difficulty was experienced in separating the two isomers, boiling 3.3° C. apart, in one fractionation.

Pennsylvania crude oil, because of the valuable lubricating oils obtained from it, is the highest priced crude in the country. However, about one-third of the crude is straight-run gasoline of low knock rating, so that, like many crudes, the amount of straight-run gasoline is greater than the gasoline obtained by cracking the fuel or gas oil. In general, straight-run gasolines knock worse than those made by cracking, and Pennsylvania straight-run is no exception. Since the knock rating of a gasoline has become one of its most important properties, it is increasingly difficult to sell straight-run product as a premium gasoline. In all other requirements or specifications for motor fuel, Pennsylvania straight-run gasoline is a premium fuel. It contains no sulfur, does not color in storage, is perfectly stable showing no tendency to form polymerization products or gums, and has the proper volatility. The tendency to knock becomes more pronounced, the greater the compression ratio used in the engine. Since the trend in automotive engine design is toward higher compression ratios, this undesirable property will cause increasing trouble.

A great amount of work is being done to increase the antiknock quality of gasoline. The most common method of obtaining higher antiknock values is to add dopes, the most important and effective of which are tetraethyllead and benzene. Because of the low knock rating of straight-run gasoline, excessive amounts of either tetraethyllead or benzene must be added, and such additions are neither practical nor economical. Another method is to blend the straight-run gasoline with cracked gasoline. This method, although widely used, is not wholly satisfactory because the large quantities of straight-run gasoline from Pennsylvania crudes require a correspondingly large quantity of cracked gasoline to give a fair knock rating on the resulting blend.

These considerations led to the conclusion that the best way to attack the problem of the knocking properties of straight-run Pennsylvania gasoline was to make as complete a study of the composition of the gasoline as time and funds would permit.

Editor's Note. This paper is the first of a series on straight-run Pennsylvania gasoline, and the information presented is very closely related to subsequent papers on the knock rating and isolation of hydrocarbons from the gasoline. These columns were used in the later work, and their performance as shown in this paper has a direct bearing on the results to be presented. Because of the close interrelationships of the various phases of this work, this paper is presented here rather than in the Analytical Edition of Industrial and Engineering Chemistry.

There is very little definite information on the composition of gasoline and the materials responsible for knock. The nearest approach to this information is the work being done on the American Petroleum Institute Project No. 6, at the Bureau of Standards, under the direction of E. W. Washburn. However, that work is being carried out on a Midcontinent gasoline and would throw little light on the Pennsylvania problem, since it is known that crudes differ widely in their properties and consequently in their composition.

The work of Boyd (*5*, *19*) and Edgar (*10*, *24*) and their associates shows that the hydrocarbons with greatest tendency to knock are the normal paraffins. However, this effect can be reduced by the addition of certain antiknocking substances, such as aromatic hydrocarbons (*15*), olefins, and the more highly branched paraffins. Callendar (*4*) and co-workers have contributed considerably to the knowledge of dopes and detonation.

The early work of Mabery (*20*) shows that the normal paraffins are present in Pennsylvania petroleum, but it is impossible to obtain from these data any idea as to the amount present. Brown and Carr (*1*) also claim to have isolated normal paraffins, but the physical data they give leaves considerable doubt concerning the degree of isolation and purity obtained. Bruun and Hicks-Bruun (*2*), at the Bureau of Standards, find all but one of the isomeric hexanes in Midcontinent gasoline, as well as benzene and toluene.

As a means of procuring information on the chemical constitution of straight-run Pennsylvania gasoline, as well as data on the proportions of the various substances present and their effect in inducing or preventing knock, it was decided to build special fractionating equipment.

A preliminary note on this work has already been given (*11*).

Requirements of Fractionation Equipment

Since the amount of any one constituent in the gasoline is small, the fractionating equipment must be of a size to give sufficient quantities of material for further study. In addition, the equipment must be constructed to give the highest possible degree of separation.

A study of rectification principles (*13*, *29*) shows that a fractionating column for the highest degree of enrichment must be adiabatic, and for simplest operation must be provided with reflux at the top of the column. In addition, for batch distillations the concentration of the lightest component in

the top of the column will be higher, the longer the column and the greater the reflux ratio (proportion of liquid returned to the column to that taken off as product). This holds true as long as there are no constant-boiling mixtures. One other point that is apt to be overlooked is the proportion of holdup in the column to the quantity of any one constituent present. In a given charge or size of still, the holdup must be as small as possible. For a column such as required for this work, there is really nothing to limit its height except the building in which it is contained and the mechanical difficulties involved in its construction. Since fabrication of metals was easier and more permanent than glass, the columns were constructed of metal.

Finally, the efficiency of a column will depend on the mechanical construction used to bring about rectification, i. e., interaction between rising vapors and descending reflux. If the common form of bubble cap is used, it must be of an efficient design; or, if a packed column is used, the packing must be such as to give a high degree of enrichment per unit of length.

Plate Columns

For a given height the choice of bubble cap or packing would depend on which gave the greater enrichment or efficiency with the least holdup of liquid, provided each could be operated with the same through-put or capacity. Plate efficiencies for petroleum hydrocarbons may be from 30 to 90 per cent. Lewis and Smoley (*17*), using an experimental ten-plate column, found efficiencies of 59 per cent for a benzene-toluene mixture, 73–9 per cent for a benzene-toluene-xylene mixture, about 80 per cent for a cracked naphtha, and as high as 95 per cent when aniline was used as the key component in the naphtha. However, they concluded that the high efficiencies observed with both aniline and pinene (90 per cent) were due to the fact that these substances showed considerable deviation from Raoult's law. The results of Carey (*25*) also indicated that, at least for a single bubble cap, efficiencies from 55 to 80 per cent could be obtained.

For a continuous operation the number of perfect distillations may be calculated for two components by the method of McCabe and Thiele (*30*). If this is done, it is found that a mixture containing 50 per cent A and 50 per cent B (where A and B are hydrocarbons) with about 4° C. (7.2° F.) difference in boiling points, can be separated to 90 per cent A as product, and 90 per cent B as bottoms by using a 30:1 ratio of overflow to product if about fifty perfect plates are present; and, from the efficiencies indicated above, there should be perhaps seventy actual plates to give the desired rectification; certainly one hundred plates would be ample.

If bubble caps were to be used it would be rather difficult to build a column of reasonable size (for example, 3 inch diameter) with less than 5 to 6 inches per plate and yet allow a reasonable vapor velocity or through-put. The column used by Lewis and Smoley (*17*) operated with a superficial vapor velocity (lineal vapor velocity in open column, i. e., between plates) of from 0.6 to 0.9 foot per second. The distance between plates was about 1 foot. Washburn, Bruun, and Hicks (*31*) described a welded twenty-plate column, but no data were given on vapor velocity or rate of distillation. Their column had about 3 to 4 inches between plates. Usual vapor velocities in plate columns are 0.6 to 1.2 feet per second. However, Chillas and Weir (*7*) advocated higher vapor velocities and they indicated in their design a maximum vapor velocity of 2.25 feet per second. In order to avoid the increased entrainment caused by these higher velocities, they used at least 18 inches between plates with a system of one or more baffles between plates.

Assuming that there could be a plate every 5 or 6 inches (*26*), and operating vehicles of 0.6 to 1.0 foot per second without decreased efficiency or excessive entrainment, a height equivalent to one perfect or theoretical plate (H. E. T. P.) of about 7 to 9 inches would be obtained with a 70 per cent plate efficiency. This basis will then permit a direct comparison with packed columns.

Packed Columns

In the literature on packed columns there are two articles which, together, may be considered to present material dealing with the more important variables in the design and operation of these columns.

The first of these is an article by Peters (*23*). He found that the H. E. T. P. varied with the mixture being fractionated. Thus, using glass-ring packing of 0.25 inch length and diameter he obtained an H. E. T. P. of 3.65 inches for ethyl alcohol (below 88 per cent) and water; 4.2 inches for ethyl alcohol (above 88 per cent) and water; 3 inches for methanol and water; 6 inches for acetone and ethyl alcohol; 8 inches for nitric acid and water; and 10 inches for benzene and toluene. No definite data on the values of reflux ratio and vapor velocity were given. From these results as well as from data on plate columns, Peters concluded that efficiency was less (H. E. T. P. was greater) for materials of high molecular weight; and that, for materials of equal molecular weight, the efficiency would be lower (H. E. T. P. greater) for mixtures of like molecules than for mixtures of unlike molecules. These results are in good agreement with those of Lewis and Smoley (*17*) using aniline and pinene. Peters also found, using acetic acid and water mixtures and 0.25-inch glass rings of length equal to diameter, that the H. E. T. P. varied directly as the diameter of the packing.

Carswell (*6*), using Peter's data, presented them in the form of the equations,

$$\text{H.E.T.P.} = K\frac{Md}{T}$$

$$\text{H.E.T.P.} = Cr$$

where M = av. mol. weight of components of mixture being fractionated
d = density of overflow
T = abs. temp.
r = radius of packing
K and C = constants for the particular column

The second of these articles is that of Hill and Ferris (*14*). This paper is concerned with the effect of different packings and different velocities on the efficiency of a column.

A laboratory column, 0.71 inch in diameter and 1.8 feet long, was used. The packings tested were glass tubes 0.22 × 0.22 inch, Lessing rings 0.22 × 0.22 inch, and iron jack-chain links 0.195 × 0.39 inch. The liquids used were carbon tetrachloride and benzene in mixtures of 2 to 6 mole per cent carbon tetrachloride. Vapor velocities varied from 3 to 28 cc. of product per minute, corresponding to 0.16 to 1.5 feet per second vapor velocity at standard conditions. The reflux used included values of ratio of overflow to vapor between 0.667 and 0.90.

Judging by their values of efficiencies[1] they concluded that the vapor velocity had little, if any, effect on the efficiency of packed columns, except when the rate was near that of flooding; and that the iron jack chain was the most efficient, the glass tubes next, and the Lessing rings least, although the difference between any of them was slight. The Lessing rings gave the highest flooding rate, the jack chain the next, and the glass tubes the lowest.

[1] They expressed their data by the equation: $\frac{C_D}{C_L} = (1.18)^K$, where C_D and C_L are the mole fractions of carbon tetrachloride in the distillate and still, respectively; 1.18 is an average value for the enrichment ratio found experimentally; and K is a constant (efficiency) for the column and still under the particular reflux ratio.

Varteressian (*28*), using the data of Rosanoff and Easley (*27*) for benzene and carbon tetrachloride, expressed the vapor-liquid equilibrium in the form:

$$\frac{y}{1-y} = 1.098\left(\frac{x}{1-x}\right)^{0.9577}$$

where y and x = mole fractions of carbon tetrachloride in vapor and liquid, respectively

The difference between the observed and calculated values in no case was more than three parts in a thousand.

These two liquids form a constant-boiling mixture. Young (*33*) gives its composition as 91.65 mole per cent carbon tetrachloride. According to the equation the composition is 91.01 mole per cent carbon tetrachloride. Varteressian repeatedly fractionated successively richer mixtures of carbon tetrachloride and benzene, and found that a distillate richer than 91.8 mole per cent carbon tetrachloride could not be obtained. If mixtures near this composition are avoided in efficiency tests, the use of this binary mixture is perfectly satisfactory for glass columns. There are apt to be corrosion difficulties if this mixture is used for any length of time in metal columns.

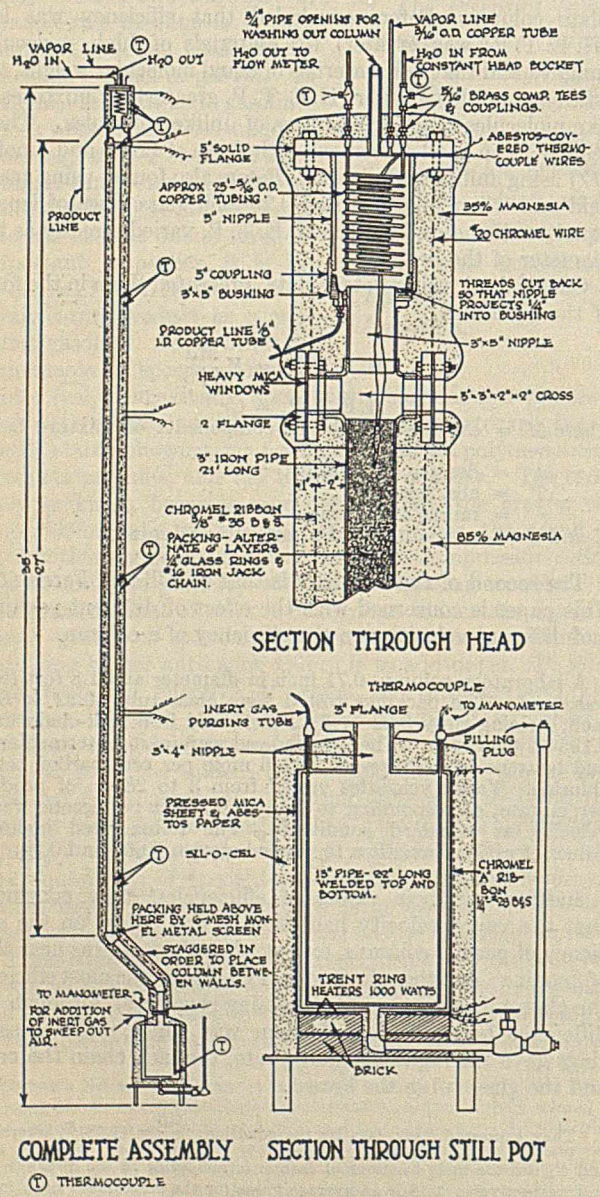

FIGURE 1. DETAIL OF COLUMN 27 FEET LONG, 3 INCHES IN DIAMETER

Analysis by refractive index or gravity is both easy and accurate.[2]

Varteressian then calculated the H. E. T. P. from the data of Hill and Ferris (*14*). A summary of his calculations is given in Table I.

TABLE I. CALCULATION OF H. E. T. P.

(Column, 1.8 feet long, 0.71 inch in diameter)

Over-all Velocity	Reflux Ratio[a]	CCl_4 In residue	CCl_4 In distillate	No. Theoretical Plates	H. E. T. P. Inches	
Ft./sec.		*Mole %*	*Mole %*			
LESSING RINGS 0.22 × 0.22 INCH						
0.16	0.667	2.85	4.42	3	7.15	
0.32	0.667	2.66	4.41	4	5.37	
0.32	0.834	2.68	5.65	5	4.30	
0.64	0.834	2.65	5.35	4.5	4.78	Av. = 4.7 in.
0.53	0.900	2.57	5.72	4.5	4.78	
1.06	0.900	2.56	5.68	5	4.30	
1.50	0.900	2.30	5.59	5	4.30	
GLASS TUBES 0.22 × 0.22 INCH						
0.16	0.667	2.76	4.89	6.5	3.30	
0.32	0.667	2.60	4.46	4.5	4.78	
0.32	0.834	2.73	5.73	4.5	4.78	Av. = 4.4 in.
0.64	0.834	2.56	5.53	5.5	3.90	
0.53	0.900	2.62	5.92	5	4.30	
1.06	0.900	2.49	6.09	5.5	3.90	
IRON JACK CHAIN 0.195 × 0.39 INCH						
0.16	0.667	2.62	4.36	3.5	6.15	
0.32	0.667	2.56	4.46	5	4.30	
0.32	0.834	2.60	5.94	6.5	3.30	Av. = 3.7 in.
0.64	0.834	2.52	5.78	6.5	3.30	
0.53	0.900	2.54	6.21	5.5	3.90	
1.12	0.900	2.37	6.58	6.5	3.30	

[a] Ratio of overflow to vapor.

Varteressian also tested an 8.75-foot column made of 3/4-inch brass pipe (0.82 inch inside diameter) and packed with brass Lessing rings,[3] 0.25 × 0.25 inch.

His results are as follows:

Over-all Velocity[a]	Reflux Ratio[b]	CCl_4 In residue	CCl_4 In distillate	No. Theoretical Plates	H. E. T. P. Inches	
Ft./sec.		*Mole %*	*Mole %*			
1.89	1	31.9	72.7	20.5	5.1	
1.43	1	36.9	71.2	17.5	6.0	Av. = 5.5 in.
0.83	1	25.4	68.2	19.5	5.4	

[a] At standard conditions.
[b] Ratio of overflow to vapor.

A few other data are reported in the literature on packed columns which substantiate those given in the two articles discussed above. Marshall and Sutherland (*21*) experimented with a column 3.25 feet in height and 0.83 inch in diameter. The materials used were ethyl alcohol and water mixtures containing as high as 92.5 per cent alcohol by weight in the distillate. The packing consisted of glass Hempel beads of 0.21 inch diameter. The vapor velocities used were between 0.33 and 1.17 feet per second at standard conditions, and the ratios of overflow to vapor were between 0.53 and 0.77. They obtained an average H. E. T. P. of 3.92 inches, which was independent of values of vapor velocity and reflux ratio.

Leslie and Geniesse (*16*) worked with chloroform and toluene mixtures, 15 to 50 per cent by weight of the former being in

[2] Gadwa (*12*) expressed the specific gravity at 20° C. (d_{20}^{20}) for this carbon tetrachloride–benzene mixture in the form: sp. gr. (20° C.) = $0.8795 + 0.7740x - 0.05654x^2$, where x is the mole fraction of carbon tetrachloride in the liquid. This equation is accurate to five parts in ten thousand. Varteressian (*28*) found the Lorentz-Lorenz formula to relate accurately the density (d_4^{20}) to the refractive index at 20° C. (n_D^{20}). The equation is

$$\left(\frac{1}{d}\right)\left(\frac{n^2-1}{n^2+2}\right) = \left(\frac{P}{100}\right)\left(\frac{1}{d_1}\right)\left(\frac{n_1^2-1}{n_1^2+2}\right) + \left(\frac{100-P}{100}\right)\left(\frac{1}{d_2}\right)\left(\frac{n_2^2-1}{n_2^2+2}\right)$$

Where n = refractive index of the mixture, d = density of the mixture, and P = per cent by weight of component 1. The subscripts 1 and 2 indicate the corresponding properties of components 1 and 2, respectively. The points so obtained agreed with the actual determinations to within five in the fourth place in refractive index. An Abbé refractometer was used.

[3] Purchased from Fisher Scientific Co., Pittsburgh, Pa.

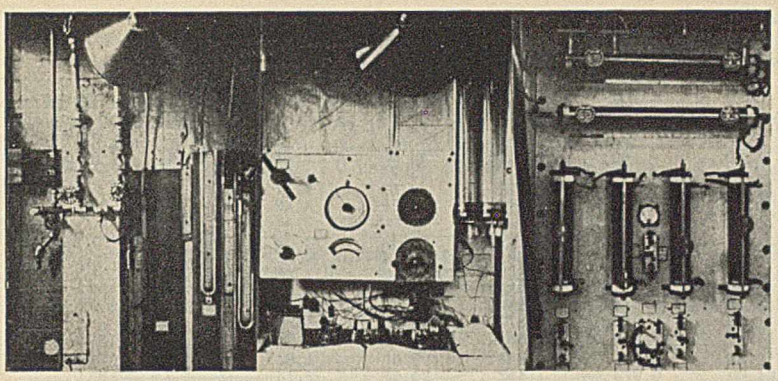

FIGURE 2. CONTROL BOARD

the feed. The column used was 4 feet high and of 0.9 inch diameter. The packing was Lessing rings, 0.22 × 0.22 inch. The vapor velocities varied between 0.36 and 0.67 foot per second at standard conditions, while the ratio of overflow to vapor was between 0.44 and 0.83. The H. E. T. P. they obtained was about 6.1 inches; and it apparently was not affected by changes in vapor velocity, reflux ratio, or composition of feed.

There is only one article in the literature in which variations in vapor velocity and in reflux ratio have been reported to have marked effect on the H. E. T. P. of a column. This is an article by Calingaert and Huggins (*3*). They used a column 5.85 feet high and 3.9 inches in diameter, packed with coke, 0.35 to 0.63 inch in size, as a stripping column for a dilute (1 to 2 per cent by weight) ammonia-water solution. The vapor velocities varied between 0.4 and 2.51 feet per second at standard conditions, and the H. E. T. P. varied from 12.8 inches to 93 inches. They concluded that the efficiency of a given column was proportional to the reflux at constant vapor velocity, or inversely proportional to vapor velocity at constant rate of product. In other words, the efficiency was proportional to the time of contact between vapor and refluxed liquid.

It seems probable that these data cannot be directly compared with those reviewed earlier. Their packing was larger and of small surface per unit of volume so that, in their case, vapor velocity and reflux ratio may have been the principal factors affecting the intimacy of contact between vapor and liquid.

Gadwa (*12*) studied the efficiency of glass rings, jack chain, and a new type of wire-helix packing. The glass rings were made from tubing cut with length equal to diameter, and measured 0.23 × 0.23 inch. The chain was No. 16 single-link iron jack chain, measuring 0.25 × 0.50 inch. The helices were made from No. 24 Lucero wire[4] wound on $^1/_8$-inch drill rod. One-, two-, and six-turn helices were tested. The six-turn helix measured about 0.15 × 0.22 inch. Part of Gadwa's data are given in Table II. His column had an effective packed length of 52.2 inches and a diameter of 0.83 inch. The column was carefully controlled and operated, and adiabatic conditions maintained by a heated air jacket.

It will be noted that Gadwa's data on glass tubes and jack chain are in good agreement with those reported above by Hill and Ferris. Both of these tests were on benzene–carbon tetrachloride mixtures and indicated that No. 16 jack chain has an H. E. T. P. of 3.7 to 3.9 inches. Very careful tests on a column, 2 inches in diameter and 6 feet high, packed with the same No. 16 jack chain, but tested with benzene-toluene mixtures, gave an H. E. T. P. of 8.2 inches.

Gadwa concluded: that the efficiency of the wire-helix packing increased about threefold for an increase from 11.38 to 20.30 sq. cm. of surface area per cubic centimeter of packing; that the efficiency was essentially independent of the mass velocity of the vapor between 12 and 28 pounds per minute per square foot for jack-chain packing; and that the efficiency of the wire-helix packing increased with increasing liquid holdup, and the holdup increased with increasing surface area of packing per unit of volume.

DESIGN OF COLUMNS

This critical survey shows that packed columns are suitable for the purpose of fractionating the straight-run Pennsylvania gasoline. They can be operated at capacities equal to bubble cap or plate columns; H. E. T. P.'s may be obtained which will allow as great if not greater enrichment per unit of length; the holdup for a packed column is considerably less than a plate column; and finally, the design, construction, and cost are in favor of the packed column. This

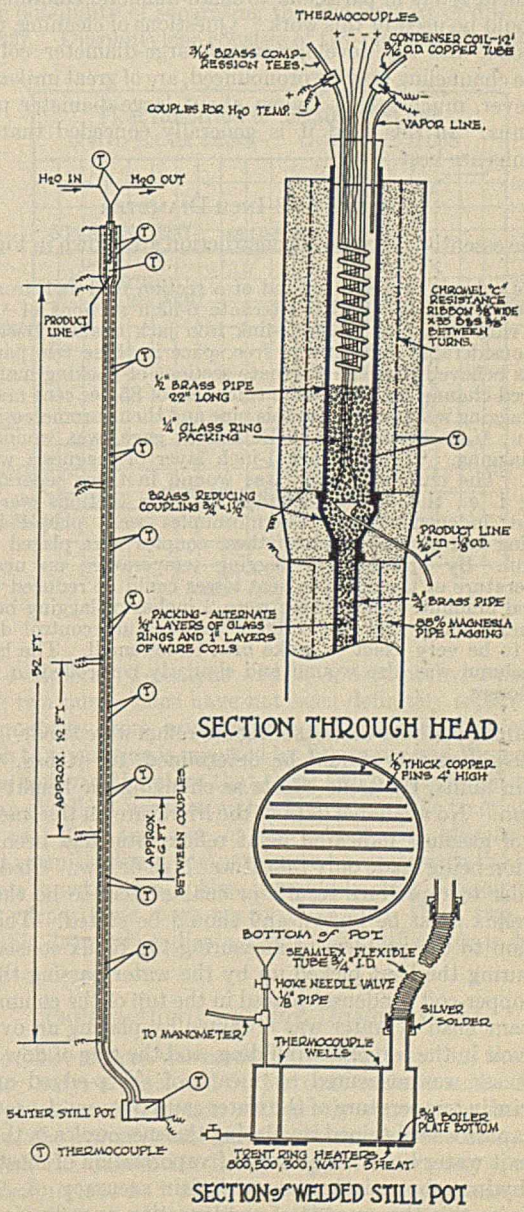

FIGURE 3. DETAIL OF COLUMN 52 FEET LONG, $^3/_4$ INCH IN DIAMETER

[4] Purchased from Driver-Harris Co., Harrison, N. J.

TABLE II. EFFECT OF TYPES OF PACKING ON COLUMNS

Packing	Free Space	Area: Without column wall	Area: With column wall	Vapor at Top	Reflux Ratio[b]	Vapor Velocity at Top	No. of Theoretical Plates	H. E. T. P.	Vapor Velocity at Flooding[d]	Holdup
	%	Sq. cm./cc. of volume		Min./sq. ft.[a]		Ft./sec.[c]		Inches	Ft./sec.[c]	Cc. liquid/cc. packing
Jack chain	76.0	6.73	8.64	13.20	0.942	0.875	14.63	3.58	1.24	0.029
Jack chain	..	...	...	12.77	0.939	0.857	12.72	4.09	..	...
Jack chain	..	...	...	27.50	0.972	1.783	12.50	4.17	..	...
Jack chain	..	...	...	26.70	0.949	1.800	12.19	4.28	..	...
Jack chain	..	...	...	25.70	0.901	1.780	15.00	3.48	..	...
Glass tubes	66.2	4.46	6.37	14.12	0.947	0.749	15.43	3.38	1.27	0.089
Glass tubes	..	...	...	13.50	0.890	0.863	13.64	3.82	..	...
Glass tubes	..	...	...	13.69	0.938	0.838	15.42	3.38	..	...
Glass tubes	..	...	...	13.40	0.878	0.888	14.32	3.64	..	...
Glass tubes	..	...	...	14.06	0.944	0.860	14.85	3.52	..	...
Glass tubes	..	...	...	14.20	0.949	0.877	15.85	3.29	..	...
Glass tubes	..	...	...	13.12	0.938	0.864	14.21	3.67	..	...
1-turn helix	79.8	22.30	22.10	13.50	0.951	0.835	28.67	1.82	1.46	0.129
1-turn helix	..	...	...	24.00	0.973	1.452	24.45	2.13	..	...
2-turn helix	85.5	14.40	16.30	13.69	0.940	0.879	10.81	4.82	1.51	0.110
2-turn helix	..	...	...	13.97	0.955	0.875	14.53	3.59	..	...
2-turn helix	..	...	...	20.95	0.939	1.410	14.60	3.57	..	...
2-turn helix	..	...	...	24.60	0.969	1.482	19.06	2.74	..	...
6-turn helix	88.4	11.38	13.28	12.58	0.955	0.855	9.79	5.33	1.62	0.082
6-turn helix	..	...	...	23.90	0.970	1.719	7.43	7.02	..	...
6-turn helix	..	...	...	25.40	0.988	1.760	8.41	6.20	..	...

[a] Cross section. [b] Ratio overflow to vapor. [c] At standard conditions. [d] Pure benzene.

argument refers in particular to small-diameter columns, such as would be used in this work. Questions of cleaning, repair, overload, and the development of large-diameter columns, where channeling may be pronounced, are of great importance. However, much less is known about large-diameter packed columns. In this field it is generally conceded that plate columns are best.

COLUMN OF 3-INCH DIAMETER

The essential features of construction are shown in Figure 1.

The column proper consisted of a section of 3-inch iron pipe, 27 feet long, packed with alternate 6-inch sections of $^1/_4$-inch glass rings and No. 16 single-link iron jack chain. Because of the considerable difference in free space in these two packings, it was believed that the alternate sections of packing materially reduced channeling. A 2-inch thickness of 85 per cent magnesia pipe lagging was placed over this pipe and then chromel resistance ribbon, $^3/_8$-inch wide × 35 B. and S. gage, was wound over this lagging. Then another 1-inch layer of magnesia was applied. The chromel ribbon was wound in three separate sections; i. e., the bottom, middle, and top sections were controlled independently. Thermocouples were placed in the winding and opposite each of these couples were placed in the column. By bringing the lagging temperature up near the temperature of the column, heat losses could be reduced to any desired amount. Since there were 2 inches of lagging between the heat source and the column, temperature control did not need to be very exact to make heat losses small. The head of the column was also wound and similarly controlled to reduce heat losses.

Various methods of measuring the reflux were tried. It was decided that this should be determined, for it has, within certain limits, the same effects as changing the height of the column. No available data in the literature on the fractionation of gasoline indicated what reflux ratio had been used, mention being made only that it was high or low. Obviously, in order to reproduce results or enable them to be checked, the reflux must be known and should be stated. The final solution to the problem of measuring the reflux consisted in measuring the heat picked up by the water passing through the copper-coil condenser placed in the top of the column. A constant head of water was obtained by placing an overflow reservoir in the top of the building, and the rate of flow to the condenser was measured by means of sharp-edged orifices. The rise in temperature of the water caused by condensation of the vapors was obtained by placing thermocouples in the inlet and exit water lines. The heat of vaporization of most gasoline hydrocarbons is known with fair accuracy (*8*, *9*, *18*), and from this the amount of condensation or reflux is easily obtained. This method can be highly recommended, for it is practically foolproof. Simply setting the orifice valve maintained a practically constant flow of cooling water over a day's operation. Checking the water temperatures in and out was, then, all that was required. In addition, this method further reduced the amount of liquid held up in the column head, since no liquid was taken out to be measured and then put back into the column. With the lagging temperature kept slightly below the column temperatures, the only source of heat for vaporization was from the still. In operation it was easy to remove 75 to 80 per cent of this heat input to the still as heat of condensation in the condenser. A part of this condensed liquid flowed into a shallow groove in the column head and was withdrawn as product, its outflow being controlled by a needle valve and the volume collected in a given time being noted. From the heat picked up by the condenser water and the heat of vaporization, the total condensation was obtained; and, since the rate of product take-off was known, the reflux ratio—namely, cubic centimeters of reflux per cubic centimeter of product—was obtained. For the most part, the columns were operated at a reflux ratio of about 30 to 1.

The still, with a capacity of 13 gallons, was electrically heated both on the sides and bottom, and was connected to the column by means of a standard 3-inch flange. As much heating surface as possible was used in order to transfer the heat by a large heating area rather than by a large difference in temperature between the heating surface and the boiling liquid. This was done to reduce cracking to a minimum.

All temperatures were measured by thermocouples led to a multipoint switch on a control board. On this board were also located the necessary rheostats, flowmeters, and product receivers. With this 3-inch diameter column, the product could easily be withdrawn at a rate of from 400 to 700 cc. per hour, using a 30 : 1 reflux ratio. The superficial lineal vapor velocities at operating temperatures usually were from 0.6 to 0.9 foot per second as measured at the top of the column. A photograph of the control board is shown in Figure 2.

COLUMN OF $^3/_4$-INCH DIAMETER

In order to rerun the fractions taken from the large column, a small column (Figure 3) was constructed with about one-tenth the capacity of the large one. This was designed to give as favorable and efficient operation as possible.

The column consisted of 52 feet of $^3/_4$-inch brass pipe and was made of approximately eight equal sections, silver-soldered together. Heat losses were controlled in the same way as in the case of the large 3-inch diameter column, the thermocouples being placed every 6 feet on the pipe, and in the lagging 1.5 inches from the pipe. On such a small column as this the pro-

portion of heat losses to total through-put was greater because of the greater proportion of surface to volume. Nevertheless, by controlling the heat losses with four independent heating sections, it was possible to operate this column as smoothly as the larger one and to get a corresponding through-put. This was about 40 to 60 cc. of product per hour at a 30 : 1 reflux ratio. Superficial lineal vapor velocities at operating temperatures were usually from 0.8 to 1.0 foot per second as measured at the top of the column.

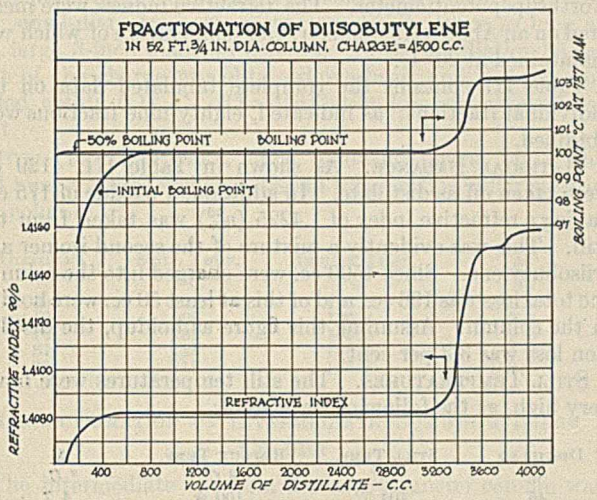

FIGURE 4

The column was packed alternately with $^1/_2$-inch layers of glass rings and 1-inch layers of No. 24 Lucero wire helices. These $^1/_8$-inch diameter coils contained about four to six turns of wire and were exactly the same as those used by Gadwa (Table II) excepting that the distance between turns was slightly greater. In this way the flooding velocity was increased. The purpose of the alternate layers of glass and helices was to reduce channeling. If more than a $^1/_2$-inch layer of glass was used, the vapor velocities were materially reduced at the flooding point. A test with a benzene–carbon tetrachloride mixture on a 6-foot length of this packing showed an H. E. T. P. of 6 inches. On this basis the 52-foot column may be considered to be equivalent to about one hundred perfect plates when tested with a mixture of benzene and carbon tetrachloride.

The reflux on this column was measured exactly as in the case of the large column, that is, by the heat imparted to the cooling water. The holdup, as tested cold with kerosene, was about 200 cc., while under operating conditions—namely, with a hot column—the holdup was about 50 cc. of liquid. This decrease in holdup was due to the lowering of the viscosity of the liquid by temperature.

True boiling temperatures were obtained by placing two thermocouples (copper-copel) in the head, which were connected so that they could be read independently or in series with each other, the latter connection giving twice the e. m. f. and permitting temperature changes to be more accurately and easily determined. The couples were calibrated over a wide range and were accurate to 0.1° C. The e. m. f. was measured by a Leeds and Northrup No. 8662 portable double-range precision potentiometer with a 0 to 16 mv. range readable to 0.003 mv.

This 52-foot column was placed in an air duct leading from the top of the building to the basement, and was suspended at the top for vertical alignment. It was provided with a 5-liter still, heated electrically from the bottom only. In order to secure better heat distribution through the liquid, thereby eliminating local overheating and cracking, copper fins were brazed to the bottom of the still.

To allow for the expansion of the column when heated, the still was connected to the column by a section of $^3/_4$-inch flexible Seamlex metal tubing. Thus the heavy still rested on a support entirely independent of the column. This construction was very satisfactory, and distillations continuing over a month could be made with only 5 to 10 per cent loss of total material. This loss included handling the cuts, determining boiling points, and all other losses.

Manometers were connected to the stills of both columns. When flooding began, the pressure immediately increased, and the heat was then adjusted to prevent the flood from filling the whole column. Since these columns were so tall, the liquid was refluxed for several hours to bring about equilibrium conditions and to concentrate the lowest-boiling material in the head before the take-off line was opened. In order to save time, the small column was fitted with a clock which automatically turned on the heat.

Efficiency Tests of Columns

In order to test these columns, it was obvious that the components should boil very close together. Since the H. E. T. P. varies with the nature of the components, the columns should be tested on hydrocarbons in order to get a true conception of the operation. However, no two pure close-boiling hydrocarbons, permitting ready analysis, were available.

The 52-foot column, when tested in a preliminary way with a benzene–carbon tetrachloride mixture, proved too efficient for the H. E. T. P. to be determined by this mixture. To prevent reaching the constant-boiling mixture of 91 to 92 per cent carbon tetrachloride, test data showed that the bottom would have to analyze less than 1.5 per cent carbon tetrachloride. At this concentration the amount present for analysis was almost too small for practical purposes. Further tests with this mixture were discontinued, attention having been called to the possibility of separating the two isomers of diisobutylene (*32*). Diisobutylene consists of two olefins (*22*)—namely,

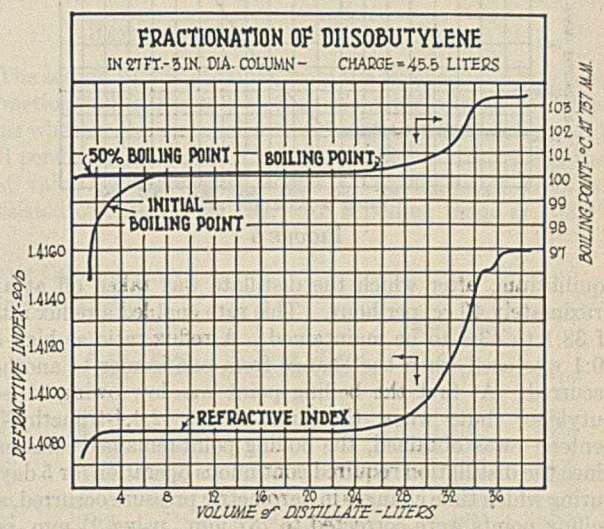

FIGURE 5

2, 4, 4-trimethyl-1-pentene and 2, 4, 4-trimethyl-2-pentene. These two pure olefins have not been definitely separated in any quantity from crude diisobutylene. The nearest approach to separation is reported by Whitmore and Wrenn (*32*). It was believed therefore that these two olefins would constitute an excellent mixture with which to test the fractionating columns. The behavior of the latter with diisobutylene would permit a direct comparison to be made with the hydrocarbons in petroleum. Also, it would be very difficult to find two hydrocarbons more nearly alike than these two. The available data (*32*) indicate about 3° C. difference in boiling points.

Preparation of Crude Diisobutylene

The diisobutylene was made in the usual way (*32*) from pure tertiary butyl alcohol and 50 per cent sulfuric acid. It was then placed under suction and gently warmed to free it of most of the isobutylene. After refluxing over sodium, it was distilled, the distillation being stopped before any quantity of triisobutylene had distilled over. It was necessary to remove the bulk of triisobutylene in this way. Otherwise, with a large quantity of triisobutylene in the still, the temperature

would have been very high toward the end of the distillation (boiling point of triisobutylene about 180° C.), and on continued refluxing some cracking would have occurred. Since the first 10 per cent of the above distillate contained a large amount of isobutylene, it was discarded. The remainder of the distillate, which was then free of most of the isobutylene and triisobutylene, was the material with which the columns were tested.

Fractionation of Diisobutylene in 52-Foot Column

The 52-foot column was charged with 4500 cc. of material having the following physical properties: refractive index (n_D^{20}), 1.4102; and specific gravity at 21.2° C., 0.717. Refluxing for about 3 hours was required to bring the column to

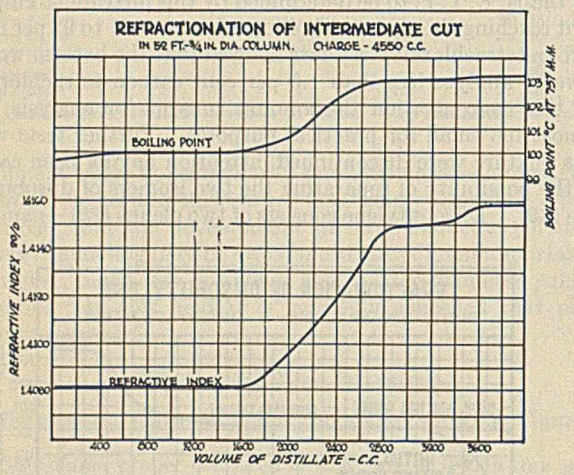

Figure 6

equilibrium, after which the distillate was taken off at approximately 40 cc. per hour. This rate enabled a reflux ratio of 38:1 to 43:1 to be maintained. A reflux ratio as high as 50:1 was used when the change from one isomer to another occurred. At first the boiling point was low owing to isobutylene; but, when the first isomer—2,4,4-trimethyl-1-pentene—was obtained, the boiling point remained constant. Since the distillation required continuous operation for 5 days, during which time changes in barometric pressure occurred, all boiling points were corrected to 737 mm., using 21 mm. per ° C. as the change in boiling point with pressure.

Usually, temperatures in the column checked with the Cottrell boiling-point apparatus to within 0.2° C., except where the fractions contained isobutylene, when the difference was much greater. This effect of the isobutylene was due to the fact that the columns were provided with a total condenser. The question of total *vs.* partial condensers cannot be discussed here. Suffice it to say that, in operating with a total condenser, a small amount of isobutylene could readily have lowered the initial boiling point of the diisobutylene. This was because there was no exit for the small amount of isobutylene in the column. It could not escape in the product line, for the product was drawn off at its boiling point. Neither could it escape through the vapor line, for, in so doing, it would have had to pass by the total condenser, and isobutylene was soluble in the cooled diisobutylene. In short, a small amount of isobutylene was trapped in the head of the column and exerted its partial pressure. For this reason the diisobutylene was boiling at some unknown, but lower partial pressure than barometric. The same explanation applied to the Cottrell apparatus. Consequently, it was far better to measure not only the initial boiling point, which was the temperature given in the Cottrell apparatus, but also, for example, the 50 per cent boiling point. In this way the small amount of isobutylene was removed, and trouble caused by it was avoided.

The results of the distillation can best be obtained from Figure 4, which shows the boiling point and the refractive index plotted against the volume distilled over. Temperatures were measured with a copper-copel thermocouple calibrated over the entire range to 0.1° C. The e. m. f. produced by this couple was measured on the Leeds and Northrup potentiometer. The refractive indices were measured on an Abbé refractometer, the temperature of which was maintained at 20° C.

Table III contains the complete tabulated data on the individual fractions; as indicated, eighty-nine fractions were obtained.

Material Balance. As shown in Table III, 4129 cc. were taken off as distillate. In addition, a residue of 175 cc., having a refractive index of 1.4225 (n_D^{20}) was taken from the still. This was evidently a mixture of the second isomer and triisobutylene. Since 4500 cc. were charged into the column, the total loss was 196 cc., and of this at least 50 cc. were holdup in the column. Assuming this figure as holdup, the distillation loss was 3.3 per cent.

Still Temperatures. The still temperatures were never very high, as the following data show:

Distilled %	Still Temp. ° C.	Reflux Temp. ° C.	Δt ° C.
46	104.7	100.0	4.7
65	108.0	100.1	7.9
81	118.0	103.0	15.0
87	138.0	103.2	34.8
90	177.0	103.2	73.8

Ninety-one and five-tenths per cent of the charge was distilled overhead, and 51 per cent boiled within 0.1° C. The bottoms had no indications whatever of being cracked.

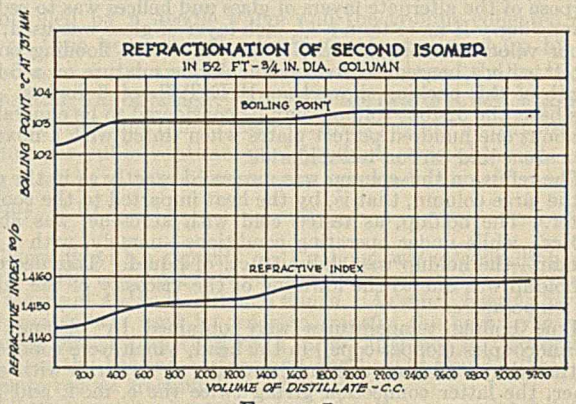

Figure 7

Proportions of the Two Isomers. From the refractive index–volume curve in Figure 4, it is seen that the volume of the first isomer—namely, 2, 4, 4-trimethyl-1-pentene—was approximately 3200 cc. The volume of the second isomer 2, 4, 4-trimethyl-2-pentene—obtained as distillate was 4129 − 3450, or 679 cc. In addition, assuming 50 cc. of second isomer as holdup in the column, and 70 cc. of second isomer in the still bottoms (calculated from the refractive indices), the total quantity of second isomer was 799 cc. Therefore, the ratio of first isomer to second was 4:1. This is in good agreement with the value of 3.7:1 found by McCubbin and Adkins (*22*) from an analysis of the ozonization products.

Fractionation of Diisobutylene in 27-Foot Column

The diisobutylene used was the same as for the distillation in the 52-foot column. The charge was 32,550 grams or 45,500 cc. The material started to boil at 69.5° C., and the temperature slowly rose to the boiling point of the pure first

isomer which was taken off at the rate of 500 to 750 cc. per hour. During the change from first to second isomer, the product rate was 250 cc. per hour, and the average reflux ratio was 28:1. This was the usual value during the run, but in some cases it varied from 19:1 to 58:1.

The results of this distillation are shown in Table IV and Figure 5, and are very similar to those obtained on the $^3/_4$-inch diameter column. However, separation was not quite as sharp in the large column as in the small, the reason being that the small-diameter column was practically twice as long as the large 3-inch diameter column. In the distillation 85 per cent of the charge was obtained overhead, and 38.5 per cent boiled within 0.1° C. The distillation loss was about 7 per cent.

Still Temperatures. The following figures show the still temperatures and the over-all temperature differences in the column:

Distilled %	Still Temp. ° C.	Reflux Temp. ° C.	Δt ° C.
39	107	100.2	6.8
58	108	100.4	7.6
74	132	102.4	29.6
81	185	103.1	81.9
85	212	103.5	108.5

Refractionation of Intermediate Cut from Large Column

The intermediate cut from the large-diameter column was next charged into the small $^3/_4$-inch diameter column. The charge was 4550 cc., or fractions 122 to 140, with refractive indices ranging from 1.4098 to 1.4150 (n_D^{20}). The refractive index of the over-all charge was 1.4123 (n_D^{20}), corresponding to 50 per cent of each of the two isomers. This fractionation was not run continuously but was stopped every night. As a result of this intermittent operation the efficiency of the distillation was greatly reduced, and the time of distillation increased. Continuous operation is essential to good separation.

Product was withdrawn at the rate of 40 to 50 cc. per hour using a 35:1 to 50:1 reflux ratio. The results of this distillation are given in Table V and Figure 6. Some of the first isomer was again obtained pure; it corresponded to 61.5 per cent of the first isomer actually present in the charge. The second isomer came off, as in previous runs, starting with a refractive index of 1.4150 and rising gradually to 1.4158. The material at 1.4158 predominated and had a 0.2° C. higher boiling point than the material of refractive index 1.4150.

The indications are that the true refractive index (n_D^{20}) for the second isomer is 1.4158, and that the 1.4150 material is second isomer containing a small amount of the first isomer. While one may suppose that two substances so nearly alike as these two isomers would form a perfect solution at all concentrations, it is nevertheless possible that the 1.4150 material represents an abnormal shape in the vapor-liquid composition curves. This point is being investigated further.

The residue in the still was not taken out but left for the next distillation. Of the charge of 4550 cc., 3993 cc. or 88 per cent were taken overhead.

Refractionation of Second Isomer

The second isomer obtained from the large column was next refractionated in the tall $^3/_4$-inch diameter column to determine whether the material with refractive index 1.4150 would still persist, and whether a refractive index of 1.4158 was the best value for the second isomer. The charge of 3730 cc. consisted of cuts 141 to 156, with a boiling range of 103.0°

Table III. Fractionation of Diisobutylene

(In column 52 feet high, $^3/_4$ inch in diameter)

Cut	B. P. in Column ° C.	Barometric Pressure Mm.	B. P. at 737 mm. Column ° C.	B. P. at 737 mm. Cottrell ° C.	Refractive Index (n_D^{20})	Total Cc.
1	88.5	730	88.75	....	1.3990	50
2	...	730	....	....	1.4063	90
3	91.5	730	91.75	95.9	1.4067	125
4	...	730	....	....	1.4072	162
5	...	730	....	....	1.4076	197
6	97.2	730	97.45	98.8	1.4079	235
7	96.7	730	....	....	1.4079	281
8	97.2	730	....	....	1.4080	332
9	98.3	730	....	....	1.4080	372
10	98.8	729	99.1	99.3	1.4081	412
11	98.5	729	....	....	1.4081	452
12	99.2	729	99.5	99.3	1.4082	492
13	99.2	729	....	....	1.4081	535
14	98.8	729	99.1	99.4	1.4082	579
15	99.6	729	99.9	99.8	1.4082	634
16	99.7	729	....	....	1.4082	689
17	99.7	729	100.0	99.95	1.4082	744
18	99.65	729	....	....	1.4082	784
19	...	729	....	....	1.4082	827
20	99.7	729	100.0	99.95	1.4082	857
21	99.7	729	....	....	1.4082	898
22	99.7	729	100.15	100.15	1.4082	948
23	...	...	....	....	1.4082	1008
24	99.8	729	....	....	1.4082	1053
25	99.7	729	....	....	1.4082	1098
26	99.7	729	....	....	1.4082	1139
27	99.8	729	....	....	1.4081	1180
28	99.7	729	....	....	1.4081	1220
29	99.7	728	100.1	100.04	1.4082	1259
30	99.7	728	....	....	1.4083	1299
31	99.7	728	....	....	1.4082	1339
32	99.1	728	....	....	1.4081	1379
33	99.8	728	....	....	1.4081	1424
34	99.82	729	100.20	100.04	1.4082	1479
35	...	...	....	100.08	1.4082	1844
36	99.8	729	....	....	1.4083	1859
37	99.8	729	....	....	1.4081	1897
38	100.0	729	....	....	1.4081	1937
39	100.0	731	....	....	1.4082	1977
40	100.0	731	100.3	100.1	1.4082	2017
41	100.0	731	....	....	1.4082	2058
42	100.0	731	....	....	1.4082	2099
43	100.0	731	....	....	1.4082	2109
44	100.1	731	....	....	1.4082	2179
45	100.1	732	100.3	100.1	1.4082	2219
46	99.9	732	....	....	1.4082	2264
47	100.1	732	....	....	1.4082	2310
48	100.05	732	....	....	1.4082	2350
49	100.05	732	....	....	1.4081	2400
50	100.0	732	....	....	1.4081	2460
51	100.0	732	....	....	1.4082	2515
52	100.0	731	100.3	100.1	1.4081	2565
53	99.95	731	....	....	1.4081	2625
54	99.95	731	....	....	1.4081	2705
55	100.0	731	....	....	1.4082	2746
56	100.0	731	....	....	1.4082	2789
57	100.05	731	....	....	1.4082	2824
58	100.1	731	....	....	1.4082	2866
59	100.1	731	....	....	1.4082	2909
60	100.1	732	100.3	100.1	1.4082	2950
61	100.15	732	....	....	1.4082	2990
62	100.15	732	....	....	1.4082	3032
63	100.15	732	....	....	1.4082	3074
64	100.15	732	100.4	100.1	1.4082	3118
65	100.25	732	100.45	100.05	1.4082	3160
66	100.3	732	....	....	1.4083	3200
67	100.3	732	100.5	100.2	1.4084	3240
68	100.6	732	....	....	1.4085	3285
69	100.85	731	101.1	100.4	1.4089	3327
70	101.4	731	....	....	1.4099	3369
71	101.9	730	102.2	100.65	1.4110	3416
72	102.5	730	....	....	....	..
73	103.0	729	103.3	102.3	1.4135	3488
74	103.1	729	....	....	....	3510
75	103.15	729	103.45	102.9	1.4147	3553
76	103.10	729	103.4	103.1	1.4150	3593
77	103.05	729	103.35	103.15	1.4150	3640
78	103	729	....	....	1.4150	3690
79	103.05	729	103.35	103.15	1.4150	3725
80	103.15	729	103.45	103.05	1.4151	3765
81	...	...	....	103.05	1.4152	3795
82	103.05	736	....	....	1.4156	3830
83	103.05	737	103.05	103.10	1.4156	3865
84	103.2	736	103.2	103.10	1.4158	3900
85	...	...	....	....	1.4158	3940
86	103.2	736	....	....	1.4158	3995
87	103.1	736	....	103.3	1.4158	4057
88	...	...	....	103.3	1.4158	4107
89	...	...	....	....	1.4157	4129

TABLE IV. FRACTIONATION OF DIISOBUTYLENE

(In column 27 feet high, 3 inches in diameter)

Cut	B. P. in Column	Barometric Pressure	B. P. at 737 mm. Column	B. P. at 737 mm. Cottrell	Refractive Index (n_D^{20})	Total
	° C.	Mm.	° C.	° C.		Cc.
1	72.0	734	72.15	....	1.3983	250
2	76.4	734	76.55	....	1.4038	500
3	82.4	735	82.50	....	1.4067	750
4	88.5	735	88.60	....	1.4076	1000
5	92.6	735	92.70	....	1.4078	1250
6	95.6	735	....	....	1.4081	1463
7	96.1	735	96.2	....	1.4080	1713
8	97.0	736	....	....	1.4082	1968
9	98.1	737	98.1	....	1.4082	2218
10	...	...	....	....	1.4082	2250
11	100.0	737	98.1	....	1.4083	2500
12	99.1	737	....	....	1.4082	2750
13	99.0	737	....	....	1.4085	3000
14	99.0	737	....	....	1.4085	3250
15	99.1	737	....	....	1.4085	3500
16	99.2	738	99.15	....	1.4085	3750
17	99.4	738	99.35	....	1.4083	4000
18	99.4	739	99.30	....	1.4083	4250
19	99.5	739	99.40	....	1.4083	4500
20	99.5	739	....	....	1.4082	4750
21	99.6	739	99.5	....	1.4082	5000
22	99.7	739	99.6	....	1.4083	5250
23	99.8	739	99.7	....	1.4083	5500
24	99.8	739	99.7	....	1.4083	5750
25	100.3	739	....	....	1.4083	6000
26	100.0	739	....	....	1.4082	6250
27	100.0	739	99.9	....	1.4083	6500
28	100.0	739	....	....	1.4083	6750
29	100.0	739	99.9	....	1.4083	7000
30	100.0	739	....	....	1.4083	7250
31	100.0	739	....	....	1.4083	7500
32	100.0	739	99.9	....	1.4083	7750
33	100.1	739	100.0	....	1.4083	8000
34	100.1	739	....	....	1.4083	8250
35	100.2	739	....	....	1.4083	8500
36	100.2	739	100.1	100.15	1.4083	8750
37	100.2	739	....	....	1.4083	9000
38	100.2	739	....	....	1.4083	9250
39	100.2	739	....	....	1.4083	9500
40	100.2	739	....	....	1.4083	9750
41	100.2	739	....	....	1.4083	10000
42	100.3	739	100.2	100.15	1.4083	10250
43	100.3	739	....	....	1.4083	10500
44	100.4	739	....	....	1.4083	10750
45	100.4	739	....	....	1.4083	11000
46	100.4	739	....	....	1.4083	11250
47	100.4	739	....	....	1.4083	11500
48	100.4	739	....	....	1.4082	11750
49	100.4	739	....	....	1.4082	12000
50	100.4	739	....	....	1.4082	12250
51	100.4	740	....	....	1.4083	12500
52	100.4	740	....	....	1.4083	12750
53	100.4	741	100.20	100.15	1.4082	13000
54	100.4	741	....	....	1.4083	13250
55	100.4	741	....	....	1.4083	13500
56	100.4	741	....	....	1.4083	13750
57	100.4	741	....	....	1.4083	14000
58	100.4	741	....	....	1.4083	14250
59	100.4	741	....	....	1.4083	14500
60	100.4	741	....	....	1.4083	14750
61	100.4	741	....	....	1.4083	15000
62	100.4	741	....	....	1.4083	15250
63	100.4	741	....	....	1.4083	15500
64	100.4	741	....	....	1.4083	15750
65	100.4	741	....	....	1.4083	16000
66	100.4	741	....	....	1.4083	16250
67	100.4	741	....	....	1.4084	16500
68	100.5	741	....	....	1.4084	16750
69	100.5	741	....	....	1.4084	17000
70	100.5	741	....	....	1.4084	17250
71	100.5	741	....	....	1.4084	17500
72	100.5	741	....	....	1.4085	17750
73	100.5	741	....	....	1.4083	18000
74	100.5	741	....	....	1.4083	18250
75	100.5	741	....	....	1.4083	18500
76	100.5	741	....	....	1.4083	18750
77	100.5	741	....	....	1.4082	19000
78	100.5	742	100.25	100.15	1.4082	19250
79	100.5	742	....	....	1.4083	19500
80	100.5	742	....	....	1.4083	19750
81	100.5	742	....	....	1.4083	20000
82	100.5	742	....	....	1.4083	20250
83	100.5	742	....	....	1.4083	20500
84	100.5	740	....	....	1.4083	20750
85	100.5	740	....	....	1.4083	21000
86	100.5	740	....	....	1.4083	21250
87	100.3	739	....	....	1.4083	21500
88	100.3	739	....	....	1.4083	21750
89	100.3	738	....	....	1.4083	22000
90	100.3	737	100.3	100.15	1.4083	22250
91	100.3	737	....	....	1.4083	22500
92	100.2	737	....	....	1.4083	22750
93	100.3	736	....	....	1.4083	23000
94	100.3	736	....	....	1.4083	23250
95	100.3	736	....	....	1.4083	23500
96	100.1	736	100.15	100.15	1.4083	23750
97	100.1	736	....	....	1.4083	24000
98	100.1	736	....	....	1.4085	24250
99	100.1	736	....	....	1.4085	24500
100	100.1	736	....	....	1.4085	24750
101	100.2	735	100.3	100.2	1.4085	25000
102	100.2	735	....	....	1.4085	25250
103	100.2	735	....	....	1.4085	25500
104	100.2	735	....	....	1.4085	25750
105	100.2	735	....	....	1.4085	26000
106	100.2	734	....	....	1.4085	26250
107	100.2	734	....	....	1.4085	26500
108	100.2	733	100.40	100.25	1.4085	26750
109	100.2	732	....	....	1.4086	27000
110	100.2	732	....	....	1.4086	27250
111	100.2	732	100.45	100.25	1.4087	27500
112	100.2	732	100.45	100.30	1.4087	27750
113	100.3	731	....	....	1.4090	28000
114	100.3	731	....	....	1.4090	28250
115	100.3	731	....	....	1.4093	28500
116	100.3	731	....	....	1.4092	28750
117	100.3	731	100.6	100.4	1.4092	29000
118	100.4	731	....	....	1.4094	29250
119	100.5	731	....	....	1.4094	29500
120	100.4	730	....	....	1.4096	29750
121	100.5	730	....	....	1.4098	30000
122	100.5	731	100.8	100.7	1.4098	30250
123	100.6	731	....	....	1.4099	30500
124	100.8	731	....	....	1.4099	30750
125	100.9	...	....	....	1.4103	31000
126	...	...	....	....	1.4104	31250
127	100.9	732	101.15	101.1	1.4107	31500
128	101.0	...	....	....	1.4107	31750
129	...	...	....	....	1.4109	32000
130	101.4	...	....	....	1.4114	32250
131	101.5	732	101.75	101.55	1.4119	32500
132	101.7	...	....	....	1.4121	32750
133	101.8	733	102.2	102.10	1.4127	33000
134	102.0	...	....	....	1.4130	33250
135	102.2	733	102.4	102.3	1.4135	33500
136	102.4	...	....	....	1.4139	33750
137	102.6	733	102.85	102.6	1.4141	34000
138	102.7	733	102.95	102.80	1.4145	34250
139	102.8	733	103.05	102.9	1.4149	34500
140	102.9	733	103.15	103.0	1.4150	34750
141	103.0	733	103.25	103.1	1.4150	35000
142	103.0	733	103.25	103.1	1.4150	35250
143	103.0	733	103.25	....	1.4152	35500
144	103.0	733	....	....	1.4152	35750
145	103.0	733	....	....	1.4154	36000
146	103.1	733	103.35	103.25	1.4154	36250
147	103.1	733	....	....	1.4158	36500
148	103.1	733	....	....	1.4158	36750
149	103.0	733	103.25	103.3	1.4158	37000
150	103.1	733	....	....	1.4158	37250
151	103.1	733	....	....	1.4158	37500
152	103.2	733	103.45	103.3	1.4159	37750
153	103.4	733	....	....	1.4158	38000
154	103.6	733	....	....	1.4158	38250
155	103.5	733	103.75	103.4	1.4158	38500
156	103.5	733	....	....	1.4158	38610

to 103.5° C. (at 733 mm.), and refractive indices (n_D^{20}) from 1.4150 to 1.4158. The first part of the distillation was run under high reflux from 40:1 to 45:1. When a refractive index 1.4158 was obtained, the take-off was increased and the reflux dropped to 28:1 to 35:1.

The results are shown in Table VI and Figure 7. These data show clearly that no further separation of this material is possible, and substantiate the values of 103.4° C. (at 737 mm.) as the boiling point, and 1.4158 as the refractive index (n_D^{20}) of the second isomer—2,4,4-trimethyl-2-pentene. The first isomer—namely, 2,4,4-trimethyl-1-pentene—boils at 100.1° C. (737 mm.) and has a refractive index of 1.4082 (n_D^{20}). The densities (d_4^{20}) of the first and second isomers are, respectively, 0.7151 and 0.7211.

The separation of these two isomers illustrates very clearly the importance of low holdup in the columns. Were it not for the low holdup for the given charge, the separation would not have been at all sharp and definite. A slightly greater holdup or a slightly smaller charge would have made it impossible to get any of the second isomer in one distillation. Since there is four times as much first isomer as second isomer, the problem of separation would have been greatly increased but for the low holdup.

TABLE V. REFRACTIONATION OF INTERMEDIATE CUT

(In column 52 feet high, 3/4 inch in diameter)

Cut	B. P. in Column	Barometric Pressure	B. P. at 737 mm. Column	B. P. at 737 mm. Cottrell	Refractive Index (n^{20}_D)	Total
	° C.	Mm.	° C.	° C.		Cc.
1	100.1	737	..	....	1.4080	85
2	100.15	737	..	99.65	1.4082	165
3	100.5	737	..	....	1.4081	250
4	100.9	737	..	99.9	1.4081	335
5	100.8	745	..	....	1.4081	425
6	100.5	741	..	....	1.4081	515
7	...	...	..	....	1.4082	615
8	...	...	..	....	1.4082	675
9	...	...	..	....	1.4081	775
10	...	...	..	100.0	1.4082	852
11	...	...	..	100.0	1.4083	942
12	100.7	740	..	....	1.4082	1057
13	100.6	740	..	....	1.4082	1172
14	100.6	740	..	....	1.4082	1272
15	...	...	..	100.05	1.4081	1400
16	...	...	..	....	1.4098	1555
17	...	...	..	....	1.4098	1600
18	101.0	737	..	....	1.4083	1715
19	101.0	737	..	....	1.4092	1780
20	100.8	737	..	....	1.4092	1875
21	100.8	734	..	100.8	1.4095	1995
22	...	...	..	....	1.4100	2065
23	...	...	..	....	1.4108	2155
24	...	...	..	....	1.4113	2200
25	100.9	734	..	....	1.4115	2285
26	...	...	..	....	1.4118	2390
27	101.6	734	..	102.6	1.4120	2470
28	102.8	734	..	....	1.4133	2605
29	103.2	734	..	102.9	1.4140	2670
30	...	...	..	....	1.4143	2733
31	103.3	738	..	....	1.4148	2793
32	...	...	..	....	1.4148	2833
33	103.3	733	..	....	1.4150	2868
34	...	...	..	103.1	1.4150	2948
35	...	...	..	103.1	1.4150	3003
36	...	...	..	....	1.4150	3073
37	...	...	..	103.3	1.4154	3153
38	...	...	..	....	1.4150	3198
39	...	...	..	103.0	1.4152	3248
40	...	...	..	....	1.4152	3308
41	...	...	..	103.0	1.4152	3360
42	...	...	..	103.1	1.4154	3435
43	...	...	..	103.3	1.4157	3580
44	...	...	..	103.3	1.4158	3650
45	...	...	..	....	1.4158	3710
46	...	...	..	103.35	1.4158	3815
47	...	...	..	....	1.4158	3878
48	...	...	..	103.4	1.4158	3993

TABLE VI. REFRACTIONATION OF SECOND ISOMER

(In column 52 feet high, 3/4 inch in diameter)

Cut	B. P. in Column	Barometric Pressure	B. P. at 737 mm. Column	B. P. at 737 mm. Cottrell	Refractive Index (n^{20}_D)	Total
	° C.	Mm.	° C.	° C.		Cc.
1	...	...	..	....	1.4145	40
2	102.4	737	102.4	....	1.4142	83
3	...	...	..	....	1.4145	148
4	...	...	..	....	1.4142	218
5	...	...	..	....	1.4145	263
6	...	...	..	....	1.4147	333
7	103.1	739	..	....	1.4146	383
8	...	...	..	....	1.4148	433
9	103.3	738	..	....	1.4148	483
10	...	...	..	....	1.4150	533
11	...	...	..	102.9	1.4150	598
12	...	...	..	103.0	1.4150	653
13	...	...	..	....	1.4151	718
14	...	...	..	103.1	1.4151	773
15	103.35	737	..	....	1.4152	828
16	...	...	..	....	1.4152	888
17	103.35	737	..	103.15	1.4152	973
18	...	...	..	....	1.4152	1028
19	...	...	..	....	1.4152	1083
20	...	...	..	....	1.4152	1133
21	...	...	..	103.15	1.4153	1178
22	...	...	..	....	1.4153	1221
23	...	...	..	....	1.4153	1264
24	...	...	..	....	1.4153	1319
25	...	...	..	....	1.4154	1380
26	...	...	..	102.80	1.4154	1423
27	...	...	..	....	1.4155	1475
28	...	...	..	....	1.4157	1560
29	...	...	..	....	1.4157	1621
30	...	...	..	103.2	1.4157	1696
31	...	...	..	....	1.4157	1770
32	...	...	..	....	1.4158	1855
33	...	...	..	103.35	1.4158	1910
34	...	...	..	103.35	1.4158	1980
35	...	...	..	....	1.4158	2045
36	...	...	..	103.40	1.4158	2130
37	...	...	..	....	1.4158	2200
38	...	...	..	....	1.4158	2265
39	...	...	..	103.40	1.4158	2337
40	...	...	..	....	1.4158	2407
41	...	...	..	....	1.4158	2492
42	...	...	..	....	1.4158	2567
43	...	...	..	....	1.4158	2634
44	...	...	..	....	1.4158	2699
45	...	...	..	....	1.4158	2814
46	...	...	..	....	1.4158	2894
47	...	...	..	103.35	1.4158	2940
48	...	...	..	....	1.4158	3030
49	...	...	..	....	1.4158	3155
50	...	...	..	103.40	1.4158	3230
51	...	...	..	....	1.4158	3330
52	103.5	737	..	....	1.4158	3515
53	...	...	..	....	1.4158	3645
54	...	...	..	....	1.4180	4295
..	650 cc. residue		..	....	....	....

CONCLUSIONS

These fractionations seem to constitute a complete and fair test of the columns. They show very clearly the actual column performance and the practicability of separating two hydrocarbons boiling about 3° C. apart. No difficulty was experienced in separating, in one distillation, a mixture which for many years was considered to be one substance.

The essential features in the design of these columns were adiabatic operation, controlled reflux, and high efficiency, with a large through-put and a minimum of liquid holdup in the column.

Inasmuch as their operation is simple and their effectiveness proved, these columns are the logical means for effecting a separation of the hydrocarbons in Pennsylvania gasoline. The results with diisobutylene indicate what may be expected in separating petroleum hydrocarbons. When the actual petroleum fractionations were made, the columns proved very effective. These results will be published shortly

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Characteristics of Vanillin and Coumarin

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VANILLA-LIKE flavors may be of three kinds: vanilla extract prepared by extracting 13.35 ounces of vanilla beans with 1 gallon of alcohol; imitation vanilla extract containing less than enough vanilla extract to account for 50 per cent of the flavoring strength or even none at all; and vanilla-vanillin and coumarin which must contain enough vanilla extract to contribute at least 50 per cent of the flavoring strength. The latter is also sometimes labeled "vanilla compound extract."

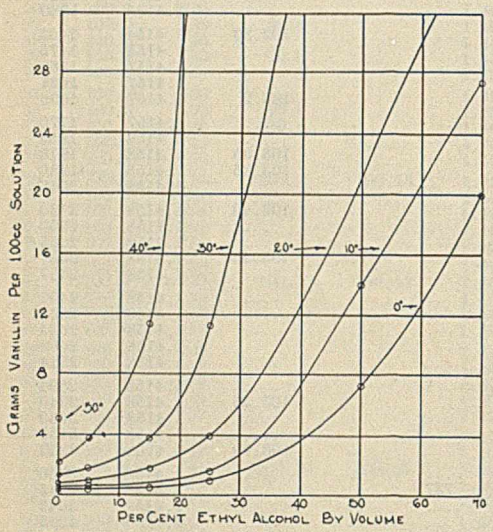

Figure 1. Data on Vanillin in Ethyl Alcohol Solutions

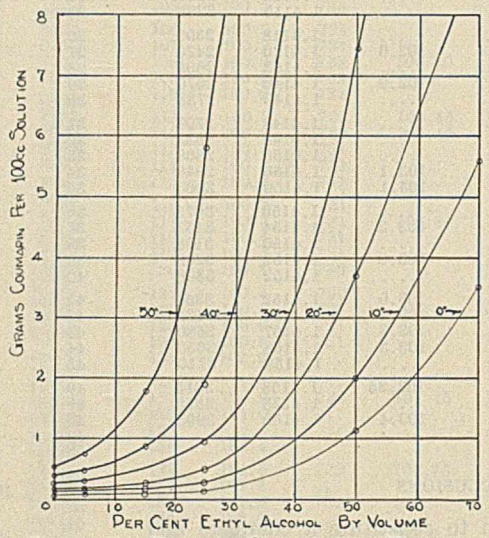

Figure 2. Data on Coumarin in Ethyl Alcohol Solutions

Flavors of the above types are largely used in baking and in the manufacture of confectionery and ice cream.

For many years the principal solvent used in making up these mixtures has been alcohol. However, in recent times there have been many attempts to decrease the amount of alcohol used or to employ a substitute for either all or part of the alcohol, owing to government restrictions on the use of the latter solvent. Glycerol has been one of the principal substitutes used. In attempting to formulate so many different mixtures, there have been numerous cases of precipitation troubles reported, especially in cold weather.

Obviously, the solution of such problems depends upon the solubility of the various solid constituents in the particular solvent mixtures used, and it is with a view to completely rounding out previously published data of this kind (*1*, *2*) that the solubilities presented in the accompanying graphs were determined.

The experimental methods employed differ somewhat from the usual and are described in detail below.

Experimental Methods

Since commercial vanillin and coumarin are of a high degree of purity, such material was used without further purification.

Ethyl alcohol–water and glycerol-water mixtures were made from good grades of commerical ethyl alcohol and glycerol. They were analyzed by specific-gravity measurements.

The solubility determinations were made as follows: The solvent and excess of the solute were placed in small flasks fitted with mechanical stirrers. The flasks were supported in a water bath, the temperature of which was maintained constant to 0.2° C. The contents of the flasks were stirred vigorously for 6 hours to insure saturation of the solutions. Solutions made in this manner proved to be of the same concentrations as those prepared by stirring super-saturated solutions at the desired temperature. They are, therefore, saturated solutions.

Samples of the solutions were obtained by means of pipets kept warmer than the solution to prevent crystallization in the pipets. The tips of the pipets were well covered with absorbent cotton to prevent contamination of the samples with undissolved substance.

It was found convenient to analyze the vanillin solutions by titrating potentiometrically the phenolic hydrogen with standard sodium hydroxide solution. The 0.1 *N* silver chloride electrode was used as a reference and a stick of antimony

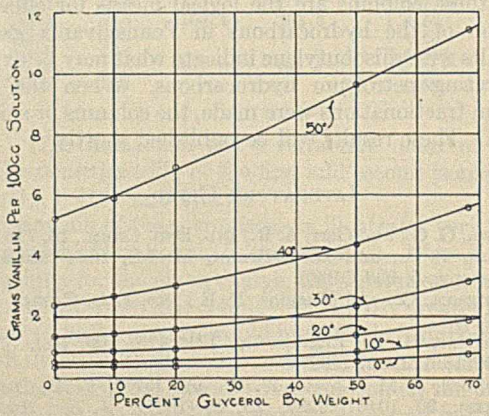

Figure 3. Data on Vanillin in Glycerol Solutions

served satisfactorily in determining the end point. In this way rapid analyses could be made with an accuracy of 1 per cent.

The ethyl alcohol–coumarin solutions were analyzed by extraction of the coumarin with chloroform and evaporation of the solvent under reduced pressure at room temperature

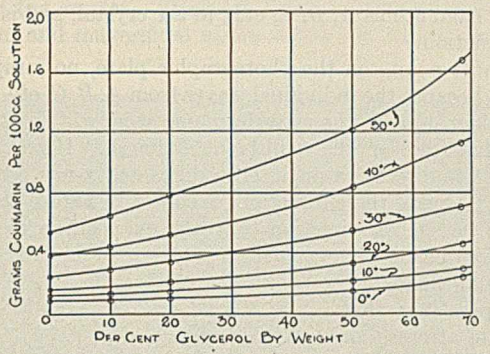

Figure 4. Data on Coumarin in Glycerol Solutions

and drying over phosphorus pentoxide. Preliminary experiments showed this method to be valid for the glycerol solutions also, since less than 1 mg. of glycerol is extracted from a 10 per cent glycerol–90 per cent water mixture by four 10-cc. extractions.

The results have been summarized in four sets of curves in which the ordinates are grams of solute per 100 cc. of solution, and the abscissas are the percentages of glycerol or of ethyl alcohol in the solvent. There is a separate curve for each temperature.

Figure 1 shows the data obtained with vanillin in ethyl alcohol–water mixtures. It is apparent that the solubility is low in cold dilute ethyl alcohol, but it rises rapidly as the concentration of ethyl alcohol increases and as the temperature rises. Most of the values in 70 per cent ethyl alcohol fall far above the graph, the highest being 76.7 grams per 100 cc. of solution at 40° C. The data at 50° C. were not completed, since vanillin melts under ethyl alcohol solutions at this temperature.

Figure 2 presents the results with coumarin in ethyl alcohol solutions. Coumarin is obviously much less soluble than vanillin, especially in dilute ethyl alcohol solutions.

Figure 3 shows the data obtained with vanillin in glycerol solutions. It will be seen that vanillin is much less soluble in glycerol than in ethyl alcohol mixtures. Not only is the solubility low in low concentrations of glycerol and at low temperatures, but it does not show the sudden rise experienced with vanillin in ethyl alcohol solutions at higher temperatures and concentrations of ethyl alcohol. The highest value obtained in this series of curves is 11.4 grams per 100 cc. of solution, compared to 76.7 grams in the case of the ethyl alcohol solutions.

Figure 4 shows the data with coumarin in glycerol solutions. Again the solubility is much lower than in the ethyl alcohol solutions. Here the maximum solubility found was 1.68 grams per 100 cc. of solution while the corresponding value for ethyl alcohol solutions was 94.9 grams.

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Structure of Asbestos

An X-Ray Study

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Commercial asbestos comprises the fibrous varieties of the amphibole and serpentine groups of silicates. Because of its unique physical properties, asbestos is one of the most important minerals in the world. During the last three years the x-ray study of the various forms of asbestos has led to a complete determination of the crystalline structure of this group of substances and to an understanding of their physical properties. It is the purpose of this paper to describe briefly the results of the x-ray study of the asbestos compounds, and to show how the fibrous nature of the material and the strength and flexibility of the fibers is now readily understood in terms of the crystalline structure.

The work to be described has been carried out by the author and his collaborators and has been published from time to time in a series of articles in the *Zeitschrift für Kristallographie* (in English). For any of the details involved in the x-ray analysis, reference should be made to these papers. The methods and principles involved in the x-ray analysis of complex structures are too specialized and technical to be considered here in any detail. Accordingly, a schematic indication of the methods employed and the more interesting discussion of the results of the analyses will be given.

Determination of Crystal Structure

A crystalline substance is characterized by an orderly arrangement of the atoms in which some small group or configuration of atoms repeats itself at regular intervals in various directions throughout space. This smallest unit of pattern which, by repeating itself throughout space, makes up the crystal is known as the unit cell. The unit cell may contain anywhere from one to several hundred atoms, and the x-ray analysis of a crystal structure consists in determining the size and shape of the unit cell and the arrangement of the atoms within that cell.

Figure 1 is a two-dimensional representation of the repeating arrangement of the atoms in a crystal. The circles, triangles, and squares may represent three different kinds of atoms. The group of atoms contained in the parallelogram, *ABCD*, represents the unit cell, and it is readily seen that the crystal as a whole is made up by regular repetition of this unit cell. In an actual crystal the unit cell is, of course, repeated millions of times. The axes in a crystal are the shortest distances of repetition or, what is the same thing, the edges of the unit cell. In the two-dimensional case *AB* and *AD* would be the two axial lengths.

The analysis of crystal structures by means of x-rays is dependent on the fact that the axial lengths are of the same order of magnitude as the wave length of x-rays, so that, when a beam of x-rays passes through a crystal, diffracted beams are produced. X-rays are electric waves wholly similar to light, except that the wave length is much shorter. Considering a train of water waves on the surface of a pond, there is a succession of crests and troughs, and by the wave length of these water waves is meant simply the distance from one crest to the next. By the wave length of x-rays is meant the distance from one electric crest to the next.

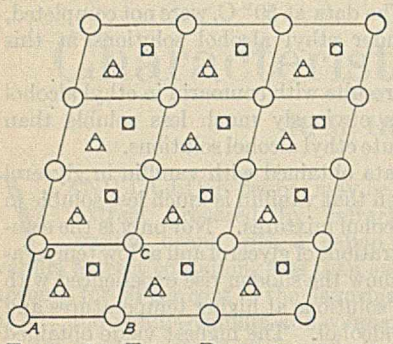

FIGURE 1. TWO-DIMENSIONAL REPRESENTATION OF THE REPEATING ARRANGEMENT OF ATOMS IN A CRYSTAL

To indicate in a rough way how the structure of a crystal is worked out from x-ray diffraction, the imaginary case of a one-dimensional crystal will be considered, that is, one in which the unit cell repeats itself in only one direction rather than in three. In Figure 2, *ABCDE* represents the one-dimensional crystal, the unit cell repeating itself at distances *AB*, *BC*, *CD*, etc. This crystal is in the path of the incident x-ray beam directed from left to right. Part of this beam passes directly through the crystal and produces the black spot, *O*, on a photographic plate situated behind the crystal. Another part of the incident beam is diffracted by the crystal; that is, each atom in the crystal scatters the incident beam and acts as a source of secondary waves, these various secondary waves moving out in all directions from the various atoms.

When two sets of water waves on the surface of a pond cross each other, it is evident that, at those points on the surface where the two individual waves are at a crest, the motion of the water will be greatest, while at other points on the surface, where one set of waves has a crest and the other a trough, the two displacements tend to cancel each other, and the motion of the water will be small. These same interference effects are produced by the individual x-ray waves coming from atoms *A*, *B*, *C*, etc., in the crystal, and is known as diffraction.

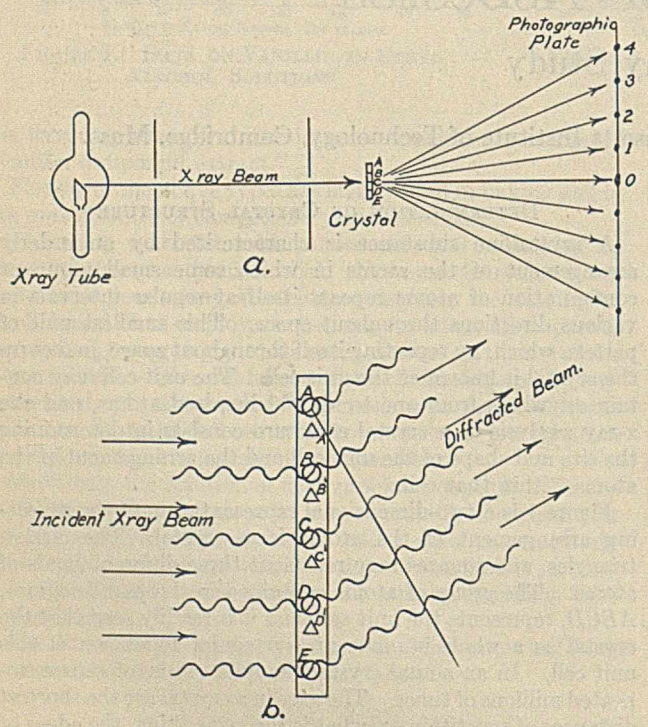

FIGURE 2. ONE-DIMENSIONAL REPRESENTATION OF X-RAY DIFFRACTION BY A CRYSTAL

b shows the coöperation of individual waves from various atoms

At most points on the photographic plate, no x-ray beam will act because the individual waves from *A*, *B*, *C*, etc., cancel each other; that is, the wave from one atom will be at a crest while that from another will be at a trough. However, in a certain few directions an intense diffracted x-ray beam will appear. One of these directions is shown in Figure 2*b* and is seen to be such a direction that at any position along the diffracted beam the individual waves are all coöperating; that is, all are at crests or all at troughs.

In those few directions in which these special conditions obtain, strong diffracted beams will be produced, and black spots will be found on the photographic plate where these diffracted beams impinge. From the positions of these diffraction spots on the photographic plate, one can calculate very simply the axial lengths in the crystal, that is, the size and shape of the unit cell.

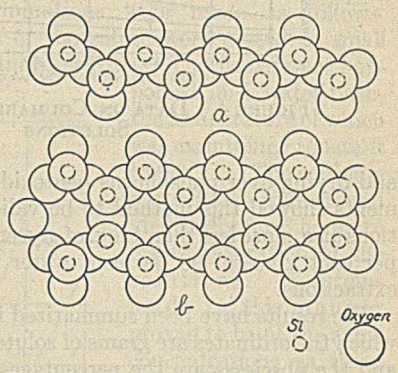

FIGURE 3. SILICON-OXYGEN CHAINS

a. Single chain in diopside
b. Double chain in asbestos

The position of other atoms within the unit cell can also be determined. Let *A′*, *B′*, *C′*, etc., represent a second set of atoms in the unit cell. Then it is evident that under the conditions represented in Figure 2*b*, if *A′* is very close to *A*, the wave from *A′* will coöperate with *A*; if *A′* is halfway between *A* and *B*, the waves from *A′*, *B′*, *C′*, etc., will tend to cancel the waves from *ABC*, etc., since, when one set is at a crest, the other will be at a trough.

This brief discussion will suffice to indicate in a rough way how the crystal structure is determined. An x-ray beam is sent through the crystalline material, and a set of diffraction spots is produced on a photographic plate properly situated. From the positions of these spots the size and shape of the unit cell of the crystal can be calculated directly, and from the intensity of the spots, the arrangement of the atoms within the unit cell.

RESULTS OF X-RAY ANALYSES

DIOPSIDE. The key to the crystalline structure of the asbestos minerals was the crystal diopside, $CaMg(SiO_3)_2$. This substance occurs in large well-formed single crystals and lends itself readily to a careful x-ray study. From a set of quantitative measurements of the intensity of the various diffracted x-ray beams, it was possible to work out completely the crystalline structure (*5*). The crystal is monoclinic with axial lengths, a = 9.71 Å., b = 8.89 Å., c = 5.24 Å., β = 74° 10′ (1 Å. = $\frac{1}{100{,}000{,}000}$ cm.). The unit cell contains four molecules of $CaMg(SiO_3)_2$. The feature of particular interest in the structure is the arrangement of silicon and oxygen atoms. Each silicon atom is surrounded tetrahedrally by four oxygens, the oxygens being at the four corners of a regular

tetrahedron with the silicon at the center. In each tetrahedral group two of the oxygens are shared with neighboring groups in such a way as to build up endless chains of tightly connected silicon-oxygen groups. This silicon-oxygen chain is shown in Figure 3*a*. In the structure these silicon-oxygen chains lie parallel to one another and in the direction of the *c* axis of the crystal. They are held together laterally by the calcium and magnesium atoms which are located in various

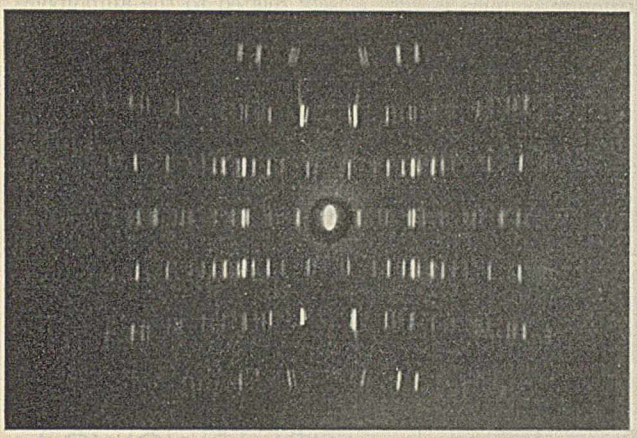

FIGURE 4. X-RAY DIFFRACTION PHOTOGRAPH OF TREMOLITE

interstices between the chains. Since Si^{++++} is a quadrivalent atom while Ca^{++} and Mg^{++} are only divalent, it would be expected that the electrical forces binding silicon to oxygen would be very strong compared to the weaker forces between calcium and oxygen or magnesium and oxygen. Thus a very definite picture is obtained of the diopside crystal and of the nature of the forces which are operating. Strings of silicon-oxygen groups lie parallel to one another, and within each string the strong silicon-oxygen forces produce a continuous system of bonds along the length of the chain. The chain will accordingly have great strength in the chain direction but be much weaker laterally, owing to the weaker calcium-oxygen and magnesium-oxygen forces which alone hold the various chains together. The picture is essentially that of a bundle of matches held together laterally by a weak cement. Diopside is not a fibrous substance, but the presence of these silicon-oxygen chains is evidenced in the crystal habit and the cleavage. It is the strong double chain (Figure 3*b*) which lies parallel to the fiber direction in asbestos that is responsible for the fibrous character.

It should be emphasized that the importance of the crystal structure of diopside is now found in the fact that a much stronger type of silicon-oxygen chain, but one which is closely related to that first found in diopside, forms the basis of the crystal structure of the various varieties of asbestos and is responsible for their important physical properties.

TREMOLITE. The next step in the approach to the asbestos group was made through the crystal tremolite, $Ca_2Mg_5(Si_4O_{11})_2(OH)_2$. Tremolite is a monoclinic amphibole occurring in the fibrous form as a variety of asbestos and occurring also in the form of single crystals. From x-ray diffraction photographs of tremolite (Figure 4) it was found that the crystal structure was very closely related to that of diopside, and that this relation was of such a simple sort that it was possible to work out directly the crystal structure of this complex substance from that of diopside which was already known (*3*, *4*). The large central spot on both Figures 4 and 5 is due to the primary x-ray beam which passes directly through the sample. The other spots are due to the diffracted beams, and it is from the position and intensity of these various spots that the crystal structure of asbestos has been worked out.

The unit cell has the dimension, $a = 9.78$ Å., $b = 17.8$ Å., $c = 5.26$ Å., $\beta = 73°58'$, and contains two molecules of $Ca_2Mg_5(Si_4O_{11})_2(OH_2)$. In tremolite each silicon is surrounded by four oxygens, and these oxygens are shared between neighboring groups in such a way as to build up endless chains of silicon-oxygen groups exactly as in diopside. The form of the silicon-oxygen chain in tremolite differs somewhat from that in diopside, as is readily seen from Figure 3*a* and *b*. It is essentially a double chain composed of two diopside chains, placed side by side and joined by a further sharing of oxygen atoms. Presumably this doubling of the chain strengthens it greatly, just as the nailing together of two boards results in an appreciable reënforcing.

The tremolite structure is composed of these strong double silicon-oxygen chains, lying parallel to one another and held together laterally by the rather weak forces exerted by the calcium and magnesium atoms. As is well known, the amphiboles have a pronounced tendency to occur as bundles of parallel fibers, and, as would be expected, it is found that the silicon-oxygen chains lie parallel to the direction of the fiber. Thus the remarkable fibrous property of the amphiboles is readily understood in terms of the crystal structure. It is due solely to the strong silicon-oxygen chains of Figure 3*b* which have great strength along the chain direction, but which are held together laterally by much weaker forces. The tremolite structure is typical of the whole group of monoclinic amphiboles, including tremolite, actinolite, hornblende, crocidolite (blue asbestos), etc. The orthorhombic amphiboles (*7*),

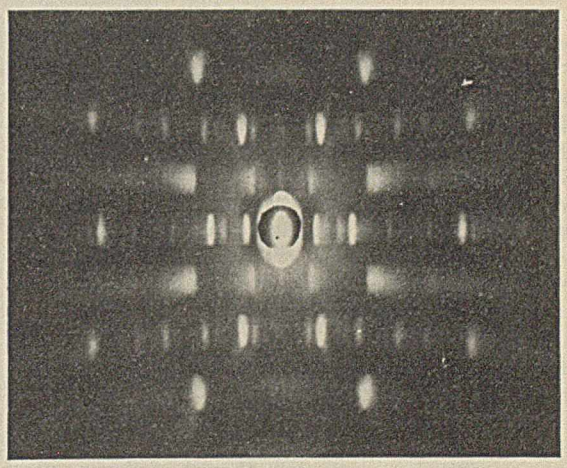

FIGURE 5. X-RAY DIFFRACTION PHOTOGRAPH OF CHRYSOTILE

anthophyllite, amosite, etc., are found to have essentially the same structure. They differ only in a doubling of the size of the unit cell with an attendant increase in symmetry, but the essential arrangement of the atoms and the double silicon-oxygen chains are exactly the same as in the tremolite structure.

CHRYSOTILE. This is a member of the serpentine group of silicates and has the composition $H_4Mg_3Si_2O_9$. From the x-ray diffraction study of chrysotile (Figure 5) it was found that certain relations must exist between this structure and that of the amphiboles, and from these relations the essential scheme of the structure was determined (*6*). Figure 6 shows the unit cell of chrysotile with the *c* axis (fiber direction) normal to the plane of the paper (*1*). The same double silicon-oxygen chains of Figure 3*b* are in chrysotile as in the amphiboles, and these are seen in Figure 6 in cross section.

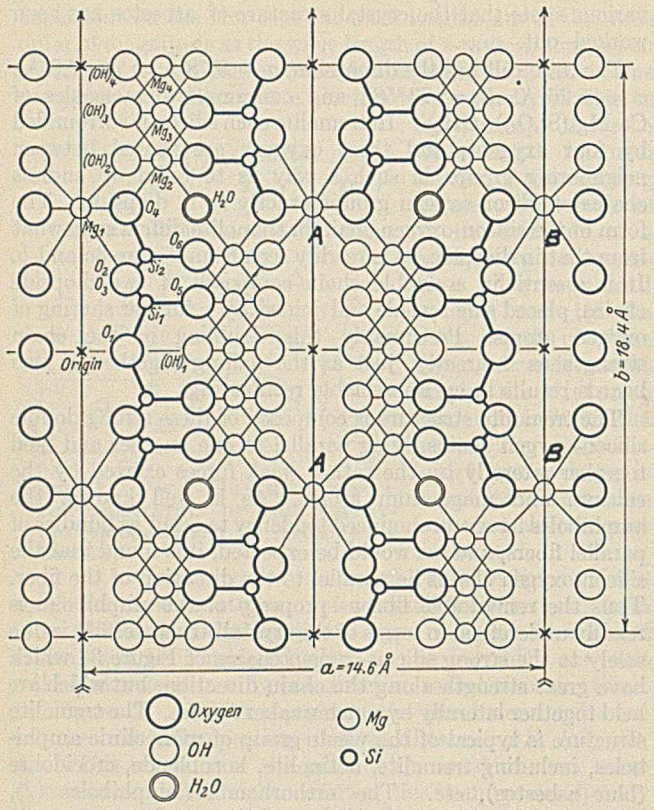

FIGURE 6. PROJECTION OF CHRYSOTILE STRUCTURE PERPENDICULAR TO *c* AXIS

The heavy lines connecting silicon to oxygen outline the cross section of the silicon-oxygen chains which stand perpendicular to the plane of the paper. The atoms lie at various heights above and below the plane of the paper, and those shown here comprise one unit cell, the length of the unit cell normal to the paper being $c = 5.33$ Å. The chains continue indefinitely through the structure, and only a unit length of chain is contained in a unit cell. The chrysotile structure differs from that of the amphiboles only in the atoms and in the atomic grouping which binds the double chains to one another laterally.

This lateral binding of the chains in chrysotile should be much weaker than in the amphiboles owing to the fact that across sections such as *AA* and *BB* the structure is held together by secondary forces only, not by direct valence attractions. From the structure then the following physical properties would be expected: The substance should be fibrous and very strong along the fiber direction—fully as strong as the fibrous amphiboles, since the same double silicon-oxygen chains are involved. It should be finely fibered and the fibers should be readily separated, since the lateral binding between the chains involves secondary forces to a large extent. Across those planes where only secondary forces act, slip will be possible, and the fibers should therefore be flexible. The structure, therefore, offers a complete explanation of the physical properties of chrysotile, explaining its fibrous nature and also the fact that fibers are so very flexible and readily separated. Owing to the fact that secondary forces play such an important role in the structure, it is readily understood why single crystal fibers never develop to any appreciable size laterally, and why the material always occurs as bundles of parallel fibers with random orientation about the fiber axis. Most of what has been said about the forces in chrysotile applies also to the amphibole varieties of asbestos, the role of secondary forces in producing weak lateral binding and a possibility of slip, however, being somewhat more evident in the structure of chrysotile than in that of the amphiboles.

MICA. Another mineral of great commercial importance because of its unique physical properties is the silicate mica, occurring in flat sheets readily separated and quite flexible. The crystal structure of the mica group has been worked out (*2*) and now provides a very simple explanation for the interesting flaky habit of this group of minerals. The crystal structure of mica is very closely related to the amphiboles, the relation being such that mica could well be called "two-dimensional asbestos."

In Figure 3 it was seen how the strong double silicon-oxygen chain of the asbestos group was produced by joining together two diopside chains. Obviously this process could be continued and a third and fourth chain joined on, etc. By this process a continuous sheet, such as that represented in Figure 7, could be built up. The relation of the mica sheet to the asbestos chain is shown by outlining more heavily that part of the sheet which comprises one chain. Each silicon atom is still surrounded by four oxygens, but in each tetrahedral group three of the oxygens are now shared with neighboring groups. The strong silicon-to-oxygen bonds run continuously in both directions throughout the sheet. From x-ray analysis it is found that the mica structure is built up from just such silicon-oxygen sheets, the sheets being parallel to one another and held together rather weakly by layers of magnesium, iron, and potassium atoms.

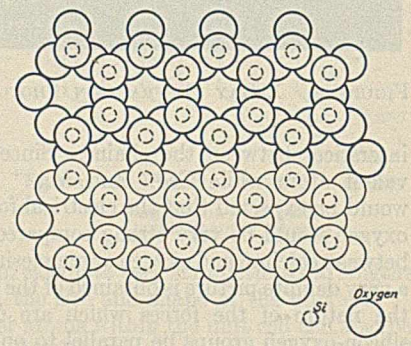

FIGURE 7. SILICON-OXYGEN SHEET AS IN MICA

These two examples may serve as good illustrations of the remarkable progress which is now being made in the x-ray analysis of complex substances and of the way in which their interesting physical properties can be understood very simply in terms of the crystal structure, the flaky habit of mica being due to the silicon-oxygen sheets out of which it is built, and the fibrous nature of asbestos resulting from the silicon-oxygen chains.

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RECEIVED October 26, 1931.

BRITISH CONFIRM CONTINENTAL DYE ALLIANCE. The British Imperial Chemical Industries, Ltd., has confirmed the report that an agreement affecting the European dye market has been concluded between them and Continental dye makers, according to a radiogram to the Department of Commerce. Details of the pact are not available but it is believed that it relates to allocation of markets, excluding the United States. It is not thought that this arrangement includes price control or interchange of technical information. Since the agreement German dye prices in England have increased 10 per cent and a further increase of prices by British dye makers is expected.

Management of Research

A Series of Articles Considering the Functions of Laboratory Organization and the Coördination of Laboratory and Plant Effort

Selection and Training of Industrial Research Personnel

WEBSTER N. JONES, Processing Division, B. F. Goodrich Company, Akron, Ohio

"SCIENTIFIC discovery and its practical application are the products of long and arduous research. Discovery and invention do not spring full grown from the brains of men. The labor of a host of men, great laboratories, long patient scientific experiment build up the structure of knowledge, not stone by stone but particle by particle. This adding of fact to fact some day brings forth a revolutionary discovery, an illuminating hypothesis, a great invention. Research, both in pure science and in its application to the arts, is one of the most potent impulses to progress. For it is organized research that gives daily improvement in machines and processes, in methods of agriculture, in the protection of health, and in understanding." In these words, President Hoover has ably pointed out the importance of research to industrial progress.

WEBSTER N. JONES

The stimulus that research in chemistry and chemical engineering received during the World War attracted the attention of our nation toward scientific investigation. The accomplishments of chemistry in the improvement of quality of products, development of new products, and lowering of cost have impressed plant executives; and many have found scientific research essential to industrial progress. In consequence, industrial research organizations have been established and expanded with great rapidity to keep abreast of the times and to meet the needs of the future. The attendant publicity has attracted the earnest consideration of the youth of the nation, with the result that American universities are now graduating annually hundreds of chemists and chemical engineers who are trained for employment in research.

During the early days of expansion in industrial research the supply of well-trained experienced research men was inadequate to meet the demand. In order to supply their needs, certain industries secured research chemists from abroad, others drew professors from our universities. Gradually the importations from other countries have almost ceased. Some of the professors have demonstrated their value to industry; others, after a baptism of commercial fire, have returned to teaching where they now work more effectively as a result of their industrial experience. The attitude of professors that entrance into industry is debasing has largely disappeared; in fact, today many professors act as consultants to large industrial research organizations. By intimate contact with industry they are enabled to give their students better educational training for an industrial research career.

The proper selection and industrial training of research personnel are the most important functions in building sound and successful industrial research organizations. The usual method is to select promising young men, thoroughly grounded in the fundamentals of chemistry, and then give them in the factory the fundamental knowledge peculiar to the industry to complete their training for handling its research problems. These men are ordinarily recruited from the graduate schools of our universities. Consequently, a college man who aspires to enter industrial research should not content himself with a four-year course of training, but should continue his work towards a graduate degree. Some chemists enter industry immediately after graduation with the expectation of later returning for advanced study after gaining a few years of industrial experience. Only a small number, however, ever fulfil this ambition. If industrial experience is sought by the student, employment during summer vacations offers a better means of securing it than by interruption of college training. Summer jobs are often available because industrial concerns employ promising young men for summer work in order to appraise them as potential permanent employees.

In passing, it may not be inappropriate to suggest that graduate schools should be very solicitous about the quality of the men upon whom they place their stamp of approval, because the reputation of a university depends upon the quality and not upon the number of its graduates. A professor should not be motivated by the desire to increase the number of his publications at the expense of a mediocre man whose future success in research is problematical. Only young men of marked promise should be encouraged to do advanced work. David Starr Jordan expressed the opinion that it is "no use loading a $10,000 education on a 50-cent boy."

The choice of research personnel is not necessarily restricted to men who have just completed their university training. Many candidates present themselves after having acquired experience with other companies. Research experience acquired in one industry should be applicable in another, but repeated shifting from one job to another inevitably raises the question of the fundamental ability of the man. Acquaintance with too wide a field of industrial research may indicate a tendency towards superficiality or even instability. On the other hand, a capable research man may be out of employment for reasons which reflect in no way upon his ability. Such a man may bring to bear upon research problems a maturity of judgment which enables him to be assimilated more quickly into another research organization than a man who has just finished his graduate study.

Young technical men with a bent for research, already

employed in technical work in the factory, should not be overlooked in making selections for research openings. Careful discrimination is necessary to insure that these men are really capable of engaging in research. When they have research ability, their services frequently prove to be of exceptional value and their rate of progress gratifying. Men who have been in close contact with the operating departments of an industry not only have gained an idea of the value of time in production and in distribution, but accept with enthusiasm the chance to secure fundamental knowledge, the importance of which their training has taught them to appreciate.

Factors in Selection of Research Workers

In the selection of productive research workers, it is necessary to consider many factors. The qualities desirable for a particular kind of work should be carefully investigated, due attention being given to health, to personal neatness, and to orderliness—traits which are sure to influence the character of their performance. Qualifications acquired by previous education and experience are useful not only in increasing the immediate value of a man's services, but also in giving a clue as to his personal inclinations. Since we all live in a world of human beings and must impress our ideas upon others, it is necessary in selecting men to consider those qualities of personality which indicate ability to make satisfactory human contacts.

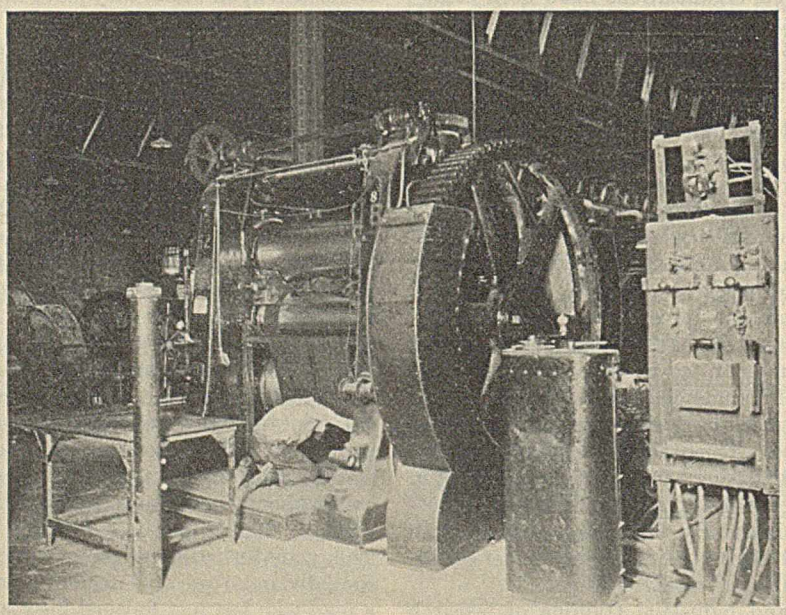
Research workers should be men of critical judgment and unquestioned integrity. It is not sufficient that they refrain from deceiving others; they should ever be alert to avoid deceiving themselves. They are primarily seekers after truth and, in enthusiasm for their work, may easily mislead themselves as well as others unless they develop a critical attitude which demands rigorous proof of that which appears to be true. This necessitates a fine balance, for it is only a step from the possession of this wholesome skepticism to the development of a cynical attitude which throttles initiative and produces a negative personality.

Many other factors enter into the selection, and, for their proper evaluation, the qualifications of those who make selections are of primary and controlling importance. In large organizations, men of mature experience in industrial research, who have wide acquaintance in university circles and a keen interest in young men, are usually chosen to make pilgrimages to the universities to interview and appraise prospective employees. These interviewers visit several selected universities, because experience has shown that a better-balanced research organization results if the research group is composed of men who reflect different methods of training. Although a specific imprint of a particular university may not be apparent in the graduate, he will, nevertheless, have acquired through his training characteristics which reflect emphasis on certain lines of thought and methods of attack upon problems. By employing men from a number of universities, it is possible to enrich a research organization with greater resources in variety of methods and originality of thought.

It is usually desirable to consider several men for each available position in order to secure men of the best qualifications. With the short time available for an interview, a very rapid appraisal must be made. It is preferable, therefore, for interviewers to travel in pairs so that each may check the other's views as to the qualifications of the candidates. Experience has demonstrated that two men operate much more effectively than one, and that impressions which are unappreciated by one are often observed by the other. Further, opportunity is provided for discussion immediately after the initial contact, and a sound appraisal of the candidates is much more likely to result. This is especially true when both interviewers independently reach the same conclusions.

The officials of the universities may, and generally do, render valuable assistance to the representatives of industry in the selection of suitable men. While no assurance can be given to a student that the school will secure a position for him, nevertheless all colleges are interested in seeing that their students are advantageously located in work for which they are qualified and in which they will acquit themselves creditably. To this end, valuable records covering the past performance of a student or reflecting the school's estimate of his fitness for particular lines of work are maintained and offered for inspection. Personal acquaintance of the interviewers with the faculty and among the associates of the candidate is often of great assistance in the selection, especially when experience has demonstrated that the judgment of these men is generally sound.

The interview between the candidate and the selectors is, in the last analysis, the actual basis for appraisal and selection. While the recommendations and records provide a valuable background and doubtless aid in formulating the appraisal, it is during the interviews that the foundation for a selection is built. Presumably, each interviewer has in mind the type of man desired for each position. Very few men, however, can describe the qualities of the desired type so exactly as to enable another to make the selection for him. It requires personal contact. Even under most advantageous conditions the actual decision is usually a compromise in which the interviewers agree upon the candidate who most nearly satisfies the standards of each. During the interview, each selector compares the qualifications of the candidate with those which he has considered essential, and secures comparative data for subsequent decision. Educational fitness and past experience can be evaluated without an interview. Past records give some measure of character and integrity.



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Health and physical condition can also be made a part of the record. Only in the interview can mental attitude, personal appearance, bearing, address, and those other intangible qualities which contribute to force and leadership be adequately evaluated.

The interview not only gives an opportunity for the investigators to evaluate the candidate, but it also provides the candidate an opportunity to appraise his prospective position by contact with representatives of the company and by their answers to the many pertinent questions which naturally arise in his mind. Through this appraisal, especially if supplemented by information concerning the company's commercial and financial standing, the candidate should be able to determine whether that particular company offers adequate opportunity for development of his capabilities for maximum advancement in his chosen profession.

In conducting the interview, the investigators should have in mind not only the type and qualifications of the men they would employ, but also a well-formed plan for securing during their visit clear answers to such vital questions as the following: Does the man use good English? Does he speak directly and clearly? When talking, does he face one squarely and look one in the eye or is his gaze wandering? Is he interested and enthusiastic or is he simply looking for a meal ticket? Is his measure of success largely financial or does he appreciate that the attainment of happiness, health, and opportunity for service to humanity are as important as a large income? Is he just a bookworm or has study enlarged his capacity to think and act? Has he hobbies and, if so, are they constructive? Does he show originality and initiative in undertakings of his own? Does he "carry through" or is his record full of projects started and abandoned short of completion? Is he capable of further growth?

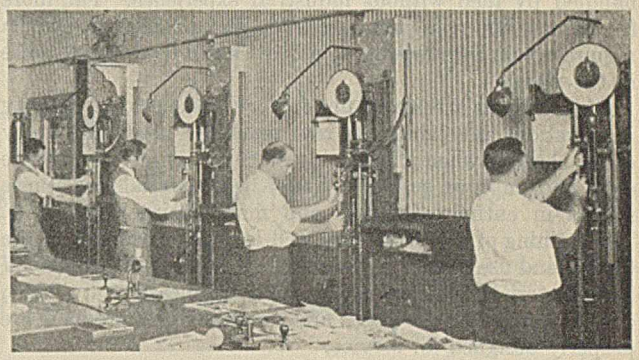
The interviewers should take pains to put the man at his ease. It must be remembered that he is under strain, and that under such conditions many very capable men are unable to show their true worth. Furthermore, the candidate is usually trying deliberately to put forth what he thinks is desired, whereas he would probably make a better impression if he were simply and naturally himself.

Training of Research Workers

University Training. The training of research workers may be considered from two distinct points of view. To the college professor, training may comprise the courses of study which should be pursued in order to build the necessary technical foundation. Questions arise, such as the proper distribution of time between those courses designed to give the student mastery of the fundamental sciences and between research problems conducted in the university laboratories. What are the best methods for development of ability to analyze problems and to think them through in a logical manner? How should the student be trained in methods of attacking his problems and of planning his research? These questions and many others rightly occupy the thoughts of the educators.

In industrial research the training of workers involves quite different factors. It starts where the educator leaves off. It is assumed that the young worker is thoroughly grounded in fundamentals and has acquired in the university laboratory familiarity with the usual research technic. It is taken for granted that the young man realizes the necessity for investigating thoroughly all of the existing information pertaining to his problems. The importance of careful observation and complete notes should be already understood. The differences which arise between laboratory experiments and operations on a plant scale have probably been repeatedly discussed in college, but nothing short of factory experience will fully impress upon the chemist the difficulties which must normally be overcome in passing from test tube to autoclave. During his industrial training the new man must be aided in adjusting himself to his new environment as smoothly as possible. He must also be given sufficient insight and familiarity in the particular industry with which he is connected so that he is enabled to work intelligently and to translate laboratory experience into the practical operations of the factory.

The aptitude shown by a new man to progress rapidly during the period of training for a specific job and his ready adaptation to new surroundings is of extreme importance in determining his subsequent value and success. Frequently, professors who have been called into industrial positions have



Rubber Testing in Laboratory of B. F. Goodrich Co.

difficulty in adjusting themselves to their new environment. The story is told that shortly after he entered the employ of an industry, a certain professor was visited by a distinguished scientist. It is the custom of most factories to require package-passes for articles carried out of the factory. The baggage of the scientist was admitted without question. The ex-professor neglected to get a package-pass when the scientist was leaving and, upon being stopped at the gate, thoughtlessly said to the guard, "Mr. Scientist is a guest of the University," Such a remark meant nothing to the guard. It was the first time that he had ever heard his company referred to as a university.

The world in which the young collegian in industry finds himself is quite in contrast to the university environment to which he has been accustomed. Considerable adjustment in behavior is demanded. An "eight o'clock" in industry means eight o'clock and there are no "cuts." The research worker should adjust himself to conform to the rules and regulations of the company and through his own efforts and attainments should become an integral part of industry. He should not regard himself as one of a specially favored class, for this inevitably puts him out of step with his fellow workers, presents opportunities for adverse criticism, and may result in lack of coöperation. A research worker needs the suggestions and support of factory men in the same measure that industry needs research.

The young man who has spent four years in obtaining a college degree, followed by three years of graduate work concentrated largely on a specific problem, is apt to lose sight of his duties toward the world at large and to center his attention too exclusively on his own interest. This concentration may lead him to isolate himself from those who have not had similar opportunities. He should take care not to make of himself an object of pointed criticism by factory workers. He may be flattered by the sound of Doctor and be offended by the omission of the title. He can profit by Charles Lamb's advice in All Fools Day: "Good Master

Raymond Lully, you look wise. Pray correct that error." A research worker has a definite obligation to society which is worthy of his consideration. He should be a leader in humanitarian and worthy economic endeavors and should not remain aloof, a mere observer or a self-centered critic.

FACTORY TRAINING. In order that research shall be of the maximum value to an industry, it is essential that the investigations shall have a background founded on precise knowledge of the problems and needs of that industry. The research worker must therefore have in addition to his college training considerable knowledge of the materials and methods pertaining to his industry; and, to supply such knowledge, the training period should include some factory experience. Industrial laboratories do, of course, have some problems which require research in pure science, and these can be handled by men without industrial experience. Far more frequently, however, problems in applied science arise which require detailed knowledge of processes and equipment in use in the plant.

Often industrial research finds a very fertile field for activity in questions involving the raw materials used. In many cases, changes when effected intelligently can greatly reduce costs and improve quality. Use of new materials sometimes results in entirely different and more desirable products. The training of new men may well include experience in the testing and use of raw materials. The testing and control of both materials and products furnish the measures by which effective production is gaged and through which products are properly designed for service.

It is neither necessary nor desirable, in providing an industrial background as part of the training of research investigators, to waste time and skill by prolonged assignment to routine operations. The scientifically trained man grasps the essentials quickly and can rapidly sense the reasons for manufacturing details. Monotonous routine in particular lines of work may dull his interest and cause him to overlook the benefit which the actual experience was intended to give. Of course, care must be taken that the inexperienced man is not exposed to the physical hazards incident to operation of machinery. This may necessitate limiting his factory activity in some lines to observation only. Nevertheless, actual performance of the essential operations of the industry by the research man, where this is feasible, is preferable to observation; and his training should include this type of experience.

In some industries a very satisfactory adjustment from university to industrial life is provided by a definite training course. In such a course the new man works for short periods in the raw-materials department and in the service laboratories, both on chemical analysis and physical testing of materials and product. He then passes as rapidly as is consistent with thorough understanding through various factory departments where, so far as possible, he is given the opportunity of handling the materials and of actually carrying out production operations. This experience is supplemented with talks by various members of the organization on the subjects in which they are expert. Opportunity for questions and answers is provided. Frequently a specially prepared text dealing with the industry is made available for study, and forms the basis for discussion classes. Throughout the course attention is given to the economic aspects as well as the scientific principles and practical methods of the industry, since a knowledge of costs of materials, manufacture, and distribution is often of great importance to the research worker. The training course should be directed and managed by technically trained men, experienced in the industry, who understand the new man's problems, and who are competent to guide and assist him during this period.

After having gone through a factory training course, the new man has a distinct advantage over one who started at the same time and immediately began laboratory work. He has made contacts throughout the organization; has become acquainted with many of the factory men; has learned a great deal about the lines of organization; and has accumulated much detailed information about the industry, its methods, processes, and equipment. Without this factory training, his feeling toward research is apt to be that of doing a very thorough and complete job of investigation to accomplish the goal which was set at the start of the problem. After having had factory training, however, the man may see the possibility of prompt application of some of the intermediate results of his research work. These often prove to be of even more value than the goal toward which he was working. Only by knowing the requirements and processes of industry can he realize the applicability of many bits of information which he might otherwise cast aside as being valueless.

Irrespective of the previous experience of the research man, an important part of his training is to learn to think in terms of the factors which determine the success of the industry. He must appreciate the effects of interruptions and speed of solving problems upon production operations. He should not only learn all there is to know of his specialty, but he should learn to broaden the sources of his information. A former professor in physics, upon entering a large industry, was given charge of the temperature-measuring instruments in the entire factory. In the narrow sense this was a laboratory job and involved testing and checking instruments to insure the limits of their sensitivity and precision. This man, however, did not confine his operations to the four walls of a testing laboratory. He soon discovered that, in many cases of inaccuracy called to his attention, the instrument was doing its part, but that the trouble in production came from such causes as improper functioning of steam traps, improper location of instruments, avoidable radiation losses, and the formation of gas films which retarded heat transfer. His duties, therefore, lured him to become a factory investigator, and before long he could be found more frequently in the factory or in the engineering division arranging for corrective measures than in his laboratory where the actual testing of instruments was conducted. He became so adroit in tracing troubles back to their sources that his services were sought by all departments of the factory from the pipe-fitters to the production executives. He did not attempt to convey the impression that he was teaching those whom he helped out of difficulty, and his influence in improving the operations of the plant was widespread and of great commercial value.

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It is equally important, apart from the very exacting discipline of scientific research, that an industrial research man learn to utilize all of the forces which exist in the organization which he serves. These must be applied constructively to promote the interests of the company and of his particular problems. In other words, it is important that he learn to coöperate wholeheartedly with the entire organization. Many zealous attempts to make haste in revolutionizing an industry through research have failed through overstepping

the lines of organization which must be maintained in order to promote smooth operation of the plant.

To enjoy fully the advantages of constructive accomplishment, a research worker should reflect optimism. The possession of a critical mind does not exclude a cheerful personality. The possession of a good-humored tenacity in the search for truth not only makes the job more enjoyable, but it inspires others with confidence and makes them want to share in the joy of the accomplishment. Very valuable attributes in a good research man are invariable optimism seasoned with judgment and the willingness to coöperate by utilizing other branches of the organization in arriving at success. Whether training can or cannot implant these attributes, they must be present in the man who hopes to succeed.

In conclusion it is pointed out that executives and others responsible for research in any growing industry should ever keep in mind that the end to be attained in the selection and training of research personnel is to build up a research organization composed of men having superior qualifications and especially initiative, creative instinct, breadth of vision, and a capacity for hard work; men who possess physical fitness to enable them to carry on energetically, tenacity of purpose to compel them to stick until the end, resourcefulness to direct them out of the beaten paths into the unexplored areas, personality such as to enable them to live amicably in their environment, and knowledge in their particular fields which will render them capable of effective work. Such an organization will contain few geniuses, for genius is indeed rare, but it will be composed of men of high average ability who are capable of consistent productive labor and combined group effort. This is the *sine qua non* of industrial research.

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Control of Research Expense

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In 1921 the great importance of planning and control began to be recognized in management. Since then many companies have required definite organizational plans for their research departments or laboratories, and in general the results have been beneficial to the directors of these laboratories, principally because their authority and responsibility are now defined.

This attention to planning and control has induced various studies of industrial research procedures, and has led in not a few instances to the installation of budget systems whereby financial requirements can be predetermined with satisfactory accuracy. Their first experience with budgetary practice was almost painful to research directors who had no knowledge of the science of management. According to our observations, however, budgets have rather quickly become the guides for the operation of a number of large industrial research laboratories.

In some companies, it is true, the administration of research is still a rather hit and miss affair. If a department desires the laboratory to make an investigation, its request is submitted to a conference committee, a decision is made as to the merit thereof, and authority is then given or withheld. But in more progressive companies a definite organization set-up has been established to plan all research laboratory activities and to control research expense. The laboratory thus has a clearly defined program for the year and can plan its personnel and work accordingly. This systematic planning gives the basis for establishing an expense budget, and experience has shown that, if the latter is controlled, satisfactory progress is made toward controlling the costs of research, to the joint benefit of management, technology, and science.

The control of research comprises questions of controlling expense as well as problems of generating desirable spirit and attitude and of producing greater activity. It must be guided by what expense is necessary and what the business can stand. There are many companies that have enjoyed growth because of the successful management of their researches. There are other companies that have died because of their failure properly to evaluate and control the costs of research. It is always essential in planning research to give due attention to the probability of the solution of the problems at a cost that is commensurate with the values involved. It must be remembered, moreover, that the expense of research must be controlled and kept within bounds without in any way constringing the initiative of the laboratorian in making investigational advancements. It is plain that the degree of effectiveness of a laboratory staff always has much to do with the cost of a research.

The average industrial research laboratory is founded for profit, and a company cannot afford a laboratory that does not at least pay for itself. The research laboratory is intended to aid in increasing earnings and in decreasing costs in the company of which it is a part. The best tool for helping to reduce costs in the laboratory and elsewhere is efficient accounting. The purpose of accounting is to control all expenditures, to analyze departments, and to present informative reports to the company officers who should have them. A competent accountant will study the methods of the department to which he is assigned, plan their accounting and procedures of recording costs so that the data procured will satisfy all requirements, and then give the management the information that is needed. If accounting records are kept close to the work, the department concerned can secure statistics that can be utilized quickly.

Apportionment of Research Expense in Industrial Management

"A pencil in the hands of a cost accountant ceases to be a writing implement; it becomes a surgical instrument."
—An Industrial Research Veteran

A question that has often come to us is, what is the most adequate accounting system to use for crediting the research accomplishments of a laboratory? We have always answered this query by explaining that a comprehensive procedure therefor has not been evolved, and that the current practice, which is conceded to be in the developmental stage and hence tentative, is based upon the evaluation of only part of the results of research—upon the so-called tangibles that can be definitely credited against the expense of scientific investiga-

tion. In consequence, we have pointed out, research expense can be reduced only partially to a method of accounting. As a matter of fact, in most instances the intangible results of research are undoubtedly more valuable than the tangibles, and consequently it is not possible at present, at least, to put an industrial research laboratory on a full accounting basis. In these cases the laboratory accounting system must consider the positive savings classifiable as tangibles that are derived from novel or improved processes, reduction or disposal of wastes, sale or licensing of patented inventions, etc. The remainder of research expense—that relating to such intangibles as maintenance of quality through control, better products, and new products—is most sensibly charged off to product and market improvements. As is well known, the cost of devising a novel product or modifying an old one is often substantial.

Intangibles are rarely realizable assets in case of liquidation, even though originally paid for at high prices, and well-managed companies generally try to amortize their intangibles just as rapidly as earnings will permit.

MANY LABORATORIES NOW HAVE ACCOUNTING DEPARTMENTS

Research laboratory management has in cost accounting a reliable sentry in guarding against uneconomical practices.

The money expended for research should therefore be recorded, and complete documentary evidence of intangibles included among assets should always be preserved. Not infrequently, in the chemical industry in particular, research efforts are principally directed to the creation of intangible assets, such as patents and formulas. As expenses are incurred in this investigational work, they are customarily charged to a ledger account; they are carried as a deferred asset and subsequently liquidated into production or marketing costs. When, however, the results of research are capitalized as patents, formulas, or good will, this consequence does not make it necessary to carry them on the books as assets for more than a transitory period. The management of a company doing research should know the cost of keeping abreast of the times and should have a cost system that reveals the sum total of calculable research accomplishment and of wasted effort.

In technology the real worth of internal expenditures for carrying on certain operations, especially the handling of raw materials, can be confirmed by securing outside competitive data. In appraising the worth of money diverted to intangibles, however, sound business judgment reinforced by technical caution must be followed.

In several of our most researchful manufacturing concerns, the cost of research is charged off currently as an item in general operating costs. All research costs, not including patent expense, are charges against expense that is written off currently as expended or at a later financial period, provided commercial products result from the expenditure. Appropriations are established for specific projects at the annual period of review, and actual costs are recorded against these projects as incurred. Projects that may arise during the year are taken care of by an emergency fund, set aside at the annual period and held available for such interim researches. In one well-known company this fund amounts to 15 per cent of the total appropriation. If it is inadequate at any time, a special extra appropriation is made for supporting promising new investigations.

Accounting experience has shown that, when charges for research expenses are deferred, it is invariably difficult to value these items. In auditing, it is first considered whether these expenditures should not have been absorbed in operating expenses when actually incurred. But if it is decided that it was proper to defer them, it is necessary to determine whether the period over which these items have been deferred is of reasonable length and not too long. The original value of a research product, such as a patent, is usually regarded as its cost (purchase price or developmental expenditure); and laboratory expenditures that have been directly unproductive of results are classed as indirect costs of such patents as have been developed from time to time.

BUDGETING OF RESEARCH EXPENSE

"Budgeting is the armory of financial management, and its sentinel is cost accounting."
—A Managemental Maxim

The use of budgets or operating schedules, for the purpose of forecasting operating results, has become an outstanding feature of the application of the principles of scientific management in the administration of industrial research. It is now recognized by many authorities that budgetary control of a research department or laboratory is a most effective mechanism for accomplishing resultful coördination within the department and with the other departments of the organization. This control, if adequate, surely reveals beneficial work, managemental defects, weak divisions and personnel, and opportunities.

The lay conception of a budget is that it is a collection or aggregate of figures relating to sums of money to be expended for definite purposes. Every properly prepared and correctly utilized laboratory budget, however, has for its cardinal purpose the induction of thought; it thereby assists research executives to look forward, to pursue the best roads to action, and to eliminate guess work and other mental as well as physical wastes. By the employment of such a budget, effectual laboratory accounting is made possible by periodic comparisons of estimates and actual results.

In these days of rapidly changing conditions, scientific management, which inexceptively operates on a factual basis, is endeavoring to develop improvements in its operational technic, so that an organization may be more quickly adjusted to meet economic changes. It is most important under these conditions that the research laboratory be alert, sensitive to change, and flexible in personnel, structure, and facilities; it will thus be always prepared, always ready to aid the organization of which it is a part. A flexible budget is a device that makes it easy to effect technical adjustments of this character whenever they are necessary. In particular, it makes it possible to do work during a coming year that cannot be foreseen.

It must be conceded here that budgetary control has several

limitations that are sometimes of serious concern in research laboratory management. In the first place, as is well known, every budgetary program is based on estimates. These estimates, however, are not supposed to be followed arbitrarily, but are intended for use with judgment and with revision as actual results reveal variations from the estimated performance. Secondly, budgetary control cannot replace management. But it is not the purpose of budgetary control to deprive a laboratory director of the essential freedom of action that ensures progressive management. Budgetary control cannot be perfected quickly; it requires time properly to make and use estimates of future plans.

In general, research results cannot be guaranteed in advance. As a matter of fact, the procedures of laboratory management do not provide for the assurance of success in the investigation of problems. It is moreover difficult to predetermine closely the time needed to solve and the amount of money required to investigate major or long-time basic production problems, which constitute the main tasks assigned to research laboratories. It happens occasionally, of course, that estimates of this type can be prepared on the basis of experience in prior investigations of similar problems; but while industrial research directors are cost conscious, they lack a full set of standards or measuring appliances for controlling the various cost elements and for determining variations in laboratory work.

PHARMACODYNAMIC AND NUTRITIONAL STUDIES ARE FREQUENTLY EXPENSIVE

Biochemistresses are the Bo-Peeps of science, but it is the cost of getting and caring for their experimental animals, and not the loss of the latter, that usually causes most concern.

Notwithstanding these obstacles, the managemental facts and mechanisms that are available can be used to evolve budgets of research, and thus provide a system of control that enhances the effectiveness of the laboratory and the cooperative position of its staff in the company organization. Such budgets, which may be monthly, quarterly, or annual, are divided into projects, with calculated costs of supplies, special equipment and general expense, and estimated salaries of personnel. Throughout the period the actual expenditures for research are checked against this laboratory budget. This system enables the officers of a company to compare expenses from year to year and to observe whether increases are justifiable.

The compilation of budgets of research should be done by the laboratory executive staff. These budgets must then be coördinated with the other activities of the company, examined and revised by the comptroller, reviewed by the general administration, and finally adopted by mutual agreement. In many companies a budget committee whose chairman is the comptroller is responsible to the president for the coördination of all budgets.

Management is rightly insisting upon the opportunity to observe the progress and accomplishments of research through the clarifying medium of the budget. Management understands or soon learns that scientific investigation cannot be charged ahead with the same accuracy as production. But the keen management of today requires reasonably close estimates of the cost of researches planned by the laboratory director and his staff, so as to determine whether the work can be begun, and, having allocated a definite amount of money to research, depends upon the director to spend this sum most advantageously.

Even in laboratories that are not operated under a budget system there is usually kept a careful record of the expenditures for salaries, supplies, insurance, etc., all classified in detail, for following in exercising economy in the conduct of work. Every laboratory manager should know enough about accounting to know when he needs an accountant.

PROCEDURES OF RESEARCH CONTROL

"In the laboratory, as in the plant, we must record the volume of work that is to be done and the rate and cost at which it is completed."
—Another Managemental Maxim

It is not rare to find that the expense of a carefully managed laboratory is largely balanced against the savings that have ensued from the tangible results of research effort. In such cases only a comparatively small charge has to be made for intangibles. As pointed out, the expense of research pertaining to the latter can be fairly charged off to product and market improvements.

If this accounting practice must have justification, support can be easily found in the fact that industrial laboratory investigations are principally basic production researches, aimed toward (1) the improvement of processes in use, (2) the betterment of products already in the line, (3) the discovery of new products, and/or (4) the evolution of novel processes. The process work of a laboratory establishes its connection with production; the research on products brings out its lineal relationship to marketing. Industrial research, production, and marketing, then, are closely interdependent in planning and effecting technologic progress. In consequence, it is plain that the value of a laboratory cannot be appraised fully in terms of definite economies resulting from its accomplishments. This conception of the place and utility of the laboratory in an industrial organization has led specialists to contend that gross sales should be chosen as a basis for determining the amount of the appropriation for research and that one per cent, at least, is the reasonable ratio of research to gross sales.

Research control that has due regard for these facts and for the time factor is capable of estimating the value of the results of laboratory work and of operating productively according to a budget. It is believed by some specialists that a docket system of research control enables the laboratory director to evaluate with most certainty the cost of the work entrusted to him and his staff and to ascertain a capacity load for the latter. This procedure also gives him the means to fix responsibility if changes are made in any of the projects under the docket. At Mellon Institute we control all researches similarly, according to definite investigational programs and fellowship budgets, by close advisory contact and conferences with the fellows, supplemented by weekly progress reports of the latter and by statements from our accounting department.

The progress chart, such as the device introduced by Gantt,

THE LABORATORY STOREROOM IS THE LARDER FOR ITS EXPERIMENTAL WORK

The stores department of a properly managed laboratory checks in and places newly received supplies, keeps apparatus and chemicals systematically and safely, and disburses these articles under the authority of requisitions.

which is used in measuring production, sales, expenses, etc., may be applied in planning certain types of laboratory work. A skeleton form for projects under a research docket and also a form for a monthly time sheet for use in determining monthly costs of researches are given in Donald's very helpful handbook (*1*). In employing the monthly time sheet, as described therein by R. G. Caswell, each research laboratory employee records his own distribution of his time to the projects on which he has been assigned to work. By its use there can be calculated the distribution of salary to the projects. Other items of expense, except supplies and special equipment which are charged to the projects for which they were ordered, are generally prorated to the respective projects in the same ratio that salary charged monthly to a particular project bears to the total laboratory salaries. Among these items are cleaning, light, heat, power, steam, water, insurance, and depreciation. The depreciation rate of laboratory equipment is generally given as 10 per cent.

The case system of research control, used with success by Arthur D. Little, Inc., was outlined by Earl P. Stevenson (*2*). In this procedure daily reports on special cards are said to afford a satisfactory means of recording the distribution by hours of the working time of the laboratory staff. The accounting department then converts this time into dollars and cents, and these figures are followed in budgeting the time of the staff for the next month. A system of this type evidently has additional utility: it enables the easy keeping of an accumulative record illustrative of the progress of researches in hand, and it facilitates a clear insight into the cost of certain researches as compared with other investigations.

GENERAL DISCUSSION OF RESEARCH EXPENSES

"The human element is basic in research, just as it is in business and industry."
—An Apothegm of Personnel Management

The expenditures for research in a large laboratory comprise the salaries and expenses of executives; office, library, shop, storeroom, and building operation and maintenance; salaries of research men and assistants; supplies and house charges, which will include as well special charges for shop and office work; and traveling expenses incurred during investigational inquiries and during the attendance of members of the research staff at appropriate scientific gatherings.

SALARIES OF RESEARCH STAFF MEMBERS. The initial salaries of research men will depend upon the standing of each man and upon the importance of the problem to be studied by him. No research specialist should ever be employed until after a personal interview. This interview can well supplant the necessity for careful weighing of certain letters of recommendation. Furthermore, as working and living conditions are important considerations for the specialist, such an interview will afford the candidate the opportunity for an inspection of the laboratory and an introduction to future associates. With no training other than that of the university, the suggested entrance salaries for the first year, according to highest degree held, are as follows: B.S., $1500 to $1800; M.S., $1800 to $2100; and Ph.D., $2500 to $3000. It may well be stipulated that, in the event of substantial progress being shown, the minimal beginning salaries will be increased at the end of six months to $1800, $2100, and $3000, respectively. In several laboratories with which we are familiar, the initial salary for the Ph.D. is $2750 for the first year. By this arrangement the salary for the year will be equalized therewith, a probationary period provided for, and the self-respect and professional attitude of the man worthily stimulated.

When the candidate possesses additional professional training, the conditions of his employment become competitive. In general, however, the salary should be comparable with that of men of equal experience already in the laboratory. Even in this case a probationary period of service is highly desirable.

Salary increases is a much debated subject, with probably more argument than over entrance salaries. Salary advancement is necessary for its psychological effect, but must be judiciously administered for the same reason. A wise policy will provide for reasonable increases based on merit, seconded by family considerations.

We all know that no man can be at his best when domestic difficulties compete with laboratory problems for his attention. Financial embarrassment will kill as much energy as home ailments. The young Ph.D. has just left a long period of financial non-production. Even under the most favorable circumstances he has undoubtedly reached the age of twenty-five, with the average probably much nearer to thirty.

Examination of our experience at Mellon Institute shows that, with few exceptions, the salaries of the research men amount to about 60 per cent of the gross cost of each industrial fellowship.

RESEARCH SUPPLIES. Although very constant over a period of years for a laboratory organization, this item may vary widely for different problems. It is often difficult to predict in advance just what the expenditure on supplies for a given research will be, although the past experience of the

laboratory will be a guide. One of the most expensive types of investigation to conduct is upon pharmacodynamic problems, in which the maintenance of a constant supply of animals of definite and pure pedigree is essential. We have understood that in some pharmacologic laboratories the expenditure for supplies, including animals, has reached 35 per cent of the total cost of research, but such experience is probably both exceptional and extreme. Our own records show an expenditure for industrial fellowship supplies, including traveling and house charges, of 20 per cent of the total fellowship receipts.

Traveling, a variable item, may be considered as a part of the experimental work. We have already alluded to the desirable practice of sending technical men to pertinent meetings of scientific societies. For the average man an amount approximating $150 should be provided each year for this purpose. Specialists of higher standing may frequently be obliged to spend much more, and for this reason it is difficult to lay down any definite provisions, but rather it is desirable to recognize that the general overhead of the laboratory should carry these charges. Averaging all traveling, on all types of research problems, at least 5 per cent of the budgeted cost should be available therefor. Probably the Mellon Institute experience on this point is a little unusual, because, in the majority of cases, a certain amount of travel is necessary in order to maintain a proper contact between the fellow and the donor's organization. Furthermore, in association fellowships, a form of research development that does not usually come into the province of the industrial research laboratory, a considerable amount of time and money may be spent in plant visits. It is often necessary, especially at the commencement of an investigation, to make a search of the literature in one or more special libraries. The cost thereof must be borne in mind as a possible traveling charge against any research.

The actual cost of storeroom supplies is generally charged against the researches. Economies in storeroom operation may be effected by securing the interest of the research chemists. In our own organization we have a social group, the Robert Kennedy Duncan Club, to which all fellows automatically belong. One of its standing committees is the storeroom committee, having a member from each floor, with a chairman in addition. This committee meets regularly with our assistant director who combines the functions of business manager and purchasing agent, for the joint purpose of awarding orders on bids previously received and of determining the general storeroom policy. Through the aid of this committee the storeroom has become of real service to all fellows. The committee has made a careful examination of all types of supplies, both apparatus and reagents, as they have been found in the storeroom and as they have been requested by fellows. The committeemen have effected standardization by elimination of many grades of reagents and many sizes of apparatus. They have determined what specifications are desirable and in a number of cases have ordered the U. S. P. grade for either C. P. or reagent quality, or both, and have formed decided opinions as to brands to be used or jobbers to be dealt with.

Recently the committee has also taken an active part in a complete inventory, house-cleaning, and rearrangement of the storeroom. Naturally this help has been of much assistance to the purchasing agent, himself a mechanical engineer. Some purchasing agents buy according to rigid specifications, which, in our own experience, are not always rigorously enforced; others buy entirely for price, while still others are worshippers of quantity discounts. Our committee has not hesitated to divide orders where the interest of the Institute is benefited, and has in every way used excellent judgment in the placement of orders.

Our business office has effected other savings in storeroom operation by the installation of a perpetual inventory of the Kardex type. By daily entry of sales and purchases, the office is in possession of accurate information regarding the actual stock that may be kept on hand most economically and yet serve practically all calls. Furthermore, the business office is able thereby to weed out all dead material and to reduce stocks of slowly moving items.

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(2) Stevenson, E. P., Natl. Assoc. Cost Accountants, *Bull.* 10, No. 19, Sect. I, 1272–3 (1929).

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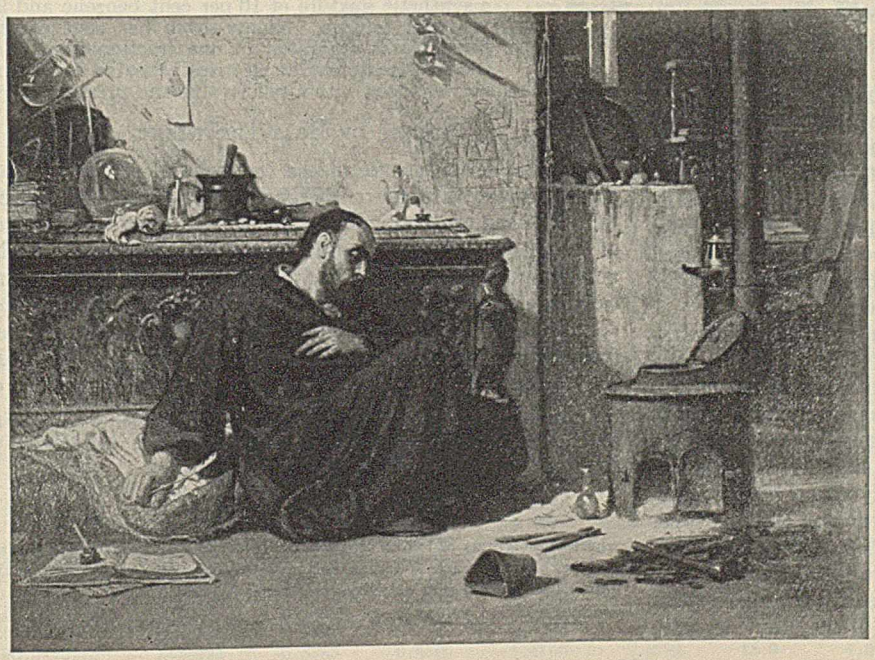

The Alchemist
by
Elihu Vedder

Elihu Vedder (1836–1923) was a famous American genre and figure painter. He executed five murals, symbolic of government, for the Library of Congress, also the beautiful mosaic "Minerva" at the head of the main staircase of the Library. Vedder probably achieved his greatest renown through his illustrations of the Rubaiyat.

(No. 18 of the Percolator Series. See page 317 in our March issue for conditions of sale.)

Highly Cracked Gasoline

A Study of Composition before and after Heat-Treatment

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THE effect of heat-treatment on various unsaturated hydrocarbons has long been known. Many unsaturated hydrocarbons are capable of polymerization at normal temperatures. For example, cyclopentadiene on standing at ordinary temperatures, is converted into dicyclopentadiene without the aid of any reagent (*11*). Other hydrocarbons, such as hexylene (*8*), trimethylethylene (*9*), amylene (*27*), methylpropylethylene (*15*), allene (*19*), isobutylene (*20*), and ethylene (*1, 6, 12, 16, 24, 25, 31*), have been caused to undergo polymerization by the application of heat and pressure. Various catalysts have been found which accelerate the polymerization of nearly all types of unsaturated hydrocarbons (*7, 13, 22, 28, 29*).

It seems desirable, in view of the great amount of interest shown in the utilization of highly cracked gasolines, especially those produced by the vapor-phase cracking process, to study the composition of such a gasoline distillate and the changes in composition effected when this material is subjected to treatment at temperatures of about 300° C. which are below the temperatures employed in cracking. Brooks and Parker (*3*) noticed that cracked gasolines produced by the vapor-phase cracking process were normally colored bright yellow and reacted energetically with sulfuric acid, producing a considerable rise in temperature and yielding black tarry materials. They also found that, if this vapor-phase distillate was treated in a steel autoclave for about 3 hours to temperatures of 315–360° C., and if the liquid was redistilled after treatment, a colorless distillate was obtained up to 205° C. and the distillate no longer reacted energetically with sulfuric acid. They therefore assumed that hydrocarbons containing conjugated unsaturated groups have been removed by polymerization, for the mono-olefins are known to be colorless.

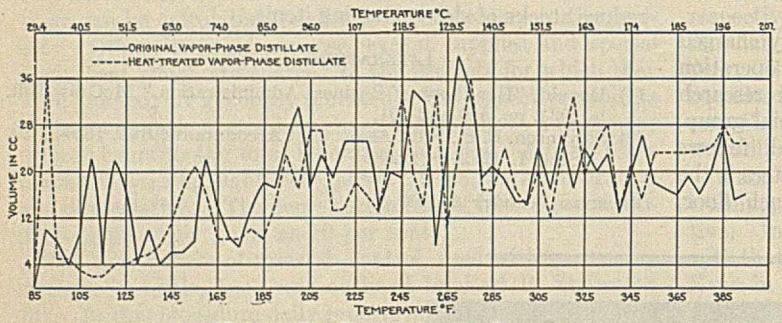

Figure 1. Distillation Curves

Lebedev (*18*) distinguishes four general types of polymerization pertaining to unsaturated hydrocarbons: (1) the stilbene type, dimers probably having cyclobutane-type structure; (2) the styrene type, yielding amorphous polymers of high molecular weight and unknown structure; (3) the acetylene type, forming benzene or its derivatives; and (4) the 1, 3-butadiene or isoprene type, forming cyclic polymers of high molecular weight. The structures of the styrene and stilbene type, when ascertained, may show that these two classes are essentially of the same type of polymerization. To the above, Brooks (*2*) adds two more general classes: (5) the allene type, yielding cyclobutane derivatives; and (6) the ethylene type, forming unsaturated acyclic polymers. The fundamental change when methylacetylene (*21*) or isopropylethylene (*23*) is subjected to heat-treatment, however, is one of isomerization into allene and trimethylethylene, respectively.

Experimental Procedure

In order to determine the changes in composition effected when a highly cracked gasoline is subjected to temperatures of about 300° C., the following procedure was adopted:

A highly cracked gasoline distillate was carefully fractionated into 10° F. (5.6° C.) fractions, and the physical and chemical properties determined on each fraction. A quantity of the same gasoline distillate was treated at 300° C. under 68 atmospheres pressure for 6 hours in a steel bomb; this treated material was then fractionated into 10° F. fractions (in the same manner as the untreated distillate was fractionated); and the changes in physical constants and composition, which had been effected in the various fractions by the heat-treatment, were noted. From the data thus obtained, general conclusions were drawn as to the types of hydrocarbons present in the most important fractions.

The vapor-phase distillate used in this investigation was produced in the commercial operation of a full-sized vapor-phase cracking still; the charging stock, which was a light solar oil, was exposed to a maximum temperature of approximately 600° C.; the time was about 10 minutes and the pressure of the order of 100 pounds per square inch. This vapor-phase distillate possessed a light yellow color, and an initial boiling point of 29.4° C.; end point of 205° C.; specific gravity of 0.7723 (d_4^{20}); iodine value (Hanus method) of 122; iodine addition value of 80.27 and substitution value of 21.1 (Johansen method, *17*); contained 35.0 per cent olefins, 17.0 per cent aromatics, 25.9 per cent naphthenes, and 22.1 per cent paraffins as analyzed by the Garner method (*10*); and contained 0.23 per cent sulfur by the lamp method.

The fractionating column used in this investigation was similar to that used by Peters and Baker (*26*). The efficiency of this column was tested on a synthetic mixture of 10 per cent benzene and 90 per cent toluene. Ninety-seven per cent of the benzene was separated in one fractionation. For the heat-treatment, an electrically heated steel bomb was used which was fitted with a relief valve and pressure gage.

Results of Heat-Treatment

The distillation curves of the treated and original vapor-phase distillates are shown in Figure 1. The specific gravities, refractive indices, and iodine addition and substitution values of the 10° F. (5.6° C.) fractions are given in Table I. The percentage of unsaturated hydrocarbons in each fraction was calculated from the iodine addition values, taking into account their probable molecular weights which were derived from known hydrocarbons having their boiling points within the range of each fraction.[1] Of course such a method of

[1] Let MW be the molecular weight of the hydrocarbon present in the fraction. Each gram mole of unsaturated hydrocarbon will add 253.86 grams of iodine. Then by the equation,

$$\frac{253.86}{MW} = \frac{X}{100}$$

where X = grams of iodine united with 100 grams of unsaturated hydrocarbon. The amount of iodine united with 100 grams of fraction is the iodine addition value as actually determined. Then,

$$\frac{\text{iodine addition value}}{X} = \text{per cent unsaturates by weight in the fraction.}$$

calculating the olefins present in the different fractions has certain limitations. Acetylenic hydrocarbons, if present, would introduce an error. However, none of the fractions yielded acetylides when treated with ammoniacal copper chloride, which indicates the absence of acetylenic hydrocarbons with the —C≡C—H structure. There is a possibility also of mixed hydrocarbons, such as the olefin aromatic type, being present in the higher-boiling cuts, but the first of this series would be styrene which boils at 146° C. Since no perfect method of analyzing such a complex mixture of hydrocarbons as is found in highly cracked gasolines exists at the present time, a certain amount of speculation is necessary in an exploratory field.

From a comparison of the percentage of unsaturated hydrocarbons in each 10° F. fraction of the original vapor-phase distillate with the corresponding fraction of the heat-treated material, it will readily be seen that in each fraction certain olefins have either been removed or chemically changed by the heat-treatment. Figure 2 shows percentage of unsaturates plotted against the middle boiling point of the fraction.

An analysis of the original and the heat-treated distillates to 201.5° C. shows that not only has there been a decrease in olefins, as already indicated by the iodine values of each fraction, but that the percentage of naphthenes has been increased by the heat-treatment (analysis by the Garner method, *10*):

	Original Vapor-Phase Distillate to 201.5° C.	Heat-Treated Vapor-Phase Distillate to 201.5° C.
	%	%
Olefins	35.0	24.5
Aromatics	17.0	15.5
Naphthenes	25.9	34.2
Paraffins	22.1	25.8

A list of the known hydrocarbons[2] which may be contained in a highly cracked gasoline distillate was compiled and their boiling points, specific gravities, and refractive indices were obtained from the literature. Using this information and the data obtained experimentally on the 10° F. fractions from the heat-treated and original vapor-phase distillates, certain conclusions were drawn as to the composition of the original distillate and the changes effected by the heat-treatment.

[2] The complete list, comprising 144 specific hydrocarbons with their boiling points, specific gravities, and refractive indices, is contained in C. R. Payne's thesis.

The fact that the substitution value (Johansen method) in the majority of the fractions boiling above 90.5° C. is increased by the heat-treatment indicates that polymerization of unsaturated hydrocarbons of lower boiling points has taken place to produce hydrocarbons containing hydrogen atoms easily replaced by halogen. This type of hydrocarbon might also be produced by the isomerization under the influence of heat.

In the fraction boiling from 85° to 95° F. (29.4° to 35.0° C.) the known olefins likely to be present are isopropylethylene, 2-pentene, trimethylethylene, and unsymmetrical methylethylethylene. The specific gravity of the fraction as determined (Table I) is 0.6647 (d_4^{20}). The analysis shows that it contains 39.1 per cent of unsaturated hydrocarbons. The average specific gravity of the known olefins possibly present is 0.651 (d_4^{20}), and the average specific gravity of the paraffins is 0.631 (d_4^{20}). A fraction so made up would have a specific gravity of 0.638 (d_4^{20}) if all the saturated hydrocarbons were paraffins. But the determined value of the fraction is 0.6647 (d_4^{20}), and the 60.9 per cent of the saturated hydrocarbons must contain some of higher specific gravity than the paraffins. The low boiling range makes the presence of aromatics very unlikely, so some naphthene is most likely present. If methylcyclobutane—boiling point 42.0° C., specific gravity 0.753 (d_4^{20})—is assumed to be present in an azeotropic mixture boiling within this range to the extent of approximately 20.0 per cent, the fraction would have a specific gravity which closely approximates the determined value. The corresponding fraction from the treated vapor-phase distillate contained 35.0 per cent of unsaturates and a determined specific gravity of 0.6509 (d_4^{20}). Using a similar line of reasoning as above, and assuming methylcyclobutane to be present to the extent of 10.0 per cent, the fraction would have a specific gravity agreeing with the determined value. This is to be expected, for methylcyclobutane would not be affected by the heat-treatment.

The fact that the percentage of naphthenes present in the fraction from the treated vapor-phase distillate is less than in the fraction from the original does not mean that naphthenes have been removed. There is really a greater amount of naphthenes in the fraction from the treated distillate, but due to its larger volume the percentage is less. The fact that the

Table I. Physical and Chemical Properties of Fractions

Fraction		Specific Gravity on:		Refractive Indices on:		Iodine Addition on:		Iodine Substitution on:		Unsaturates in:	
		Original d_4^{20}	Treated d_4^{20}	Original n_D^{20}	Treated n_D^{20}	Original	Treated	Original	Treated	Original	Treated
°C.	°F.									%	%
29.4– 35.0	85– 95	0.6647	0.6509	1.3919	1.3754	142.8	127.0	7.2	4.0	39.1	35.0
35.0– 40.5	95–105	0.6666	0.6571	1.3821	1.3739	138.2	94.1	8.1	6.2	38.0	25.9
40.5– 46.0	105–115	0.6667	0.6629	1.3810	1.3758	163.6	86.7	21.0	8.1	45.1	23.9
46.0– 51.5	115–125	0.6650	0.6641	1.3860	1.3770	166.0	72.1	1.48	1.03	45.7	19.8
51.5– 57.0	125–135	0.6792	0.6730	1.3886	1.3810	160.0	69.1	1.9	2.21	44.1	19.0
57.0– 63.0	135–145	0.6923	0.6823	1.3910	1.3854	158.5	74.6	2.8	2.9	43.1	20.5
63.0– 68.5	145–155	0.7167	0.7032	1.4031	1.3963	130.0	71.0	10.15	14.0	43.1	23.5
68.5– 74.0	155–165	0.7460	0.7219	1.4179	1.4040	126.0	68.2	10.78	15.2	41.7	22.5
74.0– 79.5	165–175	0.7626	0.7295	1.4192	1.4061	127.9	51.7	3.0	3.25	42.3	17.1
79.5– 85.0	175–185	0.7170	0.7245	1.4086	1.4053	111.9	48.0	27.2	16.0	37.5	15.9
85.0– 90.5	185–195	0.7403	0.7268	1.4105	1.4041	104.6	41.5	17.9	14.3	34.6	13.7
90.5– 96.0	195–205	0.7458	0.7289	1.4165	1.4108	82.6	47.5	23.3	19.2	31.7	18.2
96.0–101.5	205–215	0.7738	0.7521	1.4287	1.4207	72.0	35.5	20.5	26.1	27.7	13.7
101.5–107.0	215–225	0.7660	0.7612	1.4320	1.4256	73.9	31.8	33.8	28.0	28.4	12.2
107.0–113.0	225–235	0.7610	0.7550	1.4265	1.4225	72.6	30.7	20.17	21.2	27.9	11.8
113.0–118.5	235–245	0.7536	0.7552	1.4234	1.4219	81.6	35.6	28.8	31.6	31.4	13.7
118.5–124.0	245–255	0.7634	0.7609	1.4300	1.4241	63.4	23.4	27.1	28.1	27.9	10.3
124.0–129.5	255–265	0.7875	0.7742	1.4380	1.4306	63.2	22.2	26.5	37.8	27.8	9.7
129.5–135.0	265–275	0.7869	0.7844	1.4419	1.4377	62.3	22.5	23.1	60.1	27.4	9.8
135.0–140.5	275–285	0.7889	0.7820	1.4390	1.4360	54.5	21.9	26.5	47.8	24.0	9.5
140.5–146.0	285–295	0.7900	0.7802	1.4370	1.4337	53.0	27.4	34.0	51.3	26.2	13.5
146.0–151.5	295–305	0.7713	0.7868	1.4400	1.4365	51.4	14.6	38.3	45.2	25.4	7.2
151.5–157.0	305–315	0.7747	0.7943	1.4430	1.4425	40.0	14.5	31.1	48.2	19.8	7.2
157.0–163.0	315–325	0.8109	0.7963	1.4499	1.4460	37.4	14.5	31.6	70.7	18.5	7.2
163.0–168.5	325–335	0.8193	0.8090	1.4521	1.4496	32.4	16.3	29.1	38.2	16.1	8.1
168.5–174.0	335–345	0.8210	0.8120	1.4532	1.4519	29.2	11.0	27.1	37.2	16.0	6.1
174.0–179.5	345–355	0.8234	0.8162	1.4554	1.4545	22.3	2.0	64.9	42.8	12.2	1.1
179.5–185.0	355–365	0.8318	0.8227	1.4590	1.4577	24.4	0.0	43.4	45.5	13.4	0.0
185.0–190.5	365–375	0.8362	0.8293	1.4635	1.4608	19.4	0.0	49.4	48.1	10.7	0.0
190.5–196.0	375–385	0.8493	0.8437	1.4700	1.4672	13.0	4.0	43.2	72.5	7.8	2.4
196.0–201.5	385–395	0.8585	0.8569	1.4760	1.4720	15.0	4.0	28.8	71.4	9.0	2.4

volume of this fraction from the treated vapor-phase distillate is larger than that from the original material is very likely due to isomerization phenomena in the fraction boiling from 105° to 115° F. (40.5° to 46.0° C.). That fraction formed a peak in the distillation curve of the original vapor-phase distillate which was entirely absent from that of the heat-treated material (Figure 1). It seems reasonable to assume the isomerization of 1-pentene (boiling point 40.0° C.) into either trimethylethylene or 2-pentene by the heat-treatment. Trimethylethylene (*14*) is the most stable of the isomeric pentylenes, and isopropylethylene is the least stable. Trimethylethylene and 2-pentene do not rearrange into any of the other forms and would probably be found in the fraction of vapor-phase distillate boiling from 85.0° to 95.0° F. (29.4° to 35.0° C.)

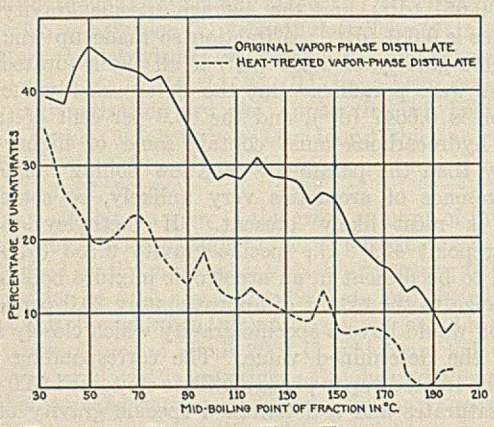

FIGURE 2. EFFECT OF HEAT-TREATMENT ON UNSATURATES IN EACH FRACTION

It was found that, if the specific gravities or refractive indices of the fractions from the original vapor-phase distillate were plotted against the middle boiling points of the fractions, three maxima occurred in each curve: the first between 68.0° and 80.0° C.; the second between 95.0° and 110.0° C.; and the third between 125.0° and 140.0° C. In the corresponding curves for the fractions from the heat-treated distillate, the first maximum was practically removed, while the last two remained. Four fractions from the original distillate and four fractions from the heat-treated vapor-phase distillate lying within the maxima in the specific gravity and refractive-index curves were analyzed for their content of unsaturated hydrocarbons, aromatics, naphthenes, and paraffins. The percentage of unsaturated hydrocarbons was determined from the iodine addition value on the fraction as previously explained; aromatics were determined by treating with fuming nitric acid at −10° C., which removed the olefins and aromatics in the acid layer. By measuring the volume loss, the percentage of aromatic and unsaturated hydrocarbons by volume was determined. But the olefins were determined in percentage by weight; and, to determine the aromatics by difference, it is necessary to take into account the specific gravities of the fractions before and after acid treatment.[3]

[3] During the course of the investigation the following equation was developed for the determination of the percentage of aromatics which facilitates this calculation:

$100 - \frac{100}{\text{sp. gr.}}$ of fraction × percentage by volume remaining after acid treatment × sp. gr. of fraction after acid treatment − percentage unsaturates by weight = percentage aromatics.

Then, to determine naphthenes + paraffins:

Percentage by volume remaining after acid treatment × $\frac{100}{\text{sp. gr.}}$ of fraction × sp. gr. of fraction after acid treatment = percentage naphthenes and paraffins.

The percentage of naphthenes and paraffins can then be determined separately from the curve formed by plotting the specific gravity of known naphthenes and paraffins against their boiling points, the specific gravity of the naphthene-paraffin mixture being known.

From the specific gravities and boiling points of known naphthenes and paraffins, and the specific gravity of the fraction remaining after acid treatment, the percentage of naphthenes and paraffins was readily calculated. While this method of analysis would not be accurate for a gasoline distillate of wide boiling range, it can be applied with a good degree of accuracy to fractions of the distillate having a boiling range of 10° F. (5.56° C.) where the hydrocarbons which can be present may be predicted on the basis of their boiling points.

ANALYSES OF FRACTIONS

The fraction boiling from 155° to 165° F. (68.5° to 74° C.) was analyzed by the above method with the following results:

	Fraction from Original Vapor-Phase Distillate	Fraction from Heat-Treated Vapor-Phase Distillate
	%	%
Olefins	41.7	22.5
Aromatics	8.8	12.5
Naphthenes	22.2	25.5
Paraffins	27.3	39.5

The percentage of olefins was decreased to almost half the original value by the heat-treatment. Averaging the specific gravities of the known aromatics, naphthenes, paraffins, and aliphatic olefins that could possibly be present in the original fraction, and multiplying these averaged values by the percentage of each of the above hydrocarbons present and then adding these values, a fraction so constituted would have a specific gravity of 0.7137 (d_4^{20}). The specific gravity as actually determined on the fraction is 0.7460 (d_4^{20}). Evidently then, there must be some hydrocarbons of higher specific gravity present which have not been included in the above calculations. Only aliphatic olefins were considered to be present when the specific gravity of the fraction was calculated above, but if part of the unsaturated hydrocarbons is considered to be cyclic in character—and this is a reasonable assumption—the calculated specific gravity can be made to agree with the determined value. For example, cyclohexene [boiling point 83° C., specific gravity 0.810 (d_4^{20})] may easily be present in the azeotropic mixture. Cyclohexadiene [boiling point 80.5° C., specific gravity 0.842 (d_4^{20})] and methylcyclopentene [boiling point 72° C., specific gravity 0.775 (d_4^{20})] might also be present. Considering only aliphatic olefins to be present, and calculating in a like manner the specific gravity of the fraction from the treated vapor phase distillate, a value of 0.7268 (d_4^{20}) is obtained as compared to 0.7219 (d_4^{20}) actually determined. This is a close agreement and strengthens the argument for the presence of cycloalkenes in the original fraction, for they would presumably be easily polymerized under the influence of heat and pressure. There seems little reason to doubt, then, that cycloalkenes were present in the fraction from the original distillate and caused the first maximum in the specific-gravity and refractive-index curves. Assuming these cycloalkenes to have been removed by polymerization upon heat-treatment, readily explains the absence of a corresponding maximum in the specific-gravity and refractive-index curves for the heat-treated distillate. The boiling range of the fraction limits the hydrocarbons which these cycloalkenes may be: (1) cyclohexene, (2) cyclohexadiene, and (3) methylcyclopentene. The very high specific gravity of the fraction argues more for the presence of the first two than of the third.

Gasoline distillates produced by the vapor-phase cracking process are known to be quite susceptible to oxidation. Some of the resulting oxidized hydrocarbons are volatile, and consequently, if they were present in high enough concentrations, they would influence the density and percentages of hydrocarbon groups present in the fractions. However, in the oxidation test of Voorhees and Eisinger (*30*) (where a

gasoline distillate is oxidized for several hours at 100° C. in a closed container, from which the air had been expelled and replaced by oxygen, and the gasoline evaporated in an inert atmosphere), showed vapor-phase distillate to deposit approximately 2 per cent of its weight in oxidized products. In this investigation special precautions were taken against oxidation of the vapor-phase distillate and resulting fractions; hence the authors believe that the physical constants and chemical analyses obtained were not influenced by the presence of oxidized hydrocarbons. All of the fractions gave negative tests for aldehydes and peroxides.

Benzene was isolated from the fraction boiling from 68.5° to 74° C. as *m*-dinitrobenzene.

The following is the analysis of the fractions boiling from 215° to 225° F. (101.5° to 107° C.):

	Fraction from Original Vapor-Phase Distillate	Fraction from Heat-Treated Vapor-Phase Distillate
	%	%
Olefins	28.4	12.2
Aromatics	31.5	37.6
Naphthenes	19.4	25.4
Paraffins	20.7	24.8

The analysis of fractions boiling from 225° to 235° F. (107° to 113° C.) gave the following results:

	Fraction from Original Vapor-Phase Distillate	Fraction from Heat-Treated Vapor-Phase Distillate
	%	%
Olefins	27.9	11.8
Aromatics	26.3	34.9
Naphthenes	19.6	18.8
Paraffins	26.2	34.5

The above four fractions occur within the second maximum of the specific-gravity and refractive-index curves. The analyses show both aromatics and naphthenes to be present in high concentrations, and, since both types of hydrocarbons have high specific gravities and refractive indices, the second maximum in the above curves is probably due to these types of hydrocarbons; these naturally remained with the heat-treated product. Toluene was isolated and identified from the fraction boiling from 107° to 113° C. as 2,4-dinitrotoluene.

Analysis of fractions boiling from 265° to 275° F. (129.5° to 135° C.):

	Fraction from Original Vapor-Phase Distillate	Fraction from Heat-Treated Vapor-Phase Distillate
	%	%
Olefins	27.4	9.8
Aromatics	21.7	28.1
Naphthenes	23.9	32.3
Paraffins	27.0	29.8

Here again the aromatics and naphthenes are present in fairly high concentrations and are probably the cause of the third maximum in the specific-gravity or refractive-index curve. The xylenes, if present in the distillate, would probably be found in this fraction in a minimum-boiling mixture. For example, practically all of the toluene (*5*) in a petroleum distillate was found to boil below 110° C., the boiling point of pure toluene. The largest fraction boiling between 98° and 99° C. contained the larger amount of toluene but the maximum concentration of toluene was found in the fraction boiling from 107° to 108° C. Likewise all the benzene (*4*) in a petroleum distillate was found as a constant-boiling mixture with the hexanes in the fractions boiling below the boiling point of pure benzene. The high specific gravity and refractive index of this fraction indicate that the xylenes are present in a minimum-boiling mixture, just as the greatest amount of toluene and benzene was found in the fractions below their true boiling points.

A comparison of the distillation data of the treated and original vapor phase distillates

	Original Vapor-Phase Distillate	Treated Vapor-Phase Distillate
	%	%
Residue above 201.5° C.	15.79	20.54

shows that some unsaturated hydrocarbons, which before treatment boiled below 201.5° C., were polymerized by the heat and pressure treatment to hydrocarbons boiling above 201.5° C.

Conclusions

As a result of this investigation the following conclusions were derived as to the composition of the original vapor-phase distillate and the changes in composition effected by the heat and pressure treatment.

1. The percentage of unsaturated hydrocarbons was decreased by the heat and pressure treatment in all the fractions isolated. The percentage of naphthenes in the whole distillate up to 201.5° C. was increased by the heat and pressure treatment.

2. Several additional changes are attributable to polymerization caused by the heat and pressure treatment.

a. Increase of material boiling above 201.5° C. from 15.79 to 20.54 per cent.

b. Disappearance of probable presence of cycloalkenes.

c. Formation of hydrocarbons containing hydrogen atoms which are easily replaceable by halogen.

3. As to the composition of the cracked gasoline:

a. Benzene and toluene were identified in selected fractions.

b. Presence of methylcyclobutane was inferred in the fraction boiling from 29.4° to 35.0° C.

c. In general the proportion of unsaturated hydrocarbons was found to decrease as the boiling point increased.

d. The physical properties, as given in Table I, in general indicate that the proportion of paraffinic hydrocarbons decreases and the percentage of naphthenes and aromatics increases as the boiling point increases.

Acknowledgment

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Impervious Crucibles of Magnesium Oxide

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Refractory crucibles of magnesium oxide have been prepared that are recrystallized to translucence and impervious to air under pressure at room temperature.

The crucibles are formed by pressing the moistened refractory powder in two steps in such a manner that the base is welded onto the walls. In this way a structure of uniform density and strength is obtained. Firing is carried out in the high-frequency induction furnace with graphite inductor at a temperature of about 2600° C.

Significant variables are the relative pressure in forming the base and walls, the fineness distribution of the refractory powder, and the duration of firing above 1800° C.

Owing to their dense structure, these crucibles are much more resistant to attack by slags than are porous crucibles.

For the experimental melting of high-temperature alloys, magnesium oxide is particularly suitable as a refractory because of its high melting point, 2800° C. (*4*), and its resistance to reduction. In melts which involve slags as in the metallurgical studies carried out at the Pittsburgh Station of the Bureau of Mines, not only is the chemical resistance to the slag to be considered, but equally important is the texture of the crucible.

It is commonly known that a porous refractory is much more rapidly attacked by slag than a dense one. As it was desired to employ magnesia crucibles in slag studies, attention was concentrated on preparing such crucibles so that they would be vitrified and impervious.

Tritton (*7*) rendered the surface of magnesia and other refractories impervious by playing an arc in the interior of the rotating crucible shape. Adcock and Turner (*1*) have formed impervious tubes of alumina by glazing the outside surface by means of the oxyhydrogen flame. In the present work it was found possible to prepare impervious crucibles of magnesium oxide by direct heating at temperatures around 2600° C. in the Ajax-Northrup high-frequency induction furnace.

Formation

The crucibles were made by pressing at loads up to 60,000 pounds in a manually operated hydraulic press. Two of the common difficulties met in this procedure are sticking of the crucible to the walls of the die during removal and nonuniform density of the product. To prevent sticking, the usual expedients of oiling and greasing the die or of lining it with paper, etc., were tried, but with indifferent success. It was finally found that the combination of keeping the walls of the core and die scrupulously clean and bright, and moistening the refractory powder, not with water, but with dilute hydrochloric acid solution rendered the removal of the crucible easy. The hydrochloric acid also served to eliminate air-drying cracks completely.

In order successfully to fire the crucible in the high-frequency furnace at the required temperatures, it was found that the structure of the green crucible must be as uniform as possible. Owing to the nonplastic nature of the moistened powder, there is no flow under pressure, so that, in pressing in one operation, some parts are highly compressed and others relatively slightly. In order to overcome this difficulty, the pressing was effected in two operations, first of the walls and then of the base; in other words, the base was welded to the walls after the latter had been consolidated. In a general way the effectiveness of such a procedure will depend upon the extent to which the physical nature of the powdered material is altered by pressing. If the alteration is great, conditions at the surface to be welded will, because of the first pressing, be different from those obtaining throughout the remainder of the powder, and a discontinuity will result at this place. If, on the other hand, the effect of pressing is merely to force the particles into closer juxtaposition, then the weld will be indistinguishable from the remainder of the pressed body.

Hagen (*3*) has classified solid substances, according to the physical properties of their compressed powders, into six categories, ranging from plastic to pulverulent and nonpressable. In the latter instance, pressure exerts no physical effect other than to bring the grains closer together. Pulverulent substances are hard and have a high melting point. Fortunately these are precisely the properties possessed by the nonplastic refractories, and this accounts for the success observed in the two-step method of pressing the crucible.

As will be discussed below, an important factor to be considered in the two-step formation of the raw crucible is the microscopic particle-size distribution of the refractory powder.

It has been found that the addition of a little phosphoric or boric acid in the water used to moisten the powder helps to overcome any tendency toward the formation of small, fine cracks during firing.

Procedure of Formation. Figure 1 shows the details of the steel mold. Die *A* is split in two halves, each of which is case-hardened on the interior. The steel core, *B*, has a taper of about 2 in 1000. Plus and minus signs indicate clearances of about 0.003 inch.

The refractory powder is moistened with about 10 per cent of its weight of water that is approximately one-quarter molar

in hydrochloric acid and one-quarter molar in *o*-phosphoric acid. With core *B* in place in die *A*, the refractory powder is well tamped into the annular space to form the walls of the crucible. Strong tamping is essential in order to eliminate entrained air that would otherwise give rise to a weak structure. Cylinder *D* is now set on *B*, and the walls formed by applying pressure to annular ring *C* and to core *B*. By means of a templet of brass, 0.003 inch thick, the excess wall is broken down with an L-shaped chisel to the level of the templet.

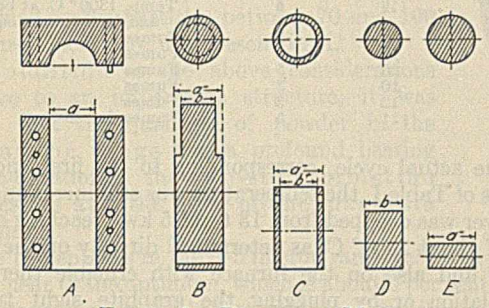


FIGURE 1. DETAILS OF MOLD

With the templet removed, the material for the base is now tamped in and the base formed by applying pressure to cylinder *E* and to *B*. To remove the finished crucible, the die bolts are loosened and made finger-tight. Core *D* is removed by twisting and pulling. The green crucible, which is fairly strong, is then removed from the die by forcing up at the base.

As noted, the use of dilute hydrochloric acid prevents sticking of the crucible to the mold during withdrawal. However, hydrochloric acid does not appear to be effective at the shoulder of *B* or on the surface of cylinder *E*, both of which are subjected to direct pressure. This may be due to the fact that some pitting takes place at these surfaces which could probably be overcome by case-hardening these parts. In lieu of this, the protection of these places by means of two pieces of paper is quite suitable for avoidance of sticking.

The green crucible is air-dried for 24 hours and then dried at 120° C. for several hours.

When the proper procedure is observed, it is found that the weld at the base and walls is about as strong before and after firing as the rest of the crucible.

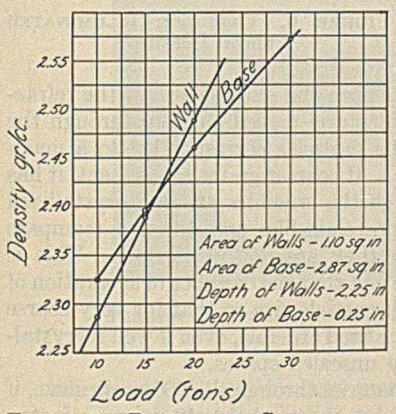


FIGURE 2. DENSITY OF COMPRESSION *vs.* LOAD

PRESSURE IN FORMING CRUCIBLE. In forming the crucible by pressure in two operations, it must be borne in mind that the degree of compression depends not only on the pressure but also on the depth of the column of powder (*8*). Consequently, in order to effect the same density of compression throughout the crucible, the pressure on the base and walls will differ. Figure 2 shows the density of the walls and base of the crucible, dried at 120° C., against the load applied in pressing. It is seen that the density of compression varies practically linearly with the load, both for the base and for the walls. This is the result obtained by Hagen (*3*) for the so-called pulverulent materials. Owing to the greater length of wall, 2.25 inches against 0.25 inch, the pressure required to compress it to a given density is about three times that required for the base.

In forming the crucible, curves, such as those shown in Figure 2, serve as guide to the relative pressure required for base and walls. In practice, an excess in pressure of 10 per cent over that required for equal density of compression is applied to the base to consolidate more thoroughly the weld of base and walls. Any wide variation of relative pressure will result in cracking of the fired crucible. Aside from the relative pressure, it is found that increase in absolute pressure increases the strength of the green crucible and promotes the ease of recrystallization to an impervious structure in firing. However, it is conceivable that, by compressing and crushing individual grains, too high pressure might tend to weaken the weld, although this condition has not been perceptible at the pressures employed, i. e., up to about 40,000 pounds per square inch on the walls and 15,000 on the base.

FIRING

While temperatures of 3000° C. can, without much trouble, be reached in the high-frequency furnace, there are certain other considerations that must be borne in mind in regard to the application of this furnace to firing crucibles.

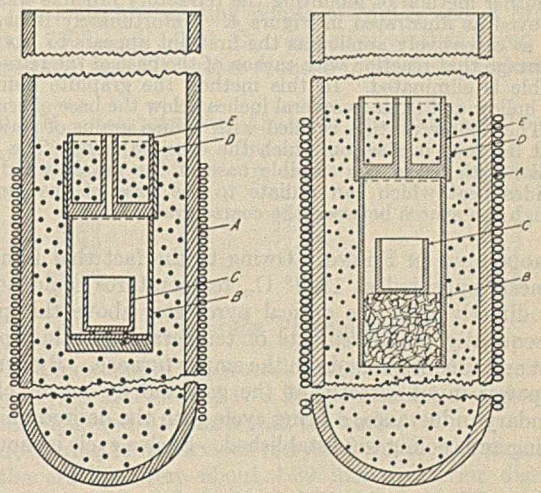


FIGURE 3 FIGURE 4
HIGH-FREQUENCY FURNACE SET-UP

Since a graphite cylinder is used as the inductor, a reducing atmosphere will necessarily be present. Fortunately magnesia does not appear to form a carbide. However, at about 1800° C., reaction between the carbon and the magnesia begins and increases rapidly with increasing temperature. To this must be added the sublimation of magnesia itself above 2000° C., although the reaction with carbon appears to be of greater significance. As a result of these effects, the crucible that has been fired to about 2600° C. will, depending on the furnace set-up and duration of firing above 1800° C., weigh 65 to 90 per cent of the original weight of the dried crucible.

Another point to be considered is the fact that high-frequency currents are induced solely in the vertical walls of the graphite inductor so that heat is radiated to the refractory crucible as from a cylindrical surface. Consequently, the base of the crucible tends to lag in temperature with respect to the rest of the crucible. The detrimental effects of this condition appear to be greatly counteracted by a uniformly dense structure of green crucible.

On the other hand, the lower temperature at the base is advantageous in firing the magnesia crucibles to recrystallization because it eliminates the excessive interaction that would otherwise take place between the magnesia and carbon when in contact.

To reduce the initial high rate of heating of the furnace, a

secondary coil whose reactance was altered by means of a water-cooled iron core was placed in series with the furnace coil.

FURNACE SET-UP. The furnace (coil diameter, 6 inches) is shown in Figures 3 and 4.

The only insulation (shown in dotted section) that could be used in attaining the high temperature was carbon black. Electric insulation for the water-cooled furnace coil was provided by silica tube *A* which served as an outer shell of the furnace. To provide insulation at the top, graphite cylinders *D* and *E* are provided. *D* is hollow while *E* has a base and peephole. Both *D* and *E* are slitted vertically so as to avoid induced electric currents. *E* fits into *D* and is filled with insulating carbon black.

One of the methods of mounting crucible *C* is shown in Figure 3. To the crucible bottom that was located near the center of the coil were cemented four large grains of periclase. A thin graphite disk was interposed between these grains and the base of the graphite inductor. Owing to corrosion by the grains and partly by the base of the crucible, the disk was replaced after each firing. It is necessary in this method of mounting the crucible that it be accurately centered and level in order to avoid slipping of the crucible to the walls of the graphite inductor during firing. The function of the graphite base in this set-up was to furnish the necessary heat by conduction to the base of the crucible.

Another method of mounting the refractory crucible was also employed as illustrated in Figure 4. Unfortunately it has not been as extensively applied as the first but appears to have the advantage that reaction with carbon of the base of the refractory crucible is eliminated. In this method the graphite inductor, *B*, is hollow and extends several inches below the base of crucible *C*. The hollow portion is filled with coarse grains of periclase, about 0.5 inch in size, on which the crucible rests. The additional length below the crucible base of the graphite inductor provides heat which can radiate to the base of the crucible through the spaces between the coarse grains.

PROCEDURE IN FIRING. Owing to the fact that fumes of magnesia appeared at 1800° C., temperatures could not be read directly with the optical pyrometer above this point. Consequently, measurements of temperature against power input and time were made on the empty furnace. By varying the power input directly at the gap and by means of the secondary inductance, a firing cycle with the desired uniform heating and cooling was established. Such a cycle is shown in

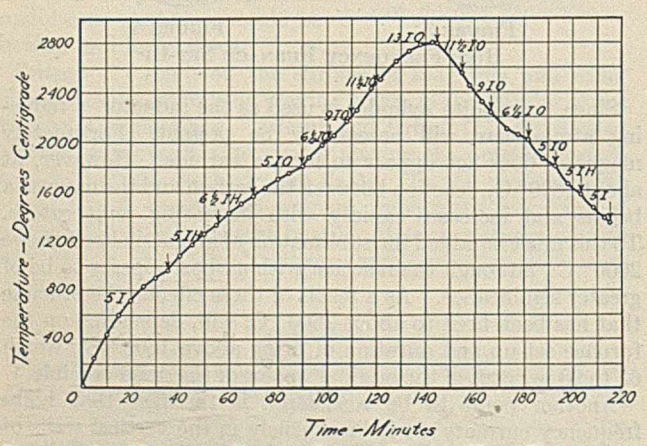


FIGURE 5. UNIFORM FIRING CURVE USING HIGH-FREQUENCY FURNACE

Figure 5. The numbers represent kilowatt power input; *IO*, *IH*, and *I* stand, respectively, for the secondary inductance out, iron core of inductance halfway in, and iron core completely in. It is seen that it takes 140 minutes on the uniform firing curve to reach the maximum temperature of 2800° C. at a power input of 13 kw.

This uniform firing cycle had to be modified owing to rapid volatilization of the magnesia above 1800° C. The modification consisted essentially in decreasing the time during which the furnace temperature was above 1800° C. from the time required for uniform heating as shown in Figure 5. Table I gives a comparison of the uniform and actual time during which the furnace was maintained above 1800° C.

TABLE I. POWER INPUT *vs.* TIME ABOVE 1800° C.

Power Input	Time of Heat: Uniform cycle	Time of Heat: Actual cycle	Remarks
Kw.	*Min.*	*Min.*	
6.5	12	5	Temp. 1800° C. at beginning, and fumes commence
9	9	5	Fumes
11.5	10	5	Fumes
13	20	5	Fumes
11.5	10	3	Fumes
9	12	3	Fumes
6.5	11	5	Fumes decreasing

In the actual cycle, corresponding to the first and third columns of Table I, the temperature was still increasing when the power was dropped from 13 to 11.5 kw., reaching a maximum of about 2600° C. as determined directly on the empty furnace and also on the furnace with crucible therein by extrapolation or by plugging the graphite sight tube so as to cut off the fumes.

A correction must be made to the actual cycle above 1800° C. because of deterioration of the carbon black insulation with time. As a measure of the insulation efficiency, the time required for the furnace temperature to drop, with power off, from 1250° to 1150° C. was noted. In terms of this time, an empirical correction was made to the duration of the maximum furnace power, in this case 13 kw.

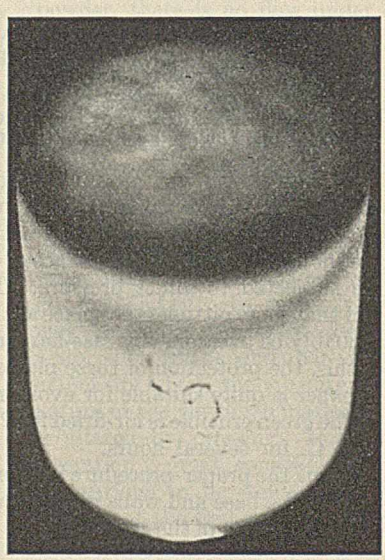


FIGURE 6. CRUCIBLE ILLUMINATED FROM INTERIOR

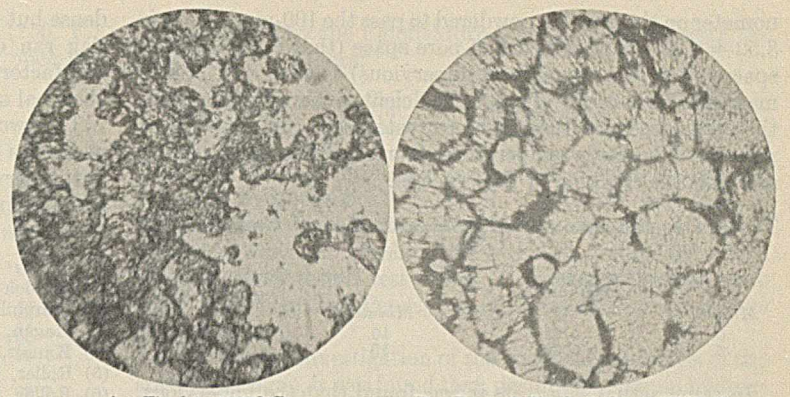
EFFECT OF PARTICLE SIZE. A particularly significant variable in this work has been the particle size of the refractory powder. The powder was passed entirely through the 200-mesh sieve; thus the particles corresponded to a maximum size of 100 microns. If coarser grains are present, it has been found that, although the crucibles are well crystallized and exhibit the same porcelain-like translucence (compare Figure 6), nevertheless they are not impervious. This is understandable from the fact that the distance of separation of the grains increases with particle size so that for very coarse grains the structure of the fired crucible, even if well recrystallized, will contain many unsealed spaces.

In fact, even for the material through the 200-mesh sieve, if the proportion of particles above about 40 microns is too great, the same situation obtains. In Table II is given the particle-size analysis of two periclase powders that were the same except in their fineness. The analysis was made in an air-analyzer for fine powders described elsewhere by one of the authors (*5*).

In Table II, powder A had been passed through a 325-mesh sieve, and powder B through a 200-mesh sieve, so that the former contained particles up to 70 microns maximum and the latter up to 100 microns maximum. The unexpectedly low percentage in the 0 to 5 micron range of powder A is apparently due to retention of these fine particles by the

oversize remaining on the 325-mesh sieve. Powder A yielded impervious crucibles easily; powder B yielded crucibles that were well recrystallized and translucent but were only occasionally impervious. This is to be attributed to the fact that powder B contained almost 10 per cent more by weight than powder A in the range above 40 microns, and at the same time B contained coarse particles between 70 and 100 microns which were not present in A.

In addition to the above considerations relative to an impervious structure, it was found that the quantity of powder in the 0–5 micron range had a profound bearing on the question of the two-step formation by pressure and the firing of the magnesia crucibles.



A. Fired to 1800° C. *B.* Recrystallized at about 2600° C.

FIGURE 8. THIN SECTIONS OF CRUCIBLES

The percentages in the 0–5 micron range recorded in Table II are near to the optimum, which is about 9 per cent. If the percentage is appreciably less, the green crucible will be too weak to remove from the mold. If the percentage in the 0–5 micron range is high, it has been found that the weld of the base and walls tends to become unsatisfactory. This is understandable from the fact that these fine grains are susceptible to deformation and crushing and thus cause a departure from the desired characteristics of a pulverulent material. In this respect Hagen (*3*) has found that the finer a material, the greater is its compressibility; that is, the more it approaches the plastic state.

In regard to the effect of particle size on firing, it was noted in this work that too great a percentage in the 0–5 micron range will cause fine cracks to appear in the finished crucible.

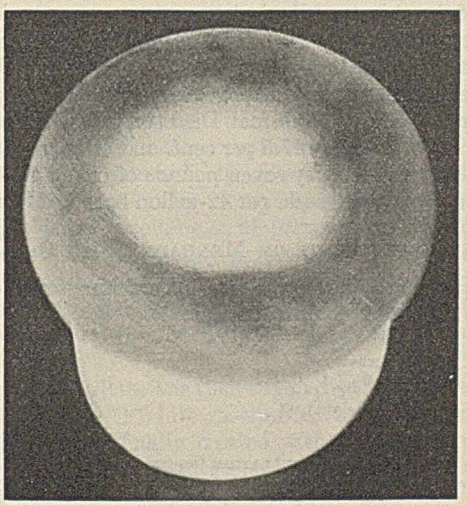


FIGURE 7. OVERHEATED AND PARTLY MELTED CRUCIBLE

Adjustment of the refractory powder to the desired microscopic particle-size distribution may be effected by means of an accurate air separator, described elsewhere (*6*).

MATERIALS AND PURITY

The material chiefly used was a high-grade fused periclase powder, the analysis of which, according to the manufacturer was as follows: MgO (by difference) 96.20 per cent; SiO_2, 1.40 per cent; Al_2O_3, 0.22 per cent; Fe_2O_3, 0.80 per cent; CaO, 1.90 per cent; loss on ignition, 0.20 per cent. A C. P. magnesium oxide was also used that was either calcined or fused in the carbon arc by the method described by Fairchild and Peters (*2*). The crucibles obtained with the purer material were much better recrystallized than the less-pure product, showing large brilliant crystal facets on the surface.

The impurities introduced by the hydrochloric and *o*-phosphoric acids in the moistening liquid amount to less than 0.1 per cent of chlorine and of phosphorus. It would appear from the relatively low melting points of $MgCl_2$ and of $Mg_2P_2O_7$ (about 700° and 1400° C., respectively) that these small percentages are still further reduced in the fired product.

TABLE II. PARTICLE-SIZE ANALYSIS OF PERICLASE POWDERS

Particle-Size Fraction	Powder A	Powder B
Microns	*% weight*	*% weight*
0–5	12.4	13.0
5–10	13.5	8.4
10–20	23.0	18.3
20–40	42.1	41.6
40–70	9.1	..
40–100	..	18.6

CRUCIBLE PROPERTIES

The dimensions of the crucibles prepared in this work were, after drying at 120° C., 1.72 inches internal diameter, 2.25 inches high, and 0.20 inch wall thickness.

After firing to impervious recrystallization, the dimensions of the crucible were about 1.39 inches interior diameter, 1.96 inches high, and 0.12 inch wall thickness. The crucibles have a metallic ring and are quite strong mechanically. Figure 6 is a photograph of one of these crucibles illuminated from the interior and shows the porcelain-like translucence that is possessed by the recrystallized crucibles. Because of the lower temperature at the base of the crucible and of the carbon inclusions on the outside surface where the crucible came in contact with carbon, these areas are not as translucent as the walls. Figure 7 shows a crucible that has been overheated and partly melted down and thus bulges at the base but which was otherwise satisfactory. This illustrates that there is a region of crucible flow at high temperatures rather than sudden melting down, so that firing to an impervious and translucent structure is rather flexible.

The physical structure of the crucibles is of some interest. Figure 8 shows thin sections[1] respectively of a crucible that has been fired to 1800° C. and of one that has been recrystallized at about 2600° C. In the recrystallization process the original small angular grains have united to form large rounded crystals. When this process is sufficiently extensive the pores are completely sealed and the crucibles are impervious to air under pressure (20 cm. of mercury was applied) at room temperatures. The empty areas of Figure 8*A* are, in the main, places where the thin section has torn away in grinding.

The density of an impervious crucible is 3.35 ± 0.02, while the absolute density of the crucible, determined with a pyc-

[1] Prepared by Alton Gabriel of this station.

nometer on the crucible powdered to pass the 100-mesh sieve, is 3.52 ± 0.02. The per cent of pore space (that is, sealed pore space, since the crucible is impervious) is then 4.8. Since magnesia has a relatively high coefficient of thermal expansion, the very dense structure of the recrystallized crucibles will not permit sudden large temperature changes without a weakening and possible cracking of the crucible.

TABLE III. SOLUTION OF MAGNESIA BY MOLTEN CaO-FeO-SiO_2 SLAG

Time of Contact	MgO in slag	Time of Contact	MgO in slag
Minutes	%	*Minutes*	%
0	3.88	10	6.71
5	5.36	15	10.21

In some actual slag tests it was found that the impervious magnesia crucibles will hold molten ferrous oxide over long periods. A slag consisting of 70 per cent ferrous oxide and 30 per cent silicon dioxide was held satisfactorily for 20 minutes at 1525 ± 20° C. Tests made by C. H. Herty, of the Pittsburgh Station of the Bureau of Mines, showed that a molten high-temperature slag, analyzing 50 per cent calcium oxide, 35 per cent ferrous oxide, and 15 per cent silicon dioxide, did not penetrate the crucible over a period of time, whereas with a dense but pervious magnesia crucible procured elsewhere, the slag ran out as it melted down. Although this slag was satisfactorily retained by the impervious magnesia crucible, chemical solution took place as shown in Table III.

The two-step formation by pressure, as described for magnesia, has been found equally satisfactory for ZrO_2 and Al_2O_3, but impervious crucibles of these materials have not yet been prepared in the high-frequency furnace with graphite inductor.

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The Cracking of Fish Oil

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THE present work was undertaken as part of a general investigation to determine whether motor fuels can be made from fish oils by the cracking process. A study of some of the reactions involved in the thermal and pressure decomposition of fish oil was also included.

In parts of the world, particularly in Japan, there is some difficulty in disposing of the waste oils from fish. Since this work was started, the cracking process has been considered by others as a means of producing valuable by-products from fish oil.

Engler and Seidner (*2*) distilled menhaden oil under pressure, using the shell still designed by Krey. A charge of 492 kg. of North American menhaden oil, specific gravity 0.930, was distilled under 10 atmospheres pressure at a temperature of approximately 320° C. (608° F.). The pressure dropped gradually during the operation to 4 atmospheres, and the temperature was gradually increased to 420° C. (788° F.). Yields of 319 kg. of distillate (amounting to approximately 60 per cent of the starting material), 77 kg. of coke and asphalt-like residue, and 96 kg. of gas were produced. The average saponifiable material in the distillate was 7.52 per cent. The distillate consisted of an upper layer of oil and a lower layer of water. Both saturated and unsaturated hydrocarbons were reported in the oil layer.

The gaseous product analyzed as follows:

	%		%
CO_2	17.4	CH_4	38.3
Olefins	7.8	Noncombustible residue	2.0
CO	34.5		

When the fish oil was distilled under atmospheric pressure, however, the gas analyzed as follows:

	%		%
CO_2	26.7	CH_4	25.2
Olefins	11.4	Noncombustible residue	1.8
CO	34.9		

One of the objects of Engler's experiments was to determine the effect of change of the conditions during pressure distillation on the composition of the gas.

In the present work, four products were obtained from the cracking of fish oil—motor fuel, Diesel oil, coke, and gas. The yield of motor fuel was 47.5 per cent, and of Diesel or furnace oil 17.0 per cent. Fifty-seven pounds of coke and 790 cubic feet of fuel gas were made per 42-gallon barrel of fish oil.

EXPERIMENTS ON MENHADEN FISH OIL

Menhaden fish oil was used for the cracking tests. This oil had the following characteristics:

Specific gravity	0.9446
Initial b. p., ° C. (° F.)	307 (585)
End b. p., ° C. (° F.)	377 (711)
Coke (by weight), %	2.9
Water, %	0.5
Sulfur	Trace

HEMPEL DISTILLATION (800-CC. CHARGE)

Distilled Over	Temperature ° C.	Temperature ° F.	Sp. Gr.
10	319	606	0.8922
20	321	610	0.8393
30	297	567	0.8877
40	311	592	0.8916
50	318	604	0.8368
60	319	606	0.8654
70	316	601	0.8762
80	310	590	0.8783

Some cracking occurred during the Hempel distillation analysis at atmospheric pressure.

CRACKING OPERATION

Menhaden fish oil from San Diego, Calif., was distilled under pressure in a steel cylindrical still equipped with vapor line and reflux pipe, and connected with a condenser and receiver with gas and liquid outlets. The pressure upon the system extended throughout the still, including the receiver.

The fish oil was cracked at pressures of 60 and 100 pounds

per square inch gage, and temperatures from 402° C. (756° F.) to 482° C. (900° F.). The cracking process was operated to produce motor fuel, Diesel oil, coke, and gas.

A summary of the results is shown in Table I.

TABLE I. RESULTS OF CRACKING FISH OIL

Specific gravity	0.9446	0.9446
Distillation pressure, lb./sq. in.	60	100
Temperature, ° C.	402–404	427–482
Temperature, ° F.	756–759	801–900
Cracked distillate:		
% of fish oil by vol.	76.6	67.9
Specific gravity	0.8137	0.7831
Water, % of fish oil	5.3	6.1
Coke, lb./barrel	47	57
Uncracked gasoline, cu. ft./barrel	690	790
Coke, gas, and loss, %	18.1	26.0
Gasoline:		
% of cracked distillate	49.0	69.9
% of fish oil	37.5	47.5
Specific gravity	0.765	0.770
Initial to end b. p., ° C.	48–224	46–225
Initial to end b. p., ° F.	118–435	115–437
Diesel oil:		
% of cracked distillate	47.0	25.0
% of fish oil	36.0	17.0
Specific gravity	0.917	0.920
Loss:		
% of cracked distillate	4.0	5.1
% of fish oil	3.1	3.4

A distillation analysis of the cracked distillate resulted as follows:

Specific gravity	0.7831
Initial b. p., ° C. (° F.)	27 (81)

HEMPEL DISTILLATION (800-CC. CHARGE)

DISTILLED OVER	TEMPERATURE	
%	° C.	° F.
10	68	154
20	97	207
30	127	261
40	147	297
50	173	343
60	198	388
70	221	430

CHEMICAL TREATMENT OF CRACKED-DISTILLATE OIL. The cracked distillate produced was treated chemically and steam-distilled into finished gasoline, and Diesel or furnace oil. The treatment comprised agitating the pressure distillate with 3 per cent by volume of a 25 per cent solution of sodium hydroxide. The sodium hydroxide sludge was allowed to settle and was then withdrawn. The oil was subjected to treatment with 1.3 per cent by volume of 98 per cent sulfuric acid, the oil and acid being thoroughly agitated. The black sulfuric acid sludge was drawn off after settling for an hour. The cracked distillate was water-washed and finally neutralized with 1.0 per cent by volume of a 10 per cent sodium hydroxide solution.

The treated distillate was then steam-distilled at a temperature of 121° C. (250° F.) into gasoline and a Diesel oil residue.

The gasoline was finally treated with a dilute solution of sodium hydroxide. It was water-white and had only a slight fishy odor.

CRACKED GASOLINE. The gasoline derived from fish oil had the following characteristics:

Specific gravity	0.7653
Color	Water-white
Odor	Slightly fishy
Sulfur, %	0.0
Initial b. p., ° C. (° F.)	46 (115)
End b. p., ° C. (° F.)	224 (435)

A. S. T. M. (100-CC. DISTILLATION)

DISTILLED OVER	TEMPERATURE	
%	° C.	° F.
10	76	169
20	96	205
30	111	232
40	128	261
50	141	286
60	156	313
70	166	331
80	181	358
90	197	387

HYDROCARBON-GROUP ANALYSIS OF CRACKED GASOLINE. The refined motor fuel was analyzed for its hydrocarbon-group content by the Egloff-Morrell method (*1*), showing the following percentages:

	%		%
Unsaturated	19.0	Naphthenes	8.0
Aromatic	35.0	Paraffin	38.0

One would judge from the percentage of unsaturated and aromatic hydrocarbons present in the motor fuel that it would have a high knock rating in an automotive engine. However, when the gasoline was tested in a standard Ethyl Gasoline Corporation test motor, it showed a knock-rating value equivalent to Pennsylvania kerosene, or an octane number of zero.

Upon further investigation of the chemical properties of the cracked gasoline, it was found that, despite the sodium hydroxide and sulfuric acid refining, the gasoline still contained oxygenated compounds which appeared in the chemical analysis as unsaturated and aromatic hydrocarbons, but which exhibited knocking tendencies. These compounds were principally aldehydes and fatty acids. The fatty acids were abundant in the fractions boiling between 104° C. (219° F.) and 205° C. (401° F.), consisting of acetic, propionic, butyric, and homologous acids. The total acidity of the cracked distillate was 7.4 per cent of free organic acids. The fractions boiling below 68° C. (154° F.) showed strong tests for aldehydes, although these compounds were detected in all the fractions up to 177° C. (351° F.) When the cracked distillate was saponified by refluxing with a strong alkali, the knock rating was increased from an octane number of zero to thirty-one. This behavior confirmed the assumption that the oxygen compounds acted as knocking compounds.

DIESEL OIL. The Diesel oil fraction may also be used for furnace oil, for gas-making, or as cracking stock to increase further the yield of gasoline.

The Diesel oil had the following properties:

Specific gravity	0.9170
Initial b. p., ° C. (° F.)	224 (435)
End b. p., ° C. (° F.)	380 (716)

A. S. T. M. (100-CC. DISTILLATION)

DISTILLED OVER	TEMPERATURE	
%	° C.	° F.
10	242	468
20	247	477
30	250	482
40	255	491
50	260	500
60	266	511
70	273	523
80	281	538
90	310	590
98	380	716

COKE AND GAS. The coke produced by cracking fish oil had a honeycomb structure. Its content of sulfur and ash was less than 0.1 per cent each. The thermal value of the coke was 15,600 B. t. u. per pound.

The incondensable gas produced had a relatively high thermal value.

SUMMARY AND CONCLUSIONS

1. Motor fuel has been produced by the cracking of menhaden oil with yields of 37.5 to 47.5 per cent.
2. The removal of saponifiable substances by refluxing with alkali increased the octane number of the motor fuel from fish oil from zero to thirty-one.
3. The production of motor fuel, Diesel oil, coke, and gas may have economic importance in some countries.

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Condensation of Phenols with Formaldehyde

I. Formation of Phenol Alcohols

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This is the first of a series of papers contributing further information, both fundamental and practical, of the general type not extensively covered in the literature, relating to the nature of phenol-aldehyde condensation and the products thereof. The present paper discusses the preliminary combination of the original materials, which precedes the condensation to resins. The later papers will deal with the chemistry and characteristics of the condensation process and of the products under alkaline and acid conditions and with different phenols.

The simplest products obtained by reaction between phenols and aldehydes are the more or less water-soluble and crystallizable phenol alcohols, formed by simple addition of single molecules of the reactants:

$$HOC_6H_5 + HCHO \longrightarrow HOC_6H_4CH_2OH$$

This reaction, in all probability, constitutes the first step in all phenol-aldehyde condensations. Any new information as to what actually occurs in this initial stage, therefore, is of some importance in connection with the general chemistry of the subject.

Previous Work

Phenol alcohols and their conversion into resins (called "saliretins") on heating, etc., have been known since 1843 (*9*); that is, long before even the reaction of phenols with aldehydes at all was known; and, when the latter fact was discovered by von Baeyer in 1872 (*5*), he attributed the formation of the resins and diphenyl methane derivatives which he obtained to the condensation of phenol alcohols primarily formed. The actual formation of phenol alcohols in this way, however, was not demonstrated until later, owing to the fact that the early investigators worked under acid conditions. The relatively rapid rate of condensation of phenol alcohols to the more complex condensation products under these acid conditions is such as to have prevented their detection.

As a forerunner of the direct synthesis, Greene (*6*), in 1880, announced the preparation of saligenin (orthohydroxybenzyl alcohol) by reaction of phenol in alkaline solution with methylene chloride; and, when formaldehyde became a commercial product in the early nineties, the direct synthesis of phenol alcohols in general soon followed.

This was accomplished by Manasse and Lederer (*7*) independently of each other, using alkaline conditions under which the further condensation of phenol alcohols is usually much slower than their formation. The broad general claims of these two investigators were practically identical, covering reaction in the presence of basic catalysts in general, that is, without reference to temperature, etc. The actual methods used in their examples differed, however.

Manasse favored the use of a strong alkali in aqueous solution, in proportions approximately equimolar to the phenol. The reaction was allowed to take place at ordinary temperature, the mixtures usually standing several days until the odor of formaldehyde had disappeared. Lederer used a weakly basic substance and heated the reaction mixture, but only long enough to complete the combination. The heating had to be stopped at this point to avoid excessive resinification. The claims of both investigators were combined in the Bayer and Company patent. In either case the method amounted simply to limiting the reaction to the phenol alcohol stage by means of the temperature in the one case, and of the time of heating in the other.

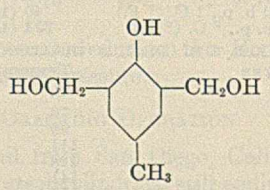
Crystalline products from phenol, the cresols, thymol, and guaiacol were described, to the extent of melting point and behavior with one or two solvents; but actual working details were given only in the case of phenol and one or two others. Yields and by-products were not mentioned. There was, therefore, no indication as to whether or not the products mentioned were the only ones formed in the various instances. The properties described by one investigator did not always tally with those of the other.

The method of Manasse was adopted as the standard method and has remained so. In the course of the following decade, the preparation of a number of alcohols was described in greater detail and with attention to establishing their identity, mainly by Auwers and his associates, working with xylenols (*3*). In 1907, Auwers (*2*) published a general review of the subject.

Polyalcohols

Up to this point, except in one instance, only equimolar proportions of the phenol and formaldehyde had been used, and the products were assumed to be monoalcohols (that is, combinations of one molecule of phenol with only one of aldehyde), if not actually identified as such. Manasse had observed in the case of guaiacol, however, that, if two molecular proportions of aldehyde were used instead of one, a second crystalline product was obtained. In this product two molecules of aldehyde were combined with one of guaiacol, and it gave up one of these two molecules on heating, yielding the original monoalcohol. The compound was not regarded as a dialcohol but as some looser form of combination. It is known, however, that aromatic nuclear carboxylic acids split off a second carboxyl group, as carbon dioxide, more readily than a single one.

Auwers made the general observation that the aldehyde entered only the ortho and para positions with reference to the phenolic hydroxyl. In the case of paracresol this limited the number of possible alcohols to two—namely, the orthomonoalcohol and the diorthodialcohol. Using the dimolecular proportion of formaldehyde, he obtained as the sole product the dialcohol,



which had been mistaken for a monoalcohol by Lederer. With equimolar proportions he obtained a mixture of the monoalcohol and the dialcohol, which he separated by means of solvents, leaving a corresponding quantity of cresol free.

Ullmann and Brittner (*10*) improved the preparation of this dialcohol by using a concentrated reaction mixture. Under these conditions the sodium salt crystallizes out in a pure state and is converted into the free alcohol by dissolving in water and neutralizing with acetic acid. The product then crystallizes out in high yield. On heating with dilute acids, it splits off formaldehyde and resinifies. Its constitution was established by analysis and derivatives.

In 1927 Amann and Fonrobert (*1*) patented a general method for making polyalcohols, which they recommended as materials for resin manufacture. It consisted in adding the phenolate solution gradually to a large excess of the aldehyde, several moles to one of the phenol. Their examples included the dialcohol of paracresol and several indefinite liquid products.

Possibilities of Alcohol Formation

In the present investigation it was found, as will be shown, that polyalcohol formation is of much more general occurrence than would appear from the literature, and that it does not require the presence of a large excess of aldehyde. Its occurrence, to a considerable extent, even in equimolar reaction mixtures is not an isolated phenomenon peculiar to paracresol. It was found also with phenol and with orthocresol and is to be expected with any phenol that forms a polyalcohol, at all. For it is then evident that the monoalcohol, which is formed first, is capable of combining with a further quantity of aldehyde; and so, as soon as any of it is formed, it must compete to some extent with the remaining phenol for the remaining aldehyde, whatever the quantity of the latter may be. An idea of the actual extent to which this occurs is gained from the results of the present work.

The possibility of polyalcohol formation and the number of alcohols possible are limited by the number of active positions available. The fact that only the ortho and para positions are active in this connection is consistent with the well-known rule of orientation and finds further confirmation in the present work.

In a series of experiments in which fifteen different phenols were each heated with formaldehyde in alkaline solution, mesitol (the only one with no free active position, but with the two meta positions unoccupied) was distinguished from all of the others by failure to react. This then limits the number of molecules of aldehyde that may be taken up in any case to three, but the maximum number of possible alcohols, as in the case of metacresol, is seven.

Polyalcohol Formation by Phenol

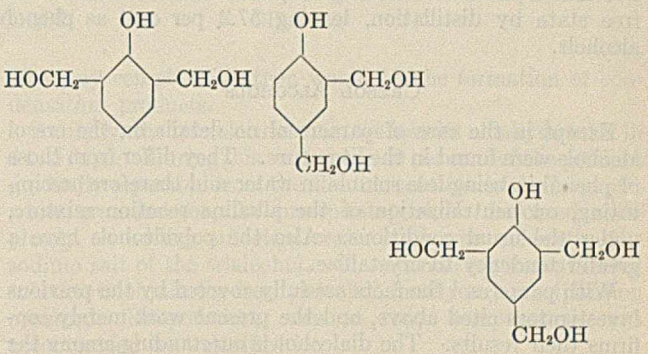
Phenol is thus theoretically capable of forming two monoalcohols, two dialcohols, and one trialcohol. Of these only the monoalcohols are known. They were obtained by Manasse by the following procedure:

> The approximately equimolar mixture of phenol, formaldehyde, and a 10 per cent sodium hydroxide solution is allowed to stand 1 day or more, until the odor of formaldehyde has disappeared, and is then neutralized. The monoalcohols are extracted with ether and, after removal of the free phenol by steam distillation or a suitable solvent, are separated from each other by means of benzene, in which the ortho compound is more soluble. Nothing is said about yields or other products.

The writer's experience with this method has been as follows: With phenol the ether extract from an equimolar reaction mixture amounted to about two-thirds of the theoretical, and about half of it was free phenol. Although the monoalcohols were readily extracted with ether, repeated extractions continued indefinitely to remove small quantities of a sirupy substance. If the aqueous solution (after the extractions) was boiled down, a copious precipitation of resin, indicating the presence of phenol alcohols, occurred after a while, accompanied by the odor of formaldehyde. If the solution was allowed to evaporate without heating, however, there was no precipitation or odor, and the residue contained a quantity of sticky sirup accounting approximately for the remaining third of the original materials. It was dissolved away from the salt by means of acetone.

The conclusion is obvious. Since all of the aldehyde entered into combination with only two-thirds of the original equimolar quantity of phenol, a considerable portion of the phenol must have combined with more than an equimolar proportion of aldehyde, forming products more soluble in water and less soluble in ether than the monoalcohols. These properties would be expected of polyalcohols because of the larger number of hydroxyl groups. The resinification accompanied by liberation of formaldehyde, on heating in aqueous solution, has been noted in the case of the known dialcohol of paracresol, and the dialdehyde compound of guaiacol also gave up formaldehyde on heating.

There are theoretically, in the case of phenol, three possible polyalcohols capable of formation by direct synthesis:



Actually three distinct fractions of the alcohols remaining in the aqueous solution after the ether extraction were separated by means of solvents.

After the nearly exhaustive ether extraction, a considerable further quantity of sirup could still be readily extracted by ethyl acetate, leaving in the aqueous solution another portion which could not be extracted. The three fractions were easily isolated, by treatment of the evaporation residue, from the original ether-washed aqueous solution exhaustively with ether, ethyl acetate, and acetone in succession.

Evidently one of the polyalcohols is soluble in ether, but its distribution coefficient (in favor of water) is so high that it is extracted to a smaller extent from the aqueous solution than the monoalcohols, from which it is further distinguished by its failure to crystallize. Only one of the three extracts crystallized on standing in the desiccator—namely, the ethyl acetate extract—and that only in one instance.

The ratio of monoalcohols to polyalcohols was found to increase with dilution of the original reaction mixture. This is in accordance with the well-known laws of chemical reactions.

If the original reaction mixture is made up with two moles of formaldehyde to one of phenol, then it must stand for several days, instead of one, before the aldehyde odor disappears. A considerable quantity of monoalcohols and some phenol are still obtained, indicating that some trialcohol must be formed. With aldehyde somewhat in excess of three moles, the odor remains indefinitely. Such a mixture, after standing many days, was put through the usual treatment. It yielded practically no free phenol and very little ether extract from the aqueous solution. The evaporation residue, however, yielded some extract both to ether and to ethyl acetate, but the

principal product was the one insoluble in either of these solvents, but soluble in acetone or water. It is evidently the trialcohol.

Apparently the taking up of the third molecule of aldehyde becomes very slow as the reaction progresses, although it was comparatively rapid in the earlier stages as shown by the formation of trialcohol from the reaction mixtures with smaller proportions of aldehyde.

When the phenol alcohols are formed under the conditions existing at the beginning of the original Bakelite process (that is, by using only a small proportion of alkali and heating), polyalcohol formation evidently takes place to an even greater extent. The homogeneous equimolar mixture of phenol and formaldehyde with 0.05 mole of normal sodium hydroxide solution per mole of phenol was heated at its boiling point under reflux. During the first 15 minutes of heating practically the whole of the formaldehyde was combined but very little resin was formed, though it forms rapidly thereafter. The reaction was stopped at this point by cooling, and the mixture remained clear even on dilution. The resin precipitated on neutralization and was removed. It was equivalent to about 1.3 per cent of the original phenol. Forty-one and five-tenths per cent of the original phenol was recovered in the free state by distillation, leaving 57.2 per cent as phenol alcohols.

Cresol Alcohols

Except in the case of paracresol no details on the cresol alcohols were found in the literature. They differ from those of phenol in being less soluble in water and therefore precipitating, on neutralization of the alkaline reaction mixture, under the usual conditions. Also the polyalcohols have a greater tendency to crystallize.

With paracresol the facts are fully covered by the previous investigators cited above, and the present work merely confirms their results. The dialcohol is outstanding among the phenol alcohols in its adaptability to isolation. The sodium salt crystallizes out even from an equimolar reaction mixture, when concentrated.

Orthocresol Dialcohol

Orthocresol theoretically can form, like phenol, both an ortho- and a paramonoalcohol, but, like paracresol, it can form only one polyalcohol—a dialcohol, in this case the orthoparadialcohol. This alcohol was not found in the literature but was prepared in crystalline form without difficulty as follows:

On allowing the alkaline reaction mixture (containing two moles of formaldehyde to one of cresol, dissolved in its equivalent of 20 per cent sodium hydroxide solution) to stand, the aldehyde odor disappeared in 2 days. No precipitation occurred. On neutralization with hydrochloric acid, an oil was thrown out which contained considerable resin and therefore crystallized only incompletely and gradually. Hardly any free cresol was present. When acetic acid was used for neutralization, however, no immediate precipitation occurred, but the dialcohol came out gradually in white crystalline form and high yield.

It was further purified by recrystallization from chloroform and melted sharply at 94° C., corrected. A molecular-weight determination gave the value 178. The theoretical value is 168. Molecular weights throughout this work were determined by the Menzies-Wright ebulliscopic method in acetone (*8*).

A New Crystalline Condensation Product

By dissolving the crude dialcohol fractionally in hot chloroform, in which it is not very soluble, the impurities accumulated in the first fractions and in the mother liquors. They consisted of a small quantity of resin and a crystalline substance which was soluble in boiling water, but which was easily distinguished from the dialcohol by its failure to melt in boiling water and by its rapid and nearly complete precipitation on cooling. It was therefore isolated by dissolving the fraction in hot water, filtering off the resin, allowing to cool and crystallize, and repeating the process on the crystalline precipitate. The dialcohol is sufficiently soluble in cold water to be removed completely in this way. The by-product was obtained as a white crystalline powder amounting to about 6 per cent of the total yield.

It crystallized from acetone in fine needle clusters and melted at 155° C., corrected. Analysis and molecular-weight determinations gave values which corresponded closely to a condensation product of two molecules of cresol with three of formaldehyde:

$$2CH_3C_6H_4OH + 3HCHO \longrightarrow C_{17}H_{20}O_4 + H_2O$$

	Found		Av.	Calcd.
Mol. weight	291	285	288	288
Carbon, %	70.91	70.79	70.85	70.83
Hydrogen, %	7.03	6.90	6.965	6.94

The substance might be one of the several possible isomers of either of the two types:

$$\left.\begin{matrix} CH_3 \\ HO \\ HOCH_2 \end{matrix}\right\} C_6H_2{-}CH_2{-}C_6H_2 \left\{\begin{matrix} CH_3 \\ OH \\ CH_2OH \end{matrix}\right. \qquad (1)$$

$$\left.\begin{matrix} CH_3 \\ HO \\ HOCH_2 \end{matrix}\right\} C_6H_2{-}CH_2OC_6H_3 \begin{matrix} \diagup CH_3 \\ \diagdown CH_2OH \end{matrix} \qquad (2)$$

In either case it could result from the condensation of the dialcohol with a monoalcohol. No condensation product of this class was found in the literature. The crystalline products reported are either simple phenol alcohols or simple diphenol methanes.

Of the two formulas above, type 1 represents a diphenol methane dialcohol. From the fact that the substance in question is crystalline, it is most probably of this type. Baekeland and Bender (*4*) have shown quite convincingly that the phenol ether (type 2) is a resin structure, whereas both phenol alcohols and diphenol methanes are, in general, crystalline substances. The alkali solubility of the substance was in the proportion of 157 grams per mole of sodium hydroxide. This is much closer to the half-molar proportion (144), corresponding to formula 1, than to the full molar proportion (288) of formula 2.

Heated to constant weight at 185° C. it is resinified, puffing up, turning brown, and hardening to a resinoid which was 87.7 per cent insoluble in acetone. The loss in weight on heating was 10.9 per cent, which is 87.2 per cent of the theoretical value for loss of $2H_2O$ (12.5 per cent). Probably the hardening interfered with complete curing by stopping the escape of the water vapor before the dehydration process was complete. The quantity of water eliminated has been found by the writer, in the case of phenol alcohols, to be a measure of the number of $-CH_2OH$ groups.

Results with Equimolar Proportions

An attempt to prepare the monoalcohols of orthocresol from an equimolar reaction mixture, from which the formaldehyde odor disappeared overnight, yielded an oily product which was found to consist largely of free cresol and the dialcohol. The remainder, about one-third of the total, appeared to be a mixture of two colorless viscous liquids which could not be induced to crystallize. These were distinguished and separated from the dialcohol by means of their lower solubility in water and miscibility in all proportions with benzene or chloroform, in either of which the dialcohol is not very soluble. They were separated from each other by virtue

of the fact that one was soluble in carbon tetrachloride and insoluble in water, while for the other the reverse was the case. They were presumably the two possible monoalcohols.

Two orthocresol alcohols, assumed to be monoalcohols, are described in the literature without details as to their preparation. One melted at 87° C. and was assumed to be the paramonoalcohol (Bayer and Company, 7), and the other at 40° C. (Lederer, 7). The first was crystallized from chloroform and was probably the dialcohol. The other was very soluble in benzene.

Metacresol

In the literature only four instances were found in which an alcohol obtained from metacresol is mentioned, and these only by the originators of the method (7). All were assumed to be monoalcohols but had different melting points—namely, 117° and 105° C. (Manasse), 110° C. (Lederer), and 122° C. (Bayer and Company), indicating either different substances or different states of purity. There is no information whatever as to how they were isolated or in what yield. They are merely mentioned among the examples of products obtained by the standard method, the details of which are given in the case of phenol.

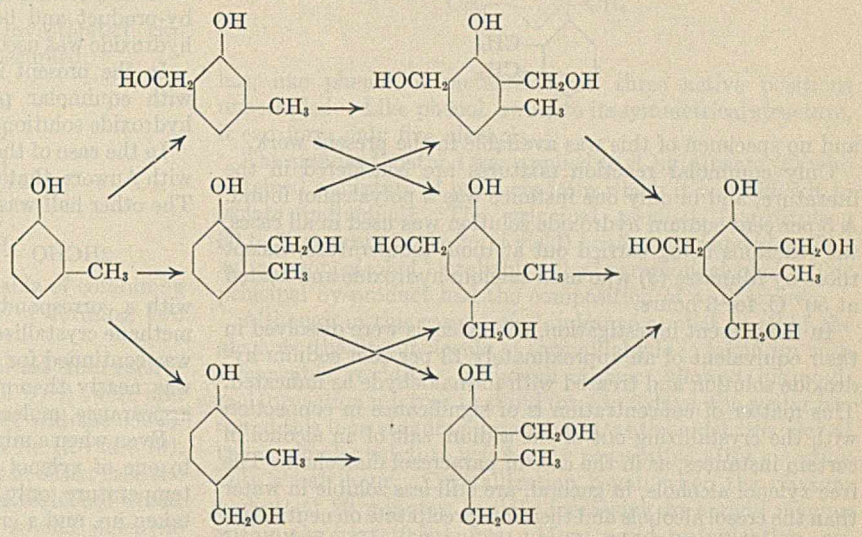
This reticence in the case of metacresol appeared understandable when the method in question was applied to it in the present work. Difficulties were encountered which do not arise in the other cases, and for which there is no provision in the descriptions given in the literature.

Having all three of its active positions unoccupied, and one ortho position different from the other owing to the adjacent methyl group, metacresol can form three monoalcohols, three dialcohols, and one trialcohol. It is characterized also by a high speed of reaction, especially of resinification. Whereas with phenol the equimolar reaction mixture can stand for a month without showing enough resinification to cause a precipitate on neutralization, extensive resinification occurs with metacresol on standing overnight. Furthermore, this resinification is rendered particularly troublesome by the fact that the alcohols of metacresol also precipitate on neutralization.

With the equimolar reaction mixture the aldehyde odor disappeared overnight. On neutralization with hydrochloric acid, the products precipitated almost completely as a tough mass. A portion of this was dissolved out by prolonged digestion with ether and was obtained crystalline by washing successively with benzene and petroleum ether, which removed mainly cresol. It dissolved in alcohol from which it was precipitated as a crystalline powder by addition of water. Its identification was not undertaken. The residue, insoluble in ether, was evidently largely resinous and was partly insoluble in sodium hydroxide solution or acetone. Probably some of this resinification occurred during neutralization and could have been avoided by diluting the reaction mixture and neutralizing with acetic instead of hydrochloric acid; but, owing to limitation of time, further work on the alcohols of metacresol was confined to the question of trialcohol formation.

Metacresol Trialcohol

If complete absorption of the aldehyde occurs in a mixture containing three moles of formaldehyde to one of cresol, the situation is greatly simplified, since, on taking up the maximum quantity of aldehyde, all of the cresol and the six possible lower alcohols (if formed) would be completely consumed in the formation of the single ultimate product—the trialcohol.



The only complication then would be the formation of condensation products.

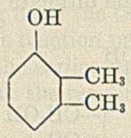
Actually, the trimolecular mixture lost its aldehyde odor in 4 to 5 days. During this time about 40 per cent of the product gradually separated from the alkaline solution in the form of a white granular soaplike precipitate, which dissolved completely on adding sufficient water and was evidently the sodium salt of the trialcohol. On neutralizing the saturated solution to obtain the free trialcohol, hardly any precipitation occurred. Evaporation, even at room temperature, was accompanied by resinification.

No satisfactory method for isolating and purifying this product was found in the time available. The only one of the usual solvents (immiscible with water) in which it was sufficiently soluble to be extracted at all from the aqueous solution was ethyl acetate, which was very inefficient both as to quantity and quality of extract. It was only sparingly soluble in cold ethyl alcohol; but, when dissolved by heating, it did not crystallize out on cooling, owing probably to the formation of resin or other products which increased the solubility. In fact, any heating or prolonged treatment seemed to result in more or less resinification or decomposition, sometimes with liberation of formaldehyde. By filtering off the sodium salt (which separated from the original concentrated alkaline solution), making it into a paste with a little water, neutralizing with acetic acid, filtering again, and washing white with alcohol, a specimen was obtained in a fairly pure crystalline condition, but with excessive losses.

Xylenols

The xylenols, as principal constituents of the coal-tar cresylic acids used in the manufacture of formaldehyde condensation products, are of considerable importance in this connection and are interesting because of the variety of structural relationships represented. Like paracresol, however, they have been more fully investigated with regard to alcohol formation, by Auwers and others, than phenol and the other cresols; thus the actual preparation of alcohols from them was not undertaken in the present work. Certain facts, however, were observed, incidental to resinification study, which are pertinent in the present connection and may be appropriately mentioned here in supplement to a brief summary of the outstanding points disclosed in the previous literature.

Of the six xylenols, all have been investigated but one—the 2,3-dimethylphenol,



and no specimen of this was available in the present work.

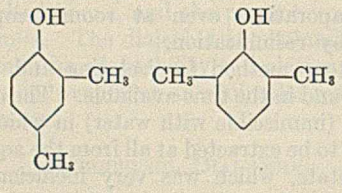
Only equimolar reaction mixtures are considered in the literature, and in only one instance was a polyalcohol found. A 5 per cent sodium hydroxide solution was used in all cases, the reactions being carried out at room temperature, except those by Manasse (*3*) who used calcium hydroxide and heated at 50° C. for 3 hours.

In the present investigation, the xylenols were dissolved in their equivalent of an approximately 13 per cent sodium hydroxide solution and treated with formaldehyde as indicated. This matter of concentration is of significance in connection with the crystallizing out of the sodium salt of an alcohol in certain instances, as in the case of paracresol dialcohol. The free xylenol alcohols, in general, are still less soluble in water than the cresol alcohols and therefore precipitate on neutralization, usually in a liquid form which crystallizes on standing.

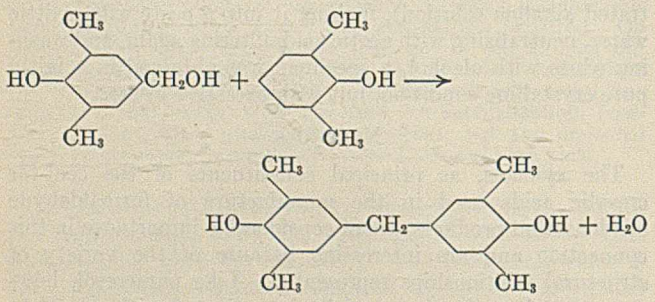
The xylenols fall into three classes with reference to the number of ortho or para positions unoccupied and to the resulting maximum number of aldehyde molecules which can be taken up and of alcohols which may be formed.

One Free Active Position and Formation of Diphenol Methanes

Two of the xylenols have but one active position:



They are therefore capable of combining with not more than an equimolar proportion of formaldehyde and can form but one alcohol each. These two xylenols, however, are characterized by the formation of the dixylenol methanes, which would result from the condensation of a molecule of the alcohol with one of xylenol, thus utilizing only half of the equimolar quantity of aldehyde:



The orthoparadimethylphenol orthoalcohol was prepared by Manasse (*3*), and the diorthodimethylphenol paraalcohol by Bamberger (*3*), who, using the standard method, obtained also a crystalline by-product, unidentified but corresponding in analysis and melting point to the dixylenol methane.

Auwers (*2*), evidently uninformed of Bamberger's work, states that the alcohol of diorthoxylenol has never been prepared and that the dixylenol methane is always obtained as the sole product. He obtained the latter substance in high yield and purity by heating the alkaline reaction mixture for two hours at 100° C. In the case of orthoparaxylenol he observed that the dixylenol methane was often formed as a by-product and became the principal product when sodium hydroxide was used instead of lime.

In the present investigation the mixtures of the xylenols with equimolar proportions of formaldehyde and sodium hydroxide solution were heated under reflux at 100° C.

In the case of the diorthoxylenol it was found, in agreement with Auwers, that only one-half of the aldehyde was taken up. The other half was consumed by Cannizzaro's reaction,

$$2HCHO + NaOH \longrightarrow HCO{-}ONa + CH_3OH$$

with a corresponding decrease in alkalinity. The dixylenol methane crystallized out copiously early in the heating, which was continued for an hour without further effect. The yield was nearly theoretical and of high purity, as indicated by appearance, molecular weight, and melting point.

Even when a mixture containing two moles of formaldehyde to one of xylenol was allowed to stand for 2 days at room temperature, only the half-molar proportion of aldehyde was taken up, and a crystalline magma separated, which was unaffected by subsequent heating at 100° C. for 1 hour. The product was identified as the dixylenol methane by molecular weight and melting point. The yield was 94.6 per cent of theory.

It is the free methylene dixylenol, liberated by hydrolysis, that crystallizes out of the alkaline reaction mixture. In the two cases just described, about 50 and 10 per cent of the yield, respectively, depending on the residual alkalinity, remained in the diluted alkaline solution and crystallized out almost completely on neutralization.

With the orthoparaxylenol an equimolar quantity of aldehyde was taken up in either case, and no crystalline or other precipitate separated until neutralization after the heating, which yielded a well-defined resin. Thus the tendency to form the dixylenol methane appears to be much less pronounced when the free active position is ortho than when it is para.

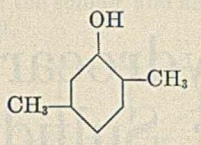
The formation of diphenol methanes is characteristic of certain phenols, rather than of the method of condensation. The best known example of this is betanaphthol. When Manasse (*7*) applied his standard method for the preparation of phenol alcohols to betanaphthol, he obtained only the dinaphthol methane. This result was confirmed by Auwers. In the present investigation the dinaphthol methane was obtained also on heating the alkaline reaction mixtures. With double the equimolecular proportion of formaldehyde, however, the greater part of the product was resin, but 25 per cent was isolated as crystalline dinaphthol methane by means of carbon tetrachloride. Another phenol, which was found to be of the diphenol-methane forming class, was pseudocumenol. It gave results similar to those obtained with the diorthoxylenol; like the latter it has but one free active position. Betanaphthol, on the other hand, has two, but here there may be a case of steric hindrance.

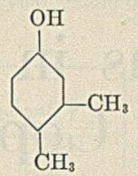
The stability of the diphenol methanes on heating the alkaline mixtures is characteristic and in marked contrast to the behavior of phenol alcohols. This is theoretically significant. Having no $-CH_2OH$ groups, they are incapable of further condensation alone. The dibetanaphthol methane, having still two active positions free, can, under sufficient provocation, acquire the $-CH_2OH$ groups necessary for further condensation by taking up more formaldehyde and thus forming a resin. With diorthoxylenol or psuedocumenol, on the other hand, this is impossible. Therefore, when the diphenol methane is formed, condensation can go no further.

Orthoparaxylenol differs in that it does not condense with its alcohol as fast as it forms the alcohol.

Two Free Active Positions and Steric Hindrance

Besides the xylenol which has not been investigated, two others have two of the active positions unoccupied:





Theoretically, either of these should be capable of combining with two molecules of formaldehyde and of forming two monoalcohols and one dialcohol.

Only one alcohol, however, has been obtained from each—namely, the 2,5-dimethylphenol paraalcohol by Auwers and Erklentz (*3*) in nearly quantitative yield (*2*), and the 3,4-dimethylphenol-6-alcohol by Auwers and van de Rovaart (*3*). This is not surprising in view of the fact that in either case the formation of a second monoalcohol or of the dialcohol would be subject to steric hindrance, since the second aldehyde molecule must enter a position directly between the hydroxyl and metamethyl radicals.

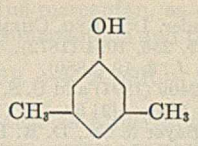
In the present investigation it was found, on allowing the alkaline mixtures of either of these xylenols with double the equimolar proportion of formaldehyde to stand at room temperature, that the aldehyde odor still remained after 5 days. The excess of formaldehyde was then determined by Cannizzaro's reaction (coincidentally with resinification) by heating under reflux at 100° C. In both cases it was found that more than an equimolar proportion of aldehyde—namely, 64 per cent of the original two moles—remained in combination with the xylenol. In all probability a larger proportion than this was taken up in the formation of the dialcohols, since polyalcohols in general give up a portion of their aldehyde on resinification. Evidently, then, a second molecule of formaldehyde is taken up by these two xylenols, but very slowly.

Auwers and van de Rovaart encountered difficulty in purifying their alcohol, owing to its high resinification tendency. Auwers and Anselmino (*3*), however, obtained it in a pure state by adding concentrated sodium hydroxide solution to the standard reaction mixture. This caused the sodium salt of the alcohol to crystallize out, as in the case of paracresol-dialcohol (*10*). The writer observed with this metaparaxylenol, using 13 per cent sodium hydroxide solution in the original equimolar reaction mixture, that, even on heating the mixture directly, the alcohol salt crystallized out suddenly and copiously on heating, and then dissolved in a few minutes as resinification proceeds. With the mixture containing the double proportion of formaldehyde, which was allowed to stand 5 days for dialcohol formation, copious crystallization also occurred, beginning on the second day and dissolving when the mixture was heated.

With the 2,5-dimethylphenol no precipitation occurred from the equimolar mixture until neutralization. With the dimolar mixtures, however, about half of the total product precipitated in a fine granular form during the period of standing for 5 days, but it was evidently neutral resin precipitated by hydrolysis. It did not dissolve on heating or diluting the mixture but was soluble in a sufficient excess of sodium hydroxide solution. With this xylenol (one of the fastest-reacting phenols in this respect) extensive resinification occurs at room temperature.

Three Free Active Positions

Only one of the xylenols—the symmetrical or dimetaxylenol,



has, like phenol or metacresol, all three active positions unoccupied. Like phenol, owing to its symmetrical structure, it can form only five alcohols.

The standard method was applied to it by Auwers (*2*) who obtained a mixture of products from which it was difficult to isolate individuals. The principal product (constituting 30 to 50 per cent of the total yield) he separated and identified as a monoalcohol, probably the paramonoalcohol. The principal by-product had the composition of a dialcohol.

Although in this case steric hindrance applies to all of the alcohols, the first molecule of formaldehyde is taken up with remarkable rapidity. Although Auwers allowed his equimolar reaction mixture to stand for 3 to 5 days, the writer has found this long standing unnecessary, as the aldehyde odor of the equimolar mixture was barely perceptible after standing only a half hour. Crystallization began when the mixture had stood 20 minutes, rapidly increasing to a rigid magma within the next 10 minutes. More rapid resinification, accompanied by solution of the crystals, occurs on heating than in the case of the metaparaxylenol.

A second molecule of aldehyde also is taken up by dimetaxylenol with comparative rapidity, though not as fast as the first. This distinguishes this xylenol from the other four investigated. Thus, with the bimolecular proportion of formaldehyde, the aldehyde odor became very weak during the first hour but was still perceptible after several hours. It vanished entirely overnight, however. Crystallization occurred but more slowly and to a smaller ultimate extent than with the equimolar mixtures, although the concentration was kept the same by increasing that of the sodium hydroxide solution to offset the dilution by the water in the additional formaldehyde solution.

To see if a third molecule of aldehyde would be taken up by the dialcohols, the corresponding quantity of formaldehyde was added to the above mixture after it had stood overnight. The crystalline precipitate disintegrated to an amorphous-looking powder during the next 24 hours. After standing 10 days the aldehyde odor was still pronounced, and the entire mixture had finally set to a solid jelly which was unaffected by the addition of water. This is the only instance in which this phenomenon was observed to occur in the cold. It occurs with phenol or metacresol when heating of the alkaline reaction mixture is prolonged beyond the period of resinification, and is due to the curing of the resin to the insoluble or resinoid form.

Thus, of the xylenols in general it may be said, in distinction to the simpler phenols, that they show a decided reluctance toward taking up the full quantity of formaldehyde corresponding to their theoretical capacity, as determined by the number of free ortho or para positions, although combining readily with a smaller quantity, which is greater the greater the theoretical capacity. This reluctance, which was observed also with the other higher phenols investigated, may be regarded simply as an instance of the resistance usually encountered in loading up the benzene nucleus with substituents.

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Action of Some Mercaptans in Hydrocarbon Solution on Copper and Copper Sulfide

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Copper sulfide and copper react with mercaptans in dilute solution in hydrocarbons, giving cuprous mercaptides, and disulfides.

The insoluble cuprous derivatives of the primary and lower secondary mercaptans remain on the surface of the copper, while those of the higher secondary mercaptans pass into solution, coloring the hydrocarbon.

Alkyl sulfides and disulfides are indifferent to copper or copper sulfide.

In the flotation process, organic sulfur compounds are selectively adsorbed by copper sulfide. Morgan and Sedbury (*2*) determined the heats of addition of some sulfur compounds with heavy metal salts, and found some of them to be large. It is well known that copper oxide was for a time used industrially in the removal of sulfur from petroleum fractions. These facts suggested a study of the removal of sulfur compounds from hydrocarbons by copper sulfide and similar materials. This investigation was started and carried through with the idea that only adsorption was involved. The results proved this to be wrong, but indicated instead unexpected reactions which are more important than the anticipated adsorption.

Removal of Sulfur Compounds

Normal Mercaptans. The study was begun with a dilute solution of *n*-butyl mercaptan in benzene, the mercaptans being readily determined by titration, and benzene being the most available pure hydrocarbon. The expected removal seemed to take place, since the titrations showed the disappearance of from 23 to 89 per cent of the mercaptan according to the proportion of copper sulfide employed.

This study was extended to the other primary normal mercaptans from methyl to *n*-nonyl, shaking 0.1, 0.2, 0.4, or 0.8 gram of copper sulfide with 50 cc. of a benzene solution of the mercaptans corresponding to 0.05 per cent by weight of sulfur. The results are shown in Figure 1, from which it appears that the action increases sharply from methyl to butyl, falls off slowly and then more rapidly with increase in molecular weight.

Four successive treatments of a butyl mercaptan solution with 0.2 gram copper sulfide (Table III) diminished the mercaptan by 90.7 per cent, compared with 88.9 per cent using 0.8 gram all at once. This indicates a surface reaction rather than adsorption.

With solutions containing progressively larger amounts of butyl mercaptan (Table IV), it was found that the amount of mercaptan removed by a given weight of copper sulfide increased at first and then became nearly constant.

The influence of the solvent was shown in comparative experiments with butyl mercaptan dissolved in *n*-heptane and in cyclohexane. These, with benzene, were taken to represent the classes of saturated hydrocarbons that are found in petroleum distillates. The results, together with those for benzene (Table V), are shown in Figure 2. The curves are of the same general shape for all of the solvents but the maxima are for the six- and seven-carbon mercaptans with the new solvents. The action of the copper sulfide on the higher mercaptans is greatest in cyclohexane, and greater in *n*-heptane than in benzene. Along with the normal mercaptans, isopropyl and *sec*-butyl were tried. These were removed to only a small degree. Secondary mercaptans are usually less reactive than the corresponding primary, but there is no apparent reason that they should be less adsorbed.

A cursory study was made using a number of supposed absorbents of various sorts. All were used in powdered form, 0.5 gram to 50 cc. of *n*-butyl mercaptan of the usual concentration in benzene. The results of duplicate experiments are given in Table I.

Table I. Removal of *n*-Butyl Mercaptan from Benzene by Various Materials

Material	Mercaptan Removed		Material	Mercaptan Removed	
	%	%		%	%
Basic cupric carbonate	99.8	100.0	Barium hydroxide	5.4	5.4
Cupric hydroxide	99.8	99.9	Silica gel, unactivated	3.0	2.4
Cupric sulfate, hydrated	68.7	85.8	Silica gel, activated	1.0	1.1
Cupric sulfide (0.4 gram)	65.0	66.0	Zinc dust	1.6	1.2
Copper, pptd. powder	50.1	50.6	Calcium carbonate	1.6	1.2
Cupric sulfate, anhyd.	44.5	43.9	Antimony sulfide, black	1.0	0.0
Cuprous chloride	28.4	32.1	Mercuric sulfide, red	1.1	0.9
Cupric oxide	9.1	8.5	Lithopone	0.4	0.2
Mercuric sulfide, black	28.4	25.0	Potassium iodide	0.2	0.4
Charcoal, cocoanut shell	34.7	31.7	Iron powder	0.1	0.4
Charcoal, bone	16.0	6.1	Antimony	0.0	0.0
Lead sulfide	25.8	27.2	Lead chloride	0.0	0.0
Antimony sulfide, red	13.3	14.5	Kieselguhr	0.0	0.0
Cadmium sulfide	10.0	10.0			

The most striking observation to be drawn from Table I is that the usual adsorbents—silica gel, charcoal, kieselguhr—show such low removal in comparison to copper sulfide. While they are not very active, the sulfides of lead, mercury, antimony, and cadmium are more so than silica gel. It is to be noted that those substances which remove 50 per cent or more, contain copper in the molecule; this indicates that the action is chemical rather than physical. That copper metal in the form of precipitated powder, which is not an adsorbent, removes such a large percentage of the mercaptan strengthens the assumption that the removal is connected with the copper atom. It is remarkable that cupric hydroxide and cupric basic carbonate remove nearly all the mercaptan, whereas barium hydroxide, a strong base, takes out only about 5 per cent.

Secondary Mercaptans. On shaking copper sulfide with similar benzene solutions of the higher secondary mercaptans, the solutions surprisingly became colored (yellow, brown, or red according to conditions). Evaporation of these solutions in a high vacuum left gummy material which was readily soluble in

benzene and which qualitative tests showed to contain copper in the cuprous condition. This was observed for pentane-2-thiol, hexane-2-thiol, heptane-2-thiol, octane-2-thiol, octane-4-thiol, and nonane-2-thiol. The solutions appear to be stable in the dark but darken in the light with the separation of precipitates. Similar phenomena were observed when copper powder, oxide, or hydroxide, or basic carbonate were used instead of the sulfide, and also with cyclohexane or *n*-heptane as solvent.

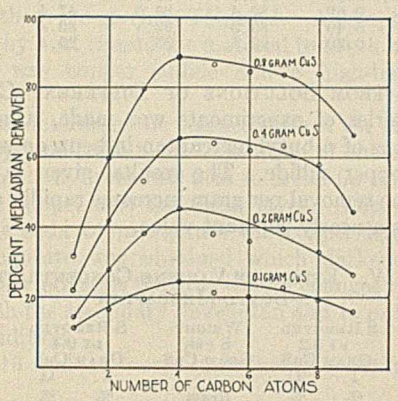

FIGURE 1. REMOVAL OF NORMAL MERCAPTANS FROM BENZENE SOLUTION BY COPPER SULFIDE

These compounds are formed more rapidly at higher temperatures in boiling benzene, *n*-heptane, and cyclohexane solutions of the mercaptans with copper or copper sulfide. When so obtained they were less stable. On analysis, these showed a higher sulfur content and a lower copper content than those prepared at room temperature. It was not possible to obtain similar solutions with many other metallic sulfides tried, or with other finely divided metals, such as zinc, iron, antimony, or tin.

A large number of experiments were made in which these colored solutions were evaporated in a high vacuum, the residues analyzed for copper and sulfur, and the difference taken as the hydrocarbon radical. These analyses are given in Table VI. The compositions of two samples approximated that of a cuprous mercaptide, while those of the others can be represented by the general formula, $CuS_{1+2x}R_{1+2x}$ or $CuSR + xR_2S_2$. The disulfides of the radicals involved are only slightly volatile under the conditions. When *n*-heptane or cyclohexane was used as solvent, the percentages of copper were very low. The cuprous mercaptides are much less soluble in these hydrocarbons. It should be possible to separate the cuprous mercaptides from the disulfides by selective solvents, but the presence of the disulfides was not suspected at the time the analyses were made.

EXPLANATION OF OBSERVATIONS. The results obtained with the primary mercaptans were just about what were anticipated (assuming adsorption), and seemed to confirm the previous supposition; those with the higher secondary mercaptans were most puzzling. The misconception as to the conduct of the primary and the mystery as to the secondary remained until after the experiments were finished. Both were cleared up by the subsequent study (*1*) of the cuprous mercaptides, aided by the working out of a method for the estimation of disulfides. The conclusion is that the copper sulfide reacts with the mercaptan, as does any other cupric salt, to form cuprous mercaptide and the disulfide:

$$2CuS + 4HSR \longrightarrow 2CuSR + RS{\cdot}SR + 2H_2S$$

That such a weak acid as a mercaptan should dissolve so insoluble a substance seems remarkable. When copper powder is used, the oxygen of the air probably takes part:

$$2Cu + O_2 + 4HSR \longrightarrow 2CuSR + RS{\cdot}SR + 2H_2O$$

It has since been found that lead mercaptides are oxidation catalysts. In experiments carried out by J. R. Sampey using copper powder, 43.9 and 41.9 per cent of the mercaptan disappeared, of which 20.7 and 20.1 per cent, respectively, (practically half), were converted into the disulfide. In two similar experiments using copper sulfide, 83.1 and 84.6 per cent of removal were obtained, of which 52.8 and 52.8 per cent, respectively, appeared as disulfide. In these the formation of disulfide may have been aided by the air.

The difference in the action of the primary and the higher secondary mercaptans is readily explained by the fact that the cuprous derivatives of the former are insoluble in benzene and remain on the surface of the copper sulfide, while those of the latter dissolve in benzene to form colored solutions. Cuprous

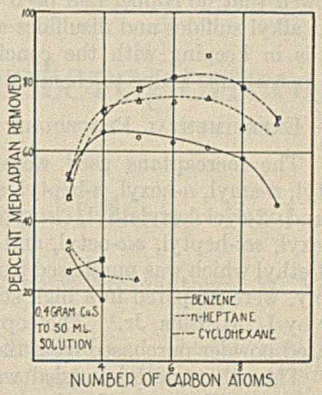

FIGURE 2. EFFECT OF VARIOUS SOLVENTS ON MERCAPTANS

mercaptides react with carbon disulfide to form benzene-soluble products of red color (*1*). Applying this test to copper sulfide, which had been shaken with a benzene solution of primary mercaptan, a deep red-colored solution was formed, indicating the presence of a cuprous mercaptide. The same phenomena appear when powdered copper is substituted for the sulfide.

The reactions here observed of mercaptans on metallic copper or its compounds must have something to do with the corrosive action of sour naphthas. It has been found by Wood, Sheely, and Trusty (*3*) that copper and brass are corroded by mercaptans in naphtha solution. The metals became covered with a coating which they supposed to be cuprous mercaptide.

ALKYL SULFIDES. Assuming that the removal of mercaptans was due to adsorption, it was expected that alkyl sulfides would be taken out of solution by copper sulfide and other adsorbents. A large number of experiments were made to test this. A 50-cc. portion of benzene solution of *n*-butyl

TABLE II. REMOVAL OF NORMAL MERCAPTANS FROM BENZENE SOLUTION BY COPPER SULFIDE

Weight of CuS	Mercaptan Removed																					
	Methyl		Ethyl		*n*-Propyl		*n*-Butyl		*n*-Amyl		*n*-Hexyl		*n*-Heptyl		*n*-Octyl		*n*-Nonyl		2-Phenyl-ethyl		2-Cyclohexyl-ethyl	
Gram	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
0.1	11.6	11.2	15.5	17.6	19.7	19.1	23.4	25.3	21.1	21.5	20.5	19.7	23.7	22.2	19.7	19.2	16.1	15.8	9.6	9.9	4.8	6.6
0.2	13.9	14.5	28.3	27.2	39.2	37.8	46.7	43.8	38.5	37.4	35.9	36.0	39.8	39.7	32.2	34.1	27.6	25.7	22.8	21.9	15.6	16.3
0.4	20.9	23.0	41.5	41.6	52.5	54.0	65.0	66.0	64.4	63.6	61.9	62.5	63.3	58.6	57.9	58.1	43.7	45.5	42.8	33.9	28.0	29.0
0.8	33.7	29.6	59.2	60.0	79.2	80.0	88.6	89.2	86.7	86.3	85.0	84.2	81.6	85.6	82.9	84.9	63.9	69.3	57.4	59.6	47.4	49.4

sulfide (0.05 per cent as sulfur) was shaken mechanically in a glass-stoppered bottle with 0.5 gram of the desired solid in powdered form. The bottle was placed in a thermostat at 25° C. for one hour, when a 25-cc. sample was withdrawn for analysis. The butyl sulfide was determined before and after treatment.[1]

Of a variety of solids tried, none showed any considerable removal. Copper metal, sulfide, oxide, hydroxide, and basic carbonate, cadmium sulfide, barium hydroxide, silica gel, zinc oxide, and lead sulfide seemed to show some adsorption, the maximum being for the copper compounds, but the amounts taken out were not much, if any, larger than the errors of analysis. Lithopone, red and black mercuric sulfides, red and black antimony sulfides, iron powder, charcoal, potassium iodide, and calcium carbonate showed no removal.

Disulfides. Similar experiments have been made with a benzene solution of *n*-butyl disulfide of corresponding strength. Precipitated copper, copper sulfide and hydroxide, and cadmium sulfide have been used. No appreciable removal could be detected in any case.[1] A solution of *sec*-heptyl disulfide was shaken for some time with both copper sulfide and copper, and then allowed to stand. After a period of several weeks no trace of yellow or red was visible in the solution, which showed that no copper had been dissolved.

The fact that alkyl sulfides and disulfides are not appreciably adsorbed is in keeping with the conclusion that the removal of the mercaptans is due to chemical action.

Experimental Procedure

Materials. The mercaptans used were methyl, ethyl, *n*-propyl, *n*-butyl, *n*-amyl, *n*-hexyl, *n*-heptyl, *n*-octyl, *n*-nonyl phenylethyl, and 2-cyclohexylethyl, isopropyl, *sec*-butyl, *sec*-amyl, *sec*-hexyl, *sec*-heptyl, *sec*-octyl, and *sec*-nonyl. All of these, except ethyl which was purchased from the Eastman Kodak Company, were prepared in a high state of purity in this laboratory by L. M. Ellis, Jr.[2] The copper sulfide used was a precipitated powder purchased from the Baker Chemical Company. The other materials tried were used as obtained commercially, without purification.

Solutions. Solutions of the various mercaptans were made in pure benzene, *n*-heptane, or cyclohexane so as to contain approximately 0.05 per cent of mercaptan sulfur. The exact amount of mercaptan in the solution was determined by titration with iodine. Experiments with weighed amounts of *n*-butyl mercaptan showed that the mercaptan in such solutions can be determined with an accuracy of about 0.1 per cent of the amount present.

Primary Mercaptans. Samples of the cupric sulfide, or other material, were weighed into glass-stoppered bottles. In the case of the cupric sulfide, these samples were very close—0.1, 0.2, 0.4, and 0.8 gram—whereas in the case of the other materials, all of them were 0.5 gram. Into these bottles were pipetted 50 cc. of the solution of mercaptan. The bottle containing the supposed absorbent and the mercaptan solution was shaken on a shaking machine for 15 minutes and placed in a thermostat at 25° C. for at least one hour. The solution was filtered through asbestos if it was not clear, and a 25-cc. sample pipetted into an excess of standard 0.025 *N* iodine solution, shaken, and allowed to stand for at least 15 minutes before back titration with standard 0.025 *N* thiosulfate, using starch as an indicator.

The percentages of the mercaptans that disappeared in the treatment have been presented in Figure 1 and are given in Table II. The results with other powders are to be found in Table I.

Successive Treatments with Copper Sulfide. An experiment was made starting with 250 cc. of the benzene solution of *n*-butyl mercaptan, shaking with copper sulfide in the proportion of 0.2 gram to 50 cc. of solution, filtering, sampling, and using an aliquot for further treatment. The results are given in Table III.

Table III. Successive Treatments of Benzene Solution of *n*-Butyl Mercaptan with Copper Sulfide

Vol. of Soln.	Weight of CuS	Total Removed		Remainder Removed	
Cc.	*Gram*	%	%	%	%
250	1.00	40.2	38.1	40.2	38.1
200	0.80	66.5	67.2	44.0	47.0
150	0.60	82.4	84.5	47.4	52.7
100	0.40	89.3	92.1	39.4	49.2
50	0.20	92.5	95.1	29.4	37.8

Removal from Solutions of Different Concentrations. A series of experiments was made, using different concentrations of *n*-butyl mercaptan in benzene with 0.2 and 0.4 gram copper sulfide. The results, given in Table IV, show that the removal per gram increases rapidly at first, but soon reaches a nearly constant value.

Table IV. Effect of Varying Concentration of *n*-Butyl Mercaptan

S Present	S Removed by 0.2 Gram CuS I	S Removed by 0.2 Gram CuS II	Weight S per Gram CuS	S Removed by 0.4 Gram CuS I	S Removed by 0.4 Gram CuS II	Weight S per Gram CuS
%	%	%	*Gram*	%	%	*Gram*
0.0198	66.0	68.8	0.0296	87.3	86.9	0.0190
0.0470	47.1	48.8	0.0496	74.7	74.3	0.0385
0.0941	31.8	34.8	0.0689	58.6	54.6	0.0689
0.1865	18.8	17.8	0.0751	31.7	31.4	0.0648
0.3754	9.5	9.4	0.0784	16.9	17.0	0.0702

Different Solvents. Runs were made with 0.4 gram copper sulfide to 50 cc. of *n*-heptane or cyclohexane containing mercaptans equivalent to 0.5 per cent sulfur. The results are given in Table V, with the averages of the figures for benzene taken from Table II. The data are plotted in Figure 2.

Table V. Effect of Nature of Solvent

Mercaptan Used	Amount Removed from Benzene	Amount Removed from *n*-Heptane	Amount Removed from Cyclohexane
	%	%	%
n-Propyl	53.2	51.9	46.9
n-Butyl	65.5	72.2	71.7
n-Amyl	64.0	74.5	78.0
n-Hexyl	62.2	74.1	81.3
n-Heptyl	60.9	75.0	87.7
n-Octyl	58.0	66.6	78.1
n-Nonyl	44.6	68.6	69.1
Isopropyl	31.9	34.1	25.6
sec-Butyl	17.2	24.77	29.0
sec-Amyl	Dissolves	23.5	Dissolves

Table VI. Composition of Residues from Benzene Solutions of Mercaptans Treated with Copper Sulfide

	Mercaptan	Amounts of Copper	Amounts of Sulfur	Amounts of Radical	Ratios of Copper	Ratios of Sulfur	Ratios of Radical
		%	%	%			
1	*sec*-Amyl	12.2	26.3	61.5	1	4.28	4.51
2	*sec*-Amyl	13.4	26.2	60.4	1	4.08	4.04
3	*sec*-Amyl	19.9	22.7	57.4	1	2.26	2.58
4	*sec*-Hexyl	21.6	20.7	57.7	1	1.90	1.99
5	*sec*-Hexyl	18.9	19.5	61.6	1	2.05	2.43
6	*sec*-Hexyl	32.2	18.5	49.4	1	1.14	1.15
7	*sec*-Hexyl	31.9	18.6	49.5	1	1.16	1.16
8	*sec*-Heptyl	21.9	21.9	56.2	1	1.97	1.91
9	*sec*-Heptyl	21.2	21.2	57.6	1	1.98	1.74
10	*sec*-Heptyl	13.3	21.7	65.0	1	3.23	3.13
11	*sec*-Heptyl	14.6	20.7	64.7	1	2.81	2.84
12	*sec*-Octyl	21.2	19.7	59.1	1	1.83	1.56
13	*sec*-Octyl	15.2	18.8	66.0	1	2.46	4.45
14	*sec*-Octyl	12.2	19.1	68.7	1	3.11	3.16
15	*sec*-Hexyl	2.05	27.3	70.7	1	25.7	25.8
16	*sec*-Hexyl	0.63	18.3	80.1	1	57.6	96.3
17	*sec*-Hexyl	2.70	26.8	70.5	1	19.4	19.3

Secondary Mercaptans. At first solutions containing 0.05 per cent of sulfur as mercaptan were used.

These were shaken with the copper compound and carefully evaporated under high vacuum in order to get the pure compound if possible. However, the quantities of material obtained were too small with which to work. To get larger amounts, approximately 2 grams of cupric sulfide or 1 gram of copper

[1] By a method which will be reported elsewhere.

[2] Prepared as part of Project 28 to be published in *J. Am. Chem. Soc.* in spring of 1932.

powder were weighed into a glass-stoppered Erlenmeyer flask. To this were added 200 cc. of a solution of a secondary mercaptan in benzene, of such strength that it contained 0.2 per cent sulfur. The flask was shaken in a mechanical shaking machine from 2 to 4 days. After the shaking was completed, the solution was filtered, and the solvent and any excess mercaptan were evaporated off at room temperature under a vacuum of about 3 mm., the distillate being condensed with Dry-Ice.

In this way, samples of 0.2 to 0.25 gram were obtained as red gummy masses which redissolved readily in benzene. The analyses of these are given in Table VI. Attempts to remove the solvent by heat caused the material to break up into what apparently was copper sulfide and a high-boiling sulfur compound.

In order to determine the valence state of the copper in the soluble compounds, the benzene solution of one of them was shaken with 1:1 hydrochloric acid to break up the compound and get the copper into the water layer. This was treated with caustic soda to precipitate the copper hydroxide. A yellow precipitate was obtained which darkened little on boiling. This indicates that the copper changes valence in its reaction with the secondary mercaptan and is present in the cuprous condition.

Samples 15 and 16 were made using *n*-heptane as solvent; 17 was made in cyclohexane. Not enough copper dissolves in a *n*-heptane solution of *sec*-amyl mercaptan to color it.

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Kinetics of a Type of Heterogeneous Reactions

II. The Mechanism of the Combustion of Lump Fuel

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In a previous paper (1) the mathematical development of a theory of the kinetics of exothermic chemical reactions occurring between a solid and a fluid, in which the products of reaction are entirely fluid, was presented. The case of the mechanism of combustion of pulverized solid fuel (individual particles less than 1 mm. in diameter) was developed in detail in order to permit of a direct and quantitative comparison with the existing reliable data available in the literature (2).

In the present paper the authors extend the theory to the combustion of lump fuel, limited, however, to the case where a single piece of solid fuel is under consideration. The results of the theory are compared with recent work by Smith and Gudmundsen. In general, it is found that the predictions of the theory are again in agreement with the experimental results.

SINCE the publication of a previous paper (*1*), the results of a new experimental study by Smith and Gudmundsen (*4*) on the mechanism of combustion of solid fuel has appeared. Since the theory as proposed and developed by the writers is of general application, it is of interest to determine whether it is in agreement with the findings of this more recent experimental study.

The experimental procedure employed by Smith and Gudmundsen (*4*) was to suspend a small sphere of electrode carbon, approximately 5 mm. in diameter, in a stream of air. The system was contained in a furnace at a constant temperature sufficiently high to maintain combustion of the carbon. The loss in weight of the carbon sphere was followed, and the surface temperature of the sphere during combustion as measured by an optical pyrometer was recorded. The velocity and moisture content of the air stream were varied in these experiments. From the results obtained, the specific reaction rates of the carbon under various conditions of temperature, air velocity, size of particles, etc., were calculated.

The physical mechanism of the combustion of solid fuel has previously been postulated by the writers (*1*). The surface temperature and the specific reaction velocity (k_s) will be considered here, as defined by Smith and Gudmundsen, i. e., milligrams loss per square millimeter of surface per second. The symbols employed in the mathematical presentation carry the significance adopted in the previous paper (*1*). Referring to Equation 20 of the earlier paper, expressing the rate of diffusion of oxygen to a uniformly burning surface, it is found that

$$M = \frac{4\pi C_0 r_1 r_2}{(r_2 - r_1)} \frac{0.178}{p} \left(\frac{T^1}{T_0}\right)^{1.754} \quad (20)$$

where

$$T^1 = \left(\frac{T_1^2 - T_2^2}{2 \log \frac{T_1}{T_2}}\right)^{1/2} \quad (19)$$

and M = mass of oxygen consumed by carbon sphere per second.

(Equations previously derived are numbered as in the previous paper. New equations required in this discussion are designated by letters.)

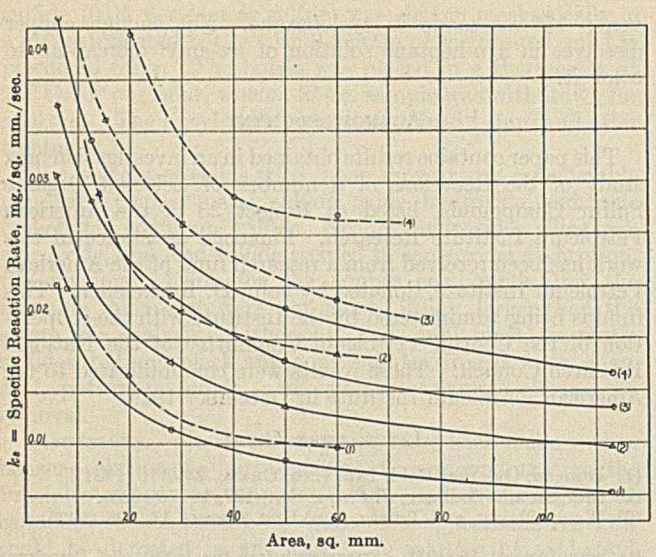

FIGURE 1. VARIATION IN SPECIFIC REACTION RATE WITH SIZE OF PARTICLE

(Ambient temperature, T_2 = 1000° C.)
— — — — Experimental curves, Smith and Gudmundsen, Figure 7 (4)
———— Theoretical curves
(1) Air velocity = v_0 = 1.09 ft./sec. (3) Air velocity = v_0 = 6.75 ft./sec.
(2) Air velocity = v_0 = 3.50 ft./sec. (4) Air velocity = v_0 = 10.25 ft./sec.

Adopting the definition of k_s as given above and giving C_1 its value for dry air,

$$C_0 = 0.00030p \frac{T_0}{T_2} \tag{1}$$

and remembering that 12 grams of carbon are consumed for every 32 grams of oxygen, it is found that

$$k_s = 0.0546 \frac{r_1 + B}{r_1 B} \frac{1}{T_2} \left(\frac{T^1}{T_0}\right)^{1.754} \tag{a}$$

The rate of reaction can now be calculated directly from this equation for given ambient and surface temperatures, if the value of the film thickness, B, is known. To determine the value of B, use is made of the fact that the heat developed by chemical reaction (H) must be equal to the heat conducted away (H_1) plus the heat radiated away (H_2).

From Equations 20, 22, 23, and 24

$$H = \frac{4\pi\ 43 r_1(r_1 + B)}{BT_2} \left(\frac{T^1}{T_0}\right)^{1.754} \tag{b}$$

When this value of H is put equal to $H_1 + H_2$, as given by Equations 8 and 21, the result is

$$E \frac{r_1(r_1 + B)}{B} = \frac{r_1(r_1 + B)}{B} F + G r_1^2 \tag{c}$$

where

$$E = \frac{43}{T_2} \left(\frac{T^1}{T_0}\right)^{1.745} \tag{d}$$

$$F = 0.000053\,(T_1 - T_2) \left(\frac{T_1 + T_2}{2T_0}\right)^{0.75} [1 + 0.0001\,(T_1 + T_2)] \tag{e}$$

$$G = 1.38 \left[\left(\frac{T_1}{1000}\right)^4 - \left(\frac{T_2}{1000}\right)^4\right] \tag{f}$$

From (c),

$$B = \frac{r_1(E - F)}{Gr_1 - (E - F)} \tag{g}$$

Substitute this value for B in Equation a, and it follows that

$$k_s = \frac{0.00127\ GE}{(E - F)} \tag{h}$$

From this equation is derived the important result that the specific reaction rate is independent of the size of the particle, provided the ambient and surface temperatures are the same, since E, F, and G are functions depending upon the temperatures only. In general, however, the surface temperature of the particle will be unknown. To find the reaction velocity in terms of known variables, it is therefore necessary to have a further equation. For this purpose the dependence of film thickness upon the velocity of the forced draught is used. Rice (3) gives the formula:

$$B = 2.0 \left(\frac{\mu D}{\rho v}\right)^{1/2}$$

where D = diameter of particle, cm.
μ = viscosity of fluid at temperature $\sqrt{T_1 T_2}$, poises
ρ = density of fluid, grams per cc.
v = velocity of fluid, cm. per second

If the values of the different factors are substituted in the above equation, the result is

$$v_0 = A \frac{r_1}{B^2} \tag{i}$$

where

$$A = 0.0154 \frac{T_1^{0.877}}{T_2^{0.123}} \tag{k}$$

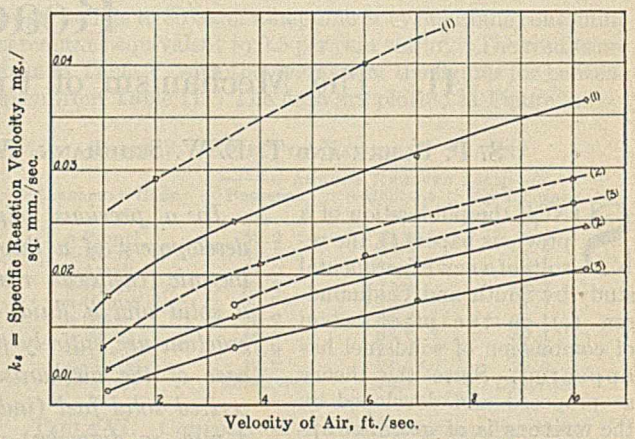

FIGURE 2. VARIATION OF REACTION RATE WITH AIR VELOCITY

— — — — Experimental curves, Smith and Gudmundsen, Figure 14 (4)
———— Theoretical curves
(1) Area of sphere = 10 sq. mm. (2) Area of sphere = 30 sq. mm.
(3) Area of sphere = 50 sq. mm.

From Equations g and h it follows that

$$\frac{1}{B} = \frac{k_s}{0.00127\ E} - \frac{1}{r_1} \tag{l}$$

Substitute this value in Equation i, and the result is

$$\frac{k_s}{0.00127\ E} - \frac{1}{r_1} = \left(\frac{v_0}{Ar_1}\right)^{1/2} \tag{m}$$

In this equation k_s, E, and A are functions of T_1 and T_2 only, and hence the value of T_1 can be determined in terms of T_2 and v_0. However, it is easier to assume values for T_1 and T_2 and then to determine the corresponding values of v_0. The values of k_s, E, and A, as calculated from Equations h, d, and k are given in Table I.

Calculations were carried out to find the relation between v_0 and T_1 for different values of the radius; Table II gives the value of v_0 for different values of T_1, r_1, and T_2.

TABLE I. VALUES OF k_s, E, AND A

T_2 ° K.: T_1		1400° K.	1500° K.	1600° K.	1700° K.	1800° K.	2000° K.
1200	k_s	0.00338	0.00581	0.00918	0.10325	0.01872	0.0334
	E	0.545	0.589	0.627	0.665	0.707	0.790
	A	3.70	3.92	4.13	4.39	4.58	5.02
1300	k_s	0.00182	0.00420	0.00732	0.01132	0.01635	0.0305
	E	.....	0.578	0.615	0.654	0.692	0.771
	A	.....	3.90	4.09	4.34	4.54	4.97
1500	k_s	.....	.....	0.00273	0.00630	0.01085	0.0238
	E	.....	.....	0.600	0.632	0.668	0.742
	A	.....	.....	4.03	4.26	4.46	4.88

TABLE II. VALUES OF v_0

(In cm. per second at 24° C.)

r_1	T_1, ° K. 1400	1500	1600	1700	1800	2000
			T_2 = 1200° K.			
0.07	..	...	...	....	14.8	129
0.1	..	...	...	14.2	55.9	282
0.15	..	...	14.5	53.3	139.3	547
0.2	..	6.05	36.0	101	237	830
0.3	2.67	23.2	83.3	180.5	433	1435
			T_2 = 1300° K.			
0.07	..	...	...	....	5.82	97.5
0.1	..	...	...	5.71	38.6	223
0.15	..	...	4.54	31.9	97	447
0.2	..	...	15.7	64.8	169	681
0.3	..	6.76	44.8	138	318	1220
			T_2 = 1500° K.			
0.07	..	...	...	....	....	41.1
0.1	..	...	...	....	3.5	114.5
0.15	..	...	...	....	25.1	254
0.2	..	...	...	7.35	54.1	404
0.3	..	...	...	27.6	119	722

A set of curves was constructed from the data so computed, and from these curves the temperatures, T_1, were read off for given air flows, expressed in feet per second at 24° C. The values of the corresponding k_s are also given.

The solid curves shown in Figures 1, 2, and 3 were drawn from the data computed in Table III. The experimental curves (broken) were drawn from the data given by Smith and Gudmundsen (*4*). A direct comparison of the experimental and theoretical results is thus afforded. It is to be noted that the experimental points are for wet air. It is believed that the relative absence of carbon monoxide effects, when using moist air, causes the combustion mechanism to be more in accord with that postulated by the writers. When using dry air, Smith and Gudmundsen obtained an increased rate of reaction of approximately 10 per cent. This is scarcely in agreement with the theory which would predict an increase in reaction rate of approximately 3 per cent, owing to the increased concentration of oxygen. Moreover, it was found experimentally that, although the absence of moisture increased the reaction rate, it decreased the surface temperature of the particles. This result definitely contradicts the present theory. The authors believe—as Smith and Gudmundsen have suggested—that the explanation of this phenomenon is involved in the production of carbon monoxide during combustion. In a subsequent paper, a quantitative treatment of the theory, modified to include the effect of carbon monoxide formation, will be presented.

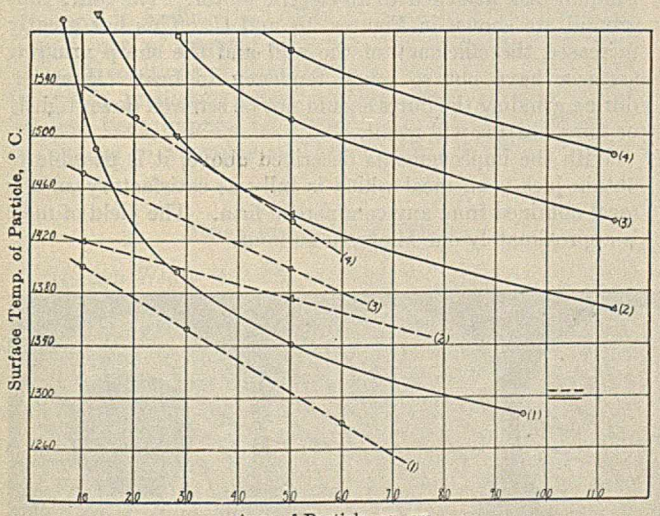

FIGURE 3. SURFACE TEMPERATURE OF PARTICLES OF DIFFERENT SIZES

(Ambient temperature, T_2 = 1000° C.)
— — — — Experimental curves, Smith and Gudmundsen, Figure 7 (*4*)
———— Theoretical curves
(1) Air velocity = 1.09 ft./sec.
(2) Air velocity = 3.5 ft./sec.
(3) Air velocity = 6.75 ft./sec.
(4) Air velocity = 10.25 ft./sec.

TABLE III. VALUES OF T_1 AND k_s FOR SPECIFIC VALUES OF r_1, v_0, AND T_2

v_0 Feet/sec.	Area (sq. mm.) 113	50.2	28	12.55	6.15
	r_1 (cm.) 0.3	0.2	0.15	0.1	0.07
			T_2 = 1200° K.		
			T_1		
1.09	1515	1587	1650	1750	1855
3.50	1618	1695	1760	1855	1967
6.75	1688	1755	1842	1940	2032
10.25	1750	1825	1893	2000	2110
			k_s		
1.09	0.0064	0.0087	0.0111	0.0159	0.0224
3.50	0.0098	0.0130	0.0164	0.0224	0.0308
6.75	0.0127	0.0163	0.0215	0.0287	0.0360
10.25	0.0154	0.0204	0.0252	0.0334	0.0429
			T_2 = 1300° K.		
			T_1		
1.09	1570	1640	1696	1790	1890
3.50	1666	1740	1800	1895	2000
6.75	1734	1812	1876	1975	2085
10.25	1785	1865	1930	2040	....
			k_s		
1.09	0.0063	0.0088	0.0111	0.0158	0.0223
3.50	0.0098	0.0132	0.0164	0.0227	0.0306
6.75	0.0129	0.0171	0.0212	0.0286	0.0370
10.25	0.0155	0.0205	0.0252	0.0336	....
			T_2 = 1500° K.		
			T_1		
1.09	1705	1760	1810	1880	1975
3.50	1782	1848	1900	1981	2078
6.75	1840	1910	1965	2065	....
10.25	1882	1955	2015	....	....
			k_s		
1.09	0.00655	0.00855	0.0114	0.0156	0.0220
3.50	0.00990	0.0137	0.0168	0.0224	0.0298
6.75	0.0130	0.0175	0.0214	0.0288	....
10.25	0.0157	0.0206	0.0250	....	....

DISCUSSION OF RESULTS

In the previous paper (*1*), excellent agreement was shown between the results of this theory and the experimental results obtained for the combustion of pulverized fuel. It is evident from the curves presented that, although the agreement is not quite so good, the theory is unquestionably confirmed in general by the experimental results obtained for the combustion of small spheres of carbon. The greatest discrepancy between theory and experiment is found in the actual magnitude of the surface temperatures of the carbon particles. Even here, however, the increase in surface temperature as the particle becomes smaller is quite in agreement with theoretical predictions. The effect of velocity on the rate of reaction (Figure 2) and the rather surprising increase in the rate of reaction with diminution in size of particle (Figure 1) are both in excellent agreement with theoretical predictions. The theory, thus far presented, does not however account for the effect of moisture on the combustion process.

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RECEIVED January 5, 1932. Presented before the Division of Gas and Fuel Chemistry at the 81st Meeting of the American Chemical Society, Indianapolis, Ind., March 30 to April 3, 1931.

Crystalline Urease

Preparation of Meal from Jack Beans

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The claim made in 1926 that the octahedral globulin crystals, which can be readily obtained from jack-bean meal, are identical with the enzyme, urease, was at first received with considerable skepticism. Recent work by Sumner and his collaborators, as well as the work by Northrop on crystalline pepsin, has done much to dispel this. This article describes a small mill for grinding jack beans to a meal suitable for preparing urease crystals. Since the burrs of the mill are of porcelain, while the other parts are of iron, there is no possibility of poisoning the enzyme by the introduction into the meal of copper or any other undesirable heavy metal. The grinding is carried out in such a manner as to ensure a minimal amount of destruction of the enzyme by heating.

In order to obtain urease crystals (*1–5*) in good yield, it is necessary to employ jack beans rich in extractable urease and to grind the beans to a fine powder without heating and without the introduction of heavy metals, such as copper. Although it is not yet certain what conditions are requisite for growing beans rich in urease, the authors have succeeded, after several failures, in learning how to grind jack beans properly.

The beans must be thoroughly dry before grinding. This can be attained by spreading them out in a thin layer on a clean blanket and leaving for about 2 weeks in a room heated during the daytime to 75° F. (23.9° C.). The beans are then broken into a meal about as coarse as chicken feed by putting them once through a large coffee mill equipped with steel burrs. Since the hulls are devoid of urease, they are removed at this stage, as far as practicable, either by picking out by hand, or by first sifting the fine material through cheese cloth and then allowing the coarse material to fall through an air blast from an electric fan and into a box. The light hulls are blown away.

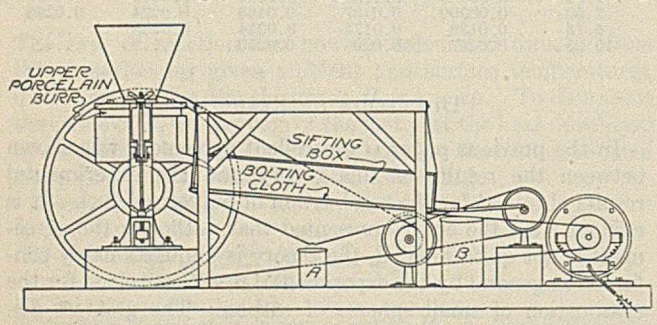


Figure 1. Mill for Grinding Jack Beans

Description of Mill

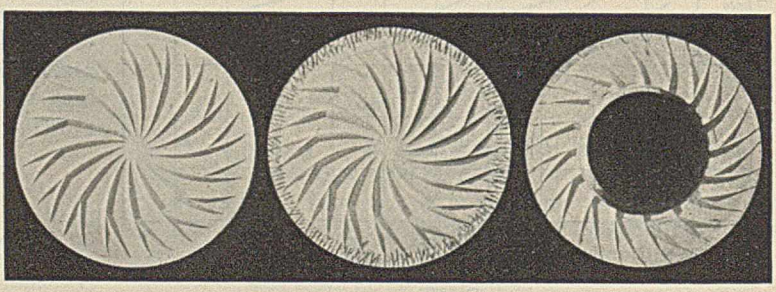
The mill here used for completing the grinding to a fine powder was made by F. A. Lentz of Berlin, Germany, and was supplied by the A. H. Thomas Company of Philadelphia. The mill had been constructed to be driven by hand and was adapted to driving by a 0.25 h. p. motor by cutting a groove in the large wheel (shown in Figure 1) and attaching a $^3/_8$-inch leather belt. In order to reduce the speed to 105 r. p. m., a reducing head, equipped with variable diameter pulleys, was inserted between the motor and the mill.

It was necessary to construct a bolting box, shown in Figure 1. The meal delivered from the mill passes into one end of this box, and the fine material is sifted through a No. 14 stretched silk bolting cloth and then falls from a hole in the bottom of the box into beaker *A*. The material which is too coarse to pass through the cloth leaves the box through a wooden tube at the other end and collects in beaker *B*, and is put through the mill again. The box is suspended from an iron framework by four iron hack-saw blades and is shaken 550 times a minute by attachment to an eccentric run by a belt from a pulley on the polishing head.

As delivered from the manufacturer, the mill had an opening in the flange above the spout, and from this opening much of the meal escaped during grinding. This loss of material was prevented by placing about the burrs and within the flange a thin strip of Russian iron, 4 by 25 inches.

Figure 2*A* shows the grinding surface of the lower porcelain burr supplied with the mill. The smooth rims at the periphery of the burrs caused the meal to cake and to heat and this heating partly inactivated the urease. Therefore grooves were ground in the lower burr and were continued in the upper burr to the periphery by means of a Bakelite-Carborundum disk attached to an electric motor. The burrs thus ground are shown in Figures 2*B* and *C*. This has greatly increased the efficiency of the mill and the sharp grinding surfaces have not so much tendency to heat. However, during grinding the burrs should not be screwed down tightly or some heating will result.

With the improvements described above, it is possible to obtain jack-bean meal which is fully as satisfactory as any meal obtained from any commercial firm. The yield of meal is approximately one kilogram an hour.



A *B* *C*

Figure 2. Grinding Surfaces of Burrs

A. Bottom burr as supplied with mill. *B.* Bottom burr as modified by grinding. *C.* Top burr as modified by grinding.

ACKNOWLEDGMENT

The authors wish to acknowledge their indebtedness to the Heckscher Foundation of Cornell University for financial aid without which this work would have been impossible, and to the A. H. Thomas Company for their generous coöperation.

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Application of Dühring's Relation to Solubilities

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It has been found that Dühring's relation can be used to predict the solubilities of non-hydrated, inorganic salts in water at various temperatures. Results are obtained of an accuracy often as good as the data themselves and rarely poorer than 5 per cent, even though but two points far apart on the solubility curve have been determined experimentally.

IN 1878 Dühring announced an empirical relation by the use of which the vapor pressure of a substance can be calculated with reasonable accuracy. Although the rule has been expressed mathematically by Dühring and others (*3, 7, 10*), the calculation is generally made graphically. If the temperatures at which one substance exerts certain vapor pressures be plotted against the temperatures at which a reference substance exerts the same vapor pressures, the points are found to lie nearly upon a straight line. Therefore, if the vapor pressure of a substance be known at two points, a straight line may be drawn in accordance with Dühring's relation, the complete vapor-pressure data for a reference substance having been taken from the literature. From this Dühring line the entire vapor-pressure curve of the substance in question may easily be calculated.

Dühring's relation has been used in recent years by a number of investigators. Badger and McCabe (*1*) and Walker, Lewis, and McAdams (*11*) call attention to its use in evaporator design and in determining the latent heat of vaporization of solutions and pure liquids (*9*). It has also been used in finding the boiling point *vs.* composition curves of solutions of organic solvents, and the vapor pressure curves of solutions of electrolytes in water (*2*). Aside from its use in predicting vapor-pressure data, Dühring's relation has been applied by Porter (*12*) to the estimation of the change in viscosity of liquids with changing temperature.

THEORETICAL DISCUSSION

Although White (*13*) has since shown it to be compatible with the integrated form of the Clausius-Clapeyron equation, Dühring's relation was first discovered as an empirical rule suggested by the close similarity of vapor-pressure curves. But it has been shown by Hildebrand (*4*) and others that the ideal case of solution is quite analogous to that of vaporization. It would therefore seem plausible that Dühring's relation should apply to solubility curves in general. Moreover, the solubility curves of salts in water, especially of salts of the same chemical nature, are similar in shape; so for this reason also Dühring's relation should be expected to apply.

Mathematically speaking, for the relation to apply to solubility curves, it is necessary only that they be of the form:

$C + KT$ = any function of M where C and K = constants
T = temperature
M = solubility in moles per 1000 grams of water

Temperature may or may not be absolute. Then, if for two salt solutions the solubility be chosen the same,

$$f(M_1) = f(M_2), \text{ and } C_1 + K_1T_1 = C_2 + K_2T_2$$

or the graph of T_1 vs. T_2 will be a straight line.

Many attempts have been made to formulate the equation for the variation of the solubility of electrolytes with temperature, but the problem is complicated by the ionization of the electrolyte and by the possible hydration of the ions. Some have introduced correction factors to allow for these effects, but equations so modified are usually made so involved that they have lost their practical utility. The ideal solubility equation is derived in the same way as is the Clausius-Clapeyron equation, and is generally deduced for organic solutions on the assumption that Raoult's law applies. Such is the case for solutions of naphthalene in organic solvents, and Hildebrand (*5*) has shown that in these instances the graph of $\frac{1}{T}$ *vs.* log N_2 (where T is the absolute temperature and N_2 is the mole fraction of solute) are straight lines. However, Hildebrand further shows (*6*) that, in the case of solutions of electrolytes in water, the simple relation no longer obtains, and the modified equation, which is even then admittedly not exact, becomes too unwieldly to be of value in predicting solubilities. Dühring's relation, however, can be easily applied, and results are obtained which are within the accuracy ordinarily required in engineering calculations.

Another relation which has been of service in predicting vapor pressures is that of White (*13*): The graph of $\frac{1}{T_1}$ *vs.* $\frac{1}{T_2}$, where T_1 and T_2 are absolute temperatures at which two substances have equal vapor pressures, is a straight line. Obviously in the case of ideal solubility above referred to, where

$$\frac{K}{T} = \log N_2 + C$$

White's rule will apply exactly. This relation has, therefore, more theoretical justification than Dühring's as yet enjoys, but the actual results of its application are sometimes hardly as accurate. Almost no deviation from the rule was noted when the nitrates of caesium, rubidium, lead,

and silver and when caesium chloride were plotted against potassium nitrate according to the inverted-temperature rule, but in several other cases the results were poor. It may be that the method tends to accentuate minor deviations. At any rate the plotting is slightly more troublesome and apt to be less accurate than when Dühring's relation is used.

Method of Applying Dühring's Relation

In Figure 1 are plotted the Dühring lines of several salts, using potassium nitrate as a reference substance. In order to make up the illustration, the temperatures at which a salt had certain solubilities were plotted against the temperatures at which potassium nitrate had the same solubilities. The Dühring lines shown are representative of a considerable number plotted using potassium nitrate as a base. Data were taken from the International Critical Tables and were expressed in moles per 1000 grams of water.

The advantage of the method lies in the fact that determinations of the solubility at two or three temperatures suffice to fix the Dühring line. The solubility at other temperatures can be predicted as follows: Take, for example, the problem of calculating the solubility of silver nitrate at 20° C. From the Dühring line for silver nitrate (line I in the figure), the solubility at 20° C. is equal to that of potassium nitrate at 64.7° C. From a curve for the solubility of potassium nitrate this solubility is 12.15 moles per 1000 grams of water. This, then, is the solubility of silver nitrate at 20° C. The value given in the International Critical Tables is 12.30 ± 2 per cent. The accuracy of plotting was within 1 per cent. Table I shows the results of calculation from a few Dühring lines.

Table I. Solubilities Calculated from Dühring Lines

(Data from International Critical Tables)

Temp.	Solubility					
	$AgNO_3$		NH_4Cl		$CsNO_3$	
° C.	Calcd.	Obsd.[a]	Calcd.	Obsd.[b]	Calcd.	Obsd.[c]
	Moles per 100 grams of water					
−15	...	...	...	4.60[d]	...	...
−5	...	5.60[d]	...	...	...	...
0	6.66	6.65	5.53	5.55	...	...
5	7.93	7.80	...	...	...	...
10	9.19	9.20	6.20	6.22	...	...
15	10.61	10.75	6.56	6.58	...	...
20	12.15	12.30	6.92	6.97	...	...
25	13.82	14.00	7.32	7.38	...	...
30	15.62	15.95	7.75	7.78	...	1.86[d]
40	19.50	19.50[e]	8.54	8.63	2.52	2.61
50	...	23.6[d,e]	9.43	9.43	3.34	3.50
60	...	...	10.29	10.34	4.37	4.52
70	...	...	11.19	11.20	5.53	5.64
80	...	...	12.17	12.15	6.98	6.92
90	...	...	13.20	13.2	8.57	8.40
100	...	...	...	14.2[d]	10.29	10.10
110	...	...	...	...	...	12.2[d]

[a] ±2%. [b] ±1%. [c] ±3%.
[d] Points used in determining Dühring lines.
[e] Accurate to only 10 per cent.

As would be expected, the rule is not exact in its application. The function of M referred to above, though it may be the same in form for all solutions, no doubt includes some factors which are different for different solutions under various conditions. The only reason Dühring's relation applies so well is that these factors are nearly alike and vary in much the same way with nearly all salt solutions of the same order of concentration. Obviously two salts with solubilities of different orders cannot be plotted against each other by Dühring's method. It has been found, however, that, in the range of slightly soluble salts where concentrations are low in any case, salts of different solubilities may be quite satisfactorily plotted against each other by multiplying the data for one salt by a constant to make the range of solubilities overlap. Solubilities thus calculated are then divided by this constant. The foregoing scheme has been used to plot calcium and strontium oxalates against barium oxalate, and in this case it worked very well.

From the Dühring lines in the figure and from a number of others investigated, it appears to make little difference whether or not the unknown salt is chemically similar to the reference substance used. It would seem that the factors in the function of solubility which change, whether because of temperature or concentration, change in the same way for all solutions of nonhydrated salts of comparable orders of solubility and are, to some extent at least, independent of the chemical nature of the salt in question. The case of solutions of hydrated salts is somewhat more complex. A few hydrated systems such as the strontium nitrates shown in Figure 1 and the zinc sulfates, form families of straight lines intersecting at the transition points. It is much more usual, however, for the Dühring line of a particular hydrate to continue straight for a while and then, as the point of transition into the next hydrate is approached,

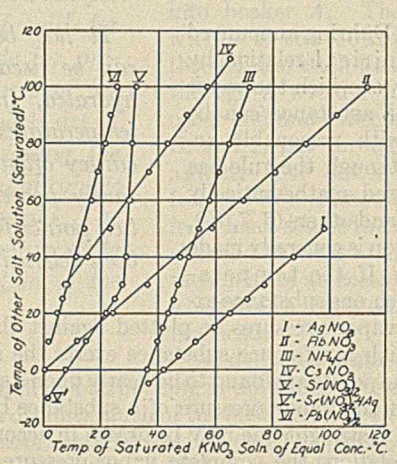

Figure 1. Dühring Lines of Various Salts

to curve sharply. Indeed there may be no straight portion. These results are what we should expect, for the theory already advanced (*8*) is that solution of the hydrates is accompanied, near the transition points at least, by concurrent dissociation of the hydrated molecule. Under these conditions Dühring's relation could not be expected to apply.

Poor results also were obtained when organic salts, such as calcium propionate, were plotted against potassium nitrate. Aside from the fact that the calcium propionate contains one molecule of water of hydration, the salts are so dissimilar that poor results would be expected. The case is interesting, however, for calcium propionate exhibits decreasing solubility. Few nonhydrated inorganic salts show this phenomenon. Anhydrous sodium sulfate decreases in solubility to a minimum, then it increases very slowly. The Dühring line is straight to the point of minimum solubility; then it changes direction sharply, giving another straight line which is vertical because further variation in temperature produces only a slight change in solubility. Strictly speaking, since the sodium sulfate solubility curve includes a hydrate, Dühring's relation should not be applied. But with it, as with several other hydrated systems, straight lines are obtained for the anhydrous salt.

One exception to the applicability of Dühring's relation has been found. In the case of thallium nitrate the Dühring line exhibits pronounced curvature. Other thallium compounds, as the hydroxide, follow the rule well, but the nitrate seems to be a real exception. No explanation has as yet been found for the behavior of this salt. It appears to be anomalous. No other exception has been noted when

inorganic nonhydrated salts were plotted against potassium nitrate, although a considerable number of cases have been investigated. The exception cautions us, however, to determine an unknown Dühring line at three points, in order to prove the line to be substantially straight before it is used in the prediction of solubilities.

ACKNOWLEDGMENT

Acknowledgment is made to A. S. Eastman of the University of Delaware for assistance in the preparation of this paper.

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Vitamins in Canned Foods

XII. Supplementary Nature of Grapefruit and Prunes

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APPARENTLY the earliest work on the vitaminic properties of prunes was that by Hess and Unger (*2*). They studied only the dehydrated fruit and came to the conclusion that it possessed practically no value as a preventive against scurvy.

Eckman (*1*) studied a number of dried fruits, including prunes, to determine their antiscorbutic properties, and concluded that peaches were the only dried fruit fed in moderate amounts that would sustain life for several months when they supplied the only antiscorbutic. Even with peaches, scurvy was not prevented but only delayed.

Osborne and Mendel (*6*) found dried prunes to have appreciable vitamin B, being considerably richer in this factor than apples or pears.

Morgan and Field (*4*) demonstrated that sulfuring prior to the drying process caused the vitamin A content in dried fruits to be retained in substantially greater amounts than if the sulfuring were omitted. It may be inserted here that sulfuring prior to dehydration of prunes is not commercially practiced. Morgan, Field, and Nichols (*5*) found sulfuring to have even more marked effects in retaining the vitamin C potency of dehydrated prunes. As fresh prunes are in season for only a short period, they froze fresh prunes to insure a supply for the feeding period. They report protective doses varying from 12 to 20 grams of frozen prunes from different seasons, but growth was subnormal. Apparently, no one has studied the vitamin content of canned prunes.

MacLeod and Booher (*3*) report some data on the vitamin C content of both raw and canned grapefruit. They found that standard guinea pigs were protected against scurvy in dosages of approximately 2.0 grams, either of juice alone or combined juice and pulp. While somewhat more canned grapefruit was necessary, the larger dose was approximately accounted for by the extent to which grapefruit is diluted in canning by the added sirup.

Osborne and Mendel (*6*) state that the vitamin B content of the fresh juice of grapefruit is about comparable to that of milk, but that no more than traces, if any, of vitamin A are present.

TYPES OF FRUIT USED

During the past year, the present authors have made a comprehensive study of both canned fresh prunes and canned fresh grapefruit. These experiments were planned to determine the effect on vitamin content, if any, of variations employed in the canning of each fruit, as well as to make a general survey of the vitamin content of these canned fruits. Both French and Italian prunes were included in the studies. The French prune is a high-sugar low-acid prune and comprises the great bulk of dried prunes on the market. Italian prunes are relatively high in acid and low in sugar, as compared with the French variety. While the French prunes of this country are grown largely in California, the Italian prunes are grown mostly in Oregon and Washington. French prunes are not commercially canned in the fresh state. While formerly practically all the Italian prunes were dehydrated or dried also, within recent years canning of the fresh prunes has grown to a considerable proportion. The high-acid and color content of the Italian prunes makes them particularly suitable for canning in the fresh state. The color of the sirup of these prunes when canned is a deep rich reddish purple.

The following lots of canned prunes were studied:

LOT SY, CANNED FRESH FRENCH PRUNES. The fruit for this lot was shaken from the tree onto canvas at the time and as is customary in harvesting for drying or dehydration. If a comparison with canned fresh Italian prunes is desired, this lot should be compared with lot 2 below.

LOT 1, CANNED FRESH (SEMIRIPE) ITALIAN PRUNES. A portion of the prunes on a few trees were picked by hand on September 2 when well colored, but when the sugar had not yet developed to a marked extent in them.

LOT 2, CANNED FRESH ITALIAN PRUNES. Two weeks after lot 1 was picked and canned, the prunes were all harvested for canning, as they had then reached the normal stage for harvesting. While the color was not much greater than that of the prunes picked 2 weeks earlier, the sugar had developed to its full extent. This lot of prunes was subjected to a vacuum of 27 to 28 inches under sirup, and the vacuum was released while the prunes were still under the sirup. In this way any air within the prunes—particularly, that surrounding the pits—would be removed.

LOT 3, CANNED FRESH ITALIAN PRUNES. Fruit from the

same batch as used for lot 2, but canned direct without first subjecting the prunes to a vacuum.

Lot 4, Canned Fresh Italian Prunes. Fruit from the same batch as used for lot 2. Prior to canning, the prunes were held submerged in a 30° (Brix) sirup for 11 hours at room temperature. The purpose of this was to enable the prunes through the respiratory process to use up any oxygen within their tissue.

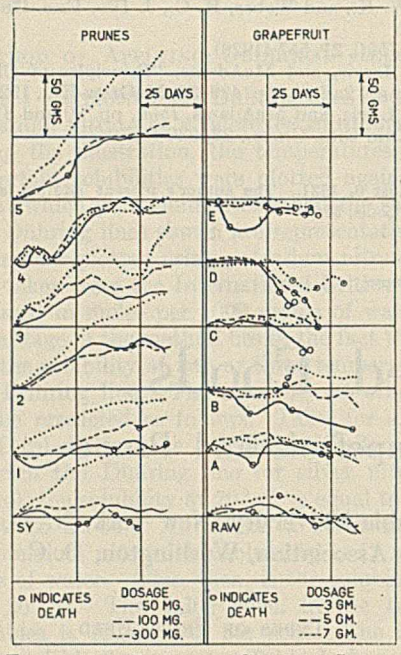

Figure 1. Average Growth Increments of Three or More Standard Test Rats Receiving Varying Dosages of Canned Prunes and of Raw and Canned Grapefruit as Sole Source of Vitamin A

Lot 5, Canned Semi-Dehydrated Fresh Italian Prunes. Fruit from the same batch as used for lot 2. Prior to canning this lot of prunes, they were subjected to the regular dehydration process at a temperature of 125° F. (51.7° C.) for 2 hours, during which time 146 pounds (66.2 kg.) were reduced to 127 pounds (57.6 kg.). As dehydration has been found to be destructive to vitamin C, it was desirable to determine whether this destruction occurs early in the dehydration process or not. Partial dehydration would permit getting more fruit into the can.

A study was also made of sun-dried and dehydrated French as well as dehydrated Italian prunes. Inasmuch as present results confirm those already published and referred to above, no further data on these will be given here.

In the canning of grapefruit two major variations in the processes are used. One variation is in the method of peeling, and the other is in the method of exhausting the can prior to closing. Grapefruit are either peeled by hand or by the so-called lye-peeling process. In the latter the grapefruit are first subjected to steam to loosen the outer peel. This is then torn away by hand. The grapefruit, then, with considerable of the white albedo portion still attached, are subjected to a hot lye bath for a few seconds. Immediately upon emerging from the lye bath, they are subjected to forceful jets of water which completely remove the albedo, softened by the lye, and wash off any adhering lye at the same time. Whether hand-peeled or lye-peeled, the grapefruit are divided into sections by hand.

After these sections are filled into the can, the can is exhausted in one of two different procedures: Either it is subjected to a mechanical vacuum and closed while under this vacuum without the application of any heat, or the filled can is passed through a hot-water box in which it is immersed to a depth of approximately 1 inch from the top. The time in the exhaust box varies approximately from 16 to 18 minutes, and the temperature of the water is commonly at 180° F. (82.2° C.). This process tends to speed up the respiratory process whereby any oxygen in the cells would be consumed, and at the same time tends to drive out oxygen in solution in the sirup. After closing the cans, they are cooked similarly, irrespective of the method of exhaust, except that the hot exhaust has some sterilizing value and permits shortening of the cook.

To cover the question of exhaust, the following two lots were packed from the same batch of fruit.

Lot A. Hand-peeled grapefruit, canned by the so-called vacuum process, in which the cans while being closed were under a vacuum.

Lot B. Hand-peeled grapefruit. Before closing the cans, they were passed through an exhaust box which required 20 minutes. The cook for lot A was 31 minutes, as against 20 minutes for lot B.

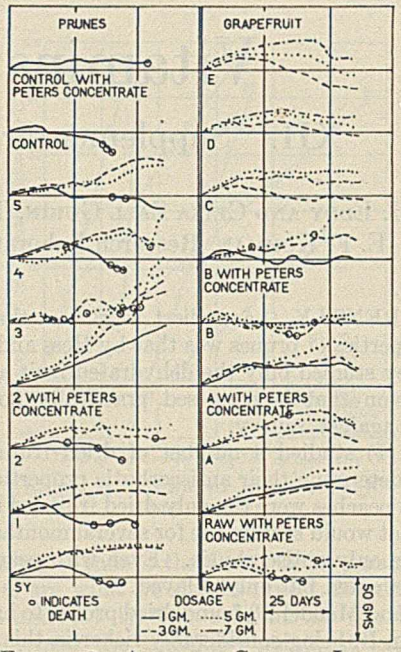

Figure 2. Average Growth Increments of Three or More Standard Test Rats Receiving Varying Dosages of Canned Prunes and of Raw and Canned Grapefruit as Sole Source of Vitamin B

Lot C. Grapefruit are sometimes picked when quite immature to supply the early city market. A grapefruit tree ordinarily blooms in April. However, some trees bloom as late as June. The fruit from this late bloom is commonly called "June-bloom" fruit. Although picked at the regular harvesting time, this fruit is quite immature. In order to secure data on it as to its relative vitamin potency, June-bloom fruit, lot C, was canned according to the same method as used in lot A. This fruit was grown in the same locality as the fruit used in lots A and B.

Studies were made to determine the effect, if any, of the lye-peeling as against hand-peeling, and also to determine any possible difference in grapefruit from different sections of Florida:

Lot D. Lye-peeled grapefruit.

Lot E. Hand-peeled grapefruit packed from the same batch of fruit as was used for lot D.

Results of Feeding Tests

The results of the feeding tests are graphically given in Figures 1 to 4, inclusive. In most cases a graph is the average growth increment of three animals. Occasionally more ani-

mals were used. In the case of the death of an animal, represented by a circle on the graph, the remainder of the graph represents the average growth increment of the remaining animals. For the sake of brevity, records as to severity of symptoms resulting from vitamin deficiency are omitted because they correlate very well with the growth record. The dosages refer to the weight of fruit fed. The actual

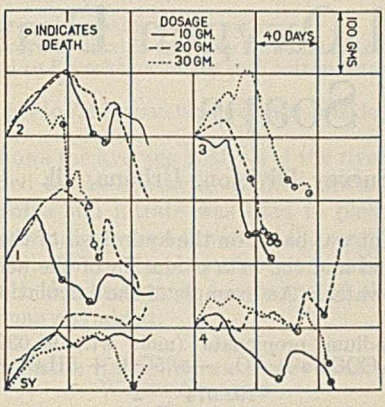

FIGURE 3. AVERAGE GROWTH INCREMENTS OF THREE OR MORE STANDARD TEST GUINEA PIGS RECEIVING VARYING DOSAGES OF CANNED PRUNES AS SOLE SOURCE OF VITAMIN C

weight fed of the canned material was increased in proportion to the dilution by the sirup added in canning. Standard animals and procedures were used as in previous reports of this series.

In Figure 1 are given the data for the vitamin A content of both prunes and grapefruit. While a dosage of from 50 to 100 mg. of prunes is adequate to produce the standard growth increment of 3 grams per week, it will be noticed that dosages ranging from 3 to 7 grams of grapefruit were scarcely able to maintain weight, and many deaths occurred before the end of the feeding experiment. There is no justification from the data in Figure 1 or from careful observation of the animals during the test to distinguish between the various lots of canned prunes, with the possible exception of lot 5, which seems to give a better growth curve. Since this lot was dehydrated to the extent of about 13 per cent, this is logical. The growth increment in all lots corresponds to that obtained by Morgan and Field from fresh prunes, and it seems, therefore, that there was no destruction of vitamin A during canning. The lack of material vitamin A in grapefruit, as evidenced by the data in Figure 1 and observation of the animals during the test, is in agreement with the findings of Osborne and Mendel.

In Figure 2 are given similar data pertaining to the vitamin B content of prunes and grapefruit. In this, equal dosages of both fruits were fed, and, it will be noted, with very comparable results. Although the addition of the antineuritic factor meets with response, this response is only moderate. One may conclude, therefore, that both prunes and grapefruit contain both the B and G factor, but in rather limited quantities. As 3 grams per day, in all cases with the prunes and in most cases with grapefruit, maintained weight over the 60-day feeding period unfortified with vitamin B concentrate, present results confirm those of Osborne and Mendel that these fruits are approximately equivalent to milk in vitamin B content, the prunes rating somewhat the higher of the two. As response, when fortified with vitamin B concentrate, seemed to be best with prunes, one may assume them to have a somewhat higher vitamin G content.

The data in Figure 3 show that response from prunes as a source of vitamin C is limited. It should be noted that the larger dosages of prunes had other physiological effects on the animals than supplying vitamins, particularly, a laxative effect. This may obscure the actual vitamin C content.

As a contrast to the data in Figure 3 on prunes, the data in Figure 4 leave no doubt as to the potency of grapefruit, raw or canned, in vitamin C. From the available data it would not be justified to conclude that there is any difference in raw or canned grapefruit, that the various methods of canning affect the vitamin C in any way, and that June-bloom fruit is any different from the more mature fruit. In all cases the 3-gram dosage was protective, and only mild symptoms of scurvy were in evidence with the 2-gram dosage. These were not present in all animals. Even on 1.5 grams, growth was fair and only three out of eighteen animals failed to survive on this dosage for 90 days.

SUMMARY

Six lots of canned prunes (including the French and Italian varieties), raw grapefruit, and five lots of canned grapefruit were studied for their vitamin A, B, C, and G content. The various lots of canned fruit represent varying packing procedures. Each lot of the two fruits was fed in at least three dosages with at least three animals on each dosage. As the various lots of canned fruit gave almost identical results, the evidence presented may be taken to represent the vitamin potency of these canned fruits in general.

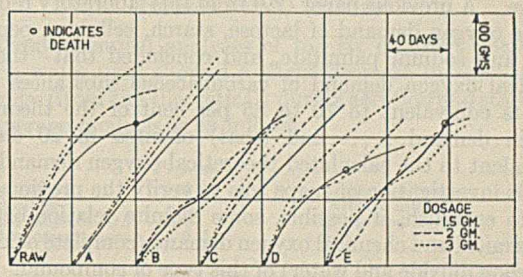

FIGURE 4. AVERAGE GROWTH INCREMENTS OF THREE OR MORE STANDARD TEST GUINEA PIGS RECEIVING VARYING DOSAGES OF RAW AND CANNED GRAPEFRUIT AS SOLE SOURCE OF VITAMIN C

While approximately 100 mg. of canned prunes contain one unit of vitamin A as defined by Sherman, as high as 7 grams of grapefruit, raw or canned, were not able to maintain weight in standard test rats. Judging from evidence available, the vitamin A of neither fruit is injured to any noticeable degree by canning.

Both varieties of prunes contain a moderate amount of vitamins B and G, being approximately comparable to milk in vitamin B potency. Like milk, too, they are richer in G than B. While there are no data available as to these vitamins in raw prunes, no difference between raw and canned grapefruit is in evidence in their content of vitamins B and G.

There is equally as great a contrast between prunes and grapefruit in their vitamin C as in their vitamin A content, but in this case the vitamin is most abundant in grapefruit. No amount of canned prunes could be fed that would completely protect guinea pigs from scurvy. Evidence on the vitamin C potency of raw prunes is available only in case of the French variety. Judging from this there is some loss of vitamin C upon canning. However, canned fresh prunes have distinctly more vitamin C value than dried prunes, the only other form in which they are generally available. Apparently canning of grapefruit has practically no adverse effect on its vitamin C.

Special interest attaches itself to the marked contrast in vitamin A and C potency of these two fruits in view of their both being tree fruits grown under similar climatic conditions.

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Preparation and Biochemical Oxygen Demand of Pure Sodium Soaps

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RECENTLY, interest has been revived in the development of a microcombustion or strictly chemical means of determining the oxygen demand of sewages in order to eliminate the time and labor necessary in the determination of biochemical oxygen demand. There are several papers in the literature covering some phase of this problem (*1–7, 9, 10, 14, 19–21*). The use of such a rapid chemical method for the determination of the oxygen demand depends on the correlation of the biochemical oxygen demand with the stoichiometric oxygen demand of the substances found in sewage. A previous paper (*20*) from this laboratory reported on the oxygen demand of lactose, starch, cellulose, peptone, urea, and sodium palmitate, and concluded that "the biochemical oxygen demand of carbonaceous substances in 30 days is equivalent to 70 to 85 per cent of the theoretical oxygen demand.....and (that) of urea in 20 days is equivalent to the calculated theoretical oxygen demand."

This investigation of soaps was to verify the previous data and to establish, if possible, some definite relation between biochemical and chemical oxygen demand (complete oxidation to carbon dioxide and water) of this type of compound.

EXPERIMENTAL PROCEDURE

PREPARATION OF SOAPS. By definition (*12*), "A soap is the salt of any monobasic aliphatic acid containing six or more carbon atoms." In this work, however, the sodium salts of the lower fatty acids are also called "soaps" since they are members of a homologous series and consequently undergo the same type of oxidation as the higher members of the series.

The preparation of the pure soaps was carried out in the following steps:

1. Purification of the acids by repeated fractional distillation or fractional crystallization.
2. Neutralization of the acid with carbonate-free sodium hydroxide solution (0.1 *N*).
3. Extraction of the water solution with petroleum ether to remove excess acid.
4. Boiling of water solution to remove esters.
5. Evaporation over steam bath and drying at 175° C.
6. Determination of melting point and purity (from sodium content).

Use of alcohol, ether, etc., for the recrystallization of the soaps was impossible, owing to formation of gels. The sodium content of the soap (index of purity) was determined by treatment with sulfuric acid, digestion to dryness, ignition, and weighing of the sodium sulfate. The isovalerate and stearate decomposed slightly during drying at 175° C., as evidenced by the change in the physical appearance (darkened slightly) and the sodium content.

The amount of soap needed for each investigation was that which, when dissolved in 2.3 liters of water, would have an oxygen demand of 5 mg. of oxygen per liter. The calculation of this amount was based on the hydrolysis of the soap to the free fatty acid and the beta oxidation of the acid to carbon dioxide and water. An example of the calculation follows:

Sodium propionate (mol. wt., 96.037)

$$2CH_3CH_2COONa + 7O_2 \longrightarrow 5CO_2 + 5H_2O + Na_2CO_3$$

$$\frac{192.074}{224} = \frac{x}{5}$$

x = 4.287 mg. sodium propionate per liter to require 5 mg. oxygen for complete oxidation.

The molecular weights used were calculated from the International Atomic Weight Table of 1927. Since these amounts were exceedingly small (48.875 mg., maximum; 4.2879 mg., minimum), weighing error was minimized by weighing ten to twenty times the amount needed and dissolving in 1 or 2 liters of dilution water so that 100 ml. of the solution contained the proper quantity.

In Table I are listed the soaps investigated with the purity and physical constants of each.

TABLE I. LIST OF SOAPS INVESTIGATED

Soap	Purity[a]	Melting Point[b] Reptd.	Melting Point[b] Obsvd.	Melting Point[c] Reptd.	Melting Point[c] Obsvd.
	%	° C.	° C.	° C.	° C.
Sodium formate	99.95	253	251–253	...	.....
Sodium acetate	99.95	324	320–321	...	.....
Sodium propionate	100.0	...	281–284	...	.....
Sodium *n*-butyrate	99.9	...	244.5–246	...	274–279
Sodium isobutyrate	100.0	...	254–256.5	...	254–256.5
Sodium *n*-valerate	99.45	...	224.5–226	...	344–345
Sodium isovalerate	94.5	...	165(?) 224–227	...	251–253
Sodium caproate	99.5	225	212–216	350	Dec. 280
Sodium heptylate	99.0	240	235–239	350	Dec. 285
Sodium caprylate	98.2	225	231–235	355	Dec. 275
Sodium palmitate	98.0	220	219–223	265	Dec. 230
Sodium stearate	90.0	225 220 215	160–170(?)	270	Dec. 200
Sodium oleate	94.0	232	185(?) 230	235	Dec. 235

[a] Purity based on sodium content.
[b] To form an anisotropic liquid } Observed melting points uncorrected.
[c] To form an isotropic liquid }

Though there has been considerable controversy (*13, 15–17*) in the past concerning the hydrolysis of soaps in concentrations of normal or greater to give the free fatty acid, there is little doubt that in the concentrations used (maximum 0.0003 *N*), there would be such a hydrolysis. The beta oxidation is the mechanism generally accepted for aërobic decomposition of the fatty acids.

OXYGEN DEMAND. The dilution method of determining oxygen demand was used throughout. The dilution water used was entirely different from any heretofore recommended (*9, 18*).[1] The attempt was made to simulate natural conditions under which wastes discharging into streams would be oxidized.

[1] Hatfield and Morkert [*Sewage Works J.*, 2, 521 (1930)] have recommended a similar water since this work was completed.

The average mineral content of several rivers of Illinois was determined from data of the Illinois State Water Survey on the analyses of fifteen 10-day composites (*11*). The following rivers were included in the average: Big Vermilion, Embarass, Fox, Illinois, Kankakee, Kaskaskia, Mississippi, Little Wabash, Sangamon, and Vermilion.

Using this as a guide, an artificial water was made in the following manner:

1. Add the various salts to the water.
2. Pass in carbon dioxide until the carbonates are dissolved.
3. Aërate 6 to 8 weeks or longer (use cotton filter to keep out dust).
4. Adjust pH to 7.4 by passing in carbon dioxide before using.

Table II shows the average analysis of the river waters and the salts added to the synthetic dilution water. It will be noted that potassium nitrate was used in place of sodium nitrate. Potassium was used in view of the recommendations of Foreman (*8*). Since the content of ammonia and organic nitrogen in the distilled water approximated that found in river water, none was added.

Table II. Average River-Water and Synthetic Dilution-Water Analysis

Salt	Av. River-Water Analysis	Synthetic Dilution-Water Analysis
	P. p. m.	*P. p. m.*
KNO_3	..	5
$NaNO_3$	4.3	..
NaCl	10.0	10
Na_2SO_4	31.8	30
$MgSO_4$	19.3	20
$MgCO_3$	71.0	70
$CaCO_3$	117.7	120
SiO_2	18.2	..
Total	272.3	255

Dissolved oxygen was determined according to Standard Methods (*19*) except that 202.9 ml. were used for titration (*22*). Samples were incubated at 20° C. by immersing the 260-ml. bottles in water. Oxygen demand was determined at weekly intervals up to 9 weeks. Duplicate determinations were discontinued when it was found that in 135 determinations the deviation averaged 0.04 p. p. m.

To conserve incubator space, reagents, and expense of sample bottles, 125-ml. bottles were used in some series. Reagents were added in half the amounts recommended (*19*). Titration was with 0.0125 *N* sodium thiosulfate, which is direct reading. A series of twenty determinations showed agreement to within 0.035 p. p. m. of the results obtained in the larger bottles.

Obviously in a study of this kind, conditions of the experiment should be as near as possible those which are encountered in practice. It has been shown (*21*) that sewage should not be used for inoculation, owing to the fact that the course of the oxidation in the control did not follow that of the substances under investigation. Use of pure cultures was out of the question because pure cultures are not encountered in practice, and, furthermore, information is not available as to what strains will aërobically oxidize all of the soaps used. Further, since soaps are known to exert a bacteriostatic action, it was apparent that the inoculum would have to be "built up." This led to the development of a special technic for obtaining a mixture of soap-tolerant organisms for inoculating purposes. The method was as follows:

1. Add 5 ml. of sewage, 5 ml. of peptone broth (5 grams per liter), and 10 ml. of soap solution to 90 ml. of dilution water (pH 7.4) in a culture bottle, arranged so that filtered air can be constantly aspirated through the solution. The concentration of soap is then about twice that in the samples for oxygen-demand determinations.
2. Incubate with constant aëration for 24 hours at 25° C.
3. Streak an agar plate (15 cc. of nutrient agar and 1 ml. of soap solution) from this culture.
4. Incubate the plate 24 hours at 25° C.
5. Pick five different colonies from the plate and transfer to a culture bottle containing 95 ml. of dilution water, 5 ml. of peptone broth, and 10 ml. of soap solution.
6. Incubate with constant aëration for 12 to 18 hours at 25° C.
7. Inoculate 2.3 liters of dilution water (containing proper amount of soap to demand 5 mg. of oxygen per liter) with 1 ml. of this culture.
8. A control inoculum is built up in the same manner and inoculated into 2.3 liters of dilution water.

The soap solution referred to is that which, when diluted from 100 ml. to 2.3 liters, has an oxygen demand of 5 mg. per liter. The culture (1 ml.) used for inoculation contained enough peptone to have an oxygen demand of 0.25 mg. per liter. Five colonies were picked in order to obtain a mixture of soap-tolerant organisms.

The results are calculated as follows:

1. Plot data for oxygen demand of soap plus inoculum, draw curve, and extrapolate to 10 weeks.
2. Plot data for oxygen demand of inoculum (i. e., control), draw curve, and extrapolate to 10 weeks.
3. Subtract curve 2 from curve 1 and obtain curve 3, representing oxygen demand of the soap.
4. Calculate percentage of theoretical oxygen demand from values on curve 3.
5. From the percentages thus obtained and the purity of the soaps, calculate the percentage of the theoretical oxygen demand (i. e., percentage of complete oxidation) of the pure soaps.

Experimental Results

Sanitary chemical analyses of the six different bottles of dilution water used showed a slight decrease in residue and alkalinity (from the theoretical) during aëration and standing. The average analysis is as follows:

	P. p. m.		*P. p. m.*
Residue	240	Organic nitrogen	0.7
Chlorides	8	Nitrate nitrogen	0.8
Alkalinity (M. O.)	200	Dissolved oxygen	7.9
Ammonia nitrogen	0.5	pH	7.4

These amounts of nitrogen together with what was added in the inoculum (very small) may not have been great enough to meet the metabolic demands of the bacteria. During the course of oxidation, the nitrate that had been added to the synthetic water was not reduced. The oxygen demand of the blanks averaged less than 1 p. p. m. in 10 weeks.

During the preparation of the cultures, the heterogeneity of the organisms was greatly reduced. Most of the inoculating cultures showed a predominance of micrococci and short rods, the latter were shown to be *Aerobacter aerogenes* and *Escherichia coli*. After inoculation, it was found that the samples contained 10,000 to 12,000 bacteria per milliliter.

In eleven series, forty-five separate investigations were made. Of these, thirty-five produced results. However, only twenty-two of these thirty-five investigations appeared to show normal oxidation as evidenced by the velocity constants.

The data (expressed in per cent of the theoretical oxygen demand) on the runs which showed normal oxidation are presented in Table III. Included for comparison are the 5-, 10-, and 20-day data as read from the curves. Also, the velocity constants are listed.

The calculation of the velocity constants was made according to the Phelps equation:

$$K = \frac{1}{t} \log \frac{L}{L - X}$$

where K = velocity constant
t = time in days
L = ultimate oxygen demand (70 days)
X = oxygen demand in t days

In deriving the value of L it was assumed that the oxygen-demand value obtained after 70 days of incubation could be

TABLE III. BIOCHEMICAL OXYGEN DEMAND OF PURE SODIUM SOAPS

(Expressed in per cent of theoretical oxygen demand)

Days	Sodium Formate	Sodium Acetate		Sodium Propionate	Sodium n-Butyrate	Sodium Iso-butyrate	Sodium n-Valerate	Sodium Iso-valerate	Sodium Caproate	Sodium Heptylate	Sodium Caprylate	Sodium Palmitate		Sodium Stearate	Sodium Oleate
5[a]	41.0	14.1	22.3	45.0	28.0	29.5	28.5	34.2	37.5	16.5	35.8	38.5	17.0	17.0	19.0
7	47.5	20.2	31.5	51.5	33.0	35.2	35.0	43.0	42.8	21.0	41.0	50.0	22.5	21.1	23.9
10[a]	55.0	28.0	43.0	56.7	39.0	40.5	42.5	52.5	52.5	27.0	48.3	62.2	29.2	24.2	29.5
14	62.0	36.3	54.8	61.2	45.0	47.0	48.7	62.0	61.0	34.0	55.0	72.5	36.0	33.3	38.6
20[a]	68.5	48.8	63.0	67.0	49.5	53.0	53.4	71.4	70.0	42.0	62.5	81.0	43.7	35.8	45.0
21	69.3	50.2	63.8	67.5	50.0	53.8	54.0	72.5	71.0	43.0	63.2	82.5	44.8	40.5	45.7
28	74.0	58.2	69.8	71.5	53.9	58.1	57.5	79.2	78.0	51.5	69.2	88.0	50.3	46.1	49.8
35	76.7	60.8	73.3	74.3	56.2	60.5	59.6	83.5	82.0	56.5	73.2	91.0	54.2	50.2	52.3
42	78.1	63.0	62.5	75.8	57.6	62.5	60.9	86.0	85.0	62.0	76.2	93.0	57.5	53.9	53.7
49	79.0	64.9	63.3	76.7	58.4	63.2	61.3	87.3	86.2	66.5	78.1	94.0	60.0	56.9	54.5
56	79.8	66.4	63.8	78.1	59.0	64.0	61.8	88.2	87.0	70.0	79.8	94.5	61.7	59.7	54.6
63	79.9	67.8	63.9	79.0	59.7	64.2	61.9	88.6	87.6	72.8	80.8	94.9	63.0	62.1	54.7
70[b]	80.0	68.5	64.0	79.8	60.3	64.4	62.0	88.8	88.0	74.0	81.0	95.0	63.7	64.4	54.8
K	0.0408	0.0328	0.0367	0.0352	0.0360	0.0392	0.0338	0.0375	0.0418	0.0371	0.0345	0.0192	0.0365	0.0211	0.0308	0.0403	0.0257	0.0202	0.0248	0.0247	0.0394	0.0256

[a] Data determined from curves.
[b] Value on 70th day, ultimate oxygen demand.

taken as the ultimate oxygen demand. Warrant for this assumption is found on comparing the oxygen-demand values obtained after 56 and 63 days with the 70-day value.

As an example of the method of computation, use will be made of the results obtained in the second run with sodium heptylate (Table III). For this experiment the value of L was 87.0 in terms of the percentage of the theoretical oxygen requirement which had been satisfied when the biochemical reaction ceased. In the same experiment, the oxygen demand after 28 days was 78.1, likewise expressed as a percentage. For that particular experiment the velocity constant obtained from the Phelps equation was

$$K_{28} = \frac{1}{28} \log \frac{87.0}{87.0 - 78.1} = 0.0353$$

The velocity constants corresponding to other periods were computed in the same manner, and the results obtained were then averaged to give the constants recorded at the bottom of Table III. In most cases (there were a few exceptions), the velocity constants corresponding to the observations made at 7 days of incubation were relatively high. It also appeared that huge errors might be introduced in the value of the velocity constant when the observed oxygen demand approached the value of L. These end values, therefore, were generally omitted in deriving the average value of the velocity constant.

The average velocity constant of all the runs was about 0.0324. This indicates that the reaction is about one-third as fast as ordinary oxygen-demand rates with K values of 0.1 at 20° C.

Those runs which did not fit the equation showed, in some cases, excessive lag phases and variable rates. In most instances, however, they reached (in 10 weeks) a percentage of the theoretical demand comparable to the demands obtained in normal runs. (A few runs required 20 weeks.)

The 20-day demand appears to have been between 80 and 90 per cent of the ultimate demand, except in a few cases where K was low. In interpreting this statement, it must be remembered that the ultimate demand was never equal to 100 per cent of the theoretical oxygen demand.

The fact that theoretically complete oxidation was not obtained may have been due to lack of sufficient nitrogen, lack of symbiotic conditions, or bacteriostatic action of the soaps. (Note the decrease in demand from formate to butyrate.) Lack of agreement between different series might be ascribed to the same reasons, since experimental errors, as already shown, would account for the difference of 0.04 p. p. m. between duplicate determinations, corresponding to an error of only 0.8 per cent with depletions of 5 p. p. m.

Table IV shows the average ultimate (10-week) demand obtained from the data in Table III and also the average demand determined from all the data, regardless of the course of oxidation. As all the data presented in Table III fit the Phelps equation given above and hence are typical orderly time reactions, no curves have been presented.

TABLE IV. AMOUNT OF COMPLETE OXIDATION OF SOAPS

Soap	Av. Ultimate (10-Week) Oxygen Demand[a]	Av. Max. Demand Obtained in Different Series[b]
	%	%
Sodium formate	80.0[c]	76.4
Sodium acetate	77.7	75.5
Sodium propionate	66.0[c]	69.2
Sodium n-butyrate	60.3[c]	66.3
Sodium isobutyrate	64.4[c]	75.6
Sodium valerate	62.0[c]	62.5
Sodium isovalerate	88.8[c]	88.8
Sodium caproate	88.0[c]	84.0
Sodium heptylate	80.0	80.0
Sodium caprylate	81.0[c]	81.0
Sodium palmitate	74.4	76.8
Sodium stearate	68.3	68.3
Sodium oleate	55.0	55.0

[a] Average of data on Table III, normal oxidation rates.
[b] Average of all data without regard to type of curve.
[c] One run only.

CONCLUSIONS

1. All of the sodium salts of the fatty acids studied are capable of being oxidized biochemically.

2. When proper bacterial conditions are obtained, the oxidation fits the curve of an orderly time reaction, and the 20-day biochemical oxygen demand has a definite relation to the ultimate (10-week) demand. The velocity constants approximate an average value of 0.0324.

3. Theoretically complete oxidation was not obtained even in 10 weeks, although, practically, oxidation had ceased at 8 weeks. The average percentage of complete oxidation varied considerably for the different soaps (55–89 per cent).

4. The biochemical oxygen demand of the sodium salts of the fatty acids apparently does not bear any definite relation to the theoretical oxygen demand for complete oxidation to carbon dioxide and water.

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Zinc in Water Supplies

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The limits of permissible zinc in drinking water have been questioned, and this investigation was undertaken to secure data concerning these limits. Methods of analysis were checked, and a method was adapted to test samples in the field. The more accurate standard method of the A. O. A. C. was used in the laboratory.

A survey was made of natural waters of the Missouri-Kansas-Oklahoma zinc district. Waters containing as high as 50 p. p. m. of zinc were found. Animals and humans were drinking waters known to contain zinc.

Water containing varying amounts of zinc sulfate was fed to rats. The rats drank 50 p. p. m. of zinc as zinc sulfate over a period of several weeks with apparently no harmful results.

Zinc in many drinking waters comes from galvanized iron pipes. If a pure zinc were used in the galvanizing, there should be less zinc dissolved by the water.

It seems advisable that, until further information is obtained, 5 p. p. m. or less of zinc should remain the standard for drinking water.

ZINC occurs in a few natural waters. Zinc sometimes occurs in tap water, having been dissolved from the zinc coating of galvanized iron pipes and storage tanks.

Underground waters occurring in zinc-mining regions frequently contain considerable zinc. The alternate exposure of the zinc ore to air and moisture favors its solution. The same principle applies to the leaching effect of the surface water on the extensive piles of waste rock material from which most of the zinc ore has been removed.

Parker and Bailey (*16*) report waters from zinc mines and concentration mills with a zinc content as high as 1852 p. p. m. Mine waters analyzed by Waring (*23*) show as high as 5500 p. p. m. of zinc. Such waters have a taste so astringent that they are not likely to be used by men or animals.

Two springs in Newton County, Mo., on the road from Joplin to Seneca, about a quarter of a mile north of Shoal Creek, known as East Spring and West Spring, were notable for their large content of zinc (*4*)—120.5 and 132.4 p. p. m., respectively. These analyses were made by Hillebrand (*8*) in 1891. He says those waters were supposed to have a peculiar composition, owing to the strong metallic astringent taste left in the mouth after swallowing.

One of the authors (Weigle) spent considerable time in April, 1931, in an unsuccessful effort to locate these springs. It seems probable that the extensive underground excavations in the zinc-ore bearing vicinity have intercepted the flow of these waters. The same explanation is given for the disappearance of all but one of the many springs at Baxter Springs, Kans.

Water coming in contact with zinc in galvanized iron pipes and cisterns frequently dissolves considerable zinc. Weinland (*24*) found 5 p. p. m. of zinc in the water supply of the chemical laboratory of the University of Tübingen. This contamination was traced to the galvanized pipes leading into the buildings.

A water which was drawn from a well through a galvanized iron pipe, several hundred yards in length, was reported by Schwarz (*18*) to contain 32.4 p. p. m. of zinc oxide. Many families using this water complained of intestinal troubles.

Abbott (*1*) reports that the water of Devil's Lake, N. D., which seemed more toxic to fish than its composition indicated, showed after careful analysis 15 p. p. m. zinc.

Jackson (*10*) says:

> I have on numerous occasions examined water for zinc which has had very marked physiological action with 5 or 6 p. p. m. of zinc present. Notably in Falmouth Foreside, a summer place near Portland, Me., where they put in new water-supply mains of galvanized piping and started to drink it early in the spring without flushing, the entire town was badly affected by it. I ordered the pipes thoroughly flushed two or three times, using well water as drinking supply in the meantime, after which no further trouble occurred.
>
> The same difficulty arose with the new annex to our Natural Science building where many of the fish and smaller animals were killed by the water which was used, and where a number of the instructors and professors were made very ill. This water contained about 8 p. p. m. of zinc. In this case also, after flushing thoroughly several times, no further trouble occurred.

Stacks (*19*) in his report on "The Effect of Artesian Water upon Galvanized Steel Pipe," which describes an investigation at Moline, Ill., says, "About 30 days after the water system had been completed and in operation, complaints were heard regarding the quality of the water as it came from the fountains, and many of the employees were taken ill with cramps, fainting spells, and nausea, soon after drinking the water." Conditions became rapidly worse and it was necessary to remove the zinc coating from the entire system of pipes.

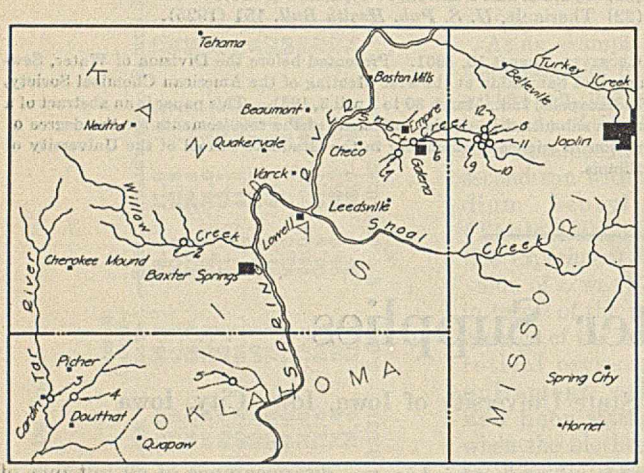

FIGURE 1. MAP OF ZINC DISTRICT SHOWING LOCATIONS OF WATERS SAMPLED CONTAINING ZINC

Hazen (*6*) reports that no harmful results were observed from the common use by the city of Brisbane, Australia, of rain water containing 17.1 p. p. m. of zinc. The water had been stored in galvanized iron tanks.

The water supply of West Berlin, Mass., drawn through 4000 feet of galvanized iron pipe, contained 18.46 p. p. m. of zinc, but appears to have produced no unpleasant results (*14*).

Mason (*13*) says he "has been unable to trace any evil effects due to the presence of zinc in drinking water, even when the quantity rose as high as 23 p. p. m. in a water which is in constant use. It might be well to add that, in the particular case just cited, the zinc was derived from a long stretch of galvanized iron pipes, and the amount of the metal present was subject to great and frequent fluctuations for reasons that were not apparent."

Krohnke (*11*) and Wittus (*25*) recommend solid zinc pipes as a substitute for lead water conduits.

Rinck (*17*) finds that the amount of zinc dissolved from solid zinc tubing in ordinary tap water is about 2 to 5 mg. per liter, and recommends the use of massive zinc pipes for conveying water.

The literature gives such conflicting reports concerning the harmful effects of zinc that it is not surprising that the standards for zinc in drinking water have been questioned. They are as follows:

Standards adopted by the Treasury Department, June 20, 1925, for drinking and culinary water supplied by common carriers in interstate commerce (*22*) (quoted and discussed by Olds, *15*) include the following concerning zinc in water: Zinc shall not exceed 5.0 p. p. m.

In the explanation of the drinking-water standards referred to above, the statement is made that "for the chemical determinations referred to in this report, the methods of analysis recommended by the Association of Official Agricultural Chemists (*3*) are satisfactory and may be substituted for those recommended by the American Public Health Association (*2*)."

Before adopting the method of the Association of Official Agricultural Chemists for the analysis of zinc in water, an effort was made to adapt the urobilin method developed by Lutz (*12*) or the method of Fairhall and Richardson (*5*), both used for the determination of zinc in foods.

The accurate determination of zinc in drinking waters by the regular gravimetric, titrimetric, or electrometric methods is impracticable for small amounts. For example, 10 liters of water containing 1 p. p. m. of zinc yields only 10 mg. of zinc on evaporation. It would be necessary to evaporate too large a volume of water to secure a sufficient quantity of zinc. Methods suitable for the determination of small quantities of zinc in small volumes of water must be used. For concentrations of zinc in water from 1 to 50 p. p. m., the ferrocyanide turbidimetric method gave very satisfactory results. The method developed by Lutz (*12*) in 1925 had such difficulties that it seemed preferable to use a less sensitive method using a larger amount of water.

The ferrocyanide turbidimetric or nephelometric method, as developed by Fairhall and Richardson (*5*) was compared with the method of analysis of the Association of Official Agricultural Chemists. The latter method was more rapid and sufficiently accurate for present purposes, and was adopted for these tests.

A method of testing samples at their source was needed. After experiments with the methods of Thresh (*21*), of Howard (*9*), and of the Association of Official Agricultural Chemists, a field test was adopted:

FIELD TEST FOR ZINC IN WATER. A 20 × 150 mm. Pyrex tube containing 1 cc. sulfuric acid (1:1) was filled two-thirds full of the water sample. Then about 1 cc. of a 10 per cent potassium ferrocyanide solution was added and the tube shaken. Since water containing 1 p. p. m. zinc thus treated will show a slight opalescence within a few minutes, and since a sample of water containing 5 p. p. m. or more of zinc will produce a strong opalescence almost immediately, it became very simple to select those waters apparently containing zinc.

WATERS OF MISSOURI-KANSAS-OKLAHOMA ZINC DISTRICT

Since it was probable that the large zinc-producing area of Missouri, Kansas, and Oklahoma would have ground and surface water supplies containing zinc, plans were made for a survey of this territory.

Out of the numerous samples tested by the field test, eleven sources of water supply were selected, and representative samples secured for laboratory analysis.

The results of the final analyses of these selected samples are shown in Table I.

TABLE I. ANALYSES OF SAMPLES FROM ELEVEN SOURCES OF WATER SUPPLY IN MISSOURI-KANSAS-OKLAHOMA ZINC DISTRICT

Sample	Zinc April[a]	Zinc May[a]	Solids in Solution April[a]	Solids in Solution May[a]	Remarks
	P. p. m.	*P. p. m.*	*P. p. m.*	*P. p. m.*	
1	0	0	0	0	Blank
2	5	..[b]	737	..[b]	....[b]
3	50	42.5	1636	1883	....
4	11.7	13.7	2151	2343	....
5	3.9	2	629	993	....
6	10	11.2	366	461	....
7	15	23.7	270	427	....
8	2.8	3.4	554	578	....
9	1.5	2.2	279	287	....
10	5	5	201	193	....
11	39	40	289	317	....
12	10.6	10	413	406	....
13	0.9	1	..	..	Check 1 p. p. m.
14	10	10	..	..	Check 10 p. p. m.

[a] 1931.
[b] Paxson mine pumps shut down.

LOCATION AND USE OF WATERS ANALYZED

Sample 1. Blank.

Sample 2. Paxson Mine, west of Baxter Springs, Kans. Pumps deliver 1500 gallons per minute. The water is cold and

has no objectionable taste. Cattle like it. The fish pond, containing fine bass, perch, and catfish, has been supplied by this water for 4 years. One man says he frequently drinks this water, sometimes for 3-week periods, with apparently no bad results. In May, 1931, the mine pumps shut down.

Sample 3. Tar River at Cardin, Okla., near bridge on Highway 7, had cattle tracks to the water's edge, indicating its use. Local people report that cattle drink this water with no apparent harm. Carp and catfish were caught in this water; also frogs and turtles were seen in the river.

Sample 4. Creek south of Picher, Okla., has clear good-looking water. Cattle use it with no apparent harm.

Sample 5. Creek in Oklahoma contains fish and supplies water for a large farming district.

Sample 6. Short Creek, Empire, Kans., furnishes drinking water to a number of cattle ranging the pastures along its banks.

Sample 7. Creek west of Galena, Kans., is used by cattle. The sample was taken south of the bridge on Highway 166.

Sample 8. Mine cave-in, 5 miles west of Joplin, Mo., 50 yards from location of sample 12, furnished drinking water for cattle. It is a good fishing pond.

Sample 9. Old mine shaft used as a well, 5 miles west of Joplin, Mo., was used by families nearby until recently. As it shows signs of caving in, they fear to go close to the shaft.

Sample 10. Cave-in (old mine shaft), 5 miles west of Joplin, Mo., is a favorite swimming hole. Hogs raised on this water look fine.

Sample 11. Creek or mine drainage near Pickett cave-in, 5 miles west of Joplin, Mo., has clear cold water. Cattle and sometimes men drink this water.

Sample 12. Short Creek, 5 miles west of Joplin, Mo., a half-mile south of Highway 66, has a chats road built through it to make a watering place. A man has watered his horse in this creek two or three times a day for 3 years with no bad results. Carp, bass, and perch have been caught here.

From the best evidence obtainable, the water containing zinc was used by man and animals without harmful results. To confirm or disprove evidence obtained from the analyses of the water in the Missouri-Kansas-Oklahoma district, tests were made with rats.

Test with Rats

No systematic effort had apparently been made by others to determine the effect of inorganic zinc salts administered to animals in drinking water.

Heller and Burke (*7*), after feeding rats food containing zinc salts, and Thompson, Marsh, and Drinker (*20*), after feeding rats solutions of organic zinc salts, report that no evil effects were noticeable.

A preliminary experiment was made here to study the effect of zinc upon rats, using pure zinc sulfate in drinking water.

Rats refused to drink a solution containing 5000 p. p. m. of zinc, possibly on account of the astringent metallic taste. The amount of solution drunk by the rats decreased as the amount of zinc increased.

After the preliminary experiment, an extended series of tests was made. Twenty-four male rats, 33 days old at the beginning of the experiment, were used for 40 days. Groups of four rats in individual cages were given during the entire period one of the six solutions: (1) distilled water, (2) tap water, and water containing (3) 50, (4) 100, (5) 500, and (6) 1000 p. p. m. of zinc, respectively, as shown in Table II.

Table II. Experiment with Twenty-four Male Rats

(Summary of averages for 40 days; four rats on each solution and in individual cages)

Water	Weight Gained	Soln.	Amount of Food	Zinc
	Grams	*Cc.*	*Grams*	*Mg.*
Distilled	172.5	1266	530.7	0
Tap	167.7	1146	489.7	0
Zinc:				
50 p. p. m.	167	1030	497	51.5
100 p. p. m.	162.7	981	506.2	98.1
500 p. p. m.	153.2	844.7	469.2	422.3
1000 p. p. m.	143.7	748.5	443	748.5

A greater amount of distilled than tap water was drunk; the gain in weight was greater and the amount of food eaten was greater. The amount of water drunk by rats on tap water, 50 p. p. m. of zinc, and 100 p. p. m. of zinc decreased with the increase in zinc content. However, there is no appreciable variation in the gain in weight and the amount of food eaten. The rats on solutions containing 500 p. p. m. and 1000 p. p. m. of zinc solution drank considerably less, ate less, and gained less. These results might be due to the astringent metallic taste of the solutions containing a high percentage of zinc sulfate.

All the rats were apparently healthy at the close of the experiments. Those on 1000 p. p. m. of zinc solution were noticeably irritable and easily startled on hot days but on cool days were apparently normal.

In reporting the harmful effects of zinc in water supplies in contact with galvanized pipes or containers, the possible effect of other impurities has not been considered—for example, cadmium and arsenic which are sometimes present in zinc used for galvanizing.

The indications that pure zinc salts in reasonable amounts in drinking water are not harmful, and the facts that pure zinc can now be made cheaply and that pure zinc is difficultly soluble, suggest the possibility that the solvent action of waters on galvanized iron pipes could be reduced by galvanizing them with pure zinc.

Note: Since presenting this paper, S. W. Sheel has made tests for arsenic in zinc from galvanized iron pipe and in various samples of commercial zinc. The amount found, a few parts per million, is so small that arsenic is eliminated as a possible cause of trouble in galvanized iron pipe of the present day.

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CHANDLER LECTURE

The Chandler Lecture for 1931 was delivered at Columbia University on February 5, 1932, by James Bryant Conant, chairman of the Division of Chemistry, Harvard University. In presenting the medal awarded at the close of the lecture, Dean H. L. McBain, of Columbia, spoke in part as follows in praise of the medalist:

To most of you his work is well known, and you know him as one of the editors of that notable series called "Organic Syntheses."

Since our choice of Professor Conant for the Chandler Lectureship, it has been announced that he is also to receive the Nichols Medal. We at Columbia are happy that the merited recognition we have given Professor Conant will be followed in the near future by the award of the Nichols Medal for a brilliant paper on chlorophyll published last year in the *Journal of the American Chemical Society*.

Many of you are familiar with his studies on hemoglobin and on free radicals, and also with his quantitative studies of organic reactions.

The Charles Frederick Chandler Foundation was established in 1910, when friends of Professor Chandler presented to the trustees of Columbia University a sum of money, and stipulated that the income was to be used to provide a lecture by an eminen chemist and also a medal to be presented to this lecturer in further recognition of his achievements in the chemical field.

The previous lecturers and the titles of their lectures are as follows:

1914	L. H. Baekeland	Some Aspects of Industrial Chemistry [Vol. 6, 769 (1914)]
1916	W. F. Hillebrand	Our Analytical Chemistry and Its Future [Vol. 9, 170 (1917)]
1920	W. R. Whitney	The Littlest Things in Chemistry [Vol. 12, 599 (1920)]
1921	F. G. Hopkins	Newer Aspects of the Nutrition Problem [Vol. 14, 64 (1922)]
1922	E. F. Smith	Samuel Latham Mitchill—A Father in American Chemistry [Vol. 14, 556 (1922)]
1923	R. E. Swain	Atmospheric Pollution by Industrial Wastes [Vol. 15, 296 (1923)]
1925	E. C. Kendall	Influence of the Thyroid Gland on Oxidation in the Animal Organism [Vol. 17, 525 (1925)]
1926	S. W. Parr	The Constitution of Coal—Having Special Reference to the Problems of Carbonization [Vol. 18, 640 (1926)]
1927	Moses Gomberg	Radicals in Chemistry, Past and Present [Vol. 20, 159 (1928)]
1928	J. A. Wilson	Chemistry and Leather [Vol. 21, 180 (1929)]
1929	Irving Langmuir	Electrochemical Interactions of Tungsten, Thorium, Caesium, and Oxygen [Vol. 22, 390 (1930)]

Equilibria and Rates of Some Organic Reactions

James B. Conant, Harvard University, Cambridge, Mass.

Photograph by Bachrach

A KNOWLEDGE of the structural formula of an organic compound enables an experienced organic chemist to make a surprising number of accurate predictions. These include not only qualitative statements about reactions and methods of synthesis but also quantitative descriptions of a variety of physical properties, such as refractive index and boiling point. We are admittedly in a less satisfactory position when it comes to predicting the energy changes involved in the transformation of the substance into other compounds or the rate of its reactions. This is in part due to the theoretical difficulties connected with the interpretation of the data and in part to the paucity of facts from which to deduce generalizations. Both these obstacles are being slowly overcome by advances in physical chemistry and by a quantitative study of more and more organic reactions. A great deal of work is being done all over the world in this field, and it would take a volume to summarize all the important and interesting results. Perhaps certain aspects of the general problems involved may be illustrated, however, by a consideration of some of the quantitative studies which we have been conducting at Harvard during the last ten years.

Relation between the Structure of Compounds and Free-Energy Change of Their Interconversion

Every equilibrium constant for a reaction occurring in solution is determined by two factors: one factor corresponds to the free-energy change referred to the substances in the gaseous state (at low pressures), and the other is the effect of the solvent molecules on the escaping tendency of the components. This last factor varies with the concentration of the reactants and the nature of the solvent except in the very rare cases where ideal solutions are at hand. It is reasonable to suppose that the simplest relationships between the structure of the compound and the free-energy change of the reaction will be found when the effect of the solvent is eliminated. This can be done by measuring the equilibrium in the gaseous state or by computing the free-energy change referred to the gaseous state by means of vapor-pressure measurements.

This second method of obtaining free-energy data referred to the gaseous state for a series of compounds is illustrated by some measurements on the free energy of reduction of quinones (*2*). As is well known, the hydrogenation of a quinone to a hydroquinone is one of the few types of organic reactions where it is possible to measure the free-energy change by an electrical method. By measuring the e. m. f. of the following

cell, one obtains directly the free energy of the reaction referred to the solid organic compound and gaseous hydrogen:

$$\text{Pt} \left| \begin{matrix}\text{Quinone (satd. soln.)}\\ \text{Hydroquinone (satd. soln.)}\end{matrix} \right\| H_2 \text{ (gas, 1 atm.)} \left| \text{Pt} \right.$$

Same solvent throughout

(In those cases in which a solid quinhydrone separates as a solid phase, the e. m. f. of the above cell must be calculated from a saturated quino-quinhydrone and saturated hydroquinhydrone cell.) The vapor pressures of a series of quinones and hydroquinones were measured by my colleague, A. S. Coolidge, and provided the necessary data for calculating the free-energy change of the reaction:

$$\text{Quinone (gas)} + H_2 \text{ (gas)} \longrightarrow \text{Hydroquinone (gas)}$$

The results are shown in Table I and Figure 1 (the values for dilute solutions were obtained by measurement of unsaturated cells in the usual manner). It is evident that in the case of the free energies referred to the gaseous state, the introduction of each additional chlorine atom decreases the free energy in a regular manner. On the other hand, when the solid state, or a dilute solution is used as the basis of reference, the effect of substitution is irregular and appears to go through a maximum. It is hardly necessary to stress the point that the results referred to the gaseous state are the significant ones both from theoretical considerations and as judged by the practical test of their regularity.

Table I. Free Energy of Reduction of Quinones in Different Standard States

Quinone	Free Energy of Reduction at 25° C.[a] Gaseous state	Solid	Dil. alcoholic soln.	Dil. aqueous soln.
	Calories	*Calories*	*Calories*	*Calories*
Benzoquinone	−26,300	−31,400	−32,800	−32,200
Chloroquinone	−28,200	−31,300	−34,000	−32,900
2,6-Dichloroquinone	−29,350	−32,200	−34,500	−33,300
Trichloroquinone	−29,950	−30,900	−33,500	...
Tetrachloroquinone	−30,300	−30,600	−32,500	...
p-Xyloquinone	−22,400	−26,850	−27,200	−27,550

[a] Hydrogen in the gaseous state in all cases.

A somewhat similar series of measurements has just been completed by Mr. Thompson in the Harvard Laboratories.[1] He has measured directly the equilibrium between a keto and an enol isomer in the gaseous phase (at low pressures), and thus obtains the free energy referred to the gaseous state ($\Delta F^\circ = -RT \ln K$). A series of substituted acetoacetic esters and similar compounds were employed; since the interconversion of the two isomeric forms does not proceed directly in the gaseous phase, it was necessary to use the liquid phase as a go-between, as it were. This was accomplished by keeping an equilibrium mixture of the keto and enol forms at a given temperature and measuring the composition of the vapor in equilibrium with this mixture. Chemical and physical equilibrium conditions were assured by introducing a small amount of solid barium hydroxide as a catalyst and agitating the liquid sufficiently to keep renewing the surface in contact with the gas phase. The composition of the gas phase was determined by withdrawing it at very low pressure (without condensation) to a noncatalytic receiver at −80° C. where it was condensed without isomerization. It was then analyzed by the usual bromine titration method. The results are summarized in Table II. A study of the data shows that the regularities in the free energy of enolization referred to the gaseous phase are for the most part lacking when the liquid-phase value of K is employed for calculating ΔF. Thus, the large difference between acetoacetic ester and its alkyl derivatives (including benzyl) is marked by the disturbing solvent effects which here are of the order of 1000 calories. In the series of alkyl derivatives themselves, the gaseous-phase results show the essential similarity of the ethyl, *n*-propyl, and *n*-butyl compounds ($\Delta F = 1220 \pm 100$ calories), and their definite but slight difference from the isopropyl derivative ($\Delta F = 1620$). It is interesting that the free energy of enolization, as determined with a dilute hexane solution, parallels the gaseous result closely. If further investigation shows that this is true for a large variety of substances, it would be a matter of some practical as well as theoretical importance, as there are a number of compounds which can not be well studied by the gaseous-phase method. As those familiar with Kurt Meyer's work know, hexane is the solvent which most favors enolization. One may suppose that in this solvent we are most closely approaching the gas condition, as the mutual attraction of the keto and enol forms are diminished by dilution, and the saturated hydrocarbon has but slight molecular attractive forces.

Table II. Free Energy of Enolization in Different Standard States

Substance	Free Energy of Enolization at 25° C.[a] Gaseous phase	Equilibrium liquid	0.1 *M* hexane soln.
	Calories	*Calories*	*Calories*
$CH_3COCH_2COOC_2H_5$	120	1500	24
$CH_3COCH(CH_3)COOC_2H_5$	1080	1880	1130
$CH_3COCH(C_2H_5)COOC_2H_5$	1310	2080	1320
$CH_3COCH(C_3H_7n)COOC_2H_5$	1120	1540	1065
$CH_3COCH(C_4H_9n)COOC_2H_5$	1280	1630	1032
$CH_3COCH(C_3H_7i)COOC_2H_5$	1620	1770	1620
$CH_3COCH(C_6H_5)COOC_2H_5$	− 900	494	− 570
$CH_3COCH(CH_2C_6H_5)COOC_2H_5$	1220	1565	850
$CH_3COCH_2COCH_3$	−1420	− 655	−1460
$CH_3COCH(CH_3)COCH_3$	167.	502	− 280
$CH_3COCH(C_2H_5)COCH_3$	315	611	...

[a] $\Delta F = -RT \ln K$.

If one should accept the cases of the quinones and the enols as typical, one might be inclined to give up all attempts to measure and correlate a series of equilibrium measurements of organic reactions. The experiments with the gas phase are time-consuming and only possible in favorable cases; the results obtained may be regarded as an abstraction without value in formulating the organic chemistry as we know it, which, after all, is the chemistry of liquid mixtures and solutions. I do not think such pessimism would be justified, however, although I do believe the results I have just considered raise serious doubts about the significance of empirical relations between structure and slight differences in free energy. The case of the chloroquinones is probably an extreme instance of the disturbing effects of the solvent or of intermolecular crystal forces. A very large accumulation of halogen atoms in a molecule would be expected to produce large intermolecular attractions. The maximum error introduced by these disturbances, even in this case, is only about 4000 calories (since quinone and tetrachloroquinone are judged to be of the same oxidizing potential when the standard state is the solid or dilute solution, whereas they really differ by 4000 calories in their oxidizing power referred to the gaseous reaction). The case of quinone compared with *p*-xyloquinone (Table I) is more typical, perhaps. Here the effect of substitution is 3900 calories when the solution is the reference state, and 5100 calories when the gaseous reaction is considered. Such differences of about 800 to 1500 calories (10 to 20 millivolts in oxidation-reduction potentials, or a power of ten in an equilibrium constant), probably represent the usual magnitude of the disturbing forces which enter into equilibrium measurements in solution. If this is the case, an attempt to correlate free-energy changes and molecular structure should be concerned with differences considerably greater than 1000 calories, unless the gas phase is taken as the reference state or unless there is a very good reason to believe that the disturbing intermolecular forces are weak or cancel in the measurements.

[1] These results will be published in full elsewhere.

Because of the limitations just considered, it is necessary to measure the free-energy change of a given type of reaction over a wide range (at least 10,000 calories), as otherwise the disturbing physical effects are as great as the measured differences between compounds. Unfortunately a direct analytical study of an equilibrium mixture is rarely able to cover more than a few powers of ten in the equilibrium constant (3000 to 6000 calories at 25° C.); this may be overcome if the reaction is highly exothermic or endothermic by measuring the equilibria of a series of compounds at different temperatures and extrapolating all the results to one standard temperature. This is the case in the dissociation of the hexarylethanes to free radicals.

Of course, there is no difficulty in measuring widely different free-energy values where it is possible to use an electrical method, as in the case of oxidation-reduction potential or the measurement of acid dissociation constants. Since acid dissociation constants have almost invariably been measured in only one solvent—namely, water—it is not always realized that they are subject to the same limitation in regard to the disturbing effects of the solvent as other free-energy measurements. The effect here, as in the other cases mentioned, seems to make uncertain the significance of changes much smaller than 1 pK unit (power of ten in K). This is illustrated by some measurements made by J. O. Halford (*8*) of Michigan in the Harvard Laboratories last year, and summarized in Table III. This table is so arranged that the strength of the acids in the three solvents (water, 50 per cent aqueous alcohol, and 40 per cent aqueous butyl carbitol) is relative to that of acetic acid in each solvent. This method of recording the data avoids the very difficult problem of the direct comparison of individual ion activities in different solvents.

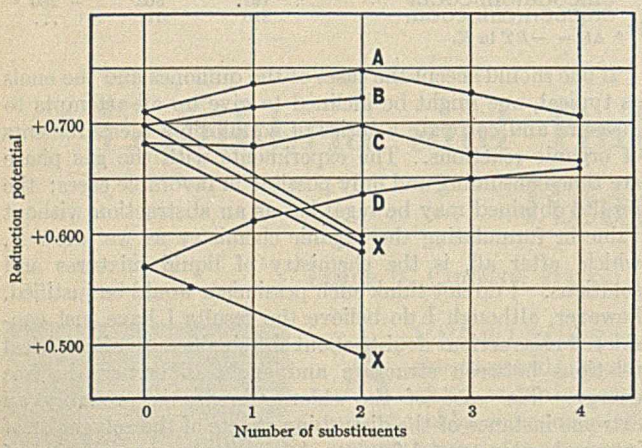


FIGURE 1. EFFECT OF SUBSTITUENTS ON REDUCTION POTENTIAL OF DERIVATIVES OF BENZOQUINONE

Reduction potentials of chloro derivatives referred to 95 per cent alcoholic solution, aqueous solution, solid state, and gaseous state, are given by lines *A*, *B*, *C*, and *D*, respectively. Points marked *X* are for xyloquinone.

It is quite clear from Table III that there are certain generalizations about the relation between acid strength and structure which are true in all solvents, while there are other relationships which hold in one of these solvents and not in another. It must be remembered that all these solvents contain some water; and, if one could obtain similar values in absolute alcohol, acetone, or even benzene, still greater variations in the relative acidities might be expected. However, the fact that the chloroacetic acids are stronger than acetic acid seems definite; the effect is here larger than the possible solvent effect; the case of formic *vs.* acetic is not so clear, and in the case of the whole group of fatty acids I feel that probably the only conservative statement is that they all have the same acid strength within the significance of the experimental results (±0.5 pK unit).

TABLE III. DISSOCIATION CONSTANTS OF A VARIETY OF ACIDS RELATIVE TO ACETIC ACID IN THREE DIFFERENT SOLVENTS

	pK RELATIVE TO ACETIC ACID IN:		
ACID	Water	60% butyl carbitol, 40% water	50% ethyl alcohol
Chloroacetic	−1.82	−1.6	−1.9
Dichloroacetic	−3.5	−2.5	−2.5
Formic	−1.06	−1.2	−1.4
Valeric	+0.07	+0.6	+0.3
Isovaleric	+0.04	+0.6	+0.4
Pivalic (trimethylacetic)	+0.28	+1.1	+0.6
Caproic	+0.11	+0.7	+0.4
Caprylic	+0.11	+0.8	+0.4
Pelargonic	+0.22	+0.9	+0.5
Lauric	...	+1.0	+0.5
Palmitic	...	+1.0	...
Stearic	...	+0.9	...

It is perhaps worth noting in passing that the use of solvents such as aqueous butyl carbitol for weak acids and glacial acetic acid for weak bases, enormously extends the number of organic compounds whose acid strength may be measured. Although there are serious theoretical difficulties in comparing such results obtained in different solvents, it seems probable that nearly as significant comparisons can be made in the nonaqueous solvents as in water. Since we seem to be precluded by the disturbing physical effects from interpreting slight changes of free energy with changes in structure, it is very important to extend our measurements over as wide a range as possible. In the case of acids this can be done only by a judicious choice of solvents. One of the strongest organic acids is the ion $CH_3CONH_3^+$, whose strength can be measured only in glacial acetic acid; one of the weakest is $(C_6H_5)_3CH$ whose salts are stable only in ether or benzene; one of the interesting problems of the future is to devise methods of comparing the acid strength of such substances and the whole host of compounds which lie in between these extremes. Some tentative estimates made in the Harvard Laboratories (*7*) suggest that a typical aliphatic acid is at least 10^{20} as strong as $(C_6H_5)_3CH$. On the other hand, it is only about 10^{-6} as strong as $C_6H_5CONH_3^+$ (*9*); thus the total spread between $(C_6H_5)_3CH$ and $CH_3CONH_3^+$ is some 34,000 calories in the free energy of dissociation.

It is perhaps worth pointing out that the measurement of the acid dissociation constants of various groups may often lead to results of value in connection with structural problems. By the use of special solvents, almost all acids stronger than phenol may be measured. If one does not attempt the impossible task of attempting to distinguish between slight differences, the results of the measurements are usually unambiguous. Such results obtained by the e. m. f. titration method in homogeneous solution stand out in contrast to the erroneous conclusions that are occasionally drawn from qualitative experiments involving two phases. The classical example of this sort of error is the widespread belief that stearic acid is a very weak acid. The results given in Table III show that none of the higher fatty acids is significantly weaker than the first few members of the series. The apparent weakness in aqueous solutions is, of course, the result of their insolubility.

INFLUENCE OF ACIDITY ON RATE OF CERTAIN REACTIONS

As is well known, there is, in general, no connection between the rate of a reaction and the free-energy change. For this reason, that portion of organic chemistry which is concerned solely with rates of reaction will be little concerned with thermodynamic relationships. There are a few instances however, where, for very special reasons, rates and equilibria are intimately connected. Three such instances will be considered in this paper; one of these, which concerns ir-

reversible oxidation and reduction reactions, has been reviewed elsewhere and will therefore be mentioned only in passing.

In the coupling of diazonium salts with phenols, the acidity of the solution is usually regulated by the addition of the salt of a weak acid; sodium acetate, sodium bicarbonate, and sodium carbonate are thus commonly employed in the manufacture of azo dyes. In order for the reaction to proceed rapidly, the acidity must be kept below a certain value; this value depends on the nature of the diazonium salt and the phenol. A great mass of qualitative information of this sort suggested that the rate of the coupling reaction was a function of the hydrogen-ion activity of the solution. This was shown to be the case by a quantitative study of the rate of coupling of five different diazonium salts with a variety of phenols and naphthols (*4*). A colorimeter method was employed for following the reactions, and the hydrogen-ion activity was controlled by the use of buffer solutions of known pH value. The rate corresponded closely to that of a bimolecular reaction over a wide range of changes of concentration of the reactants. The general reaction may be illustrated by the case of diazotized aniline and a sulfonated naphthol.

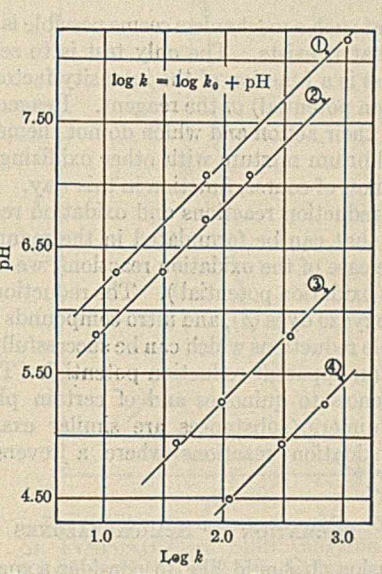
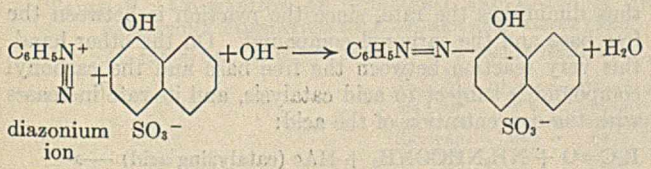


FIGURE 2. RATE OF COUPLING OF FOUR PAIRS OF COMPONENTS AT DIFFERENT pH VALUES

(Temperature, 15.0° C.; μ, 0.24)
1. Diazotized *o*-anisidine + R salt
2. Diazotized *o*-anisidine + N. and W. salt
3. Diazotized sulfanilic acid + R salt
4. Diazotized sulfanilic acid + N. and W. salt



The relationship between the rates of the reaction and the pH value of the buffer solutions is illustrated by Figure 2. The lines correspond to the general equation:

$$\log k = \log k_0 + \text{pH}$$

where k = bimolecular rate constant at given pH value
k_0 = a constant dependent on the nature of the diazonium salt and the phenolic substance

It was established that the pH value of the buffer and not the concentration of acid or base was the determining factor. It might be noted in passing that the ionic strength of the buffer solutions was kept constant although the salt effect is not great.

The equation just given shows that for a given azo dye the rate of formation is a function of the pH value of the solution. The reason for this appears to be that there is a rapid reversible step controlling the rate of the entire process. This reversible step involves the hydroxyl ion; for a given concentration of diazonium salt and phenol the amount of reactive intermediate depends on the hydroxyl-ion activity used. Hence the rate is controlled by the pH value of the buffer:

$$\text{ArN}_2^+ + \text{OH}^- \rightleftharpoons \underset{\text{reactive intermediate}}{\text{ArN=NOH}} \text{ (rapid reversible step)} \quad (1)$$

$$\text{ArN=NOH} + \left\{\begin{matrix}\text{phenolic}\\ \text{compound}\end{matrix}\right\} \longrightarrow \text{azo dye} + \text{H}_2\text{O (relatively slow)} \quad (2)$$

If A and B represent the initial concentration of diazonium salt and phenol, respectively, it is clear that the amounts of the two reactants in the rate-determining step (2) are:

$$(\text{ArN=NOH}) = K(A - x)\,[\text{OH}^-]\,\frac{Y_C}{Y_A} \text{ and } (B - x)$$

where x = amount reacted at time t
Y_C and Y_A = activity coefficients of diazonium salt and reactive intermediate, respectively

The differential equation for the rate is therefore:

$$\frac{dx}{dt} = k'K\,[\text{OH}^-]\,\frac{Y_C}{Y_A}\,(A - x)(B - x)$$

Substituting for $[\text{OH}^-]$, $Kw/[\text{H}^+]$ it is evident that

$$k \text{ (the usual bimolecular constant)} = k'KKw\,\frac{Y_C}{Y_A[\text{H}^+]}$$

At constant ionic strength the ratio of activity coefficients is constant so that we may write:

$$k_0 = k'KKw\,\frac{Y_C}{Y_A} \text{ and } k = \frac{k_0}{[\text{H}^+]}$$
$$\text{or } \log k = \log k_0 + \text{pH}$$

This is the equation which expresses the experimental results.

It will be noted that, in the value of k_0 which is characteristic for each pair of reactants, there is a rate constant, k', and an equilibrium constant, K. The latter will be a characteristic of the diazonium salt; the former would be expected to vary for each set of reactants. It appears, however, that the rate of coupling is determined almost entirely by the nature of the phenolic compound. This was discovered by the empirical observation that it was possible to assign numerical values to each diazonium salt and each phenol such that their sum corresponded closely to $\log k_0$. This essentially independent behavior of each diazonium salt and each phenolic substance makes the coupling reaction peculiarly susceptible to quantitative formulation. This is shown by Table IV. The coupling value has been defined as the pH at which $K = 10(\log k = 1)$; that is, it is $-\log k_0 + 1$. It is evident from the table that the coupling values for each pair of reactants is very close to that calculated from the empirically determined constants, A and B, which are probably directly related to $\log K$ and $\log k'$, respectively.

A situation analogous to that with the coupling reaction has been found to exist in regard to a number of irreversible oxidation and reduction reactions. Here the mobile equilibrium which feeds the irreversible step is an oxidation-reduction reaction involving four substances, all of which gain or lose hydrogen (or electrons) with such rapidity that a state of equilibrium is always at hand. In place of a series of buffer solutions with varying hydroxyl-ion activity, we employ a series of rapidly acting oxidizing or reducing agents of known potential. A specific illustration will make this clear (*3*). The reduction of the unsaturated 1,4-diketone, dibenzoyl-

TABLE IV. COUPLING VALUES ($-\log k_0 + 1$)[a]

(Temperature = 15° C.; μ = 0.24)

	Sulfanilic Acid, $A = 0$		p-Bromoaniline, $A = 0$		Aniline, $A = 1.1$		p-Toluidine, $A = 1.5$		o-Anisidine, $A = 2.1$	
	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
1-Naphthol-4-sulfonate, $B = 3.5$	3.5	3.45	...	....	4.6	4.70	5.0	5.31	5.6	5.85
2-Naphthol-3,6-disulfonate, $B = 4.2$	4.2	4.28	4.2	4.43	5.3	5.22	5.7	5.60	6.3	6.22
1-Naphthol-3,8-disulfonate, $B = 5.1$	5.1	4.90	5.1	4.77	6.2	6.37	6.7	6.83	7.3	7.35
2-Naphthol-6,8-disulfonate, $B = 6.4$	6.4	6.46	6.4	6.10	7.5	7.60	7.9	8.02	...	....
p-Phenolsulfonate, $B = 8.3$	8.3	8.35	...	....	...	....	...	....	...	....

[a] The numbers for each pair of components represent the coupling value (pH at which log k = 1) as calculated according to the relationship $A + B$ = coupling value, and found experimentally. The values of A and B for each component are given under the name and were assigned empirically so that the best agreement would result in this table.

ethane, is irreversible. When a mobile reducing agent, such as a hydroquinone or the leuco form of a dye is employed, the reaction appears to proceed as follows:

$$\left(\begin{matrix}\text{Fast}\\ \text{reversible}\end{matrix}\right) C_6H_5COCH{=}CHCOC_6H_5 + \underset{\text{reducing agent}}{AH_2} \rightleftharpoons \qquad (1)$$

$$C_6H_5\underset{\underset{OH}{|}}{C}{=}CH{-}CH{=}\underset{\underset{OH}{|}}{C}\,C_6H_5 + A$$

$$C_6H_5\underset{\underset{OH}{|}}{C}{=}CH{-}CH{=}\underset{\underset{OH}{|}}{C}C_6H_5 \xrightarrow[\text{slow}]{\text{relatively}} C_6H_3CO\ CH_2CH_2COC_6O_5 \qquad (2)$$

hypothetical intermediate (di-enol)

The amount of di-enol formed in the mobile equilibrium depends on the oxidation-reduction potential of the reagent system (AH_2–A) and of the diketone–di-enol system. The more powerful the reducing agent employed, the more di-enol will be formed in step 1 and the greater the speed of the overall process of irreversible reduction (through step 2). As would be expected from this mechanism, the rate is independent of the dilution, since the rate-controlling step is monomolecular. By varying the ratio of AH_2 to A or by choosing another reagent $A'H_2$–A' of different potential, the speed of the reaction can be varied. Just as it is convenient to define a coupling value for the formation of an azo dye in terms of an intensity factor (the pH value at which the reaction proceeds at a certain rate), so it is convenient to define an apparent reduction potential as the potential of a reagent which will cause a definite amount of reduction in a given time (30 per cent in 30 minutes). Such a method of formulation enables one to express in numerical terms the behavior of a compound in an irreversible process. The apparent reduction potential has no thermodynamic significance, of course, since both an equilibrium term and a rate term are involved in it. It is to be clearly distinguished from a real oxidation-reduction potential which can be measured in the case of reversible reduction and oxidation processes, such as are involved in the case of quinones and dyes. The difference between the apparent reduction potential of a substance and the free energy of reduction is well illustrated by the case of dibenzoylethylene. The apparent reduction potential is about +0.27 volt (H_2 electrode as zero and the European convention in regard to sign being employed). The free energy of reduction as calculated from heats of combustion and the entropies of the two ketones (measured by Parks, *10*) is −23,900 calories, which corresponds to +0.52 volt as a true oxidation-reduction potential. If the system dibenzoylethylene–dibenzoylethane–reducing agent could be made mobile by some catalyst, a tenfold excess of reducing agent of potential about 0.52 volt would cause nearly complete reduction, and a similar excess of oxidizing agent of potential 0.52 would oxidize the ethane to the ethylene in fair yields. In reality, however, no appreciable reduction occurs until we use a reducing mixture of potential as low as +0.27 volt, and no oxidizing agent has been found which will oxidize the ethane to the ethylene derivative.

In applying these ideas to a new class of substances, one must be certain that a reversible step really is involved; the mere fact that such a mechanism seems possible is of course no guarantee that it exists. The only test is to see if the rate of the process is a function of the intensity factor (the oxidation-reduction potential) of the reagent. Reagents which are not rapid in their action and which do not themselves form a mobile equilibrium mixture with other oxidizing or reducing systems cannot, of course, function in this way. A number of irreversible reduction reactions and oxidation reactions have been found that can be formulated in the manner just outlined (in the case of the oxidation reactions, we may speak of an apparent oxidation potential). The reduction of 1,2-diketones, hydroxyazo dyes (*5*), and nitro compounds are examples of irreversible reductions which can be successfully formulated in terms of an apparent reduction potential. The oxidation of aminophenols to quinones and of certain phenolic compounds to dimeric substances are similar examples of irreversible oxidation reactions where a reversible step is involved (*6*).

FORMATION OF SEMICARBAZONES

In conclusion, I should like to consider some equilibrium and rate measurements made in the Harvard Laboratory by Paul D. Bartlett[2] on semicarbazone formation. This is a case where an equilibrium controls the rate but, in addition, acid catalysis is involved. The results illustrate the great importance to organic chemistry of the general theory of acid and basic catalysis developed by Brönsted and Lowry in the last few years (*1*). The general reaction may be illustrated by the reaction of acetone:

$$(CH_3)_2\,CO + NH_2NHCONH_2 \rightleftharpoons (CH_3)_2C{=}NNHCONH_2 + H_2O$$

The reaction is reversible, and this fact must be taken into account, of course, in formulating the kinetic equations where the back reaction is appreciable.

A study of the reaction rate in a variety of buffer solutions has shown that two opposing factors are at work. On the one hand, an increase in acidity of the solution beyond about pH = 4.9 decreases the amount of free semicarbazide by salt formation (the pK of $NH_3^+NHCONH_2$ is 3.66 at 25° C.) and thus diminishes the rate, since the reaction is between the free base and the carbonyl compound. On the other hand, this very reaction between the free base and the carbonyl compound is subject to acid catalysis, and its rate increases with the concentration of the acid:

$$R_2C{=}O + NH_2NHCONH_2 + HAc\ (\text{catalyzing acid}) \longrightarrow R_2C{=}NNHCONH_2 + H_2O + HAc$$

(partially removed as $NH_3^+NHCONH_2$ by increase in $[H^+]$)

In an ordinary set of buffer solutions covering a narrow range, increase of acidity is effected by increasing the concentration of free acid. Therefore, rate measurements in such buffers show a pronounced maximum, as shown in Figure 3. Such a smooth curve might easily lead to the erroneous conclusion that the rate was controlled solely by the pH value of the buffer. Measurements made at constant pH but varying

[2] Unpublished results.

concentration of buffering materials, however, show that the rate is proportional to the concentration of catalyzing acid. The apparent regularity shown by the curve in Figure 3 is thus the result of an accidental conformity between pH and acid concentration—a consequence of the usual way of making a series of buffers. The two curves shown in Figure 4 further illustrate this point; it will be seen that the phosphate and acetate curves are not connected.

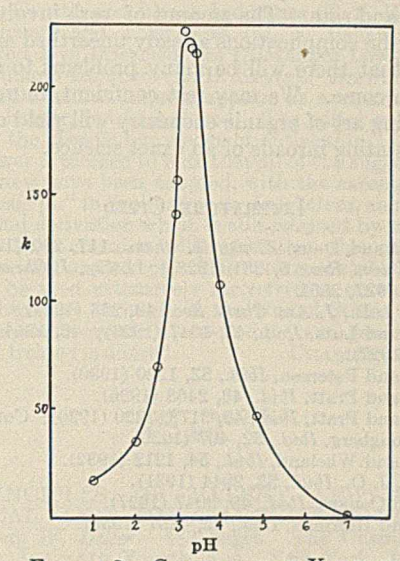


FIGURE 3. CONDENSATION VELOCITY OF FURFURAL AND SEMICARBAZIDE IN 0.5 M, $NaH_2PO_4 + H_3PO_4$, CITRATE AND ACETATE BUFFERS

In general, in cases of acid catalysis, the specific catalytic effect of the acid is greater, the stronger the acid. For this reason the most effective catalyst for semicarbazone formation would be an acid only slightly weaker than the semicarbazide ion, $NH_3{}^+NHCONH_2$. Such an acid is acetic (about 1 pK unit weaker); a large concentration of this acid can be introduced into the solution, and, by an appropriate increase in sodium acetate concentration, the pH value can be kept sufficiently high so that only a small portion of the semicarbazide is combined with the acid. To some extent these optimum conditions are approached when potassium acetate and semicarbazide hydrochloride are employed in the preparation of semicarbazones. It would probably be advantageous, however, to increase the concentration of the catalyst (acetic acid), at the same time keeping the pH high by the addition of acetate ion.

TABLE V. COMPARISON OF EQUILIBRIA AND RATES OF SEMICARBAZONE FORMATION OF KETONES AND ALDEHYDES

(At 25° ± 0.01° C. in 0.07 M Na_2HPO_4 + 0.03 M NaH_2PO_4)

	$K \times 10^5$ Hydrolysis Constant of Semicarbazone	Velocity Constants of Semicarbazone Formation = k_2	Hydrolysis $k_1 \times 10^5$
Acetaldehyde	2.9	361	1040
Benzaldehyde	0.30	2.05	0.62
Furfural	0.76	0.73	0.55
Pivalaldehyde (trimethylacetaldehyde)	1.85	20	37
Pyruvic acid	0.51	7.37	3.8
Acetone	324	6.02	1800
Cyclohexanone	214	36	7600
Pinacolone	1260	0.068	86

It is evident that, in comparing the equilibria and the rates of semicarbazone formation with a variety of carbonyl compounds, the experiment should be performed in such a manner that a definite amount of catalyst is present in each case and that practically all the semicarbazide and condensation product should be present as the free base. A phosphate buffer of pH about 7 and a concentration of catalyst ($H_2PO_4^-$) of about 0.06 M meets these specifications. The results obtained under such conditions are summarized in Table V.

A consideration of Table V brings out a number of points of interest. In the first place, it is clear that there is no apparent relation between the speed of formation of the semicarbazone and its stability as measured by the hydrolysis constant, K. Considering first the relation between structure and rate of semicarbazone formation, acetaldehyde is found at the top of the list, with its trimethyl substitution product about a tenth as reactive, but some ten times more reactive than benzaldehyde or furfural. The latter is the least reactive of all the aldehydes and differs from acetaldehyde by nearly a thousandfold. Of the ketones, cyclohexanone is the most reactive (as would have been expected from previous work), and acetone and pyruvic acid are essentially equal and about a sixth as rapid in semicarbazone formation as the cyclic ketone. The large drop in reactivity caused by substitution of three methyl groups (0.068 for pinacolone compared with 6.0 for acetone) is in accord with a large variety of qualitative and quantitative facts of organic chemistry. A comparison of benzaldehyde, furfural, acetone, and trimethylacetaldehyde gives very little support to the idea that the rate of carbonyl reaction is determined solely by so-called steric effects. It would seem that the facts are much too complicated to be explained solely by such a simple hypothesis. However, if one confines one's attention to a particular limited class of compounds, such as the aldehydes ($C_nH_{2n}O$), the concept of steric hindrance affords a plausible explanation of relation between rates and structure. The comparison of acetone, pinacolone, and acetaldehyde and its trimethyl derivative illustrates this.

Turning now to the equilibrium constants, we find all the ketones (except pyruvic acid) falling into one class and the aldehydes into another. Within the ketone class the variation in the hydrolysis constant is only threefold, the most highly substituted ketone being the most completely hydrolyzed. The variation among the aldehydes is tenfold, but the difference between the least-hydrolyzed ketone semicarbazone (always excepting pyruvic acid) and the most-hydrolyzed aldehyde semicarbazone is a hundredfold. It would appear that the carbonyl compounds, as far as the energy relationships are concerned, show a rather simple relationship between structure and semicarbazone formation, the equilibria constants being determined by the same sort of factors which determine the dissociation constants of acids. For convenience, these factors may be termed the "polarity" or "negativity" of the attached groups. Thus we may say that the more negative the atoms or groups X, Y in the compound, XCOY, the less hydrolyzed is the semicarbazone. The contrast between aldehydes and ketones corresponds to the difference in strength of formic and the other aliphatic acids. The fact that pyruvic acid semicarbazone is even less hydrolyzed than that of acetaldehyde is in accord with the greater strength of oxalic acid (pK ≐ 2.8) as compared with formic acid (pK = 3.7).

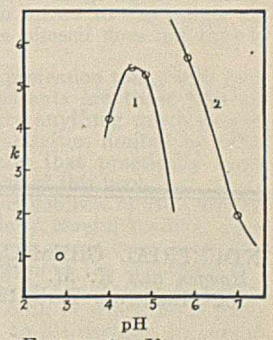


FIGURE 4. VELOCITY OF CONDENSATION OF ACETONE AND SEMICARBAZIDE AT 0° C. IN 0.045 M BUFFER SOLUTIONS

1. Acetate buffers
2. Phosphate buffers

Some of the conclusions summarized in Table V can be demonstrated by qualitative experiments which also serve to emphasize the difference between rates and equilibria in controlling organic reactions. The most striking of these experiments involves a comparison of cyclohexanone and

furfural. The differences in rates of semicarbazone formation are in favor of the former by a factor of about fifty; the hydrolysis of the aldehyde semicarbazone is only one three-hundredth of that of the ketone, however. As a result, if one mole of semicarbazone and one mole each of cyclohexanone and furfural are allowed to react, practically the entire final product is furfural semicarbazone. Because of the differences in the rates of reaction, however, the initial product in such an experiment is almost wholly cyclohexanone semicarbazone. The effect of these differences in rate and equilibrium constants can be shown very simply by allowing semicarbazide to react with a mixture of cyclohexanone and furfural in alcoholic solution and isolating the semicarbazone after a few seconds and after a few hours. (Because of the solubility of cyclohexanone semicarbazone in water, it is necessary to precipitate the product by pouring a sample of the mixture into a saturated ammonium sulfate solution in which the cyclohexanone semicarbazone is almost insoluble.) In such an experiment, starting with 0.01 mole each of semicarbazide hydrochloride, furfural, and cyclohexanone, and 0.05 mole of potassium acetate in 50 per cent alcohol, a sample precipitated after 20 seconds yielded cyclohexane semicarbazone, while after 2.5 hours a similar precipitate was found to be pure furfural semicarbazone.

It is worth noting that, if one had attempted to draw conclusions about the relative reactivity of the two carbonyl compounds from one of the above experiments alone, the conclusions would have been diametrically opposite, depending on whether the product was isolated after a few seconds or after a few hours. This is an illustration of the difficulties of attempting to deduce generalizations in regard to the behavior of organic compounds from qualitative experiments when the nature of the reaction is not fully understood. There seems no escape from the conclusion that significant comparisons of quantitative measurements can be made only on the basis of a thorough knowledge of a reaction. This requires first a detailed study of the yields of all the products and later a physico-chemical study of the factors which control the equilibrium and rate. The amount of work involved in such studies and the complications already unearthed are welcome guarantees that there will be many problems to solve for a long time to come. We may rest confident, moreover, that the fascinating art of organic chemistry will yield only slowly to the devastating inroads of an exact science.

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BOOK REVIEWS

INDUSTRIAL CHEMICAL CALCULATIONS. *By P. A. Hougen and K. M. Watson.* 502 pages. John Wiley and Sons, Inc., New York, 1931. Price, $4.50.

The publishers of this excellent book should have followed seventeenth century practice, and, in place of "Preface," titled the authors' introductory remarks "An Explication of Subjects Propounded." Based on the reading of many books, it would seem that prefaces are sometimes drafted before a book is written, and, as the book takes its final shape, and the authors fair promises fail of realization, the preface remains as a will o' the wisp beckoning along the unwary. Professors Hougen and Watson evidently wrote a postscript which they retitled "Preface," as their book is a successful accomplishment of all the promises of the preface, including the difficulty of selecting material equally well suited as preparation for advanced courses in chemical engineering, and as a text for the industrialist lacking precise training or recent practice in chemical engineering calculations.

The authors have intentionally avoided condensed calculations, and, in the presentation of a series of solutions of well-selected typical problems, have indicated each necessary step in such detail that the methods can be readily applied to other related problems, and can also serve as useful training in quantitative reasoning and methods of calculation.

While the book has 13 chapters, its contents fall in orderly manner into six sections. The first portion of the book develops, in systematic manner, the fundamental methods of calculation of the basic chemical and physical relationships used in the solution of all industrial chemical problems. The second part shows the application of these methods to a large number of the more simple problems of gaseous mixtures, solutions, crystallization, etc.

The third part presents thermophysical relationships with emphasis placed on the thermochemistry of industrial reactions and combustion processes. The fourth section is devoted to the application of the previously developed methods in the solution of studies of several complete chemical processes, such as sulfuric acid production by the chamber process, blast furnace operation, etc. The fifth and sixth sections are rather short and are devoted to the discussion of distillation and chemical equilibria, respectively.

The authors can certainly be complimented on a work marked by clarity of definition, the terms and methods used being so well and succinctly explained, that possibility of confusion is eliminated without the mental fatigue sometimes associated with excessively detailed explanations. A. E. Marshall

INDUSTRIAL CHEMISTRY. VOLUME I. INORGANIC. VOLUME II. ORGANIC. Edited by *Allen Rogers.* 5th edition. 1517 pages. D. Van Nostrand Co., Inc., 250 Fourth Ave., New York, 1931. Price, $13.00.

It was the writer's privilege to review also the fourth edition of this standard work on industrial chemistry, now extensively used in our colleges and as reference source for a general description of present important industrial chemical processes. The book has been quite fully rewritten, brought up to date, and enlarged by some 300 pages. It is a distinct improvement over previous editions.

The book is still divided into 2 volumes, Inorganic and Organic. Former chapters on Commercial Organic Chemicals and on Dehydrated, Dried, and Evaporated Foods have been omitted as such, although their main features have been incorporated elsewhere. The chapter on Water for Industrial Use is now published under the authorship of D. D. Jackson and W. D. Turner; the chapter on Fuel and Power Generation, by J. C. W. Frazer;

the chapter on the Petroleum Industry has been rewritten by Gustav Egloff; the chapter on Soap and Soap Products is now written and signed by Martin H. Ittner; Shellac now appears as a separate chapter under the authorship of A. C. Langmuir; the chapter on Sugar has been rewritten by Claude S. Hudson; and the chapter on the Cellulose Industry has been rewritten by Gustavus J. Esselen. The following chapters, some of which are particularly well done, have been added under separate chapter headings, although they were in part treated elsewhere in the previous edition: Soda and Allied Industries (T. P. Hou); Electrolytic, Caustic and Bleach Industries (T. P. Hou); Industrial Instruments and Their Uses (M. F. Behar); Industrial Chemicals and Dye Intermediates (Alexander Lowy); Solvents and Nitrocellulose Lacquers (D. B. Keyes). Brewing and Malting Wine and Distilled Liquors appears as a separate and very interesting chapter, but is unsigned. The editor will, therefore, be accorded the specific knowledge of authorship.

The reviewer is pleased to note that all of the suggestions in his previous review have been adopted, with the exception that the publishers use "ph" in "sulfur" or its derivatives, an ancient error in spelling and derivation which is still retained by many writers in English. Most chemists will regret that this old, incorrect, and disappearing form is kept. The book is one which, as already stated, will be used extensively for reference on the subject of industrial chemistry throughout the United States, particularly where a comparatively short, up-to-date, and general review of each subject treated is desired. CHARLES L. PARSONS

THE PRINCIPLES OF PATENT LAW FOR THE CHEMICAL AND METALLURGICAL INDUSTRIES. *By Anthony W. Deller.* 483 pages. The Chemical Catalog Company, Inc., 419 Fourth Ave., New York, 1931. Price, $6.00.

ELEMENTARY texts on chemistry, written for patent attorneys and other nonchemists, are characterized by the brief and lucid statement of important facts and principles and the omission of complex experimental and analytical data which would tend to confuse the layman and which are important only to the profession. Patent attorneys writing for chemists might well follow the same precedent. Deller's chapters on Form and Construction of Patents and on Infringement follow this desirable principle, and are genuinely good and informative.

However, in many other sections of his text the author has attempted to convey the principles of patent law to the layman by the quotation of statutes, Supreme Court cases, and Patent Office rules, without any very apparent effort to interpret these complex matters for the benefit of the chemist. As one example, only 9 pages are devoted to the important subject of interferences, and these pages constitute largely a rearrangement of the complex Rules of Practice. The reviewer feels that the original edition has the virtue of being more authoritative and just as intelligible.

After a brief discussion of the classes of chemical inventions and before giving any explanation of the significance of the jargon used in chemical claims, the author devotes 52 pages to the quotation of 219 chemical patent claims, which, in the absence of the specifications from which they were taken, give the reader little but a general impression of the ingenuity of the attorneys in obscuring inventions. Later, the author devotes an additional 19 pages to the quotation of more chemical claims. The discussion of chemical claims would have been greatly clarified by a review of important decisions of Patent Office tribunals, i. e., the cases of Ellis, Dosselman and Neymann, Markush, Phair, etc.

The book is prolix. Forty-two pages of foreign-trade and manufacturing statistics (1926 vintage) have been included to guide the chemist in determining the countries in which he should file foreign applications. Another 20 pages are devoted to a quotation of a table showing the chronology of American chemical advance. A part of a bankruptcy statute is quoted on page 349 and again on page 355. The Patent Recording Statute is quoted at length, first on page 350 and again on page 351.

There were some remarkable omissions in the preparation of this text. For example, the 49 pages of matter pertaining to foreign patents does not include information for the chemist to the effect that French patents issue immediately and without examination; and that hence (1) they serve as advance signals of patents filed in other countries, and (2) their factual merit cannot be taken seriously. Nor is the chemist advised that German and Dutch patents, since they issue slowly and after painstaking examination, are more apt to be limited to genuinely novel subject matter. While 6 pages are devoted to technical rules and legends of interest to Patent Office draftsmen, no example is given of a good disclosure of invention, a well-drafted patent application, or an actual preliminary statement. The number of jurors permitted in the obsolete jury trial of patent infringement cases is carefully stated, although no mention is made of the number of members of the Board of Appeals, nor of their qualifications or method of hearing cases. BRUCE K. BROWN

THE LAW OF PATENTS FOR CHEMISTS. *By Joseph Rossman.* 304 pages. Inventors Publishing Co., Washington, D. C., 1932. Price, $3.50.

THE world today is so flooded with books that it seems almost unbelievable that a new book can be produced which actually meets the publisher's ideal that it shall "fill a long-felt want." Yet this is exactly what Rossman has accomplished in his "Law of Patents for Chemists." The chemical industry and the chemical profession have been slow to realize the value of patents, but in recent years there has been an increasing tendency to recognize and utilize the full possibilities of chemical patents. Yet prior to the publication of this book, no work of this sort which would meet satisfactorily the needs of the chemists of this country was available. It is extremely fortunate that such a book has now been written by an author with the unusual qualifications of Doctor Rossman.

Today no chemist, no matter what branch of the science motivates his professional activities, can afford to ignore the subject of chemical patents. Chemical industry has long been convinced that only by efficient utilization of patent protection can research be made profitable. Now even the worker in pure science has come to realize that he can no longer ignore patents, even though he uses them merely to insure to the public the benefits of discoveries from which he himself does not care to profit.

The only members of the chemical profession today who have no reason for interest in chemical patents are those who are convinced that they will never produce anything worth patenting, and even those may find their activities limited by other chemists' patents. It follows logically that practically every chemist will be benefited by the reading of this book.

The first 9 chapters of the book cover subjects of vital interest to the chemist, and merit an especially careful reading, since questions dealt with are those which in many cases a chemist will meet and will attempt to solve without the assistance of a patent attorney, such as the decision as to whether to patent or keep secret, and when to patent, both of which he is likely to settle for himself as preliminaries to his decision to consult patent counsel.

Part III, Obtaining the Patent, should be read by the chemist with full realization that cursory knowledge of patent procedure does not justify him in exercising his legal right to prepare and prosecute his own application any more than a superficial knowledge of chemistry justifies a patent attorney in handling an application for a chemical patent without the assistance of a competent chemical adviser.

Chapter XVII treats especially of Abandonment, and is likely to prove informing not only to the amateur in chemical patents but to many of those who consider themselves reasonably expert in this field.

Probably the section of most nearly universal interest to chemists is the chapter on Patent Rights, especially that part in which is discussed the complicated subject of Employer-Employee Relations. This extremely illuminating explication of a matter which is so frequent a cause of misunderstanding between chemists and their employers might be studied to advantage by every member of both these classes.

Other sections of less specific interest to the average chemist are those dealing with the Enforcement of Patent Rights, since the matter of litigation is not one concerning which he normally finds it necessary to make decisions. There is in this section, however, a discussion of Chemical Equivalents which is one of the most important and helpful portions of the book.

After what has been said, it probably will appear mere repetition to say that this book should be read and parts of it carefully studied by every chemist, especially every young chemist who has or expects to have any connection with the subject of chemical patents, and that the members of the chemical profession are indebted to Rossman for his very successful labors in their behalf. CARL S. MINER

FORENSIC CHEMISTRY AND SCIENTIFIC CRIMINAL INVESTIGATION. *By A. Lucas.* 2nd edition. 324 pages. Edward Arnold & Co., London; Longmans, Green & Co., 55 Fifth Avenue, New York, 1931. Price, $6.00.

In 1920 the author published a small book entitled "Legal Chemistry and Scientific Criminal Investigation." The success of this small volume encouraged him to write a larger book in 1921 with the title "Forensic Chemistry." In the succeeding ten years, important advances have been made in the use of scientific methods for the detection of the criminal. This has necessitated a very thorough revision and the incorporation of much new material. While the book is not as large or as complete as "Criminal Investigation" by Hans Gross, it is really much more useful since the only English translation of Gross' book was made in 1904.

The new edition is well written and, on the whole, is up to date. An expert in a particular field will feel perhaps that his subject has been slighted, but obviously the author could not do justice to all in a textbook of about 320 pages. The book comprises 16 chapters, as follows: Introduction; Blood Stains; Clothing; Counterfeit Coins; Documents; Dust, Dirt, Stains and Marks; Explosives and Explosions; Fibres, Woven Fabrics, String and Rope; Finger Prints; Fires and Insurance Frauds; Firearms, Cartridges and Projectiles; Microscopy, Photography and Ultra-Violet Rays; Poisons; Preservation of the Human Body after Death; Robbery from Letters and Parcels; Tobacco.

The author is to be specially commended for the excellent bibliographies accompanying each chapter and the numerous references throughout the text. In the introduction he has incorporated many useful suggestions and much sound advice for the benefit of those who may have occasion to work in this most interesting field. He closes his introduction with the statement (with which the reviewer heartily agrees), "...the criminal is becoming so scientific, not only in his work but also in the means he adopts to escape detection, that a scientist is needed to cope with him; that is to say, a scientist must be set to catch a scientist."

J. H. Matthews

THE POTASH INDUSTRY. A STUDY IN STATE CONTROL. *By George Ward Stocking.* 343 pages. Richard R. Smith, Inc., 12 E. 41st Street, New York, 1931. Price, $3.00.

This treatise deals with the industrial, economic, and political career of the German potash industry; it is based on a year's resident study in Germany, interviews with German industrialists, and extensive reading of pertinent documents, made possible through the Fund for Research in the Social Sciences of the University of Texas. It follows, with many interpretive discourses and digressions, the vicissitudes of the German industry in its efforts, with and without governmental assistance, to adjust overexpansion to the demands of dividends and capital structures. Although it is not quite apparent to what group of readers the book is addressed, it is written as a matter of preparation (if not forewarning) in anticipation of an overexpansion of a contemplated Texas potash industry, which industry it has been commonly hoped would result from the potash discoveries in that state.

While the history of the German industry has been frequently reviewed, and its progress recorded from year to year, here is the most detailed study from the economist's viewpoint that has appeared in our language. To those interested, the book is commended.

Part I, The Setting, containing a single chapter entitled "The Background in Theories and Institutions," opens with a brief discussion of the condition of the German industry as it was in 1920, presenting "a picture of confusion and disorder." Causes and circumstances offered in explanation of this state of affairs are presented in terms of the physical facts of potash, its occurrence in nature, and the economic characteristics of its production and sale as reflecting the politico-economic ideas and systems of control under which that great natural resource has been exploited.

Part II, The Sequence of Events, opens with the subject, "The Illusion of Orderly Development," in which is outlined the growth of the industry from 1863, and with each overexpansion, the formation of succeeding though not altogether successful syndicates for mutual self-help; following chapters are entitled, respectively, The Confusion of Uncontrolled Capacity; The American Controversy and the Potash Law of 1910; The Aftermath and the War Period; Post-War Reorganization: The Socialists Try Their Hand; and The Triumph of Business Enterprise.

Part III, The Net Gain, deals with the subjects, Mercantilism in Practice, The Fruits of Mercantilistic Control, Has the Potash Industry Been Socialized?, Does The Consumer Pay? (in which is found an illuminating discussion of the recent status of the *Kuxe*, a much discussed element of uncertainty in analyses of German costs), and What of the Future?

The remaining 50 pages deal with the prospective Texas industry under the subtitle, "The Conclusion: Prospects and Problems of an American Potash Industry," wherein is confined the discussion of the anticipated Texas industry. Here the author is handicapped by being forced to deal with a hypothetical set of conditions. His comparison of production costs as they have been forecast for Texas with those established in Germany is by far the most useful so far presented, owing to his familiarity with the latter. While this comparison is somewhat unfavorable to Texas, the author displays the optimism common to all of us interested in the development of an American potash industry. In his opinion, "Should the ventures now in progress (in Texas) prove commercially successful, they will afford a tremendous stimulus to potash wildcatting. Capital may be expected to rush in with characteristic speculative abandon" (page 337).

Anticipating such eventualities in Texas, the author would naturally be looked to for advice, based on his study of German experience, as to what to do in case such a situation should arise, or to avoid its arising. While the book by title is a study in state control and "is offered as a point of departure for a program of control for American potash," the reader is left to his own interpretation to determine the extent to which state control as contrasted with individual initiative has functioned in the German industry to induce order or chaos. Likewise does he fail to find that the author has summarized his deductions in terms of definite council as to what must be done in the way of state control (or its avoidance) to safeguard the economic future of the embryonic Texas potash industry. To combat the American slogan, "Less government in business," state control, if advocated, must be presented more cogently and more concretely than is here to be found.

J. W. Turrentine

RECENT ADVANCES IN PHYSICAL CHEMISTRY. *By Samuel Glasstone.* 470 pages, 32 illustrations. P. Blakiston's Son & Co., 1012 Walnut Street, Philadelphia, 1931. Price, $3.50.

Into this compact volume the author has brought a wide range of subjects which are at present engaging the attention of chemists. The headings of the chapters summarize the contents: Electron Theory of Valency, The Parachor, Dipole Moments, Molecular Spectra, Homogeneous Gas Reactions, Photochemical Reactions, The Properties of Surfaces, Heterogeneous Catalysis, Solubility, Strong Electrolytes, Acid-Base Catalysis. Under these titles the major portion of the newer theories are mentioned, and adequate references to original papers are given. The treatment is that of a guide rather than of an expounder.

The book is intended for two classes of readers: first, "those chemists who, having started on a professional career after completing a university course, find they have neither time nor opportunity to keep in touch with modern developments in physical chemistry." To these readers we heartily recommend the book. It is easily read and gives an excellent summary of the latest views on many physico-chemical phenomena. We do not, however, think that the book should be recommended without modification to the second class mentioned—namely, advanced students at the university. Too much emphasis is laid on the theories of the subject, many of them not far removed from speculation, and too little attention is paid to a clear and distinct demarcation of the line where knowledge stops and theorizing begins. The very fact that none of the substantial advances in chemical thermodynamics is adequately treated detracts from the value of the book to advanced students.

This text is reminiscent of a remark of the *Sceptical Chymist* about the sailors of Solomon's fleet bringing home from their arduous voyages not only gold and silver, but also apes and peacocks. While it would be entirely unjust to imply that the author has brought before us only the plausible, interesting, and even brilliant hypotheses and generalizations which catch the eye

and appeal to the imagination, we would emphasize that, in leaving in the background so much of the gold and silver of systematic experiment and useful exact knowledge, the author has fallen short of his title. But this is a feature which this book has in common with many other texts on physical chemistry. Some day it will be realized that physical chemistry is also advancing slowly but surely along lines other than molecular structure, dilute gas reactions, and the properties of contaminated water.

R. E. GIBSON

THE INGENIOUS DOCTOR FRANKLIN. Edited by *Nathan G. Goodman.* 244 pages. University of Pennsylvania Press, Philadelphia, 1931. Price, $3.00.

THE book is a compilation of selected letters of Benjamin Franklin on scientific subjects. In bringing these letters together and editing them for publication, Mr. Goodman has performed a valuable service, and the resulting volume not only faithfully reflects the broad interests of Benjamin Franklin but makes easily available some enjoyable bits of writing.

There are some fifty-seven letters which treat on all manner of topics—from economies possible through daylight saving as measured by the decreased use of candles (a suggestion made to the *Journal of Paris* in 1784), to the last letter in the book which concerns toads found in stone near Paris in 1782.

The Rules of Health and Long Life, which are given, wisely discuss factors which are today recognized as important. After discussing at some length "the art of procuring pleasant dreams," Doctor Franklin concludes that "what is necessary above all things, a good conscience." Another letter gives directions for learning to swim, another is on choosing eyeglasses, and still another describes his own bifocals, the first to be made. Topics in physics, meteorology, natural history, geology, chemistry, mechanics, agriculture, medicine, and mathematics are briefly treated. He discusses fireplaces, the Gulf Stream, hydrogen balloons, and the restoration of life by sun rays.

Since the letters were written to close friends, they are in his most persuasive style. While much that he discusses has since been surpassed, nevertheless his ideas as expounded in these letters retain a certain vitality and give a good idea of Franklin's rare personality. The editor of the book and the University of Pennsylvania Press deserve our thanks for making this volume available.

THE SORPTION OF GASES AND VAPOURS BY SOLIDS. *By James William McBain.* 577 pages, 147 figures. George Routledge & Sons, Ltd., 68–74 Carter Lane, E. C. 4, London, 1932. Price, 25 s.

MCBAIN gives an exhaustive treatment of the subject, including an imposing list of references. Many of these are increased in value by extended comment.

The early chapters review the history of sorption and the various methods of measurement. Then follows the long section presenting and discussing experimental data. Of course, active charcoal is always in the limelight, but so is silica and even glass and the metals. A most interesting discussion of chabazite and the record-breaking smallness of its capillaries is a feature of one chapter. Only the smallest molecules, as vapor, can penetrate chabazite, it appears.

Heat of wetting, heat of sorption, and the effect of adsorbed gases upon the structure of charcoal, of iron, and of palladium make up the body of Chapter XIII.

A theoretical section concludes the book. The compressed-film theory is questioned, and much evidence cited as against condensation as a general explanation of sorption. Yet the author does, and wisely too, admit that often capillary condensation occurs in addition to sorption. Like Langmuir, he considers adsorption the result of time lag between condensation and evaporation of molecules striking a surface. The electrical interpretation of sorption concludes the book.

Altogether, this is a most useful and comprehensive test. It is to be hoped that it will soon be followed by a second volume on adsorption from liquids.

HARRY N. HOLMES

INTRODUCTION TO AGRICULTURAL BIOCHEMISTRY. *By R. Adams Dutcher and Dennis E. Haley.* 484 pages, 98 figures, 67 tables. John Wiley and Sons, Inc., New York, 1932. Price, $4.50.

HERETOFORE, most teaching of so-called agricultural chemistry to college students has been from the background of chemists with training and experience in general, and of inorganic chemistry, supplemented by study of results of empirical field tests or annual feeding experiments. Recently, however, a group of chemists, of whom the authors of this book are examples, have been developing the applications of biochemistry in the field of agricultural science and practice. Specifically, this means the study of the chemistry of plants and animals from the standpoint of their behavior as biological units rather than solely as units of farm production. The present book, the first of its kind in this field, is the result of some twenty years of teaching chemistry to students of agriculture from this viewpoint.

Several of the chapters, dealing with The Soil, Fertilizers, Insecticides and Fungicides, Mineral Nutrients of Plants, etc., are presented more largely from the former farm-practice viewpoint than from their biochemical aspects; but, in the main, the latter dominate the subject matter. The senior author's own special interest is reflected in the unusually extensive presentation of the biochemical basis for animal and human nutrition.

The book is divided into three parts dealing, respectively, with General and Introductory, discussions of the chemistry of living matter; The Plant, chiefly from the nutritional point of view; and The Animal, again chiefly from the nutritional standpoint. The material presented is accurately stated, up to date, and well chosen. It is excellently illustrated, an unusual feature being the large number of pictures of prominent chemists who have contributed to the agricultural applications of this science.

This pioneer book in a new field is exceptionally well prepared and appears destined to be widely used as a text and reference.

R. W. THATCHER

ERGEBNISSE DER ANGEWANDTEN PHYSIKALISCHEN CHEMIE. BAND I. Edited by *Max LeBlanc.* 417 pages. Akademische Verlagsgesellschaft, Leipzig, 1931. Price, paper, 28.50 marks; cloth, 30 marks.

THIS book is the first volume of a series to be published on the results of applied physical chemistry, the object being to show the extent to which physical, or, in a broader sense, theoretical chemistry, has penetrated industry and the practical results achieved. According to the editor, one volume containing from five to six separate and self-contained contributions is to be issued each year. In the first volume, the articles have no relation to each other and are selected from the widely different fields of solid fuels, steel-making, sugar from wood, rubber, ore-dressing, and coal-washing.

The first article, by Richard Heinze, is a good technological review of the newer processes for the improvement of fuels. Briquetting, drying, pulverization, gasification, high- and low-temperature carbonization, and hydrogenation of brown coal and bituminous coal are discussed in the usual manner of books on fuel technology, without any particular emphasis on physical chemistry. In fact, a number of important physico-chemical investigations, such as those of Haslam and co-workers on gas production and water-gas reactions, are omitted entirely. Only 3 of the 259 references pertain to American workers.

On the other hand, Edward Maurer and Wilhelm Bischof, the authors of the second article on the physical chemistry of the manganese reaction in steel-making, have not limited themselves to German investigators and have made a determined effort to fit the physical chemistry of aqueous solutions to the steel-making process. The third article, by F. Bergius, reviews previous work on the preparation of sugar from wood and similar substances, and describes the development of his own process and its economic application.

The fourth article, by M. Kröger and M. LeBlanc, is a valuable physico-chemical contribution to the fundamentals and limitations of the elastic properties of rubber and similar substances. The fifth, and last, article on modern problems in ore-dressing and coal-washing, by S. Valentine, is likewise an excellent review of the physics and physical chemistry involved in gravity concentration and froth flotation.

It is a pity that such diverse subjects should be included in a single volume. One cannot expect a rubber chemist, a steel

metallurgist, or an ore-dressing engineer to invest eight dollars in a volume which is largely devoted to other subjects. Consequently, the book will find only limited circulation in libraries of general technology. A. C. FIELDNER

ENZYKLOPÄDIE DER TECHNISCHEN CHEMIE. BAND VIII. NATRIUMVERBINDUNGEN BIS SALOPHEN. *By Fritz Ullmann.* 2nd revised edition. 860 pages. Urban & Schwarzenberg, Berlin and Vienna, 1931. Price, paper, 45 marks; bound, 54 marks.

VOLUME VIII of this encyclopedia is quite up to the standard of the first seven volumes, all of which have been briefly reviewed in previous issues [IND. ENG. CHEM., **21**, 393, 889 (1929); **22**, 200, 1024 (1930); **23**, 248, 973 (1931)]. The present volume includes detailed treatises in German on various subjects between the topics indicated in the title, among some of the more important being nickel, sodium compounds, ovens of various types from laboratory ovens to metallurgical furnaces, oxalic acid, ozone, paper, phenol, phosphorus and its compounds, photography, platinum, pumps, mercury and its compounds, radioactivity, perfumes, yeasts, etc. An index to the volume, as of previous volumes, is inserted separately, together with a table of contents showing the author of each subject treated. Little can be said that has not already been said covering previous volumes; it is simply the eighth of a series of one of the largest and best works ever published in the field of chemical technology. As the reviewer has stated previously, the books will be an important encyclopedic reference work in all libraries of importance.

CHARLES L. PARSONS

TRAITÉ DE CHIMIE MINÉRALE. TOME I. Edited by *Paul Pascal.* 860 pages, 17 × 26 cm., 160 figures. Masson et Cie, 120 Blvd. Saint-Germain, Paris, 1931. Price, unbound, 150 francs plus 22.5 francs postage.

THIS is the first of a series of 12 volumes forming a Treatise on Inorganic Chemistry to be published during the course of the years 1931 and 1932, under the editorial direction of Paul Pascal assisted by sixty-four collaborators. It consists of an Introduction (P. Pascal), and chapters on Air (A. Dansette), Liquid Air (R. Tremblot), Water (J. Barbaudy), Hydrogen (J. Barbaudy), Hydrogen Industry (P. Baud), Oxygen (J. Barbaudy), Combustion and Detonation of Gaseous Mixtures (P. Laffitte), Ozone (J. Guéron), Hydrogen Peroxide (J. Barbaudy), Fluorine (A. Damiens), Chlorine (A. Chrétien), Bromine (P. Pascal), Iodine (P. Pascal), and Industry of the Halogens and Their Derivatives (P. Baud).

The plan of the work contemplates a critical presentation of the material interpreted from the point of view of physical chemistry without neglecting the descriptive aspects of the subject. The treatment is modern throughout, and there is a good balance between the articles contributed by the several authors.

A notable feature of the book is the 48-page section of the introduction devoted to graphs and their application to the succinct presentation of experimental data. Many such graphs, as well as numerous tables of physical constants, are found in the body of the work. An admirable method of indicating at the bottom of each page the location of the references given there is employed, and the collective bibilography at the end of each chapter is divided into tenths by heavy numerals, thus greatly facilitating its use. The bibliographies are critical rather than exhaustive, but are in no sense incomplete. The index is well prepared and permits the rapid location of desired material. A table of contents is given.

The paper and printing are of excellent quality. The volume is unbound in accordance with French custom, thus permitting each purchaser to select his preferred binding.

It is of interest to note that a similar Treatise on Organic Chemistry is to be published in the near future under the editorial direction of Victor Grignard.

The present volume is a distinct contribution to the literature of the subject, and, if the succeeding volumes of this and the companion treatise maintain the high standard of the one under review, they will form a necessary part of every library.

COLIN MACKENZIE MACKALL

MEHLCHEMIE. NEUE ERKENNTNISSE AUF DEM GEBIETE DER MULLEREI UND BACKEREI. *By Karl Mohs.* 3rd edition, revised. 172 pages, 24 illustrations. Theodor Steinkopff, Dresden and Leipzig, 1931. Price, 8 marks.

THE third edition of Mohs' interesting book is similar to its predecessors in purpose and scope. Some of the text has been revised and expanded and brought up to date. It will be remembered that Mehlchemie is written for practical bakers, millers, and the grain and flour trade, and not for professional chemists. The author disclaims any intention of writing a scientific textbook, and has gone in for "popular science" in the best sense of that much abused term. He gives the baker and miller a little "painless chemistry" in the first chapter, followed by three others on something about plant physiology, the proteins, and dough as a colloid system. Cereal chemists will find much of interest in the latter.

The exposition of hydrogen-ion concentration and buffer action, as compared with the interplay of costumed guests at a masked ball, is ingenious, but in the experience of the reviewer similar attempts to translate theory into familiar analogies is not always successful. Straight exposition is often more satisfactory.

An excellent list of references, brought up to date, ends the book, with the inclusion of recent papers by American research workers in the cereal field. C. B. MORISON

DIE GLASFABRIKATION. 2 BAND. *By Robert Dralle.* 710 pages. R. Oldenbourg, Munich and Berlin, 1931. Price, bound, 64 marks; paper, 60 marks.

THIS volume is much more specific than Volume 1 and might be regarded as a practical text on glass-making. It comprises seven general sections by as many authors, as follows: Sheet Glass (Hermann); Plate Glass (Lutz); Wire, Ornamental Glass, etc., (Wollner); Bottle Glass (Keppler and Hermann); Hollow Ware (Springer); Illuminating Ware (Frommel); Optical Glass (Eckert).

The treatment of these various subjects is quite detailed and includes discussion of both old methods and the recent developments in the glass industry. Generally, each subject is discussed in detail, so that it is possible to obtain quite comprehensive information on any one of the above subjects without reading the entire text; some improvements (as in furnaces and machines), made since Volume 1 was published, are described. Numerous references to Volume 1 are given; hence Volume 2 will be more valuable if read in connection with Volume 1.

The index, complete for the two volumes, is a subject index only, and its appearance (after five years) is a desirable addition to Volume 1. Although the book (both volumes) reflects more German ideas than American, it contains much information that will be of value to American glass manufacturers. A. N. FINN

CROMATURA ELETTROLITICA. COME S'IMPIANTA—QUANTO COSTA. LE APPLICAZIONI DECORATIVE E MECCANICHE. *By Osvaldo Macchia.* 489 pages, 204 figures, 45 tables. Ulrico Hoepli, Galleria de Christoforis 59–65, Milan, 1932. Price, paper, 50 lire.

THE author, who is a chemist at the Royal Industrial Institute at Fermo, has published several papers on chromium plating, and is hence well qualified to review the subject. This book is the most comprehensive summary of chromium plating that has appeared. The bibliography includes nearly two hundred authors, and admirably supplements that published a few years ago by R. Schneidewind. Most of the subject matter is familiar to American readers; in fact, many of the illustrations and tables are quoted from American publications. The chief value of the book to American investigators, therefore, will be to help them check up on their reference lists, and incidentally to get a European point of view on chromium plating. One possible source of confusion is that only the middle initial is given in many references—for example, M. Baker (for E. M. Baker), G. Fink (for C. G. Fink), etc. This practice should certainly be corrected in any revision of the book. WILLIAM BLUM

MARKET REPORT—MARCH, 1932

THESE PRICES UNLESS OTHERWISE SPECIFIED ARE THOSE PREVAILING IN THE NEW YORK MARKET, MARCH 15, FOR COMMERCIAL GRADES IN CARLOAD QUANTITIES

Newer Chemicals

Acetaldehyde, drums, lc-l., wks.	lb.	.18½
Acetaldol, 50-gal. drums	lb.	.27
Acetylene tetrachloride, *see* Tetrachloroethane		
Acid, abietic	lb.	.12
Adipic	lb.	.72
Linoleic	lb.	.16
Ammonium linoleate, drums	lb.	.15
Amyl furoate, 1-lb. tins	lb.	5.00
Aroclors	lb.	.40
Butyl carbitol, *see* Diethylene glycol monobutyl ether		
Cellosolve, *see* Ethylene glycol monobutyl ether		
Furoate, tech., 50-gal. drums	lb.	1.00
Carbitol, *see* Diethylene glycol monoethyl ether		
Cellosolve, *see* Ethylene glycol monoethyl ether		
Acetate, *see* Ethylene glycol monoethyl ether acetate		
Crotonaldehyde, 50-gal. drums	lb.	.32
Dichloroethyl ether, 50-gal. drums	lb.	.06
Diethylene glycol, drums	lb.	.14
Monobutyl ether, drums	lb.	.24
Monoethyl ether, drums	lb.	.15
Diethylene oxide, 50-gal. drums	lb.	.50
Dioxan, *see* Diethylene oxide		
Diphenyl	lb.	.30
Ethyl acetoacetate, 50-gal. drums	lb.	.65
Carbonate, 90%, 50-gal. drums	gal.	1.85
Chlorocarbonate, carboys	lb.	.30
Ether, absolute, 50-gal. drums	lb.	.50
Furoate, 1-lb. tins	lb.	5.00
Ethylene chlorhydrin, 40%, 10-gal. cbys	lb.	.75
Dichloride, 50-gal. drums	lb.	.05
Glycol, 50-gal. drums	lb.	.25
Monobutyl ether, drums, wks.	lb.	.24
Monoethyl ether, drums, wks.	lb.	.17
Monoethyl ether acetate, drums, wks	lb.	.19½
Monomethyl ether, drums	lb.	.21
Oxide, cyl	lb.	2.00
Furfuramide(tech.), 100-lb. drums	lb.	.30
Furfuryl acetate, 1-lb. tins	lb.	5.00
Alcohol, tech., 100-lb. drums	lb.	.50
Furoic acid (tech.), 100-lb. drums	lb.	.50
Glyceryl phthallate	lb.	.26
Glycol stearate	lb.	.18
Isopropyl ether, drums	lb.	.10
Lead dithiofuroate, 100-lb. drums	lb.	1.00
Magnesium peroxide, 100-lb. cs.	lb.	1.15
Methyl acetate, drums	gal.	1.20
Cellosolve, *see* Ethylene glycol monomethyl ether		
Furoate, tech., 50-gal. drums	lb.	.50
Paraldehyde, 110-55 gal. drums	lb.	.20½
Phosphorus oxychloride, 175 cyl.	lb.	.20
Propyl furoate, 1-lb. tins	lb.	2.50
Strontium peroxide, 100-lb. drums	lb.	1.25
Sulfuryl chloride, 600-lb. drums, crude	lb.	.15
Distilled	lb.	.40
Tetrachloroethane, 50-gal. drums	lb.	.09
Trichloroethylene, 50-gal. drums	lb.	.10
Triethanolamine, 50-gal. drums	lb.	.40
Trihydroxyethylamine linoleate	lb.	.40
Trihydroxyethylamine stearate	lb.	.35
Vinyl chloride, 16-lb. cyl	lb.	1.00
Zinc dithiofuroate, 100-lb. drums	lb.	1.00
Perborate, 100-lb. drums	lb.	1.25
Peroxide, 100-lb. drums	lb.	1.25

Chemicals Previously Quoted

Acetanilide, U. S. P., powd., bbls.	lb.	.24
Acetic anhydride, 92-95%, cbys.	lb.	.21
Acetone, drums, wks	lb.	.10¼
Acetphenetidin, bbls	lb.	1.25
Acid, acetic, 28%, c/l., bbls.	100 lbs.*	2.75
56%, c/l., bbls	100 lbs.	5.10
Glacial, c/l., bbls	100 lbs.	9.14
Glacial, U. S. P., c/l., carboys	100 lbs.	9.64
Acetylsalicylic, bbls	lb.	.75
Anthranilic, 99-100%, drums	lb.	.85
Benzoic, tech., bbls	lb.	.40
Boric, bbls	lb.	.06½
Butyric, 100% basis, cbys	lb.	.80
Chloroacetic, mono-, bbls., wks.	lb.	.18
Di-, cbys	lb.	1.00
Tri-, bbls	lb.	2.50
Chlorosulfonic, drums, wks	lb.	.04½
Chromic, 99%, drums	lb.	.13¼
Cinnamic, bottles	lb.	3.25
Citric, U. S. P., cryst., bbls	lb.	.33½
Cresylic, pale, drums	gal.	.49
Formic, 90%, cbys., N. Y.	lb.	.10¼
Gallic, U. S. P., bbls	lb.	.74
Glycerophosphoric, 25%, 1-lb. bot	lb.	1.40
H, bbls., wks	lb.	.65
Hydriodic, 10%, U. S. P., 5-lb. bot	lb.	.67
Hydrobromic, 48%, cbys., wks.	lb.	.45
Hydrochloric, 20°, tanks, wks.	100 lbs.	1.35
Hydrofluoric, 30%, bbls., wks.	lb.	.06
60%, bbls., wks	lb.	.13
Hydrofluosilic, 35%, bbls., wks.	lb.	.11
Hypophosphorus, 30%, U. S. P., 5-gal. demis	lb.	.85
Lactic, 22%, dark, bbls	lb.	.04
48%, light, bbls., wks	lb.	.11
Mixed, tanks, wks	N unit	.07
	S unit	.08
Molybdic, 85%, kegs	lb.	1.25
Naphthionic, tech., bbls	lb.	nom.
Nitric, C. P., cbys	lb.	.11
Nitric, 36°, c/l., cbys., wks.	100 lbs.	5.00
Oxalic, bbls., wks	lb.	.11
Phosphoric, 50%, U. S. P.	lb.	.14
Picramic, bbls	lb.	.65
Picric, bbls., c/l	lb.	.30
Pyrogallic	lb.	1.50
Salicylic, tech., bbls	lb.	.33
Stearic, d. p., bbls., c/l	lb.	.07½
Sulfanilic, 250-lb. bbls	lb.	.14½
Sulfuric, 66°, c/l., cbys., wks.	100 lbs.	1.60
66°, tanks, wks	ton	15.00
60°, tanks, wks	ton	10.50
Oleum, 20%, tanks, wks	ton	18.50
40%, tanks, wks	ton	42.00
Sulfurous, U. S. P., 6%, cbys.	lb.	.05
Tannic, tech., bbls	lb.	.23
Tartaric, U. S. P., cryst., bbls.	lb.	.24½
Tungstic, kegs	lb.	1.40
Valeric, C. P., 10-lb. bot	lb.	2.50
Alcohol, U. S. P., 190 proof, bbls.	gal.	2.57
Amyl, from pentane, tanks	lb.	.203
Amyl, Imp. drums	gal.	1.75
Butyl, drums, c/l., wks	lb.	.148
Cologne spirit, bbls	gal.	2.69
Denatured, No. 5, comp. denat., c/l., drums	gal.	.34½
Isoamyl, drums	gal.	4.00
Isobutyl, ref., drums	gal.	1.00
Isopropyl, ref., drums	gal.	.60
Propyl, ref., drums	gal.	1.00
Wood, *see* Methanol		
Alpha-naphthol, bbls	lb.	.57
Alpha-naphthylamine, bbls	lb.	.32
Alum, ammonia, lump, bbls., wks.	100 lbs.	3.30
Chrome, casks, wks	100 lbs.	5.00
Potash, lump, bbls., wks.	100 lbs.	3.35
Soda, bbls., wks	100 lbs.	3.45
Aluminum, metal, N. Y.	100 lbs.	22.90
Aluminum chloride, anhyd., commercial, wks., drums extra, c/l.	lb.	.05
Aluminum stearate, 100-lb. bbl.	lb.	.20
Aluminum sulfate, comm'l, bags, wks	100 lbs.	1.25
Iron-free, bags, wks	100 lbs.	1.90
Aminoazobenzene, 100-lb. kegs	lb.	1.15
Ammonia, anhydrous, cyl., wks.	lb.	.15½
50,000-lb. tanks, wks	lb.	.05625
Ammonia, aqua, 26°, tanks, wks., contained NH_3	lb.	.05½
Ammonium acetate, kegs	lb.	.33
Bifluoride, bbls	lb.	.21
Bromide, 50-lb. boxes	lb.	.35
Carbonate, tech., casks	lb.	.08
Chloride, gray, bbls	100 lbs.	5.25
Lump, casks	lb.	.10½
Iodide, 25-lb. jars	lb.	5.20
Nitrate, tech., cryst., bbls	lb.	.08½
Oxalate, kegs	lb.	.22
Persulfate, cases	lb.	.26
Phosphate, dibasic, tech., bbls.	lb.	.10¾
Sulfate, bulk, wks	100 lbs.	1.00
Amyl acetate, tech., from pentane, tanks	lb.	.175
Aniline oil, drums	lb.	.14½
Anthracene, 80-85%, casks, wks.	lb.	.60
Anthraquinone, subl., bbls	lb.	.50
Antimony, metal	lb.	.06½
Antimony chloride, drums	lb.	.13
Oxide, bbls	lb.	.08½
Salt, dom., bbls	lb.	.22
Sulfide, crimson, bbls	lb.	.25
Golden, bbls	lb.	.16
Vermilion, bbls	lb.	.38
Argols, red powder, bbls	lb.	.07
Arsenic, metal, kegs	lb.	.27
Red, kegs, cases	lb.	.09⅜
White, c/l., kegs	lb.	.04
Asbestine, bulk, c/l	ton	15.00
Barium carbonate, bbls., bags, wks	ton	56.50
Chloride, bbls., wks	lb.	.03¾
Dioxide, drs., wks	lb.	.12
Hydroxide, bbls	lb.	.05¼
Nitrate, casks	lb.	.07¼
Barium thiocyanate, 400-lb. bbls.	lb.	.27
Barytes, floated, 350-lb. bbls., wks.	ton	23.00
Benzaldehyde, tech., drums	lb.	.60
F. F. C., cbys	lb.	1.40
U. S. P., cbys	lb.	1.15
Benzidine base, bbls	lb.	.65
Benzol, tanks, wks	gal.	.20
Benzoyl chloride, cbys	lb.	1.00
Benzyl acetate, F. F. C., bottles	lb.	.75
Alcohol, 5-liter bot	lb.	1.20
Chloride, tech., drums	lb.	.30
Beta-naphthol, bbls	lb.	.22
Beta-naphthylamine, bbls	lb.	.58
Bismuth, metal, cases	lb.	1.00
Bismuth, nitrate, 25-lb. jars	lb.	.95
Oxychloride, boxes	lb.	2.95
Subnitrate, U. S. P., 25-lb. jars	lb.	1.20
Blanc fixe, dry, bbls	ton	70.00
Bleaching powder, drums, wks.	100 lbs.	2.00
Bone ash, kegs	lb.	.06
Bone black, bbls	lb.	.08¼
Borax, bags	lb.	.02½
Bordeaux mixture, bbls	lb.	.11½
Bromine, bot	lb.	.36
Bromobenzene, drums	lb.	.50
Bromoform, jars	lb.	1.80
Butyl acetate, drums, c/l	lb.	.159
Cadmium bromide, 50-lb. jars	lb.	1.40
Cadmium, metal, cases	lb.	.55

* Contract price.

Cadmium sulfide, boxes	lb.	.60
Caffeine, U. S. P., 5-lb. cans	lb.	2.40
Calcium acetate, bags	100 lbs.	2.50
Arsenate, bbls	lb.	.05½
Carbide, drums	lb.	.05½
Chloride, drums, wks., flake	ton	21.00
Cyanide, 100-lb. drums	lb.	.30
Nitrate, bags	ton	35.00
Phosphate, monobas., bbls	lb.	.08
Tribas., bbls	lb.	.11
Calcium carbonate, tech., bags,	100 lbs.	1.00
U. S. P., precip., 175-lb. bbl.	lb.	.06½
Camphor, Jap., cases	lb.	.47
Carbazole, bbls	lb.	.75
Carbon, activated, drums	lb.	.08
Carbon bisulfide, drums	lb.	.05
Carbon black, cases	lb.	.06
Carbon dioxide, liq. cyl	lb.	.06
Carbon tetrachloride, drums	lb.	.06¼
Casein, stand. gr., bbls	lb.	.06½
Cellulose acetate, bbls	lb.	.80
Cerium oxalate, kegs	lb.	.33
Charcoal, willow, powd., bbls	lb.	.06
China clay, bulk	ton	8.00
Chloral hydrate, drums	lb.	.70
Chlorine, liq., c/l., cyl	lb.	.04
Chlorine, tanks	100 lbs.	1.75
Chlorobenzene, mono-, drums	lb.	.10
Chloroform, tech., drums	lb.	.15
Chromium acetate, 20° soln., bbls.	lb.	.05
Coal tar, bbls., wks	gal.	.10
Cobalt, metal, kegs	lb.	2.50
Cobalt oxide, bbls	lb.	1.25
Cod-liver oil, bbls	bbl.	30.00
Copperas, c/l., bulk	ton	14.50
Copper, metal, elec	100 lbs.	6.00
Copper carbonate, bbls., 52/54%	lb.	.16½
Chloride, bbls	lb.	.22
Cyanide, drums	lb.	.39
Oxide, red, bbls	lb.	.15½
Sulfate, c/l., bbls	100 lbs.	2.75
Cotton, soluble, bbls	lb.	.40
Cream tartar, bbls	lb	.19¼
Cyanamide, bulk, N. Y.	Ammonia unit	.97½
Diaminophenol, kegs	lb.	3.80
Dianisidine, bbls	lb.	2.35
Dibutylphthalate, drums, wks	lb.	.23½
Diethylaniline, drums	lb.	.55
Diethylene glycol, drums	lb.	.14
Diethyl phthalate, drums	lb.	.23
Diethyl sulfate, tech., drums	lb.	.30
Dimethylaniline, drums	lb.	.26
Dimethylsulfate, drums	lb.	.45
Dinitrobenzene, drums	lb.	.15½
Dinitrochlorobenzene, bbls	lb.	.13
Dinitronaphthalene, bbls	lb.	.34
Dinitrophenol, bbls	lb.	.23
Diphenylamine, bbls	lb.	.34
Diphenylguanidine, bbls	lb.	.30
Epsom salt, tech., bbls., c/l., N. Y.	100 lbs.	1.70
Ether, nitrous, bot	lb.	.80
Ether, conc., drums	lb.	.09
Ethyl acetate, tanks, c/l	lb.	.09
Bromide, drums	lb.	.50
Chloride, drums	lb.	.22
Methyl ketone, drums	lb.	.30
Ethylbenzylaniline, 300-lb. drums	lb.	.88
Ethylene dichloride	lb.	.05
Chlorohydrin, anhyd., drums	lb.	.75
Glycol, c/l., wks	lb.	.25
Feldspar, bulk	ton	6.50
Ferric chloride, tech., bbls	lb.	.05
Ferrous chloride, cryst., bbls	lb.	.06
Ferrous sulfide, bbls	100 lbs.	2.50
Fluorspar, 98%, bags	ton	31.00
Formaldehyde, bbls	lb.	.06
Formaniline, drums	lb.	.37½
Fuller's earth, bags, c/l., mines	ton	15.00
Furfural drums, tech., contract, works	lb.	.10
Glauber's salt, bbls	100 lbs.	1.00
Glucose, 70°, bags, dry	100 lbs.	3.14
Glycerine, C. P., drums	lb.	.11¼
G salt, bbls	lb.	.42
Hexamethylenetetramine, tech., drums	lb.	.46
Hydrogen peroxide, 25 vol., bbls.	lb.	.05½
Hydroquinone, kegs	lb.	1.20
Indigo, 20%, paste, bbls	lb.	.12
Iodine, crude, 200-lb. kgs	lb.	4.20
Iodine, resubl., jars	lb.	4.65
Iodoform, bot	lb.	6.00
Iridium, metal	oz.	160.00
Kieselguhr, bags	ton	50.00
Lead, metal, N. Y	100 lbs.	3.25
Lead acetate, bbls., white	lb.	.10½
Arsenate, bbls	lb.	.10
Oxide, litharge, bbls	lb.	.05¾
Peroxide, drums	lb.	.20
Red, bbls	lb.	.06¾
Sulfate, bbls	lb.	.06½
White, basic carb., bbls	lb.	.07¼
Lime, hydrated, bbls	100 lbs.	.85
Lime, live, chemical, bbls., wks.	100 lbs.	1.05
Limestone, ground, bags, wks	ton	4.50
Lithopone, bbls	lb.	.04½
Magnesite, crude	ton	32.00
Calcined, 500-lb. bbls., wks	ton	40.00
Magnesium, metal, wks	lb.	.30
Magnesium carbonate, bags	lb.	.06
Chloride, drums	ton	36.00
Fluosilicate, cryst., bbls	lb.	.10
Oxide, U. S. P., light, bbls	lb.	.42
Manganese chloride, casks	lb.	.07½
Dioxide, 80%, bbls	ton	80.00
Sulfate, casks	lb.	.07
Mercury bichloride, cryst., 50 lbs.	lb.	1.59
Mercury, flasks, 76 lbs	flask	74.50
Meta-nitroaniline, bbls	lb.	.67
Meta-phenylenediamine, bbls	lb.	.80
Meta-toluylenediamine, bbls	lb.	.67
Methanol, pure, synthetic, drums, wks	gal.	.37½
Tanks, wks	gal.	.35½
Methyl acetone, drums	gal.	.50
Salicylate, cases	lb.	.42
Methyl chloride, cylinders	lb.	.45
Michler's ketone, bbls	lb.	3.00
Naphtha, solvent, tanks	gal.	.26
Naphthalene, flake, bbls	lb.	.03¾
Nickel, metal	lb.	.35
Nickel salt, single, bbls	lb.	.10
Double, bbls	lb.	.10
Niter cake, bulk	ton	11.50
Nitrobenzene, drums	lb.	.08½
Oil, castor, No. 1	lb.	.10
China wood, bbls	lb.	.06¾
Coconut, Ceylon, tanks	lb.	.03½
Cod, N. F., tanks	gal.	.25
Corn, crude, tanks, mills	lb.	.03⅛
Cottonseed, crude, tanks	lb.	.04
Lard, edible, bbls	lb.	.11¼
Linseed, bbls	lb.	.07
Menhaden, crude, tanks	gal.	.20
Neat's-foot, pure, bbls	lb.	.08¾
Oleo, No. 1, bbls	lb.	.06⅝
Olive oil, denat., bbls	gal.	.70
Foots, bbls	lb.	.04¾
Palm, Lagos, casks	lb.	.03¾
Peanut, crude, bbls	lb.	.07
Perilla, bbls	lb.	.05½
Rapeseed, bbls., English	gal.	.39
Red, bbls	lb.	.06½
Soy bean, crude, bbls	lb.	.043
Sperm, 38°, bbls	gal.	.68
Whale, bbls., natural, winter	gal.	.56
Ortho-aminophenol, kegs	lb.	2.15
Ortho-dichlorobenzene, drums	lb.	.08
Ortho-nitrochlorobenzene, drums	lb.	.28
Ortho-nitrophenol, bbls	lb.	.85
Ortho-nitrotoluene, drums	lb.	.16
Ortho-toluidine, bbls	lb.	.20
Palladium, metal	oz.	19.00
Para-aminophenol, kegs	lb.	.78
Para-dichlorobenzene	lb.	.15½
Para-formaldehyde, cases	lb.	.38
Paraldehyde, tech., drums	lb.	.20½
Para-nitraniline, drums	lb.	.48
Para-nitrochlorobenzene, drums	lb.	.25
Para-nitrophenol, bbls	lb.	.45
Para-nitrosodimethylaniline, bbls	lb.	.92
Para-nitrotoluene, bbls	lb.	.29
Para-phenylenediamine, bbls	lb.	1.15
Para-toluidine, bbls	lb.	.40
Paris Green, 250-lb. kegs	lb.	.23
Phenol, drums	lb.	.14¼
Phenolphthalein, drums	lb.	.80
Phenylethyl alcohol, 1-lb. bot	lb.	7.00
Phosphorus, red, cases	lb.	.42
Phosphorus trichloride, cyl	lb.	.18
Phthalic anhydride, bbls	lb.	.15
Platinum, metal	oz.	37.00
Potash, caustic, drums	lb.	.06⅛
Potassium acetate, kegs	lb.	.28
Bicarbonate, casks	lb.	.09½
Bichromate, casks	lb.	.08
Binoxalate, bbls	lb.	.14
Bromate, cs	lb.	.35
Carbonate, 80–85%, calc., casks	lb.	.049
Chlorate, kegs	lb.	.08
Chloride	ton	34.55
Cyanide, cases	lb.	.55
Meta-bisulfite, bbls	lb.	.11
Permanganate, drums	lb.	.16
Prussiate, red, casks	lb.	.37½
Yellow, casks	lb.	.18½
Titanium oxalate, bbls	lb.	.21
Pyridine, drums	gal.	1.50
Resorcinol, tech., kegs	lb.	.65
Rochelle salt, bbls., U. S. P	lb.	.16
R salt, bbls	lb.	.42
Saccharin, cans	lb.	1.70
Salt cake, bulk	ton	14.00
Saltpeter, gran., bbls	lb.	.06
Silica, ref., bags	ton	22.00
Silver nitrate, 16-oz. bot	oz.	.23¼
Soda ash, 58%, light, bags, contract, wks	100 lbs.	1.15
Soda, caustic, 76%, solid, drums, contract, wks	100 lbs.	2.50
Sodium acetate, bbls	lb.	.04½
Benzoate, bbls	lb.	.42
Bicarbonate, bbls	100 lbs.	1.85
Bichromate, casks	lb.	.05
Bisulfite, bbls	lb.	.04
Bromide, bbls., U. S. P	lb.	.31
Chlorate, kegs	lb.	.05¾
Chloride, bags	ton	12.00
Cyanide, cases	lb.	.16½
Fluoride, bbls	lb.	.07
Metallic, drums, 12¼-lb. bricks	lb.	.19
Naphthionate, bbls	lb.	.52
Nitrate, crude, 200-lb. bags, N. Y	100 lbs.	1.76½
Nitrite, bbls	lb.	.07
Perborate, bbls	lb.	.18
Peroxide, cases	lb.	.21
Phosphate, trisodium	100 lbs.	3.20
Picramate, kegs	lb.	.69
Prussiate, bbls	lb.	.11½
Silicate, drums, tanks, 40°	100 lbs.	.75
Silicofluoride, bbls	lb.	.05½
Stannate, drums	lb.	.18
Sulfate, anhyd., bbls	lb.	.02
Sulfide, cryst., bbls	lb.	.02½
Solid, 60%	lb.	.03½
Sulfocyanide, bbls	lb.	.28
Thiosulfate, reg., cryst., bbls	lb.	.02½
Tungstate, kegs	lb.	.70
Strontium carbonate, tech., bbls.	lb.	.07¼
Nitrate, bbls	lb.	.09
Sulfur, bulk, mines, wks	ton	18.00
Sulfur chloride, red, drums	lb.	.05
Yellow, drums	lb.	.03½
Sulfur dioxide, commercial, cyl	lb.	.07
Sulfuryl chloride, drums	lb.	.10
Thiocarbanilid, bbls	lb.	.26½
Tin	lb	.22¼
Tin tetrachloride, anhydrous, drums, bbls	lb.	.16
Oxide, bbls	lb.	.23½
Titanium dioxide, bbls., wks	lb.	.21
Toluene, tanks	gal.	.30
Tribromophenol, cases	lb.	1.10
Triphenylguanidine, drums	lb.	.58
Triphenyl phosphate, bbls	lb.	.60
Tungsten, powder	lb.	1.65
Urea, pure, cases	lb.	.11
Whiting, bags	100 lbs.	1.00
Xylene, 10°, tanks, wks	gal.	.26
Xylidine, drums	lb.	.36
Zinc, metal, E. St. Louis	100 lbs.	3.195
Zinc ammonium chloride, bbls	lb.	.05½
Chloride, granulated, drums	lb.	.05¾
Oxide, Amer., bbls	lb.	.05¾
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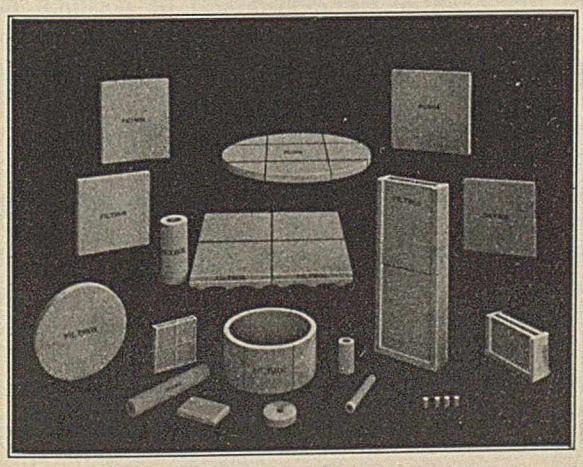

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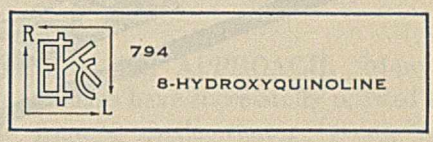

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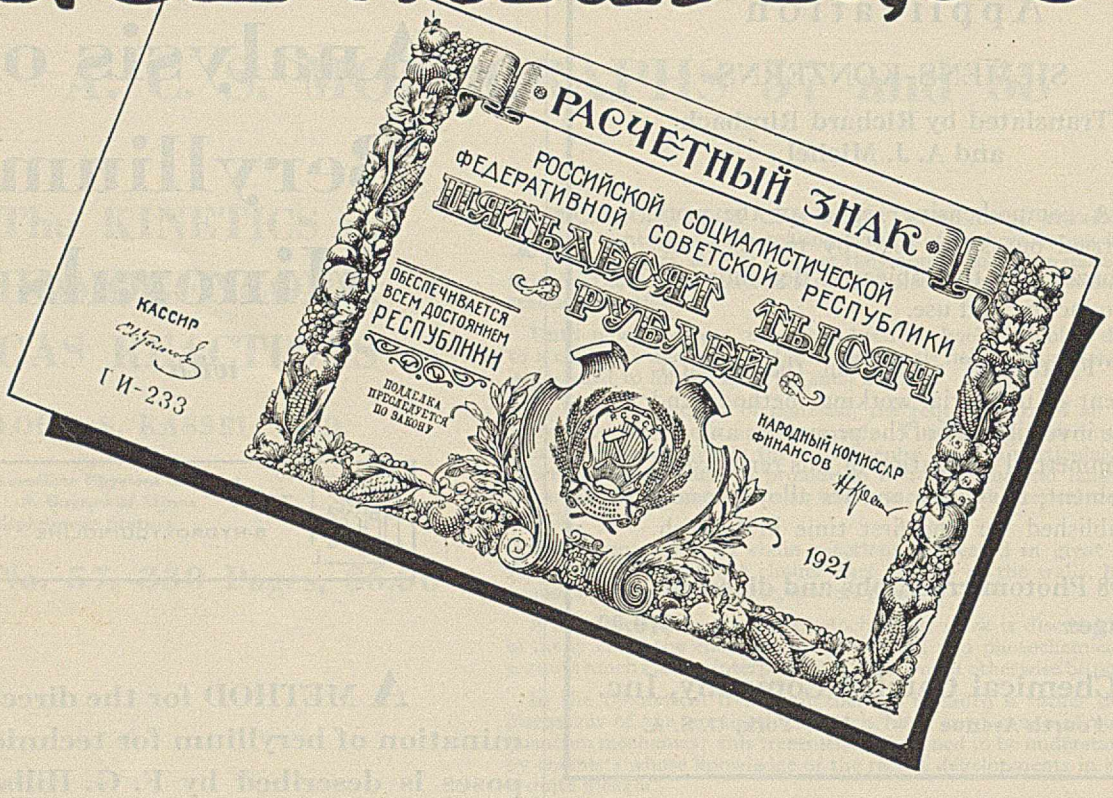

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