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"Uncle John"

By this affectionate nickname John Edgar Teeple was known to a very wide circle of chemist friends, and even those who always addressed him as "Doctor Teeple" soon came to see why the more familiar salutation was in such common use. For years he had carried on his work, notwithstanding the severe handicap which ill health imposes. He was optimistic and cheerful in circumstances which would have made the average person impossible, and many times he met one with a smile when other people would have been quite inaccessible. He last sat as a Director of the American Chemical Society at the annual meeting of the board in December. Immediately thereafter he became a patient at the new Medical Center, where in due course a thorough diagnosis was made in which a single principal source of trouble was located. Then came the work of preparing him for an operation, which he subsequently withstood surprisingly well. One crisis after another was met and passed, but successive hemorrhages could not be withstood, and he died March 23 at the Presbyterian Hospital.

John E. Teeple was a comparatively young man, having been born in 1874. His academic and professional record need not be recited here. These have been set forth on the occasion of medal presentations and when he was president of The Chemists' Club, and may be found in the usual places where such data are printed.

There was combined in this man a number of rare qualities. His keen business judgment was sound. Many who went to him perplexed for advice came away with thoughts crystallized and doubts cleared. He was coöperative—a quality lacking in so many of us. He was friendly and even-tempered. We have seen him in serious moods, but we have never known him to lose his temper. He never sought the limelight. He was ever available to discuss and advise on matters of interest to the other fellow, and yet in his quiet way he performed important service for industry and directed research of the highest scientific merit. He enjoyed a large consulting practice, and from his experience grew his oft-quoted expression of "patient, educated money." Among his hobbies was research on the Maya civilization. He deciphered many of the records and did outstanding work on the Maya calendar. His report on this archeological problem was published as a scientific publication of the Carnegie Institution of Washington under the title "Maya Astronomy." During the last two years of his life Doctor Teeple held an appointment as research associate of the institution.

Doctor Teeple performed a great service as Treasurer of our Society. His counsel was continually sought on Society matters, just as it was sought by business men who knew his ethical standards to be so high and his opinions founded on such calm, painstaking considerations that they were highly prized and unquestioned. The work which he did must now be done by others. That is the way of the world. But his place cannot be filled.

Cost Accounting de Luxe

The scientist in industry, whatever his title, should be the first to recognize the utility of correct cost accounting. The manufacturer who engages in modern competition without a knowledge of his costs, based on thorough-going methods and accurate analysis of his operations, is riding for a fall. Like most other human devices, cost accounting can be overdone.

A manufacturer was at a loss to understand why his principal competitor continually undersold him in a certain line of products. A careful study was instituted covering the costs of raw materials of all the operations, advertising, selling, etc., and the difficulty was ultimately discovered. This manufacturer had a little-used building in which this product was fabricated. The building had been erected for some especially heavy work. The foundations were deep and the entire construction represented such an investment that products manufactured in it carried an unusually high overhead.

Rather than upset the cost-accounting factors, the concern erected a cheaper type of structure which could be easily used, and in that, with the lower overhead, found itself able, by the books, to meet competition. The expensive structure vacated stands ready for the occasional heavy piece of work, which in consequence will cost the purchaser much more than it otherwise would, and the manufacturer has more of his capital tied up in brick and mortar.

Doubtless the cost accountants feel they have won a victory, but somehow the thing does not look right to us. The books may show a lower cost for this item, but not for the business as a whole. Let us have cost accounting, but not *in absurdum*.

Service of Paper

Beginning with our February issue we have presented a series of articles on purified wood fiber. These have set forth in some detail pioneer work on large-scale manufacture of alpha-cellulose from wood and have indicated the tests applied to obtain data, not only for the direction of the work, but for the evaluation of the product. The series has been received favorably and has inspired discussion.

What determines the service life of paper? Precedent holds that long life can be achieved only by papers made from pure rags. Unfortunately, the pure rag of yesteryear is not the pure rag of today. The term is no longer significant. There have been too many changes in the textile industry to permit that. True, the belief is still held that no paper made from cellulose derived from wood will give the service life of one made from cellulose from the fibers of flax and cotton. Investigations indicate that it is not the source of the cellulose which is the determining factor. It is rather the purity of that cellulose and the freedom of the finished sheet from excess chemicals and certain types of fillers and sizes which heretofore have brought wood cellulose into a certain disrepute.

> Cellulose from wood, as it can be prepared today, is a raw material decidedly improved over that with which we worked but a few years ago. Cellulose has become a center of research. More is known of its molecular structure and of its properties. This information serves as a basis for comparing cellulose from various sources and has not been neglected by those who use cellulose from wood in paper-making.

It is important—very important—that questions affecting the service life of paper be settled and settled rightly. The facts advanced in the series by Doctor Richter should go far toward stimulating the research which will enable the correct answer to be found.

Dextrose

BY WHATEVER name you may prefer to call it, the comparatively simple compound which chemists know as "dextrose" has been the center of one of the most important contentions since the enactment of the Federal Food and Drugs Act and the promulgation of the several regulations for its enforcement.

There have been two rather distinct schools of thought on this whole question of prepared foods. The precedents which bear upon the interpretation and enforcement of the act are, to a large extent, based on the status of foods prior to this era of intensive food research. There are those who maintain that such precedents should be rigorously followed. The other school of thought maintains that, in the interests of all concerned, a more open attitude of mind toward new products as they are developed and proved would be more logical and constructively helpful. The differences of opinion concerning the justification for and the probable consequences of the ruling of the Secretary of Agriculture on December 26, 1930, are governed largely by which of the two schools has influenced a given individual. Certain it is that the decision rescinding the requirement that the presence of added corn sugar should be stated on food labels accomplished, through an administrative act, something which had not been possible by legislation, notwithstanding years of effort. The best friends of refined dextrose wish the action might have been taken as a result of convincing research and investigation, rather than on the political basis which was so evident in the statement of the Secretary.

Confusion has developed because of the many statements made and written, which have clouded the real issues. It may be helpful to give a little of the historical background.

Some take exception to the name "corn sugar," believing that it should have been reserved for such a sugar as has been and can be manufactured from the stalk of maize or Indian corn. It is held that that product should be the one known as corn sugar, just as cane and beet sugar are named to indicate their direct production from the raw materials. These men believe that corn starch sugar would be the better name, since it is the starch of the corn, and not the juice of the corn stalk, from which corn sugar is made. However, the present designation has become so widely accepted, whereby products derived from corn starch are known as corn sugar and corn sirup, that a change is not to be expected. It might be argued that dextrose from any source, be it starch or cellulose, might be entitled to be known as corn sugar. The trade-mark "Cerelose" was doubtless chosen to indicate cereal origin for the dextrose marketed under that name.

While there unquestionably exists a direct relation between pure food and good health, nevertheless contrary to the ideas of some, the Federal Food and Drugs Act is not primarily a public health measure. The enforcement of the pure food law naturally has given a form of protection which, though secondary to the purpose of the law, has made the public feel far more safe concerning its food supply. The primary purpose is the prevention of adulteration or fraud. Public food officials in the enforcement work are largely guided by the interpretations which the Supreme Court has made in several cases, of which the vinegar decision is typical. The law is to be interpreted to guarantee to the consumer that grade of food having the constituents which, according to common understanding and public conception, the consumer expects in that food. Thus, the housewife knows that the baker does not use the exact ingredients in his cake that she uses in hers. Her concept of commercially baked foods and home-baked foods differs. When the commercially baked food differs from the common understanding or public conception, then it must be labeled to show that deviation. Likewise, the common understanding of a salad oil is not exclusively olive oil; it is any wholesome edible oil that has been suitably refined. The examples might be multiplied.

At the time the Federal Food and Drugs Act was passed, the food industry as a whole was suffering because some manufacturers were putting out a product different from that which the general understanding would indicate as suitable. For the good of the industry, as well as of the consumer, it was necessary to take steps that would insure the purchaser's obtaining the food he had a right to expect. Deviations from a reasonable concept were to be stated on the label.

By reference to the Food and Drugs Act of June 30, 1906, and its amendments, we find in Section 7 "that for the purposes of this act an article shall be deemed to be adulterated: in the case of food:

> First. If any substance has been mixed and packed with it so as to reduce or lower or injuriously affect its quality or strength.
>
> Second. If any substance has been substituted wholly or in part for the article.
>
> Third. If any valuable constituent of the article has been wholly or in part abstracted.
>
> Fourth. If it be mixed, colored, powdered, coated, or stained in a manner whereby damage or inferiority is concealed.
>
> Fifth. If it contain any added poisonous or other added deleterious ingredient which may render such article injurious to health. *Provided*, That when in the preparation of food products for shipment they are preserved by any external application applied in such manner that the preservative is necessarily removed mechanically, or by maceration in water, or otherwise, and directions for the removal of said preservative shall be printed on the covering or the package, the provisions of this act shall be construed as applying only when said products are ready for consumption.
>
> Sixth. If it consist in whole or part of a filthy, decomposed, or putrid animal or vegetable substance, or any portion of an animal unfit for food, whether manufactured or not, or if it is the product of a diseased animal, or one that has died otherwise than by slaughter.

From the above will be seen the basis for the contention that to substitute corn sugar for sucrose would constitute deception. The other point of view is that deception cannot be proved where the substance is wholesome and of food value, and that since there is no harm there is no fraud.

White crystalline corn sugar, now produced on the order of 135 million pounds annually, has been used for years in candies, ice creams, and bakery goods. Here it meets a special need and its character is said to be well suited to the requirements. However, no large-scale operations have been carried out, even experimentally, in the manufacture of preserves, jellies, canned foods—in other words, for the industry which one might suppose would be in position to profit most by the wide use of this new sugar. So long as the label statement was required, the food manufacturers were not interested in making experiments for themselves, and strangely, the advocates of corn sugar have not seen fit to determine the data for themselves on a scale sufficiently large to be convincing. The canners of foods generally did not advocate the ruling of the Secretary, but since its announcement the National Canners Association and several organizations distributing food have passed resolutions condemning it.

It must be said to the credit of the industry that the corn sugar of today, the descendant of the uncertain glucose of earlier days, is a beautiful pure-white crystalline product. We have not heard its wholesomeness or its food value questioned. The hydrated product has a sweetness approximately one-half that of sucrose. This is the average of many determinations in various laboratories. Some investigators have found a value less than 50 per cent, while one group reported 75 per cent of the sweetness of sucrose. In the system sucrose-dextrose-water at 30° C. a saturated solution of sucrose contains 68.11 per cent; of dextrose, 54.64 per cent; and a mixture of the two when saturated contains 47.1 per cent of sucrose and 26.59 per cent of the hydrated dextrose. This difference in solubility, according to some observers, produces in jellies, preserves, etc., a crystalline product if more than 25 per cent of the sugars added are in the form of dextrose. These same observers state that when approximately 25 per cent of added dextrose has been reached there is a decided difference in the flavor of the product, which some hold to be objectionable. The dextrose molecule is aldehydic and combines with the amino substances in sweet corn, producing a brown color when the pack is made with corn sugar. Some investigators find this tendency to coloration with invert sugar generally. When dextrose is added the reaction is more pronounced.

The statement has been made that the ruling would help increase the market for corn, estimated anywhere from 5 million to 100 million bushels per annum. Statements attributed to the manufacturers of corn sugar have pointed out that any gain in production would come slowly and that the minimum figure given may easily be the maximum increase obtained for many years. The corn products industry buys what is known as "cash corn," and this represents about 10 per cent of the corn crop reaching the primary markets. Of this the industry consumes about one-third. It would seem that any substantial increase in demand would affect this market. We are all interested in any greater uses for farm products, but we doubt whether the corn farmer should expect, for a long time to come, any noticeable change in the price of his corn as the result of the new ruling.

Pure dextrose has been the study of several physiological chemists and has been used as a therapeutic agent. However, the usefulness of the resulting valuable data is threatened with destruction through its misuse. In a recently distributed circular we find the following paragraph:

> There is a very little question of what such a sugar can do to improve the desirability of manufactured food products. A sugar which can of itself, and without the necessity of undergoing chemical change, wipe out the poisonous toxins of fatigue and sickness; and which, with proper physical exercise, can reduce the fatty accumulations of the body, tending to keep them normal under all ordinary circumstances; and which, because it is the same vital sugar which Nature herself uses, can help the feeble to new life and the strong to a greater enjoyment of their strength, needs no advocate.

Does it not seem that dextrose is sometimes handicapped by the over-enthusiasm of its friends?

In the face of the federal ruling, there is a strong indication that the states will not uniformly accept it. In thirty-eight states federal rulings pertaining to food and drugs are automatically adopted. In the remaining states these rulings apply only in the case of articles in interstate commerce. The food officials of several states are in disagreement with the Secretary's ruling, and some state officials have announced their intention of asking the legislatures for a law that will enable them to require labels stating the presence of added corn sugar. Food manufacturers have been endeavoring for years to obtain uniformity in labeling, for one can readily see the complications that would arise in packing, labeling, and marketing goods where different labels must be used for different states. While success has not been so complete as could be hoped, the present indications are that the decision will add to these difficulties.

The corn sugar question as it now stands depends upon acceptance by state officials and the public. It also may have a direct bearing upon the enforcement of the pure food laws. Selling as it does at approximately 50 cents per hundred pounds less than sucrose, it cannot be expected to find a place solely on the basis of its sweetness. Obviously, it would be uneconomic to employ a substance half as sweet (hydrated dextrose as marketed) at a cost of but 50 cents less per hundred, unless the character of dextrose particularly fitted it for a given purpose. Corn sugar will ultimately find its own place and fill it well, but the place will be determined by its physical and chemical characteristics, including its sweetness, and also the price at which it can be obtained. Where it can be used with real advantage it will be sought after, but universal application is not to be expected. Further, its introduction into foods should proceed slowly. Otherwise there will be disappointments and loss, unless preliminary investigation can be followed by large-scale trials before the foods are regularly put into commercial channels.

So far as the pure food law and its enforcement are concerned, one group holds the consequences to be grave. Another sees a step toward fairmindedness where new products are involved and an opportunity for the results of careful research in food. Those with the first point of view insist that, whatever the chemists may include in the designation "sugar," it must be admitted that the public concept of sugar is sucrose and nothing else. If dextrose is to be used in commerce interchangeably with sucrose, then what is salt? A chemist applies that term to a great variety of compounds other than sodium chloride. What is flour? What is alcohol?

We can but wait for the consequences of this ruling. Meanwhile the manufacturers of food products should be careful to insist upon experimental packs and a thorough investigation in each case before making changes in their formulas which would alter taste, color, and physical properties. This means too much in the psychology of our foods to take undue risks. The good relations of the canning industry with the public also may be involved. The interests of the manufacturers of corn sugar are intimately tied in with this same problem.

The manufacture of corn sugar and other corn products is properly classed in the chemical industry. We, therefore, are interested in their successful development and wide utilization. The corn products industry often purchases corn too high in moisture to withstand long storage and transportation. In this it benefits the corn grower. The finished products are already important factors in high-grade human foods. Because they have merit, we insist they should be used on their merits and for their own sake advocated only in those cases where it is well known and experimentally demonstrated just what may be expected of them.

The Initial Corrosion Rates of Metals[1]

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The initial corrosion rates of aluminum, zinc, iron, copper, nickel, tin, and silver in oxygenated water have been studied. The electrochemical series in the ordinary sense was found to be inadequate in predicting the corrosion tendencies of metals in oxygenated water. Calculations based on free-energy changes show that all the metals studied tend to corrode in saturated solutions of their hydroxides containing dissolved oxygen. These metals were found to corrode at appreciable rates during the initial period. The approximate initial rates of corrosion, expressed as cubic centimeters of oxygen consumed per square decimeter per minute per average cubic centimeter of oxygen per liter, are in the above order 0.028, 0.020, 0.020, 0.0054, 0.0049, 0.0045, and 0.0007.

The corrosion rates were found to decrease or become zero after the initial period, indicating the formation of films which reduced the rate of diffusion of the ions and dissolved oxygen.

IN A previous paper [IND. ENG. CHEM., 22, 1197 (1930)] the writers have shown that various steels, including the stainless types, corrode at finite rates of the same order of magnitude, when submerged in oxygenated water. The rate for stainless steels becomes essentially zero after only a few minutes because of the formation of a protective film of corrosion products. For the purpose of further showing the effect of such protective films on corrosion rates, similar studies were made using other metals which would be expected to corrode when submerged in water.

Theoretical Considerations

The usual criterion for predicting whether a metal will tend to corrode is its position in the electromotive series, and this is referred to extensively in discussions of corrosion problems, because of the general acceptance of the electrochemical theory of corrosion. However, when factors which affect reversible electrode potentials are neglected, a literal application of the series is of little value. The electromotive series is based on measurements of the potential of different metal electrodes in the following cell:

$$\text{Metal} \left| \begin{array}{c} \text{Metal ion, } 1\,M \\ \text{H ion, } 1\,M \end{array} \right| \text{H}_2 \text{ (1 atm.)}$$

Obviously, such a cell will not measure the correct tendency of reactions to proceed when the activities[2] of the metal and hydrogen ion are other than one molal. When considering normal corrosion in water, it may be assumed that the metal-ion and hydrogen-ion concentrations correspond to saturation of the solution with the metallic hydroxide, particularly at the metal surface. Since the concentrations of the saturated solutions of hydroxide vary for the different metals, not only may the absolute values of the electromotive forces be different, but also the relative positions may change. A further criticism of the use of the electromotive series as determined by the above cell is that it is not applicable to corrosion reactions in which dissolved oxygen takes part.

The first of the objections to the direct use of the electromotive series may be overcome by correction for concentration. The solubility product of silver hydroxide, for example, is 10^{-8}, and the saturated solution is therefore 10^{-4} molal in Ag^+ and OH^- ions. The hypothetical cell may be represented as:

$$\text{Ag(s)} \left| \begin{array}{c} \text{AgOH} \\ 10^{-4}\,M \end{array} \right| \text{H}_2 \text{ (1 atm.)}$$

The electromotive force of this cell is a measure of the tendency of silver to corrode in oxygen-free water according to the following reaction:

$$2\text{Ag(s)} + 2\text{H}_2\text{O(l)} = 2\text{Ag(OH)(s)} + \text{H}_2 \text{ (1 atm.)}$$

This equation, however, does not represent the reaction which occurs during the corrosion of a metal in oxygenated water. The equation for the correct reaction may be written as follows:

$$4\text{Ag(s)} + 2\text{H}_2\text{O(l)} + \text{O}_2 \text{ (0.21 atm.)} = 4\text{AgOH(s)}$$

and may also be considered as taking place in an electrolytic cell represented as follows:

$$\text{Ag(s)} \left| \begin{array}{c} \text{Ag(OH)} \\ \text{Satd. soln. O}_2 \\ (10^{-4}M) \\ \text{(0.21 atm.)} \end{array} \right| \text{O}_2 \text{ (0.21 atm.)}$$

The electromotive force of this type of cell is a more exact measure of the tendency of a metal to corrode in water saturated with oxygen and the metal hydroxide. Its numerical value may be calculated from the free-energy decrease accompanying the reaction by means of the equation $-\Delta F = EMF$. The necessary data on solubility products of metallic hydroxides, potentials of the molal hydrogen electrode, the molal oxygen electrode, and the molal metallic electrodes, and the free-energy content of water are available in the literature and are sufficient for the calculation of the free-energy values.

For comparative purposes the values of free-energy decreases accompanying the reactions and electromotive forces of the hypothetical cells have been calculated for a number of metals, and are shown in Table I.

Table I—Free-Energy Decreases and Electromotive Forces of Corrosion Cells

METAL	SOLID CORROSION PRODUCT	OXYGEN CELL		HYDROGEN CELL	
		Free-energy decrease[a]	E. m. f.[b]	Free-energy decrease[a]	E. m. f.[b]
			Volts		*Volts*
Aluminum	$Al(OH)_3$	+162030	+2.34	+77885	+1.12
Zinc	$Zn(OH)_2$	+71514	+1.61	+15414	+0.33
Tin	$Sn(OH)_2$	+61090	+1.33	+4990	+0.11
Iron	$Fe(OH)_2$	+56880	+1.23	+780	+0.02
Iron	$Fe(OH)_3$	+81855	+1.18	−2295	−0.03
Nickel	$Ni(OH)_2$	+52650	+1.14	−3450	−0.07
Copper	$Cu(OH)_2$	+27378	+0.59	−28722	−0.62
Silver	AgOH	+1410	+0.06	−26643	−1.15

[a] $\Delta F_{25}°$ (cal.) per gram atomic weight of metal.

[b] A positive electromotive force indicates that metallic ions tend to form while a negative electromotive force indicates that the reaction tends to proceed in the opposite direction.

From the table it may be seen that, if only hydrogen evolution is considered, nickel, copper, and silver would not tend to corrode and iron would not tend to go to the ferric state. That is, in water containing no oxygen the free-energy decreases and the voltages of the hypothetical cells are negative for the solution of these metals. When oxygen is dissolved in the water, the free-energy decreases and the voltages of the hypothetical cells are positive and all these metals, therefore, tend to corrode. In making use of this

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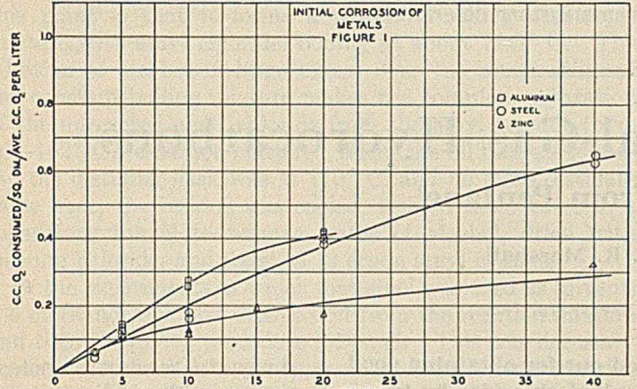
[1] Received January 19, 1931.

[2] Throughout this paper the activities of the ions are considered equal to their concentrations, which is correct for low concentrations.

table it must be remembered that free-energy decreases show only the tendencies for reactions to take place and are in no sense measures of rates.

From a consideration of the values in Table I it was concluded that all the metals listed should show finite initial corrosion rates in oxygenated water. An investigation was therefore undertaken to determine whether or not these metals do corrode, and to ascertain the part played by resistant films in the protection of these metals. Since corrosion would take place, if at all, on oxide-free metal surfaces, the initial-corrosion-rate method described in the previous paper was used in determining corrosion rates.



Experimental Procedure

The experimental procedure used was essentially that described in the previous article. Rotating cylinders of the various metals were rendered oxide-free by treatment with 10 per cent hydrochloric acid. The adhering acid was removed by washing with a stream of oxygen-free water until the effluent was neutral. The specimen was then subjected to the action of oxygenated water, and the corrosion measured by determining the decrease in oxygen concentration during the test. The only departure from the previous procedure was the treatment of copper and nickel with 30 per cent hydrochloric acid and the silver with 5 per cent nitric acid.

Results

As in the previous paper, the results are calculated as cubic centimeters of oxygen (at standard conditions) consumed per square decimeter of metal, corrected for differences in oxygen concentration. The correction was made by dividing by the average oxygen concentration (cubic centimeters per liter) during the run. The values of oxygen consumed are a measure of the total corrosion, and these values are plotted in Figures 1 and 2 against time in minutes. The scales used in the two figures are different because of the low rates of corrosion of tin, copper, nickel, and silver.

Table II—Initial Corrosion Rates of Metals

METAL	O_2 CONSUMED/SQ. DM./MIN./ AV. CC. O_2/LITER
	Cc.
Aluminum	0.028
Zinc	0.020
Iron	0.020
Copper	0.0054
Nickel	0.0049
Tin	0.0045
Silver	0.0007

The curves show that oxygen is consumed during the first few minutes by all metals used, but the slopes of the curves decrease after a short period of corrosion. The slopes of the curves are the rates of consumption of oxygen and, therefore, measures of the corrosion rates. Every metal used shows some decrease in corrosion rate, but the most marked decreases noted are for nickel, tin, and silver, whose rates become essentially zero after 15 minutes.

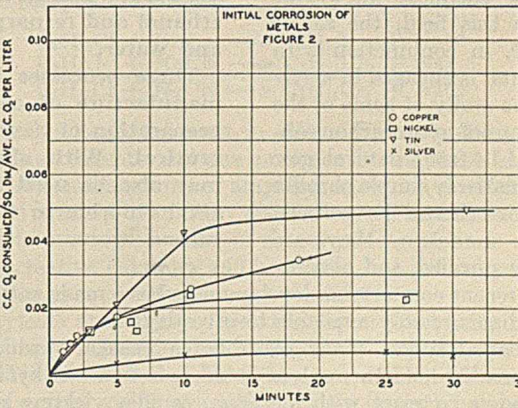
Since it is impossible to obtain an accurate value of the slope at zero time, approximate rates have been estimated by drawing a straight line through the origin and the curve at the 2-minute intercept. The approximate rates so obtained are shown in Table II.

Discussion

As mentioned previously, the free-energy decreases or the electromotive forces of the hypothetical cells indicate positive tendencies for all these metals to corrode in oxygenated water. The experimental data substantiate this conclusion, since the initial corrosion rates are not only finite but readily measurable. In this connection it should be pointed out that, although aluminum, zinc, tin, and iron should corrode in water free from oxygen, the time of exposure to neutral deoxygenated water was short and the rate of hydrogen evolution would be so low as to have no effect on the measurements.

The fact that the electromotive series is not the proper criterion for expressing the tendency of the metal to corrode is evidenced by the fact that both silver and copper have finite corrosion rates in oxygenated water. These metals are both below hydrogen in the electromotive series and accordingly would not be expected to corrode. On the basis of the free-energy decreases, however, these metals were expected to have finite initial corrosion rates in oxygenated water.

As previously stated, all the metals studied corrode during the initial period, but it is important to note that in every case the curves flatten with increased duration of exposure. Tin and nickel, which are known to have a high resistance to corrosion in oxygenated water, consume oxygen at a high rate during the initial period. However, the rate quickly drops to zero, pointing to the formation of a very resistant film. The fact that the rates of oxygen consumption for copper and silver decrease with time indicates that stable metals, such as copper and silver, are resistant to oxygenated water because protective films are formed after very short contact.



It is interesting to note that the initial corrosion rates of most of the metals used are not widely different, considering the characteristics of metals and their corrosion products. Although the lowest rate (silver) is one-fortieth that of the highest (aluminum), the next lowest rate (tin) is only one-seventh that of the highest. In other words, the initial corrosion rates of six metals tested, including some above and some below hydrogen in the electromotive series, from aluminum to copper, vary only seven fold.

Since the initial corrosion rates of the first three metals listed in Table II are essentially the same, it may be that the corrosion rate is determined by the rate of diffusion of oxygen[3] to the metal surface, rather than by the rate of oxidation of the metal. This cannot be true, however, of the other four metals used, since the initial corrosion rates are considerably lower and indicate that the oxidation rate of metals is controlling.

Conclusions

1—The electromotive series as ordinarily used is not the proper criterion for judging the probability of corrosion of a metal in oxygenated water.

2—The free-energy decreases, assuming oxygen and water to react with metals to form metallic hydroxides in saturated solution, are more exact measures of the tendencies to corrode.

3—Aluminum, copper, iron, nickel, silver, tin, and zinc all show finite initial rates of corrosion in oxygenated water.

4—The initial corrosion rates of all metals tested decrease after a relatively short time, indicating the formation of partially or completely protective films in all cases.

5—Metals such as nickel, tin, copper, and silver do not seriously deteriorate on exposure to oxygenated water, not because of a negative corrosion tendency, but because of the formation of an impermeable corrosion product which prevents further deterioration.

[3] All experimental work was done under constant conditions of liquid agitation and hence the rate of oxygen diffusion through the liquid would be constant.

Syntheses from Natural-Gas Hydrocarbons

I—Caproic Acid from Pentane[1]

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Conditions have been worked out for obtaining good yields of alkyl cyanides from alkyl chlorides by treatment with sodium cyanide. Yields of 70 per cent with a recovery of 25 to 28 per cent of unchanged chloride have been obtained with normal amyl chloride. Other primary chlorides also react satisfactorily. Secondary alkyl chlorides and bromides give poor yields (around 30 per cent) and tertiary amyl chloride or bromide gives no nitrile at all under these conditions. By the use of sodium iodide, which acts as an intermediate compound catalyst, the yield can be raised to 90 per cent or more.

The hydrolysis of amyl cyanide by means of 67 per cent sulfuric acid is complete in 30 minutes.

Amyl and butyl chlorides resemble carbon tetrachloride, ethyl iodide, benzene, hexane, etc., in forming binary minimum boiling azeotropic mixtures with ethanol and ternary azeotropic mixtures with ethanol and water.

These processes have been found suitable for the manufacture of caproic acid, which is used in the preparation of hexylresorcinol, a well-known pharmaceutical. With slight modifications these methods may also be used for the conversion of any primary alkyl chloride to the fatty acid containing one more carbon atom.

THE need for a more intimate and extended knowledge of the chemistry of the non-benzenoid hydrocarbons and their immediate derivatives has been frequently stressed by J. F. Norris, B. T. Brooks, and other eminent authorities. Indeed, anyone gaining even a slight familiarity with hydrocarbon chemistry is impressed by the dearth of information on even the commonest reactions. With the object of contributing to fundamental chemical knowledge within this field, the senior author, in conjunction with students, is engaged in a systematic study of some of the reactions of hydrocarbons obtainable from natural gas. The relatively simple paraffin hydrocarbons have been chosen because they are readily purified, and also because recent commercial developments have made certain intermediates readily available to investigators.

Perhaps the best known controllable reaction to which paraffins readily lend themselves is halogenation. Alkyl halides are known to react with metallic cyanides yielding nitriles, from which fatty acids, esters, amines, amides, alcohols, and other classes of compounds are readily prepared. It might be supposed that the latter reaction had been rather thoroughly studied, but we were unable to find that any case had been reported where an alkyl chloride had been successfully treated with sodium cyanide to yield an alkyl cyanide. Butyl bromide has been converted to valeronitrile by means of sodium cyanide reacting in aqueous alcoholic solution (*1*), and alkyl chlorides under similar conditions have been shown to react with potassium cyanide yielding nitriles (*2*). Preliminary tests showed that aqueous alcoholic solutions of amyl chloride and sodium cyanide yield capronitrile slowly upon refluxing. The main object of the research was to determine the optimum conditions and yield.

Materials

The normal amyl chloride (b. p. 105–107° C.) was obtained by the rectification of a sample produced by the chlorination of natural-gas pentane by the Sharples Solvents Corporation.[2] The sodium cyanide was Mallinckrodt U. S. P. IX, granulated. Other reagents were of C. P. grade.

Procedure

Weighed amounts of sodium cyanide, water, alcohol, and amyl chloride were placed in the order named in a 500-ml. Pyrex Florence flask. The flask was fitted with a reflux condenser, placed on a water bath, and the contents were refluxed for a definite time. Shellacked cork connections were used throughout, owing to the tendency of rubber to absorb amyl chloride vapor. At the end of the run the flasks were removed from the bath, cooled, and fitted with two-hole corks containing a 100-cc. separatory funnel and a tube leading to a Liebig condenser. The flask was immersed in an oil bath and the entire liquid contents of the flask were distilled out, water being added from the funnel to drive over

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[1] Received December 6, 1930.

[2] The writers wish to thank R. R. Read, director of Chemical Research Laboratories, Sharp and Dohme, for a sample of especially pure normal amyl chloride which was used in most of these experiments.

the last traces of amyl cyanide. Since this compound is practically insoluble in water, the distillation was considered complete when no drops of nitrile were observed floating upon the surface of the water dropping from the condenser. This procedure left behind sodium chloride, unreacted sodium cyanide, and traces of tar. The distillate contained amyl chloride, amyl cyanide, water, and alcohol.

The distillate was treated with anhydrous potassium carbonate, which completed the separation of the water into a lower layer, the upper layer containing alcohol, amyl chloride, and amyl cyanide. The upper layer was separated, 95 per cent ethanol added to bring total volume of ethanol up to 75 cc., and distilled. The reason for adding the ethanol at this point is that it forms a minimum-boiling azeotropic mixture with amyl chloride, boiling at about 72.5° C. The addition of alcohol in large excess over the composition of the constant-boiling mixture makes the complete separation of the unreacted amyl chloride from the amyl cyanide (b. p. 161–162° C.) a simple matter. When the oil bath surrounding the distilling flask was at 110° C. and no more distillate came over, the residue was cooled, treated with water in a separatory funnel to remove traces of alcohol, dried with calcium chloride, and weighed as crude amyl cyanide.

In the experiments in which methanol was used as solvent, the methanol was first distilled off from the reaction mixture and then the above procedure followed. This was necessary because methanol does not form an azeotropic mixture with amyl chloride. When isopropanol was used as solvent it was employed in the distillation in the same way as ethanol.

Results

In Table I the amount of alcohol used was varied, the other reagents being held constant at 53 grams (0.5 mol) of amyl chloride, 27 grams (0.55 mol) of sodium cyanide, and 27 grams of water. The figures refer to percentage of the theoretical yield of amyl cyanide obtained by refluxing for 48 hours.

Table I—Effect of Varying Concentration of Alcohol on Yield of Amyl Cyanide

ALCOHOL	YIELD WITH VARYING QUANTITIES OF ALCOHOL				
	25 ml.	50 ml.	75 ml.	100 ml.	125 ml.
	%	%	%	%	%
Methyl	..	17.6	23.75	41.5	35.7
Ethyl	8.2	25.5	44.5	51.2	54.9
Isopropyl	3.7	17.6	21.0	17.6	17.6

At every concentration ethanol showed higher yields than the others. Further work was therefore confined mainly to this solvent.

The results expressed in Table II were obtained by varying both the concentration and amount of ethyl alcohol, other conditions remaining as before.

Table II—Effect of Varying Both Concentration and Amount of Ethanol in Ethanol-Water Mixtures on Yield of Amyl Cyanide

ETHANOL	YIELD WITH VARYING AMOUNTS OF SOLVENT						
	75 ml.	90 ml.	105 ml.	125 ml.	150 ml.	200 ml.	300 ml.
%	%	%	%	%	%	%	%
80	65.0	69.5*	63.5	60.0	56.0	40.7	36.6
85	48.5	60.5	60.5	53.2	52.5	37.5	28.0
90	47.0	52.0	55.0	49.5	46.4	31.7	20.0
95	43.0	44.5	47.5	47.5	..	..	..

These data would appear to indicate that better results might be expected with a smaller percentage of ethanol in the solvent, but data in Table I, where slightly more dilute alcohol was used, show a decrease in yield and indicate that greatly improved results could not be expected in this direction.

Another series of experiments proved that increasing the amount of sodium cyanide or the time of refluxing improves the yield only slightly, a maximum yield of 72.2 per cent having been obtained when a 20 per cent excess of sodium cyanide is allowed to react for 96 hours. When a temperature of 104° C. was used (pressure 50 pounds gage) a yield of 59.6 per cent was obtained in 24 hours. Other conditions were the same as in the starred result in Table II.

The yields are all based upon the amyl chloride used. In the best runs, where from 68 to 70 per cent of the amyl chloride was converted to cyanide, it was always possible to recover from 25 to 28 per cent of unchanged amyl chloride.

Effect of Sodium Iodide

Since alkyl chlorides are known to react rapidly with sodium iodide, forming alkyl iodides and sodium chloride, and alkyl iodides are known to yield alkyl cyanides rapidly when treated with sodium cyanide, a run was made using equimolar portions of amyl chloride and sodium iodide with a 10 per cent excess of sodium cyanide, refluxing with 90 ml. of 80 per cent ethanol for 24 hours. A yield of 90 per cent of crude amyl cyanide was obtained.

Hydrolysis of Amyl Cyanide

This reaction may be carried out in either acid or alkaline solution, but is best accomplished by using equimolar portions of amyl cyanide and 67 per cent sulfuric acid. The mixture is placed under a reflux condenser and warmed until the exothermic reaction has started. Heat is then withdrawn until the more violent part of the reaction has subsided, after which the mixture is again warmed. At the end of 30 minutes no odor of the isocyanide is apparent and the product is entirely soluble in aqueous sodium hydroxide indicating complete conversion to caproic acid. Practically no discoloration accompanies this step. Water is added to prevent the crystallization of ammonium bisulfate and the upper layer is separated. Distillation showed it to be practically pure caproic acid.

Discussion

The highest yields of amyl cyanide from amyl chloride were by the use of sodium iodide, which acts as an intermediate compound catalyst.

$$\begin{array}{l}
\mathrm{C_5H_{11}Cl + NaI \longrightarrow C_5H_{11}I + NaCl} \\
\underline{\mathrm{C_5H_{11}I + NaCN \longrightarrow C_5H_{11}CN + NaI}} \\
\mathrm{C_5H_{11}Cl + NaCN \longrightarrow C_5H_{11}CN + NaCl}
\end{array}$$

Two disadvantages inherent in this technic are the greater cost of the reagents and the presence in the final reaction mixture of small amounts of amyl iodide, which is not readily separated from the cyanide by distillation. The sodium iodide method is proving of value in the cyaniding of some of the more uncreative chlorides and bromides, but is hardly necessary in the case of normal amyl chloride.

The yields are largely dependent upon the purity of the normal amyl chloride used. Separate experiments have established the fact that secondary amyl chlorides and bromides give poor yields of cyanides, while tertiary halides give none at all under the conditions of these experiments.

The methods described above are capable of being extended to other primary alkyl chlorides, with excellent yields. In case the boiling point of the chloride is too low—e. g., *n*-butyl chloride—it is best to use pressure above atmospheric. Iron does not interfere with the reaction, so an ordinary autoclave may be used.

Literature Cited

(1) Adams and Marvel, *J. Am. Chem. Soc.*, **42**, 318 (1920).
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Chemistry of the Doctor Sweetening Process[1]

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The sweetening of petroleum distillates with doctor solution is a complicated chemical process. The litharge originally present in the reagent promptly changes to lead sulfide, which then acts catalytically in a variety of ways. The lead sulfide itself adsorbs mercaptans. The lead sulfide, however, is partly or wholly reconverted into sodium plumbite by the action of air used for blowing. Finally, the alkaline solution of mercaptans (in the aqueous phase) is directly oxidized by atmospheric oxygen.

The normal operation of the doctor process yields sodium sulfide, and this also is altered by aeration, being converted finally into sodium thiosulfate. All of these various reactions occur simultaneously, each at the rate determined by the concentrations of the substances involved.

On the basis of some new experimental work, suggestions are made for improving the technic of commercial sweetening operations.

"SOURNESS" in petroleum distillates is understood to mean the presence of compounds belonging to the group of mercaptans, R–S–H, where R is any hydrocarbon radical. Hydrogen sulfide also imparts sourness to gasoline, but it is so readily removable by washing with alkalies that it no longer constitutes a problem of petroleum refining.

Reactions in Doctor Process

The presence of mercaptan in petroleum distillates is recognized by means of the official doctor test. This test takes place in two stages. The first consists in shaking the distillate with an alkaline solution of lead oxide (sodium plumbite):

$$2\,R{-}S{-}H + Na_2PbO_2 = R{-}S{-}Pb{-}S{-}R + NaOH \qquad (1)$$

The product is lead mercaptide, which is usually deeply colored and soluble in the petroleum phase.

The second step consists in adding a small amount of elementary sulfur. The reaction is:

$$R{-}S{-}Pb{-}S{-}R + S = R{-}S{-}S{-}R + PbS \qquad (2)$$

resulting in the formation of a disulfide and of lead sulfide.

Commercial sweetening by means of doctor solution corresponds in general to these two equations.

There are, however, two important facts to be considered. Equation 1 calls for 1 mol of lead oxide for every 2 mols of mercaptan; Equation 2 calls for 1 atom of sulfur for every 2 mols of mercaptan. In actual practice, however, 1 mol of original lead oxide is capable of sweetening, not 2, but from 10 to 20 mols of mercaptan. This points to either a regeneration of the lead sulfide formed in Equation 2 or a catalytic action of the lead sulfide itself. Moreover, it is customary to agitate the mixture of doctor solution and petroleum distillate by means of air. Under these circumstances we sometimes find the amount of sulfur required according to Equation 2 to be considerably diminished, but we may also find that more sulfur is needed than corresponds to this same equation. On the average, however, over a large series of operations the amount of sulfur required corresponds somewhat closely to that demanded by the equation.

In the event that less lead oxide is taken than corresponds to Equation 1 or, what amounts to the same thing, in the event of lead sulfide acting catalytically to facilitate the sweetening process, we must consider two other chemical processes as going on.

$$PbS + 2NaOH = PbO + Na_2S + H_2O \qquad (3)$$
$$2R{-}S{-}H + S + 2NaOH = R{-}S{-}S{-}R + Na_2S + 2H_2O \qquad (4)$$

where Equation 3 shows a regeneration of lead sulfide and Equation 4 a direct oxidation of the mercaptan to disulfide by means of sulfur and sodium hydroxide, lead sulfide acting purely catalytically.

Note—Equation 3 is thus written for the sake of simplicity. Actually the reaction will run from right to left, as long as sulfide ion is present. Solution of lead sulfide in sodium hydroxide can take place only if the resulting sulfide ion is oxidized to SO_4^{--} or $S_2O_3^{--}$.

Previous Explanations of Process

Each of the secondary processes summarized by Equations 3 and 4 has been defended as giving a proper explanation of the sweetening process as practiced on a large scale.

Morrell and Faragher (*6*) incline strongly to the regeneration of lead sulfide as given in Equation 3, with the addition that the conversion of lead sulfide into lead oxide takes place through the intermediate formation of lead sulfate. Lead sulfate is then decomposed by sodium hydroxide, giving lead oxide and sodium sulfate.

Wendt and Diggs (*10*), on the other hand, view the process according to Equation 4. They point out that lead sulfide is easily wetted by both oils and aqueous solutions. Moreover, they assign to it the power of adsorbing organic sulfides on its surface, so that the particles of lead sulfide offer a meeting place for all the necessary substances required for the sweetening process. Further support for the idea of Wendt and Diggs is found in the work of Greer (*4*), who has shown that merely filtering sour petroleum distillate through a bed of metallic sulfides, such as lead or copper, will yield a sweet product.

It will be shown in the present paper that there is no antagonism between the interpretation of Morrell and Faragher, on the one hand, and that of Wendt and Diggs on the other. As a matter of fact, both of these side reactions take place simultaneously. Such a reconciliation of these extreme views might indeed have been expected from the information available from other sources. Thus, the process of the Standard Development Company (*8*) uses no lead oxide whatever, but sweetens with a mixture of lead sulfide, sodium hydroxide, and sulfur. The use of air, according to this process, is optional. In the process of Rowsey (*7*) no sulfur whatever is used. The sour distillate is agitated with a large quantity of lead sulfide and of sodium hydroxide solution, air being blown in in fine bubbles. Finally, in the process of Low (*5*) no sulfur and no lead sulfide are employed. The distillate is heated with solid sodium hydroxide under moderate pressure with air. In Low's process, in the absence of oxygen there is no sweetening.

Much of the confusion that has attended the discussion of the sweetening process in chemical literature has been due to investigators using the doctor test itself to check their operations. According to them, a gasoline was either sweet or sour. But suppose that we find a given procedure removes 90 per cent of the mercaptan originally present.

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[1] Received October 6, 1930.

Surely this is an important guide as to what has happened. Merely to ascertain that the gasoline is still sour is not very helpful.

The doctor test is extraordinarily sensitive. Thus, Borgstrom and Reid (*3*) give, as an upper limit of sensitivity of the doctor test, a mercaptan concentration of 0.00023 molar. The present writer has found that by dilution of known weights of mercaptan solution a definite test can be obtained with a concentration as low as 0.00006 molar. Inasmuch as the average sour gasoline has a mercaptan molarity of about 0.01, the upper limit of Borgstrom and Reid corresponds to a removal of about 98 per cent of mercaptan, whereas the lower figure given above corresponds to a 99.5 per cent removal.

In the work to be described all the estimations of the extent of mercaptan removal have been made by the method of Borgstrom and Reid (*3*), which has been found entirely satisfactory.

Action of Air on Mercaptan in Presence of Sodium Hydroxide

In these experiments 100-cc. portions of sour gasoline were shaken at room temperature (20–25° C.) with varying amounts of sodium hydroxide solution of different strengths for varying periods of time. The flasks had been carefully cleaned in a current of live steam. The total volume of each flask was 315 cc. when stoppered. The rubber stoppers were new and were cleaned by boiling in dilute sodium hydroxide solution. The gasoline was a sour cracked distillate (original mercaptan molarity 0.0098) to which some isoamyl mercaptan was added. The final mercaptan molarity was 0.0118 as determined by titration with silver nitrate solution. The chemical process taking place, leaving out of consideration for the moment certain side reactions to be considered later, is:

$$4\,R{-}S{-}H + O_2 = 2\,R{-}S{-}S{-}R + 2H_2O \qquad (5)$$

From this equation it is seen that each mol of mercaptan requires $^1/_4$ mol of oxygen or $^5/_4$ mols of air for completion of the reaction. From this we may calculate that 1.00 volume of a 0.01 molar mercaptan solution requires 0.28 volume of air. The mercaptan solution actually employed needed 0.28 × 118, or 33 cc., of air per 100 cc.

Table I gives the experimental data. The amount of mercaptan consumed was determined by titration in each case and is given in terms of the molarity of mercaptan of the remaining gasoline solution, as well as in percentages.

Borgstrom, Dietz, and Reid (*2*) have determined the solubility of various mercaptans in alkalies of different strengths by shaking gasoline solutions of varying origin and containing added mercaptans of increasing molecular weight. They took no account of the volume of air present during shaking, and the time of shaking (*1*) was not always the same. It seems very likely that their figures showing the distribution of mercaptans between gasoline and sodium hydroxide solutions are vitiated by the oxidizing effect clearly demonstrated in Table I.

The normality of oxygen in 2 *M* sodium hydroxide solution saturated with air is about 0.001. If the reaction between oxygen and mercaptan takes place in the aqueous-alkaline phase, then an air-saturated solution of sodium hydroxide might be expected quickly to oxidize one-tenth of its volume of gasoline of a mercaptan molarity equal to 0.01. To test this, 10 cc. of the above gasoline were stirred for 10 minutes with 150 cc. of 2.5 *M* sodium hydroxide in such a manner that no air came in direct contact with the sodium hydroxide solution during the period of stirring. The gasoline gave a mere trace of reaction with doctor solution (see above as to limits of mercaptan detectable by this test).

To check further whether or not oxidation occurred in the aqueous-alkaline phase, a larger portion of gasoline was stirred with an equal quantity of sodium hydroxide solution for 15 minutes, and the two phases thereupon separated. The gasoline phase contained mercaptan equal to 0.0017 molar a few minutes after separation. In a second portion, after standing 24 hours in a closed flask with plenty of air space, the molarity was found equal to 0.0010. A third portion was washed with water, filtered, and allowed to stand 24 hours. The molarity had not changed (found 0.0018 *M*; titration error is about 0.0001 *M*).

Table I—Action of Air on Mercaptan in Presence of Sodium Hydroxide[a]

(100 cc. gasoline, mercaptan 0.0118 *M*, at 20–25° C.)

Expt.	Sodium Hydroxide		Air in Flask	Time of Shaking	Mercaptan Remaining	Mercaptan Removed	Partial Pressure of Oxygen[b]	
	Cc.	*Mols*	*Cc.*		*Mol*	%	Final	Av.
1	25	2	190	1 hour	0.0067	43	0.93	0.96
2	50	2	165	10 min.	0.0069	42	0.91	0.95
3	50	2	165	1 hour	0.0054	54	0.89	0.94
4	50	2	165	2 hours	0.0046	61	0.88	0.94
5	100	2	115	1 hour	0.0038	68	0.81	0.90
6	100	2	115	2 hours	0.0033	72	0.79	0.89
7	100	2	115	4 hours	0.0006	95	0.73	0.86
8	50	2	165	15 min.	0.0065	45	0.91	0.95
9	50	2	165	1 hour	0.0055	53	0.89	0.94
10	50	2	165	5 hours	0.0009	92	0.82	0.91
11	50	2	165	7 hours	0.0005	96	0.81	0.91
12	1	12	214	1 hour	0.0068	42	0.93	0.96
13	10	12	205	1 hour	0.0049	59	0.91	0.95
14	25	12	190	1 hour	0.0046	61	0.89	0.94
15	50	12	165	1 hour	0.0032	73	0.85	0.92
16	1	12	214	15 min.	0.0058	51	0.94	0.97
17	1	12	214	1 hour	0.0038	68	0.90	0.95
18	1	12	214	2 hours	0.0012	90	0.86	0.93
19	1	12	214	6 hours	Sweet	100	0.85	0.92
20	1	2	214	1 hour	0.0046	61	0.91	0.95
21	1	2	214	2 hours	0.0036	70	0.89	0.94

[a] There are some discrepancies in this table (see expts. 12 and 17). Oxidations with gaseous oxygen are notoriously difficult to check, due to the marked influence of traces of either catalysts or inhibitors. In spite of experimental fluctuations, the table gives an unmistakable picture.

[b] Original oxygen pressure, 1.00.

Obviously, small amounts of sodium mercaptide were dissolved or suspended in the gasoline and slowly oxidized in the second sample. The third sample, owing to washing and filtration, apparently contained no sodium mercaptide in solution.

According to Equation 5 the oxidizing reaction we are here discussing takes place between 4 molecules of mercaptan and 1 molecule of oxygen. Experience in a great variety of fields shows that pentamolecular reactions involving oxidation with gaseous oxygen are practically non-existent. The usual mechanism, wherever accurate studies have been made, seems to be according to the following equations:

$$2\,R{-}S{-}H + O_2 = R{-}S{-}S{-}R + H_2O_2 \qquad (6)$$
$$2\,R{-}S{-}H + H_2O_2 = R{-}S{-}S{-}R + 2H_2O \qquad (7)$$

The secondary reaction (7) is very rapid and would be completed practically as soon as the primary reaction (6). An indication of the correctness of this assumption is found in Table III of Borgstrom, Dietz, and Reid (*2*), and in Borgstrom's (*1*) Table IV. These authors used gasolines of different origins and compositions. More particularly, they were careful to determine the relative amounts of unsaturated hydrocarbons in these gasolines. It is well known that unsaturated carbon compounds act as accelerators in oxidation with gaseous oxygen. It is very significant that greater amounts of mercaptan were found to be extracted from gasolines containing larger proportions of unsaturated hydrocarbons. Borgstrom has determined, not true solubility, but solubility plus oxidation, and the sum of these two factors is greater when the solvents are higher in unsaturated content.

The atmospheric oxidation of mercaptans takes place either in the alkaline phase or at the interface between this and the gasoline phase. From this we may draw two conclusions. First, it is not mercaptan, but the mercaptide ion that is actually oxidized. The data given by Borgstrom, Dietz, and Reid (*2*) on the solubility of mercaptans in aqueous alkalies of increasing concentration indicate that in these solutions mercaptans are largely ionized. The second conclusion is that the rate of oxidation is governed by the diffusion of atmospheric oxygen into the alkaline film. Walker, Lewis, and McAdams (*9*) give a more complete discussion of this diffusion question.

A first glance at Table I might lead to the conclusion that oxidation is more rapid when the air volume retained in the shaking flasks is large. Inasmuch as the diffusion of gaseous oxygen into the film where reaction takes place is governed by the partial pressure of oxygen in the system, a calculation has been made of this partial pressure at the end of the shaking period and of its average value during the shaking period. It will be seen that the average partial pressure of oxygen has not varied greatly and that these changes must have only a secondary effect on the rate of oxidation.

Inasmuch as the rate of oxidation is governed by the alkaline film and its oxygen content, we may infer that the rate of oxidation will probably be increased by increasing (1) the air pressure, (2) the area of the film by agitation, and (3) the surface of contact by the addition of suitably selected, finely divided solids. The second inference would seem to be borne out by experiments 12 and 16 to 21, where very small volumes of alkali gave results as good as, or better than, larger volumes. This is probably due to the better film formation when these small volumes of alkali are spread on the surface of the glass shaking vessel under the given shaking conditions. Experimental results justifying the last conclusion will be found in Table II.

Table II—Effect of Various Catalysts on Mercaptan Removal
(100 cc. gasoline (mercaptan 0.0118 *M*) + 25 cc. 2*M* NaOH + catalyst; air volume 190 cc.)

CATALYST		TIME	MERCAPTAN IN GASOLINE
	Mol		*Mol*
Cadmium sulfide	0.001	1 hour	Sweet
Zinc sulfide	0.001	1 hour	0.0015
Lead sulfide	0.0005	15 min.	Trace
Bone black	(2.0 grams)	30 min.	Sweet
Bone black[a]	(2.0 grams)	30 min.	0.0094
Barium sulfate	0.002	30 min.	0.0050
Sulfur	0.03	10 min.	Sweet
Clay (Palex 2)	(2.0 grams)	30 min.	0.0026
Water glass[b]	(10 cc.)	2 hours	0.0026

[a] No alkali used.
[b] No alkali added; 10 cc. water added.

Influence of Catalysts on Oxidation Rate

Among the catalysts tried were the sulfides of lead, cadmium, and zinc, barium sulfate, animal charcoal, a variety of Florida earth, flowers of sulfur, and sodium silicate. The results given in Table II call for no further discussion, except in the case of sulfur.

Powdered sulfur is shown to be a true catalyst for the atmospheric oxidation of mercaptans. This is apparently due to the fact that it acts as a solid rather than chemically. Table III gives comparative results of the action of air and alkali on gasoline under parallel conditions, with and without the addition of approximately calculated amounts of flowers of sulfur.

Table III—Effect of Small Amounts of Sulfur as Catalyst on Mercaptan Removal[a]
[100 cc. gasoline (0.0118 *M*) + 50 cc. 2 *M* NaOH; air volume 165 cc.; added sulfur 0.020 gram (0.015 gram calcd.)]

TIME	MERCAPTAN IN REMAINING GASOLINE	
	Air only	Sulfur present
	Mol	*Mol*
15 min.	0.0065	0.0044
1 hour	0.0055	0.0037
5 hours	0.0009	0.0006
7 hours	0.0005	0.0007

[a] Titration error equal to 0.0001 to 0.0002.

It will be seen that at the start sulfur has a slightly accelerating influence but that this is far less than that shown in Table II, where fifty times as much sulfur was present. Moreover, in a second experiment in which 0.020 gram of sulfur was added dissolved in 20 cc. of xylene, practically no catalytic effect of the dissolved sulfur could be observed.

Action of Air on Lead and Sodium Sulfides

As most commercial sweetening processes employ lead sulfide and air, it seemed desirable to trace the fate of lead sulfide when not present in great excess. Authorities seem to differ as to the influence of sodium sulfide on the course and rate of the sweetening process. Inasmuch as sodium sulfide is always produced during catalytic sweetening under ordinary working conditions (Equation 4), the adverse effect of its presence must be small. Varying amounts of lead sulfide, with or without sodium sulfide, and of sodium sulfide alone were shaken with sweet and sour gasoline under the conditions previously described. The results are summarized in Table IV.

Table IV—Effect of Lead and Sodium Sulfides and Air in Sweetening Process
(Gasoline 100 cc. (0.0118 *M*); 2 *M* NaOH 85 cc.; volume of reagents made to 15 cc.; air volume 115 cc.)

EXPT.	REAGENT		TIME	MERCAPTAN IN REMAINING GASOLINE
	Pb	S		
	Mol	*Mol*	*Min.*	*Mol*
1	....	....	15	0.0050
2	0.005	....	15	Very sour; too black to titrate
3	....	0.005	15	0.0046
4	0.005	0.005	15	Sweet
5	0.0002	0.0002	15	0.0040
6	0.0002	0.0005	15	Sweet
7	0.0002	0.0010	15	0.0026
8	0.0002	0.0020	15	0.0028
9	0.0002	0.0025	60	Sweet gasoline used

In experiment 9 the lead sulfide disappeared almost completely. Examination of the reaction products showed that the gasoline contained traces of free sulfur and that the alkaline solution contained lead as plumbite and was entirely free of sulfide and sulfate ions. Practically all of the oxidized sulfide was present as thiosulfate ion.

From these experiments it is clear that the presence of sodium sulfide during catalytic mercaptan oxidation is detrimental only in that it competes with the mercaptan for the sulfur and for the oxygen, according to the equation:

$$Na_2S + S + 1^1/_2O_2 = Na_2S_2O_3 \qquad (8)$$

Thus, when a relatively small amount of sodium sulfide is present, it can have little influence on the rate of mercaptan oxidation. If, however, large amounts are present, much of the added sulfur and of the oxygen added during air agitation is diverted from the primary mercaptan oxidation. This explains why in the case of the more refractory mercaptans it may frequently be necessary to add much more sulfur for sweetening purposes than is calculated from the amount of mercaptan actually known to be present. If the amount of sodium sulfide present occupies a middle range, then the sulfur loss due to thiosulfate formation may be compensated by the mercaptan oxidation due to added air.

Conclusion

The experimental evidence disposes of any conflict between the views of Morrell and Faragher (*6*) and of Wendt and Diggs (*10*). Lead oxide is regenerated from lead sulfide when the latter is blown with air (Table IV, expt. 9); therefore, one equivalent of litharge is capable of oxidizing far more than the two equivalents of mercaptan to be expected from our ordinary equations. On the other hand, Greer (*4*) can sweeten sour gasoline with lead sulfide alone, without using air, sulfur, or sodium hydroxide. Sweetening is due to surface adsorption in this case. British patent (*8*) uses lead sulfide, sulfur, and sodium hydroxide without air. No lead oxide is formed in this case, and mercaptan oxidation seems to be due to absorption on the particles of lead sulfide, followed by a reaction of the absorbed film with sulfur. It has been shown in the present work that mercaptans can be oxidized with air alone, in the presence of sodium hydroxide solutions, as well as that finely divided inert solids may accelerate such atmospheric oxidation.

It is therefore possible to draw several useful conclusions concerning the practice of sweetening with doctor solution. Air used for agitation should be very finely divided. Several methods of accomplishing this are known. The ordinary agitator is inefficient for this purpose.

The amount of sodium sulfide in the alkaline mixture containing suspended lead sulfide should be kept at a minimum. For this reason it is advantageous to remove hydrogen sulfide with a caustic wash before sweetening. The air-blowing of spent doctor sludge is useful chiefly to destroy its content of sodium sulfide.

The ordinary method of adding sulfur in small amounts until the gasoline is sweet can be greatly improved by first making an analytical estimation of the amount of mercaptan present, and adding all of the calculated quantity of sulfur, very finely divided, at one time. Except for the resulting corrosiveness, it would be desirable to add an excess of sulfur. It seems likely that methods can be developed for removing any excess of dissolved sulfur from sweetened gasoline.

The addition of finely divided solids, as shown in Table II, will hasten the process of sweetening, but it will probably be necessary to follow the sweetening process by a filtration.

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Partial Oxidation of Methane in the Presence of Oxides of Nitrogen[1,2]

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Small additions of nitrogen oxides have a marked effect on the partial oxidation of methane. Complete data on this reaction in small scale glass apparatus have been obtained under varying conditions of heating time, temperature, gas composition, and amount of catalyst, using nitric acid vapor, nitrogen dioxide, and nitric oxide. Under the conditions studied here, the production of formaldehyde by the partial oxidation of methane in the presence of oxides of nitrogen would not be commercially feasible. Suggestions have been made as to the possible mechanism of the reaction.

The partial oxidation of methane is of considerable interest in connection with the chemical utilization of natural gas. Any method which gives promise of yielding partially oxidized products of immediate usefulness, such as formaldehyde, is deserving of consideration. No doubt considerable unpublished work has been done on this problem. However, the early published attempts (*3*) to produce formaldehyde by reaction between methane and oxygen or air mixtures succeeded in converting only about 0.03 per cent of the methane to formaldehyde per pass. A patent by Bibb (*1*) claims the conversion of much larger quantities by adding small amounts of nitric acid vapor or its decomposition products. Layng and Soukup (*8*) have investigated the oxidation of methane by air in the presence of nitrogen dioxide. They report a conversion of 3.7 per cent of the methane per pass under their experimental conditions. The total decomposition of methane was about 42 per cent in this experiment. Frolich, Harrington, and Waitt (*6*) have studied the reaction between natural gas (98.3 per cent methane) and nitrogen dioxide in the absence of oxygen. They found as much as 3.4 per cent methane converted to formaldehyde and 32.5 per cent methane decomposed. The temperature used in various experiments ranged from 440° to 680° C. and the heating times from 2 to 13 seconds. Bibb and Lucas (*2*) give the results of many experiments on mixtures of methane and air, using low concentrations of nitric acid vapor. The maximum yield of formaldehyde was 5 per cent. The methane used contained small quantities (3 per cent or over) of ethane.

The thermal decomposition of nitrogen dioxide to form nitric oxide and oxygen has been studied by Bodenstein (*5*). Using his data and assuming the original partial pressure of nitrogen dioxide to be 0.02 atmosphere, with the oxygen partial pressure constant at 0.5 atmosphere throughout the reaction, the following values for the nitrogen dioxide remaining at equilibrium were found: at 500° C., 0.0088 atmosphere; at 600° C., 0.0044 atmosphere; at 700° C., 0.0022 atmosphere. Bodenstein measured the rate of decomposition up to 383° C. Assuming as usual that $k = \text{constant}\ \sqrt{T}\, e^{-\frac{Q}{RT}}$, the time required for 90 per cent of the dioxide to decompose under the above conditions is approximately: at 500° C., 115 seconds; at 600° C., 19 seconds; at 700° C., 4 seconds. For very short heating times, therefore, the nitrogen dioxide cannot reach its equilibrium value by thermal decomposition alone in the absence of catalytically active surfaces. If, however, other very fast reactions occur, in which nitrogen dioxide is reduced to nitric oxide, then the concentration of nitrogen dioxide would not be fixed by these values.

Experimental Work

The methane used in the present work was obtained by the fractionation of Pittsburgh natural gas. Numerous analyses by a Bureau of Mines Orsat never showed ethane,

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[2] Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

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but traces of carbon dioxide, carbon monoxide, oxygen, and nitrogen were usually present. Methane and oxygen or air were measured into an 8-liter flask by water displacement to give any ratio of methane to oxygen desired.

The nitrogen dioxide was usually made by dropping fuming nitric acid on copper turnings. The gas was dried by passing through an ice trap and over phosphorus pentoxide. It was condensed in a trap surrounded by a carbon dioxide–acetone bath. A slow stream of air was continually passed through the apparatus to convert all nitric oxide to the dioxide. The nitrogen dioxide as used was a clear red-yellow liquid, freezing to a white solid. One portion was made by heating lead nitrate, the gas being dried as above. One experiment was made using nitric oxide prepared from potassium nitrite and iodide with sulfuric acid (*14*). The nitric oxide after drying could be kept over mercury and was mixed with an excess of oxygen before entering the reaction tube. All of these preparations gave approximately the same results in use.

The oxides of nitrogen were introduced in various ways. In the first experiments a definite portion of the methane-oxygen mixture was passed through liquid nitrogen dioxide to give the concentration desired. Later the oxide was introduced by slowly bubbling pure nitrogen through the liquid dioxide. The trap containing the dioxide was always immersed in a Dewar flask filled with ice. The vapor pressure of pure liquid nitrogen dioxide has been measured by Sheffer and Treube (*11*). Since the rate of gas flow was very slow through the liquid dioxide, saturation was easily obtained and the amount of dioxide used could be calculated from the amount of gas passing through the trap.

The reaction tube in the first experiments was a straight quartz tube about 2 mm. i. d. This was jacketed by a heavy copper block, which in turn was surrounded by an electric tube furnace. A thermocouple placed in a well in the copper block was used to determine the temperature. This was uniform to within 10° C. throughout the length of the block and never varied more than this amount during a run. Later experiments were made using a quartz tube with a side arm through which the nitrogen dioxide could be introduced by a stream of nitrogen. Finally, to study long preheating times of the nitrogen dioxide, a quartz U-tube was made of 2-mm. tubing. Into the bottom of the U-tube was sealed a 1-mm. quartz capillary tube. This extended up to a bulb of 6-mm. quartz tubing. The U-tube and capillary were surrounded by a heavy copper cylinder and placed in the tube furnace. The chamber above was also jacketed with copper and surrounded by another furnace. The nitrogen dioxide was introduced through the chamber at the top and could be preheated to any temperature desired. Thermocouples in both copper jackets measured the temperature. The mixture of methane and oxygen (or air) entered the U-tube on one side and the exit gas came out the other side.

In the early experiments the exit gases were washed free of formaldehyde in a series of two or three efficient water bubblers. Tests showed that all formaldehyde was removed. A great deal of trouble was caused by formaldehyde condensing as paraformaldehyde in the end of the reaction tube. When the quartz U-tube was used, a quartz-to-Pyrex seal in the exit side led to a trap cooled by a carbon dioxide–acetone bath. This was followed by a water bubbler. On completing a run the trap was warmed to room temperature and all gases evolved were slowly washed through the bubbler with nitrogen. Gentle heating with continued nitrogen flow then sublimed the paraformaldehyde into the water. The total volume of exit gas was always measured by water displacement in a large flask.

The water containing the formaldehyde was made up to a definite volume and the formaldehyde determined in a portion of this. Two methods were used. In the first experiments, with high percentages of methane, the iodometric method of Romijn (*10*) was used. To remove traces of nitric oxide or dioxide which would interfere with the end point, the formaldehyde solution was made slightly alkaline with sodium hydroxide and distilled just to dryness. Tests showed no decomposition of formaldehyde under this treatment. Duplicate analyses for each run were always made.

When the methane content of the initial gas was as low as 17 per cent, it was found necessary to use another method for determining the formaldehyde. The potassium cyanide method (*4, 10, 12*) proved very satisfactory. The two methods checked when tried on standard solutions of formaldehyde. Undoubtedly the greatest error in the determination of the yield of formaldehyde lay in the recovery of all the formaldehyde in a soluble form. Some modifications of paraformaldehyde are insoluble in both hot and cold water (*13*).

Samples of inlet and exit gas were collected over mercury during a run and analyzed on the Orsat. More accurate gas analytical methods would have been desirable, but the time required for such methods would have been excessive.

The experimental results are given in Table I. The reaction time as given was calculated for the straight quartz tube assuming the gas came instantly to the temperature of the tube. In the case of the U-tube experiments the reaction time was taken as the time of heating after addition of the nitrogen oxides. "Preheating time" and "preheating temperature" refer to the heat treatment given the oxides of nitrogen before mixing with the methane and oxygen mixture. When nitric acid vapor was used as the source of nitrogen oxides, it was introduced by bubbling the inlet gas through two bubblers in series. Each bubbler was filled with c. p. concentrated nitric acid (sp. gr. 1.42). The amount of nitrogen oxides used, whether HNO_3 or NO_2, is given as cubic centimeters of gas calculated as NO_2. The materials balance for oxygen was secured by assuming that all the hydrogen from the methane which could not otherwise be accounted for went to the formation of water. It is evident that where a total of more than 100 per cent is found the gas analysis is at fault. In experiments 1 to 18 the apparatus had several connections made with rubber tubing, and occasionally leaks occurred at these points. Experiments 19 to 26 were made in an all-glass (and quartz) apparatus with more consistent results.

Experiments 1 to 6 show the effect of various temperatures and heating times on the reaction. The effect of nitrogen oxides is clearly brought out by comparing experiments 7 and 15 with 1 and 14. Even with the addition of ethane the decomposition at 600° C. with a heating time of 0.35 second is inappreciable. Increasing or decreasing the amount of dioxide, as in experiments 8 to 12, does not affect the yield of formaldehyde proportionately. Comparing experiments 13, 14, and 3, it is seen that either small amounts of ethane or the use of nitric acid instead of nitrogen dioxide increases the yield of formaldehyde.

One interesting result is the large decrease in yield of formaldehyde when the methane is heated before the oxides of nitrogen are added. Experiments 16 to 18 and 20 to 26 show this clearly. Use of Pyrex or quartz reaction tubes gave the same result. Preheating of the oxides of nitrogen for a time that gave the equilibrium concentration of nitric oxide at these temperatures before mixing with the methane did not alter the reaction. Experiment 19 is the only one in which the nitric acid was introduced along with the cold methane, and here there was found the same large decomposition of methane and high yield of formaldehyde as before.

Table I—Results on Reactions between Methane and Oxygen

	STRAIGHT QUARTZ TUBE															PYREX U-TUBE			QUARTZ U-TUBE							
Experiment number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26
Initial volume, gas, cc.	5000	5850	5000	5000	5000	4000	5000	5000	5000	5000	4948	5100	4850	4850	4850	5192	5240	5210	4850	4935	4927	4917	4917	4919	4919	5079
Oxygen, cc.	1930	2260	1930	1930	1930	1930	1930	1930	1930	1930	1870	1945	835	839	829	1945	1930	675	845	854	873	840	840	820	840	951
Methane, cc.	2685	3145	2685	2685	2685	2685	2725	2725	2725	2725	2640	2695	737	723[a]	737[a]	2695	2725	1800	825	825	825	825	825	825	825	832
Final volume gas, cc.	3730	4580	3230	3150	4700	4480	4950	3950	4530	4400	4060	3950	4680	4630	4880	4820	5070	5110	4540	5050	5010	4980	4890	4940	4920	5210
Temperature, ° C.	700	600	600	600	500	500	700	700	600	600	700	700	600	600	600	600	600	600	600	600	600	600	600	600	600	600
Reaction time, sec.	0.11	0.15	0.27	0.66	0.32	0.55	0.14	0.08	0.09	0.09	0.19	0.22	0.34	0.35	0.35	0.13	0.20	0.14	0.45	0.42	0.41	0.41	0.41	0.41	0.39	0.44
Preheating temp., ° C.											700	700				600	600	600			685		630	655	680	700
Preheating time, sec.											1.0	1.0				1.6	1.6	1.6			54.0		71.0	67.0	60.0	70.0
Nitrogen oxide used	NO_2	NO_2	NO_2	NO_2	NO_2	NO_2	None	NO_2	NO_2	NO_2	NO_2	NO_2	HNO_3	HNO_3	None	NO_2	NO_2	NO_2	HNO_3	NO_2	NO_2	HNO_3	HNO_3	HNO_3	NO_2	$NO+O_2$
Volume nitrogen oxide used, cc.	163	149	113	120	118	104	0.0	388	382	254	63	77	25	25	0.0	124	159	134	27.0	85.0	77.0	26.0	26.0	27.0	69.0	48.0
Volume CH_2O (g) formed, cc.	55.8	64.5	52.4	47.5	16.7	14.8	4.9	90.3	68.2	90.5	56.8	45.7	20.0	29.0	0.0	53.1	28.1	30.0	25.7	7.4	9.6	10.3	16.1	12.3	9.1	8.6
Methane:																										
Unchanged, %	56.1	69.7	57.7	52.7	89.4	85.1	102.3	75.2	90.5	87.1	64.1	56.8	87.0	80.7	101.3	96.0	96.6	98.9	74.3	98.2	97.2	97.2	99.0	97.1	95.3	97.0
Going to CO, %	38.4	24.9	32.4	36.3	2.8	5.4	0.0	18.5	4.6	5.9	32.3	39.3	5.7	12.4	1.3	1.6	0.8	0.9	20.4	1.8	1.8	1.2	0	1.2	1.8	1.2
Going to CO_2, %	1.5	1.7	1.9	2.0	0.2	1.3	0.0	2.1	1.1	1.1	2.7	3.3	1.8	1.2	0.0	0.9	0.3	0.3	2.5	0.0	0.6	1.8	0	0.6	1.8	0.0
Going to CH_2O, %	2.1	2.1	2.0	1.8	0.6	0.6	0.2	3.4	2.5	3.4	2.2	1.7	2.7	3.7	0.0	2.0	1.0	1.7	3.0	0.9	1.2	1.2	1.9	1.5	1.1	1.0
Total accounted for, %	98.1	98.4	94.0	92.8	93.0	92.4	102.5	99.2	98.7	97.5	101.3	101.1	97.2	98.0	102.6	100.5	98.7	101.8	100.2	100.9	100.8	101.4	100.9	100.4	100.0	99.2
Oxygen:																										
Unchanged, %	16.4	42.8	13.2	9.8	91.8	79.4	87.3	47.5	79.3	74.7	31.9	18.4	85.8	76.8	100.5	89.4	93.4	84.8	64.0	96.0	93.2	93.2	96.6	95.8	94.4	95.9
Going to CO, %	26.7	17.3	22.4	25.2	1.9	3.8	0.0	13.1	3.2	4.2	23.1	27.2	2.5	5.8	0.6	1.1	0.5	1.2	10.0	0.9	0.9	0.6	0.0	0.6	0.6	0.5
Going to H_2O, %	45.2	34.8	50.4	60.6	13.3	19.8	0.0	29.6	11.0	15.0	37.4	45.1	9.5	12.0	0.0	2.1	3.4	0.0	21.1	1.4	1.5	1.3	0.0	1.7	2.7	1.6
Going to CH_2O and CO_2, %	3.6	3.7	3.9	4.0	0.6	2.1	0.1	5.2	3.3	3.9	5.0	5.7	2.8	2.8	0.0	2.6	1.2	3.0	4.1	0.4	1.2	2.4	1.0	0.7	2.4	0.5
Total accounted for, %	91.9	98.6	89.9	99.6	107.6	105.1	87.4	95.4	96.8	97.8	97.4	96.4	100.6	97.4	101.1	95.2	98.5	89.0	99.2	98.7	96.8	97.5	97.6	98.8	100.1	98.5

[a] In these experiments, 27 cc. of ethane were added to the initial amount of methane. Percentages were calculated on total carbon present.

In experiment 25 the inlet gas was bubbled through water and the nitrogen dioxide introduced into the hot gas. It would appear that water vapor has no effect on the reaction.

Several experiments not shown in the table were made to determine whether the oxides of nitrogen were decomposed by the reaction. The procedure used was to replace the formaldehyde absorbers by bubblers containing concentrated sulfuric acid. Since an excess of oxygen was always present in the exit gas, any nitric oxide in the exit gas would be converted to the dioxide and absorbed in the acid. The nitrometer method of Lunge (*9*) was used, giving a direct measure of the nitrogen dioxide absorbed. A blank experiment was always made first, using either air or nitrogen without methane. The amount of nitrogen dioxide found in the exit gas was then compared with that found when the methane-oxygen (or air) mixture was used. With all other factors the same, no trace of nitrogen dioxide could be found using nitric acid as the source of nitrogen oxides. When nitrogen dioxide was used, only about one-eighth of the nitrogen dioxide introduced was recovered in the exit gas. These experiments show that almost all the oxides of nitrogen are not recoverable after reaction with methane.

Discussion of Results

The main products of the reaction are water and carbon monoxide. The percentage of methane converted to formaldehyde does not vary widely, although the conditions were varied so that from 3 to 50 per cent of the methane was decomposed.

A detailed mechanism to account for all the observed results is difficult to formulate. A number of steps probably occur. In the experiments where the oxides of nitrogen were introduced along with the cold methane, the first step may be the formation of a loose compound between the oxide and methane. As the gas travels down the hot tube (the temperature rising) this compound is broken up, probably to give formaldehyde, while the nitrogen oxide liberated combines with more methane. The formaldehyde is decomposed to give mostly carbon monoxide and hydrogen. The oxides of nitrogen are gradually reduced (probably to nitrogen) by direct reaction with methane or hydrogen (*7*). The hydrogen also combines with the oxygen present to form water. The decomposition of the addition compound and that of formaldehyde must both occur at a relatively high temperature, since experiments at 500° C. showed relatively little reaction.

When the methane is heated (as in the U-tube experiments) before the addition of the nitrogen oxides, the main reaction may be the direct formation of formaldehyde with reduction of the nitrogen oxides. In none of these experiments did the total volume of methane decomposed exceed the volume of nitrogen oxide added. The formaldehyde then partially decomposed to give carbon monoxide and hydrogen. The ratio of hydrogen to carbon monoxide is much higher in the U-tube experiments, which would be expected if no oxides of nitrogen were present to accelerate the burning of hydrogen. This direct formation of formaldehyde is unaffected by long preheating of the nitrogen oxides or the use of nitric acid rather than nitrogen dioxide.

Under the conditions prevailing in the present work the production of formaldehyde alone by this method would not be commercially profitable. The oxides of nitrogen are entirely destroyed in the reaction when only a small amount of methane is decomposed (efficiency of conversion high), and when some of the oxides are recoverable the conditions are such that a major portion of the methane goes to carbon monoxide and water. In the experiments described in this paper the volume of formaldehyde gas formed was never more than the volume of oxides of nitrogen used. From the published data of Layng and Soukup (*8*) this is also true for their work. Bibb and Lucas (*2*) give the amount of nitric acid used for only one experiment and here it appears that 1 mol of nitric acid was used to give 3 mols of formaldehyde. It is unfortunate that more data on this point are not available.

The production of traces of other organic products along with the formaldehyde was not investigated in the present work. Previous work indicates the possibility of the presence of these products. From the materials balances presented here, however, it does not seem likely that other products were formed in amounts sufficient to make the process, as here carried out, commercially profitable.

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Prediction of Critical Temperatures and Heats of Vaporization[1]

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A method has been developed whereby the critical temperature of a non-polar liquid may be estimated from its boiling point, molecular weight, and liquid density (Equation 7). The error in the use of this method is in general less than 2 per cent.

Two methods are presented for the estimation of the latent heat of vaporization of a non-polar liquid at any desired temperature or pressure without experimental determinations (Equation 8; Figures 2 and 3). The data necessary are the critical temperature and the normal boiling point. The errors involved are generally less than 5 per cent except for relatively small values of the latent heats.

The latent heat of vaporization of a liquid, either polar or non-polar, may be estimated at any desired temperature from Figure 2 if one experimental value is available and the critical temperature is known.

Previous Methods for Critical Temperatures

GULDBERG has pointed out that for many compounds the ratio of the critical temperature to the normal boiling point is approximately a constant when both are expressed on an absolute scale. However, this rule constitutes only a very rough approximation, the value of the ratio as experimentally determined varying from about 1.3 to 1.8 for different types of normal compounds. Several modifications of Guldberg's rule have been proposed. Prud'homme (*15*) points out a "rule of three temperatures"—that the ratio of the sum of the normal boiling point and the melting point to the critical temperature, when all are expressed on an absolute scale, varies between 1.0 and 1.1 for most substances. The same author in other publications suggests various other relationships between the temperature of fusion and ebullition and the critical data. These expressions yield results which are in only fair agreement with the experimentally observed facts. Fielding has proposed a modification of the form of Guldberg's rule through the use of two constants, one of which is additive to the ratio of critical temperature to boiling point. Another formula by the same author attempts to relate critical temperatures to critical pressures. These two formulas are discussed by Moles (*12*), who concludes that neither is an accurate expression. Friend (*2*) points out that the latter of Fielding's formulas follows from the van der Waals equation.

Herz (*3*) proposes numerous relationships between the critical constants and the molecular weight, boiling point, total number of atoms in the molecules, total number of valences in the molecule, and the specific heat.

Van Laar (*6*) discusses the applicability of a rule which he had proposed regarding the additivity of atomic values of the van der Waals constant, b, and a similar additivity of values of $\sqrt{a}$. From a table of atomic values of b and $\sqrt{a}$, the van der Waals constants of a great variety of compounds may be calculated with rather surprising accuracy. From the van der Waals constants the critical temperature and pressure may be calculated. The same author also develops an expression relating the critical temperature to the expansion coefficient and density (*7*).

A brief recent review of a Paris thesis by Longinescu (*10*) discusses the results of an analysis of molecular forces of attraction from the kinetic standpoint. The relationship between heat of vaporization and surface tension from the standpoint of the kinetic theory is also pointed out by Audubert (*1*). It is postulated that the work of bringing a molecule from the interior to the surface of a liquid should be equal to the work done in bringing the molecule from the surface to the external atmosphere. On this basis Audubert derives an expression for the heat of vaporization in terms of molecular dimensions and surface tension which leads to the deduction of Trouton's and Guldberg's rules.

Proposed Prediction of Critical Temperatures

None of the expressions resulting from the work discussed above is of a form that is both convenient and sufficiently accurate for use in the prediction of critical temperatures in the majority of technical problems. For technical use a relationship is required which is applicable to a large general class of materials and which requires only data that are ordinarily available or may be easily determined. It is hoped that ultimately such expressions may be deduced in a theoretically sound manner from thermodynamic or kinetic theory. The present state of development of these theories

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leaves opportunity for the usefulness of an accurate empirical relationship, even though its entire theoretical significance is not yet apparent.

The following empirical generalization was deduced:

> The ratio of the absolute temperature at which a liquid is in equilibrium with a specified molal concentration of its saturated vapor to the absolute critical temperature is a function only of the molal volume of the substance in the liquid state at the temperature of the equilibrium.

It is found that this statement is supported by practically all the reliable data for non-polar compounds, which would not be expected to be associated or dissociated in either the liquid or vapor state. This comparison between critical temperatures and temperatures corresponding to constant vapor concentration may be carried out at any selected vapor concentration within the range in which the simple gas law is applicable. At high concentrations it is probable that the rule would no longer hold. The vapor concentration that has been arbitrarily selected is 1.0 gram-mol in 22.4 liters, which is the concentration in equilibrium with a compound boiling at 273° K. at a pressure of 1 atmosphere. The temperature corresponding to this vapor concentration will not differ greatly from the normal boiling point for most substances, and the molal volume of the liquid may be taken as that at the normal boiling point.

An approximate relationship between the normal boiling point of a liquid and the temperature at which the molal volume of its saturated vapor is 22.4 liters may be derived from the Clausius-Clapeyron equation. From the simple gas law the temperature (T_e) corresponding to a molal vapor volume of 22.4 liters is expressed by:

$$T_e = 22.4\ P/R \tag{1}$$

The approximate Clausius-Clapeyron equation expresses the relationship between vapor pressure and temperature:

$$\frac{d\ \ln_e P}{dT} = \frac{ML}{RT^2} \tag{2}$$

where L is the heat of vaporization and M is the molecular weight. The heat of vaporization, L, may be assumed to be constant over narrow temperature ranges. Integrating between the limits,

$$P = 1.0,\ T = T_s \text{ and } P = P, \text{ and } T = T_e$$

where T_s is the normal boiling point,

$$\ln_e P = \frac{ML}{R}\left(\frac{1}{T_s} - \frac{1}{T_e}\right) \tag{3}$$

Writing Equation 1 logarithmically and substituting in it the value of $\ln_e P$ from (3),

$$\ln_e T_e = \ln_e[22.4/R] + \frac{ML}{R}\left(\frac{1}{T_s} - \frac{1}{T_e}\right) \tag{4}$$

Hildebrand (4) has shown that the molal entropy of vaporization of normal liquids is constant when they are in equilibrium with the same concentration of their saturated vapors. From this rule, using an average of the data of the literature, the molal heat of vaporization of a normal liquid when in equilibrium with a molal vapor volume of 22.4 liters is represented by the following expression:

$$ML = 9.8RT_e \tag{5}$$

Substituting (5) in (4) and replacing R by its numerical value of 0.082 liter-atmospheres per degree Kelvin,

$$\ln_e T_e = \frac{9.8T_e}{T_s} - 4.2 \tag{6}$$

Equation 6 relates the normal boiling point of a liquid to the temperature at which it is in equilibrium with a molal vapor volume of 22.4 liters.

From this equation the data represented in Figure 1 were calculated. From this curve may be determined the temperature at which any normal liquid of known boiling point is in equilibrium with a molal vapor volume of 22.4 liters.

The molal volume, in cubic centimeters per gram-mol, of a liquid at its boiling point is equal to M/d_s, where M is the molecular weight and d_s the density at the boiling point, in grams per cubic centimeter. From the data of the International Critical Tables, values of the boiling points, T_s, the critical temperatures, T_c, and the densities, d_s, were obtained for normal liquids of widely varying boiling points and molecular weights. By means of Figure 1 the corresponding values of T_e were calculated. Values of $\log_{10}(T_e/T_c)$ were plotted against the corresponding values of $\log_{10}(M/d_s)$. The data followed very closely along a straight line having a slope of 0.18. From this curve the following equation was derived:

$$\frac{T_e}{T_c} = 0.283(M/d_s)^{0.18} \tag{7}$$

This equation is applicable only to non-polar liquids.

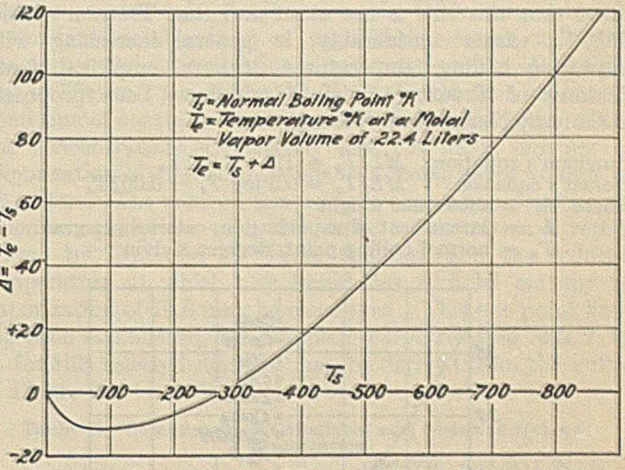

Figure 1—Temperatures of Constant Vapor Concentration

In Table I values of T_e/T_c obtained from the experimental values of T_c of a number of non-polar compounds are compared with values of $(T_e/T_c)'$ which are calculated from the molecular-weight, density, and boiling-point data by means of Figure 1 and Equation 7. It will be noted that in general the difference between the observed and the calculated values is less than 2 per cent. The method appears to break down in the cases of liquids of very low boiling points such as hydrogen and helium.

Table I—Comparison of Calculated and Observed Critical Temperatures

LIQUID	M	T_s, °K.	T_c, °K.	d_s	M/d_s	T_e	$(T_e/T_c)'$ (calcd.)	T_e/T_c (obsd.)
H_2	2.0	20.4	33.2	0.0709	28	14.3	0.515	0.430
He	4.0	4.2	5.2	0.126	31.8	2.2	0.526	0.425
Ne	20.2	27.2	44.4	1.204	16.8	20.0	0.456	0.450
O_2	32.0	90.1	154	1.14	28.0	80.0	0.515	0.519
A	39.9	87.4	151	1.40	28.5	75.9	0.516	0.505
Kr	82.9	121.3	210	2.60	32.0	110.3	0.528	0.525
N_2	28.0	77.3	126	0.808	34.6	66	0.535	0.524
CH_4	16.0	112	191	0.42	38.0	101	0.544	0.530
C_2H_2	26	189.5	309	0.61	43	181	0.558	0.585
C_2H_4	28	169.3	283	0.57	49	160	0.572	0.565
C_2H_6	30	185	305	0.546	55	176	0.580	0.576
$CH_3C:CH$	40	245	401	0.67	60	242	0.592	0.602
CS_2	76	319	546	1.25	61	325	0.595	0.595
I_2	254	457	826	3.71	68	484	0.604	0.586
$C_2H_4:CH_2$	42	226	365	0.61	69	221	0.605	0.605
C_3H_8	44	235	369	0.585	75	230	0.618	0.622
C_4H_{10}	58	273	426	0.601	96	273	0.642	0.640
C_6H_6	78	353	561	0.80	97	363	0.645	0.647
CCl_4	154	350	556	1.48	104	360	0.654	0.648
$(C_2H_5)_2O$	74	307	466	0.68	109	311	0.660	0.667
C_6H_5Cl	112	405	632	0.98	114	423	0.665	0.670
C_6H_{12}	84	354	554	0.72	116	364	0.666	0.657
$n C_5H_{12}$	72	309	470	0.61	118	318	0.667	0.676
$n C_6H_{14}$	86	342	507	0.62	139	351	0.689	0.691
$C_3H_7.C_3H_7$	86	331	500	0.63	136	338	0.685	0.675
$n C_7H_{16}$	100	371	539	0.62	161	383	0.709	0.710
$n C_8H_{18}$	114	398	569	0.61	187	415	0.725	0.730

By the use of Figure 1 and Equation 7 it should be possible to predict, with sufficient accuracy for technical purposes, the critical temperature of any normal liquid whose molecular weight, boiling point, and liquid density at the boiling point are known. Since temperature coefficients of expansion are in general small, errors in estimating the liquid density at the boiling point from density data at other temperatures will ordinarily be small. The general procedure for the estimation of a critical temperature may be outlined as follows:

(*a*) From Figure 1 determine the absolute temperature, T_e, which corresponds to a saturated vapor concentration of 1 gram-mol in 22.4 liters.

(*b*) From Equation 7 calculate the value of T_c.

Previous Methods for Latent Heats of Vaporization

Of the many methods proposed for the estimation of latent heats of vaporization, that of Trouton is most familiar and widely used. Trouton's rule states that the molal entropy change of vaporization at the normal boiling point is a universal constant for normal liquids. It has long been recognized that this rule is not exact and that Trouton's ratio, ML/T_s, varies considerably, in general increasing with increasing boiling temperatures. Several empirical modifications of Trouton's original rule have been proposed, notably by Nernst and by Bingham:

Bingham's equation: $ML/T_s = 17 + 0.011T_s$
Nernst's equation: $ML/T_s = 9.5 \log T_s - 0.007T_s$
where M = molecular weight
L = latent heat of vaporization, calories per gram
T_s = normal boiling point, degrees Kelvin

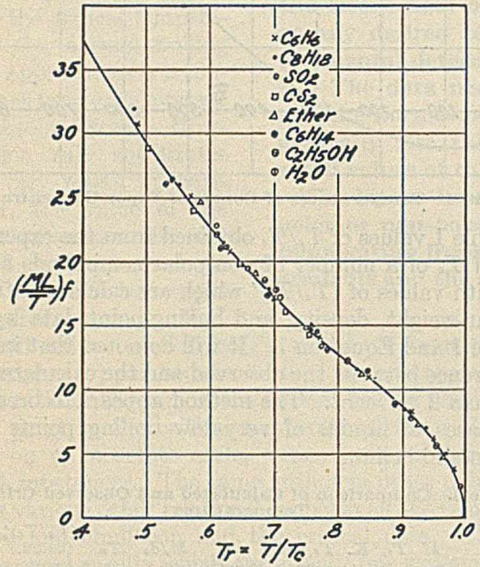

Figure 2—Form of Variation of Molal Entropy of Vaporization with Temperature

In comparing the accuracy of these equations, Mortimer (*13*) finds that neither is applicable over wide ranges of boiling points. At high boiling temperatures the equation of Nernst passes through a maximum and finally yields negative results. The results of Bingham's equation are much too high for materials of high boiling points.

Hildebrand (*4*) has proposed a restatement of Trouton's rule. He has pointed out that the molal-entropy change of vaporization is a constant, not at the normal boiling points, but at temperatures which correspond to a constant molal volume of saturated vapor. It was shown that this rule is in good agreement with the experimental data of materials having a wide range of boiling points. The comparison may be made at any selected value of molal vapor volume, but becomes less accurate at small volumes approaching the critical value and breaks down entirely at the critical conditions. On the basis of Hildebrand's relationships, Mortimer (*13*) has developed the following empirical expression for latent heat of vaporization at the normal boiling point:

$$ML = 4.23(-68 + 4.877T_s + 0.0005T_s^2)$$

Mortimer finds good agreement between the results of this equation and experimental data of materials with wide ranges of boiling points.

A method for convenient use of the Hildebrand principle has been pointed out by Lewis and Weber (*8*) and by McAdams and Morrell (*11*). The values of Trouton's ratio are plotted against 1000 P/T, a factor proportional to the molal vapor concentration, in the range of applicability of the simple gas law. From this curve it is possible to predict values of latent heat of vaporization at various temperatures and pressures. This method gives good results in the range corresponding to low vapor pressures, but breaks down at the higher temperatures and pressures approaching the critical values.

At low pressures the modified Clausius form of the Clapeyron equation may be used to calculate latent heats from only a vapor-pressure curve. This method is not applicable at high pressures. A convenient method for the use of this principle has been pointed out by Lewis and Weber (*9*) and by White (*19*). These authors plot the boiling-point data of the substance in question against those of some reference substance such as water, obtaining approximately straight lines from which the latent heat at any selected temperature is readily calculated.

Schultz (*17*) has found that, by plotting the molal entropy of vaporization of a material against that of some reference substance at the same pressure, approximately straight lines result over wide ranges of conditions. This method for the extrapolation of latent-heat data becomes uncertain at high pressures in the region of the critical point. In a later paper (*18*) the same author attempts to determine the slopes of his curves by means of specific-heat data. The assumptions involved in this scheme appear rather uncertain.

Nutting (*14*) has proposed the following equation relating latent heat of vaporization to temperature:

$$L = A(T_c - T)^n$$

where A and n are constants, the latter equal to about $^1/_3$, and L is the latent heat at temperature T. Similar equations involving the critical temperature have been proposed by Prud'homme (*16*) and Winter (*20*).

With the exception of the Clapeyron equation, all the methods discussed above are based on empirical relationships. An interesting theoretical contribution has been made by Kistyakowsky (*5*). From an extension of the third law of thermodynamics an equation is said to have been deduced for the latent heat of vaporization at the normal boiling point. This equation contains no empirical constants and agrees with the entire range of experimentally observed values with surprising accuracy. The general equation is as follows, Q being the molal heat of vaporization in cubic centimeter-atmospheres, R the gas law constant, and T_s the absolute temperature of the normal boiling point:

$$Q = RT_s \ln_e (RT_s)$$

With the constants evaluated and the units converted to calories, Trouton's ratio becomes:

$$ML/T_s = 8.75 + 4.571 \log_{10} T_s \qquad (8)$$

where L = latent heat of vaporization, calories per gram
M = molecular weight
T_s = temperature of normal boiling point, ° K.

This is offered as a fundamental law expressing the latent heat of vaporization at a pressure of 1 atmosphere, but is applicable only to non-polar liquids. In the present state of the theory the extension of this relationship to apply up to the critical conditions is not apparent.

Proposed Method for Estimation of Latent Heat at Any Temperature

None of the methods discussed above permits accurate prediction of latent heats over wide ranges of conditions from only readily determined and generally available data. As a basis for the deduction of such a method, curves were prepared expressing the data of the International Critical Tables for heats of vaporization at various temperatures. Values of Trouton's ratio, ML/T, were plotted as ordinates and corresponding values of the reduced temperature, $T_r (= T/T_c)$, as abscissas. A fanshaped family of curves resulted, converging at the point where $T_r = 1.0$ and $ML/T = 0$. It was found that these curves for different materials were of the same shape, constituting an "affin" group. By multiplying the values of the ordinates of any one curve by the proper constant factor it could be made to coincide with any one of the other curves. This similarity of the various curves is indicated in Figure 2, which shows a composite curve of the available data on latent heats of vaporization over wide ranges of pressure. The ordinates of each of the curves representing an individual compound were multiplied by the proper constant factor to superimpose the curves in the best agreement. It will be noted that the agreement of the individual points with the composite curve is almost within the limit of accuracy of the data. Included in the data on which Figure 2 is based are such highly polar compounds as ethyl alcohol, water, and ammonia.

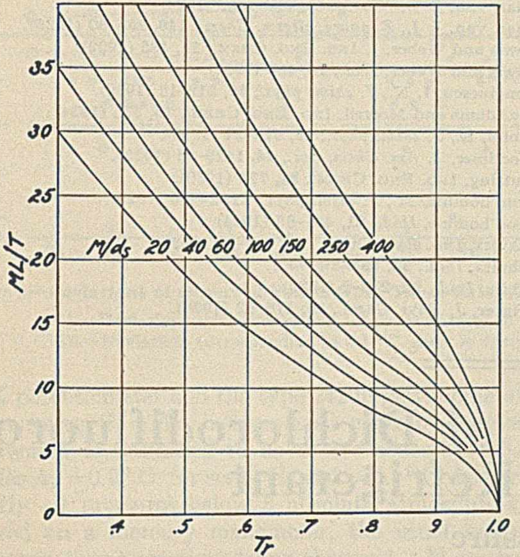

Figure 3—Chart for Estimation of Heats of Vaporization

Extension of experimental data to apply at other temperatures (applicable to all liquids). From Figure 2 the latent heat of vaporization of any liquid, polar or non-polar, at any desired temperature may be predicted if the value at any one temperature and the critical temperature are known. The critical temperature of a non-polar material may be estimated by the method proposed in the preceding section. If the known value of molal entropy of vaporization is $(ML/T)_1$ at a temperature, T_1, corresponding to a reduced temperature, T_{r_1}, the value at any other reduced temperature, T_{r_2}, may be estimated as follows: From Figure 2 read the values of the ordinates (y_1) and (y_2) corresponding to T_{r_1} and T_{r_2}, respectively. Then

$$(ML/T)_2 = (y_2/y_1).(ML/T)_1 \qquad (9)$$

A graphical method such as this is considered preferable to the use of the rather complicated empirical equation necessary to represent the curve of Figure 2.

General methods of prediction without experimental data (applicable only to non-polar liquids). A general method for the estimation of latent heats of non-polar liquids without any experimental values results from combination of Equation 8 of Kistyakowsky with the use of Figure 2 and Equation 9. Kistyakowsky's equation may be used for calculating the heat of vaporization at the normal boiling point. The heat of vaporization at any other temperature may then be estimated from Equation 9. In Table II are values of $(ML/T)''$ calculated by this method, compared with the experimentally observed values (ML/T) taken from the International Critical Tables.

By combining the curve of Figure 2 with the Hildebrand principle, a useful chart, applicable to non-polar liquids, may be constructed. According to the Hildebrand principle a constant molal entropy of vaporization corresponds to a constant molal concentration of saturated vapor. A straight line on Figure 2 parallel to the T_r axis would then indicate a condition of constant vapor concentration in the range where the concentration is relatively low. A molal entropy of vaporization of 19.6 corresponds to a molal vapor volume of 22.4 liters. The reduced temperature of any non-polar liquid when in equilibrium with this vapor concentration is represented by Equation 7. From this equation the reduced temperature at which any liquid has a molal entropy of vaporization of 19.6 may be calculated. This one point having been established, the complete curve relating ML/T to T_r for this selected material may be derived from the curve of Figure 2.

Table II—Comparison of Calculated and Observed Heats of Vaporization

LIQUID	T, ° K.	T_r	M/d_s	$(ML/T)'$ (calcd.)[a]	$(ML/T)''$ (calcd.)[b]	ML/T (obsd.)
H_2	20.4	0.615	28	15.3	14.7	10.6
He	4.2	0.81	31.8	9.0	10.3	10.9
O_2	90.1	0.585	28.0	16.5	17.7	18.0
	68.1	0.442	28.0	23.5	25.2	26.1
A	87.4	0.578	28.5	17.0	17.6	17.2
N_2	77.8	0.617	34.6	16.0	17.4	17.1
	63.1	0.500	34.6	21.5	23.5	22.9
CH_4	114	0.597	38	17.1	17.6	19.4
C_2H_6	233	0.764	55	11.7	12.1	12.5
	272	0.895	55	7.5	7.7	8.2
CS_2	273	0.500	61	25.0	25.2	24.9
	319	0.585	61	20.0	20.2	20.0
	373	0.674	61	15.7	15.8	15.4
	413	0.758	61	12.4	12.5	12.4
I_2	457	0.553	68	22.3	20.9	31.8 (?)
C_3H_8	243	0.657	75	17.7	18.7	17.7
	273	0.740	75	13.8	14.5	14.4
	293	0.794	75	11.6	12.2	12.5
nC_4H_{10}	273	0.640	96	19.8	19.8	19.5
	293	0.686	96	17.5	17.5	17.3
C_6H_6	273	0.486	97	29.8	29.7	30.6
	353	0.630	97	20.5	20.4	20.8
	433	0.772	97	13.5	13.4	14.1
	533	0.950	97	6.0	6.0	6.4
CCl_4	273	0.491	104	29.7	29.4	29.4
	350	0.630	104	20.6	20.4	20.4
	433	0.778	104	13.3	13.2	13.5
	533	0.960	104	5.5	5.5	5.8
$(C_2H_5)_2O$	273	0.585	109	23.7	24.2	25.0
	307	0.658	109	19.7	20.1	20.2
	373	0.800	109	12.9	13.2	13.4
	453	0.971	109	4.8	4.9	4.9
C_6H_5Cl	404	0.640	114	20.7	20.7	21.5
C_6H_{12}	353	0.637	116	21.2	20.4	20.4
nC_6H_{14}	341	0.672	139	20.6	20.3	20.0
nC_7H_{16}	371	0.689	161	20.6	20.5	20.6
nC_8H_{16}	398	0.700	187	21.0	20.6	20.4

[a] On basis of Hildebrand principle, from Figure 3.
[b] On basis of equation of Kistyakowsky from Equation 8 and Figure 2.

In Figure 3 is plotted a family of curves each of which was derived, in the manner described above, to correspond to a selected value of the factor M/d_s of Equation 7. From this chart Equation 7 and Figure 1, the latent heat of vaporization of any non-polar material at any desired temperature,

T, may be predicted if the molecular weight, M, normal boiling point, T_s, and the density at the normal boiling point, d_s, are known. This method is applicable only to non-polar liquids. The procedure is as follows:

(a) Estimate the critical temperature of the material by means of Figure 1 and Equation 7 as previously described.

(b) Calculate the reduced temperature, T_r, corresponding to temperature T.

(c) On Figure 3, by interpolation between the curves, locate the point corresponding to T_r and the value of M/d_s of the material.

(d) Read the corresponding value of ML/T from the scale of ordinates.

In Table II are values of $(ML/T)'$ which were calculated on the basis of the Hildebrand principle from Figure 3. The agreement of these calculated values with those experimentally observed is in general good, but not so good as that of the values calculated from the equation of Kistyakowsky. The difference between the results of the two methods becomes marked when they are applied to liquids having high molal volumes such as the higher hydrocarbons. For these substances the latent heats predicted by this application of the Hildebrand principle are considerably higher than those based on the Kistyakowsky equation. Unfortunately reliable experimental data in this range are not available. However, in view of its scientific basis and the fact that it is in good agreement with practically all observed data, it would seem that the equation of Kistyakowsky should offer the more reliable basis. It is therefore suggested that this equation, in conjunction with the curve of Figure 2, be used for the estimation of latent heats of vaporization of non-polar liquids at any desired temperatures.

Acknowledgment

It is desired to acknowledge the important encouragement and assistance given by the Universal Oil Products Company in the initiation and development of the work herein reported, and particularly the criticisms and helpful suggestions of W. F. Faragher, O. L. Kowalke, and W. H. McAdams.

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Thermodynamic Properties of Dichlorodifluoromethane, a New Refrigerant

II—Vapor Pressure[1]

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The vapor pressures of dichlorodifluoromethane from −70° C. to the critical temperature (111.5° C.) have been measured by a static method. An equation, suitable for thermodynamic calculations, is given:

$$\log_{10} p = 31.6315 - \frac{1816.5}{T} - 10.859 \log_{10} T + 0.007175\, T$$

where p is the pressure in absolute atmospheres and T is the temperature in degrees Kelvin. The calculated normal boiling point is −29.8° C.; the Trouton and Hildebrand constants are, respectively, 20.0 and 27.1. A table of calculated vapor pressures at 10° C. intervals is given.

THE vapor pressure of a refrigerant is of more obvious practical value than any of the other thermodynamic properties, and its determination has repeatedly occupied the attention of this laboratory since an early stage in the development of dichlorodifluoromethane. Three series of measurements, hereafter designated as A, B, and C, have been made by the static method, using six samples of the refrigerant.

Purity of Samples

The crude material as manufactured at the semi-works plant was known to contain only impurities removable by fractional distillation and readily detectable if present. All laboratory samples were obtained from the middle cut of the final fractional distillation as practiced in the regular plant operation. Dryness was established in samples 1, 2, 3, and 4 by bubbling the vapor through sulfuric acid. Samples 5 and 6 were dried over phosphorus pentoxide. Filling the apparatus by distillation insured the absence of oil, and the removal of successive small fractions by evaporation at constant pressure, both before and during a series of measurements, made certain the absence of air. The remote possibility of an unknown impurity which was not readily removable by fractional distillation was checked in the case of 5 and 6 by fractional freezing. This was found to have no observable effect on the vapor pressure. As a final test for purity, samples 5 and 6 were slowly evaporated almost to dryness at constant temperature without perceptible change in vapor pressure.

Measurement of Temperatures and Pressures

Temperatures were measured with copper-constantan thermocouples using an ice junction. The wire from which these couples were made was checked for uniformity and was calibrated at the melting point of mercury, the transition point of sodium sulfate, and the temperatures of condensing steam and condensing naphthalene.

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[1] Received January 26, 1931.

The observed microvolts at these fixed points determined an almost linear deviation plot from the microvolts calculated from the copper-constantan tables in the International Critical Tables. These tables and the deviation plot were used to convert potentiometer readings into temperature. For series A a Leeds and Northrup type 8657C potentiometer with self-contained galvanometer was used; for series B the same potentiometer was used with a Leeds and Northrup type 2420b external galvanometer; a Leeds and Northrup type K potentiometer and the type 2420b galvanometer were used in series C. The instrumental error in temperature measurement is estimated to be of the order of ±0.3° C. for series A, ±0.2° C. for series B, and ±0.1° C. for series C.

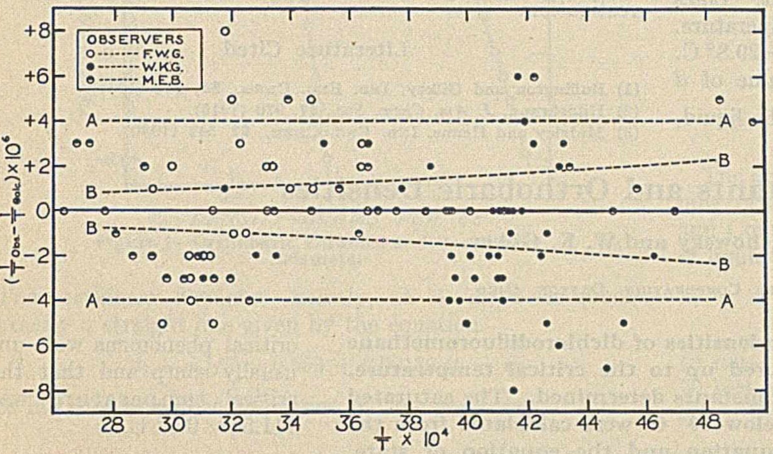

Figure 1—Deviations of Observed Points from Those Calculated by Equation 3

AA—Deviations corresponding to 1.0 per cent error in pressure.
BB—Deviations corresponding to 0.1° C. error in temperature.

Nearly all pressures below 5 absolute atmospheres were measured on a mercury manometer, the usual barometric and temperature corrections being observed. Measurements of higher pressures were made with Bourdon tube gages calibrated before and after use against a dead-weight gage, whose constant was determined by direct comparison with the mercury manometer. The average error in the pressure measurements is estimated to be ±0.5 per cent, although in a few instances it may be as great as 1.5 per cent.

Apparatus

The apparatus was essentially the same for all measurements, though certain changes were made to suit the varying requirements imposed by the wide range of pressures. A container, partially filled with the liquid, was connected to the pressure gage by small-bore tubing. For most of the low-temperature measurements the container was a Pyrex bulb connected to the manometer by a short section of rubber tubing; a Dewar flask containing gasoline cooled by solid carbon dioxide furnished a satisfactory bath. At the higher pressures small welded steel cylinders, fitted with valves, held the liquid, and connection to the pressure gage was made with $^1/_8$-inch copper tubing; an oil bath of large heat capacity with a manually controlled electric heater was used. The baths were thoroughly stirred and thermal equilibrium was established by violently shaking the containers. Temperatures and pressures could be held constant within the sensitivity of the instruments for 3 or 4 minutes.

Data

Space does not permit reproduction here of the ninety-eight individual measurements made. The essential information is contained in Table I, in connection with the final equation 3 and deviation plot (Figure 1).

Derivation of Equation

The equation

$$\log p = 4.321 - 1047/T$$

as quoted by Midgley and Henne (*3*) was derived from the data of series A only. Although this equation satisfactorily represents the data from which it was derived, it does not extrapolate correctly and is obviously inadequate for thermodynamic calculations involving derivatives. Soon after it was published the data of series B were obtained and the combined data represented by an equation in which the logarithm of the pressure was expressed as a function of a series in $1/T$. The Jackson Laboratory of E. I. du Pont de Nemours and Company pointed out that this equation gave too much curvature in regions above and below those covered by the data from which it was derived, so a third series, C, covering the range from −70° C. to the critical temperature, was made.

For final representation of the combined data, an equation of the form

$$\log p = A + \frac{B}{T} + C \log T + DT \qquad (1)$$

was chosen because it was known to represent other vapor pressure data satisfactorily and also because its derivative

$$\frac{d \log p}{d\left(\frac{1}{T}\right)} = B - CT - DT^2 \qquad (2)$$

is a parabolic function of the temperature, a matter of considerable practical convenience.

Table I—Experimental Data

Observation	Sample	Observer	Temp. Range °C.
		SERIES A	
1–19	1	F. W. G.	0 to 70
20	2	F. W. G.	0
21–24	3	F. W. G.	0 to 36
25–30	4	W. K. G.	0 to 49
		SERIES B	
31–49	4	W. K. G.	−35 to − 8
50–63	5	W. K. G.	−57 to −29
		SERIES C	
64–98	6	M. E. B.	−71 to 100

Table II—Vapor Pressures Calculated from Equation 3

Temp.	Pressure (Absolute)		Temp.	Pressure (Absolute)	
° *C.*	*Atm.*	*Lbs./sq. in.*	° *C.*	*Atm.*	*Lbs./sq. in.*
−70	0.1217	1.79	30	7.337	107.9
−60	0.2240	3.29	40	9.456	139.0
−50	0.3870	5.69	50	11.99	176.3
−40	0.6340	9.32	60	14.98	220.2
−30	0.9915	14.6	70	18.48	271.7
−20	1.490	21.9	80	22.54	331.3
−10	2.162	31.8	90	27.20	399.8
0	3.045	44.8	100	32.58	478.9
10	4.174	61.4	110	38.58	567.1
20	5.592	82.2	111.5	39.56	581.5

The data were plotted as $\log_{10} p$ against $1/T$ on a large scale and a smooth curve was drawn through the points. The slopes, $d \log p/d\left(\frac{1}{T}\right)$ of this graph were plotted against absolute temperatures and approximately fitted by an equation having the form of (2). This equation was then integrated, the boiling point supplying the constant of integration. As was to be expected, this first approximation to the integral did not fit the vapor-pressure data accurately. The final equation was obtained by successive approximations using the Trouton and Hildebrand (*2*) relations to indicate the general trend of the slope curve in the regions to which they apply. The final equation is

$$\log_{10} p = 31.6315 - \frac{1816.5}{T} - 10.859 \log_{10} T + 0.007175T \qquad (3)$$

where p is the vapor pressure in absolute atmospheres; T is the temperature in degrees Kelvin (° C. + 273.1).

Discussion

Figure 1 shows the deviations of the observed data from the equation. The data of each observer are well represented by the equation. These deviations are random with respect to observer, sample, and order of observations on each sample. The dotted lines AA show the deviations from the equation assuming a 1 per cent error in pressure measurement. Lines BB show those due to an error in 0.1° C. in temperature. The boiling point as calculated from the equation is −29.8° C. The Trouton constant as calculated from the value of $d \log p / d\left(\frac{1}{T}\right)$ at the boiling point, the density of the liquid, and the equation of state (*1*) is 20.0. The Hildebrand constant is 27.1.

Acknowledgment

The writers gratefully acknowledge the assistance and suggestions of R. M. Buffington, under whose direction this work was done, and of F. R. Bichowsky. They also wish to thank F. B. Downing and A. F. Benning, of the Jackson Laboratory of E. I. du Pont de Nemours and Company, for constructive criticisms offered during the course of this investigation.

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III—Critical Constants and Orthobaric Densities[1]

F. R. Bichowsky and W. K. Gilkey

Frigidaire Corporation, Dayton, Ohio

The orthobaric densities of dichlorodifluoromethane have been measured up to the critical temperature, and the critical constants determined. The saturated vapor densities below 50° C. were calculated from the vapor-pressure equation and the equation of state. Above 50° C. they were obtained by determination of dew points. Liquid densities from −40° to 50° C. were determined by a dilatometric method, and above 50° C. by Faraday's method, using glass floats. The critical temperature, pressure, and density are, respectively, 111.5° C., 39.56 atmospheres, 0.555 gram per cubic centimeter.

In order to calculate the heats of vaporization and other thermodynamic properties of dichlorodifluoromethane from the vapor pressures, the orthobaric densities are needed.

Density of Saturated Vapor

The density of the saturated vapor may be calculated from the equation of state (*1*),

$$p = \frac{RT}{V^2}(V + B) - \frac{A}{V^2}$$

where $A = 23.7\left(1 - \frac{0.305}{V}\right)$

$B = 0.59\left(1 - \frac{0.622}{V}\right)$

p = pressure in atmospheres
V = volume in liters per gram mol
T = absolute Centigrade temperature

by introducing the corresponding pressures and temperatures from the vapor-pressure equation (*2*),

$$\log_{10} p = 31.6315 - \frac{1816.5}{T} - 10.859 \log_{10} T + 0.007175\, T$$

and solving for the volume. The computed values are given in Table I.

Table I—Volume and Density of Saturated Vapor, as Calculated from Equation of State and Vapor-Pressure Equation

Temp. ° C.	Density Grams/cc.	Volume Cc./gram	Temp. ° C.	Density Grams/cc.	Volume Cc./gram
−40	0.004097	244.1	10	0.02379	42.04
−30	0.006199	161.3	20	0.03149	31.75
−20	0.009037	110.7	30	0.04111	24.33
−10	0.01280	78.13	40	0.05313	18.82
0	0.01765	56.67	50	0.06856	14.59

These values have a probable error of ±1.0 per cent.

At temperatures above 50° C. this equation of state fails and we depend on two determinations of the dew point. The values are d = 0.202 at 94.4° C. and 0.168 at 86.7° C. These dew-point determinations were made in small glass tubes and are probably accurate to ±1 per cent.

Direct observations of the critical point showed that the critical phenomena were unusually sharp and that the critical temperature was 111.5 ± 0.5° C.

Density of Liquid

Preliminary determination of the density of the liquid gave the density at 0° C. as 1.40 and the coefficient of expansion, 0.00233. These values have been superseded by very careful determinations, by a dilatometric method, of the density by F. B. Downing and A. F. Benning, of the Jackson Laboratory of the E. I. Du Pont de Nemours and Company. Their values are given in Table II.

Table II—Densities of Liquid

Temp. ° C.	Density Grams/cc.	Temp. ° C.	Density Grams/cc.
−37.8	1.5095	13.8	1.3521
−28.4	1.4822	25.6	1.3081
−23.9	1.4689	35.1	1.2725
−17.8	1.4511	35.2	1.2722
− 9.5	1.4254	46.9	1.2260
0	1.3946	56.5	1.1834

The densities at higher temperatures were determined by Faraday's method—that is, by the use of small floats in a sealed tube. The values obtained were 0.9785 at 91.1° C., 0.910 at 98.9° C., 0.814 at 106.7° C. The estimated error was ±0.5 per cent.

Computed Densities—Rectilinear Diameter—Critical Constants

These various determinations, together with the points determining the rectilinear diameter, are shown graphically in Figure 1. Table III gives interpolated densities at even temperature intervals.

Table III—Density of Liquid and Saturated Vapor

Temp.	Density		Temp.	Density	
	Liquid	Vapor		Liquid	Vapor
° C.	Grams/cc.	Gram/cc.	° C.	Grams/cc.	Gram/cc.
−40	1.517	0.004097	50	1.213	0.06856
−30	1.486	0.006199	60	1.165	0.0875
−20	1.456	0.009037	70	1.115	0.111
−10	1.425	0.01280	80	1.056	0.142
0	1.393	0.01765	90	0.988	0.182
10	1.362	0.02379	100	0.898	0.242
20	1.329	0.03149	110	0.725	0.390
30	1.293	0.04111	111.5	0.555	0.555
40	1.255	0.05313			

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[1] Received January 31, 1931.

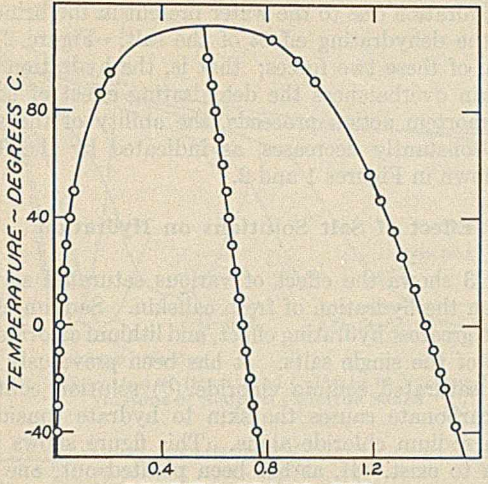

Figure 1—Orthobaric Volumes and Rectilinear Diameter

The rectilinear diameter—namely, $(d_l + d_v)/2$—is almost exactly a straight line given by the equation

$$(d_l + d_v)/2 = 0.555 + 0.00139\ (t_c - t)$$

or in terms of reduced densities and temperatures,

$$(d_l + d_v)/2d_c = 1 + 0.963\ (1 - T/T_c)$$

The coefficient 0.963 is that of a normal liquid (*3*). The critical volume is 1.80 cc. per gram. The critical density, d_c, is 0.555 gram per cc. A short extrapolation of the vapor-pressure curve gives for the critical pressure, p_c, 39.56 atmospheres. The critical temperature is 111.5° C. The ratio of the absolute boiling point to the critical temperature is 0.632. The conventional constants *a* and *b* of the van der Waals equation are:

$$a = \frac{27}{64(273.1)^2}\,\frac{T_c^2}{P_c} = 0.02116$$

$$b = \frac{1}{8 \times 273.1}\,\frac{T_c}{P_c} = 0.00445$$

Acknowledgment

The authors wish to thank F. B. Downing and A. F. Benning, of the Jackson Laboratory of E. I. Du Pont de Nemours and Company, for permission to publish the accurate series of liquid density determinations given in this paper.

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Hydration of Animal Skin by Volume-Change Method

IV—Effect of Various Factors upon the Hydration of Calfskin[1]

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Department of Chemical Engineering, Lehigh University, Bethlehem, Pa.

The hydration of calfskin has been measured quantitatively. The effects of post-mortem action, upon the potential hydration capacity of calfskin, have been shown. It is pointed out that if the hydration capacity of hides and skins is to be conserved, the skins should be cured as soon as possible after death.

The effects of salt solutions of various concentrations upon the hydration of fresh calfskin are shown and the relation of these salts to curing is pointed out.

A new method of measuring quantitatively the amount of hydration is given, which is based upon the change in specific gravity of the tissue as measured by the displacement method. By this method, as well as by the dilatometric method, it is shown that hydration is different from swelling.

PREVIOUS papers (*3*, *4*, *5*) have described the hydration changes that take place during the soaking and liming of heavy hides. A method of measuring hydration by the volume change method was described. This method consisted in placing 20 grams of animal skin (cut into 1-cm. edge cubes) in the dilatometer bottle (120 ml. capacity). The ground-glass connection was then well lubricated and inserted in the bottle, care being taken to rid the system of all air bubbles. The apparatus was then placed in a thermostat maintaining a temperature ±0.5° C. of the desired temperature.

In the previous papers various factors affecting the hydration were discussed and it was shown that hydration and swelling were not parallel effects. It was further pointed out that, though swelling could be accounted for by the Donnan membrane theory, hydration, at least to some degree, must be considered as due to residual valence forces. It was further shown that the hydration as measured by the dilatometric method was a compression of the water within the skin and that this compression was of the order of 1000 atmospheres per gram of gelatin in 150 ml. of water at 0° C.

In the previous work, the hydration as measured with the dilatometer was merely qualitative and it is the purpose of this work to demonstrate the extent of hydration in a more quantitative manner. In the previous work only the millimeter contraction of the system was noted. In the present work the capillary tubes were accurately calibrated before use and the millimeter contraction was changed over into milliliter contraction. By this means the actual number of milliliters of liquid compressed by the material was known.

Effect of Post-Mortem Action

It was shown by McLaughlin (*1*) that post-mortem action radically affected the ability of fresh animal skin to swell. This swelling, often termed "hydration," was measured by the weight-gain method. The effect of post-mortem action upon the hydration of fresh calfskin is shown in Figure 1. It is readily seen, first, that there is a drastic change in the potential ability of the skin to hydrate from 3 per cent in

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[1] Received September 27, 1930. Presented before the Division of Leather and Gelatin Chemistry at the 80th Meeting of the American Chemical Society, Cincinnati, Ohio, September 8 to 12, 1930.

[2] Barrett and Co. Leather Research Fellow, Lehigh University.

practically fresh skin to less than 1 per cent after 48 hours post-mortem action; second, that the degenerative activity of bacterial and autolytic enzymes progressively increases with the post-mortem time—in other words, the bacterial-enzymatic period of lag changes from 12 hours in the case of practically fresh skin to $4^1/_2$ hours for a post-mortem period of 24 hours and to $^3/_4$ hour for a post-mortem period of 48 hours.

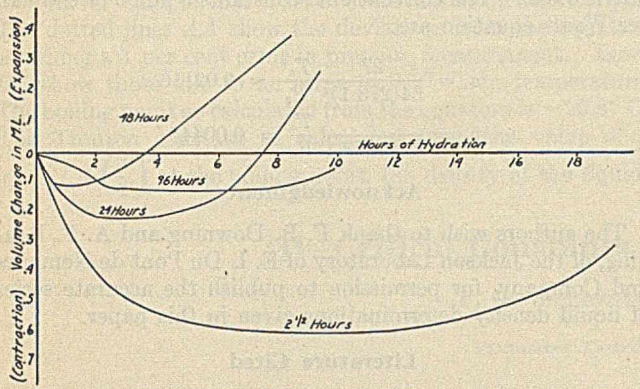

Figure 1—Effect of Post-Mortem Action upon Hydration of Calfskin in Water

The curve representing 96-hour post-mortem effects is somewhat out of line with reference to earlier periods. This can readily be understood when the complexity of post-mortem action is taken into account. The water in a biological organism may exist in part as liquid water, acting as a solute and dispersing medium for salts and hydrophilic colloid materials. It appears, however, that in the true cell a large portion of the water exists as "bound" water—that is, enclosed in the colloidal micelle. This bound water may exhibit entirely different properties. It would appear that there exists in the normal tissue an equilibrium such that bound $H_2O \rightleftharpoons$ free H_2O.

External conditions may readily cause the shifting of such an equilibrium. It can readily be conceived that post-mortem activity (mainly enzymatic) would cause a disruption of such equilibrium and alter any potential hydration capacity of the tissue. Since we have postulated (*3*) hydration to mean water bound to the hydrophilic colloid by auxiliary valences, this theory would account for post-mortem change in hydration capacity.

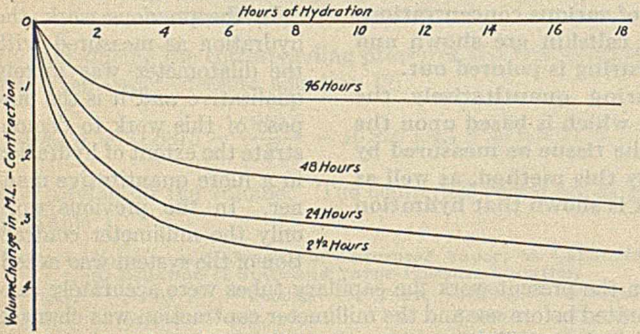

Figure 2—Effect of Post-Mortem Action upon Hydration of Calfskin in Saturated Sodium Chloride Solution

In the curing of hides and skins with brine, the action of the saturated brine is considered to be one of dehydration, as expressed in the usual sense of the word. When fresh calfskin is placed in brine, instead of an immediate dehydration, there is actually a further hydration of the skins, as expressed in the light of this work. However, as post-mortem action ensues this hydration becomes less and less, as shown in Figure 2. If a fresh skin that is fully hydrated is placed in a saturated salt solution, dehydration immediately takes place and two forces are at work: first, the tendency to further hydration due to the water present in the brine; and second, the dehydrating effect of the salt. Figure 2 shows the mean of these two forces; that is, the hydration ability of the skin overbalances the dehydrating effect of the salt. As post-mortem action proceeds, the ability of the skin to hydrate constantly decreases, as indicated by the 96-hour action shown in Figures 1 and 2.

Effect of Salt Solutions on Hydration

Figure 3 shows the effect of various saturated salt solutions upon the hydration of fresh calfskin. Sodium chloride shows the greatest hydrating effect, and lithium chloride shows the least of the single salts. It has been previously shown (*3*) that saturated sodium chloride (*6*) solution containing sodium carbonate causes the skin to hydrate considerably less than sodium chloride alone. This figure shows such a condition to exist. If, as has been pointed out, one of the functions of the brine is to dehydrate the hide or skin, we must alter our concept of curing, for sodium chloride, at least during the first 24 hours, does not dehydrate, but actually causes a further hydration of the fresh skin.

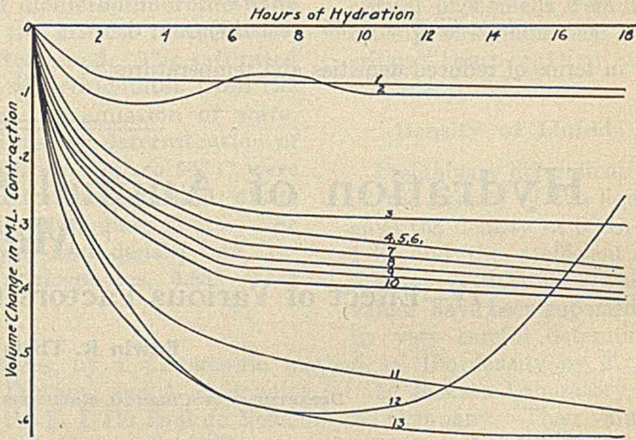

Figure 3—Hydration of Fresh Calfskin in Saturated Salt Solution

Curve	Saturated Solution of	Curve	Saturated Solution of
1	NaCl + 5% Na_2CO_3	8	Na_2SO_4
2	LiCl	9	NaCl
3	$MgSO_4$	10	0.05 *N* NaOH
4	KCl	11	$Ca(OH)_2$ + excess lime
5	$CaCl_2$	12	H_2O control
6	NaCl + 5 *M* $CaCl_2$	13	$Ca(OH)_2$
7	K_2SO_4		

On the other hand, if actual dehydration is a primary requisite for the proper curing of hides and skins, then such salts as lithium chloride, potassium or sodium sulfate, or, still better, sodium chloride containing sodium carbonate should be used for brining. This fact was pointed out by Thomas, and later by Wilson (*7*).

In practice we know that a sodium chloride brine gives a satisfactory cure. We also know that hides or skins immersed in a saturated brine lose weight very quickly. But since by the dilatometric (volume-change) method we have shown an actual hydration of the skin during brining, this weight loss must be due, not to any loss of compressed or bound water, but to a loss of the loosely held water within the tissue. Therefore, one of the functions of the brine during curing must be the loss of the loosely held water within the skin, and not a dehydration as we now speak of it. For this reason we must again contrast the terms "hydration" and "swelling."

It has been pointed out to the writers that the volume contraction observed by dilatometric measurement might be due to occluded gases within the skin—in other words, to a displacement of the gases by the liquid. If such were the case, we should expect to find almost the same volume

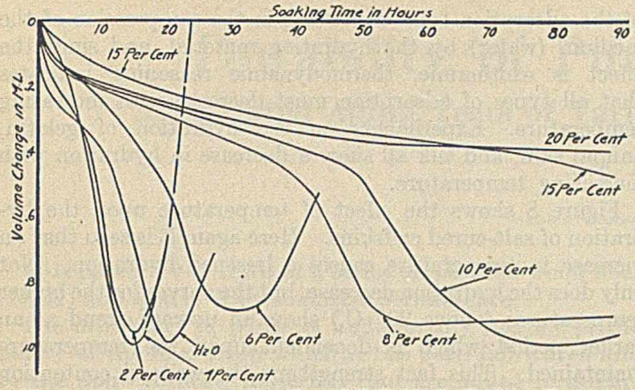

Figure 4—Hydration of Dry-Cured Calfskin in Various Concentrations of Sodium Chloride Soaks

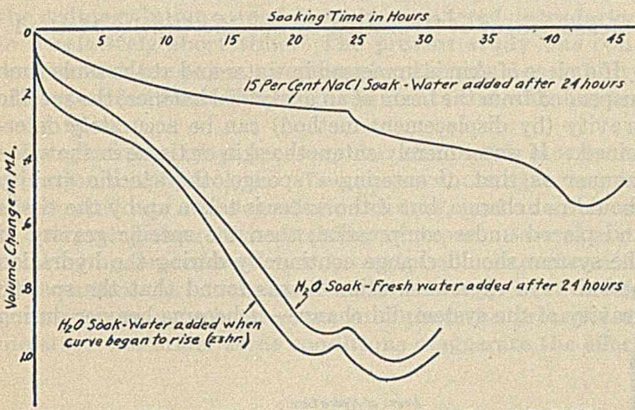

Figure 5—Effect of Various Soaks upon Dry-Cured Calfskin

change when saturated salt solutions are used. Again, it is possible to displace all the occluded air from the skin and still have a distinct change in volume of the system as measured by the dilatometer.

Figure 3 also shows the hydration of fresh calfskin when placed in sodium and calcium hydroxide solutions. For the same normality calcium hydroxide causes a distinctly greater hydration.

Relation of Salt Soaking to Curing

In tannery practice dry skins are often soaked in salt solution previous to a water soak. The changes that take place during the soaking of dry calfskin in various concentrations of salt are very interesting from the hydration standpoint. Various workers have noted that a small concentration of salt (2 to 4 per cent) often expedites bacterial action, whereas a higher concentration, 5 per cent or above, will markedly cut down such action. Figure 4 shows the effect of salt concentration upon the hydration of calfskin. With 2 to 4 per cent salt the skin hydrates very quickly, reaching a maximum in about 15 hours. At the end of this period, however, bacterial-enzymatic action sets in, as shown by the upward trend of the curves. Above 5 per cent salt degeneration is retarded and the dehydrating effect of the salt sets in; thus a skin soaked initially in a strong brine will not hydrate so much or so rapidly as one soaked in water.

The hydration curve for dry-cured skin differs somewhat from the salt-cured skin. The hydration takes place in two stages; it proceeds very slowly during the first 10 hours, and then increases very rapidly. The addition of a small amount of sodium chloride causes a distinct change in this two-stage reaction. In the case of water the initial stage of hydration takes about 12 hours, while with a 2 per cent sodium chloride solution it is only about 8 hours. The addition of sodium chloride up to and including 4 per cent aids very materially the hydration of the skin. At higher percentages of sodium chloride this effect is retarded.

Dry-cured skins must have altered materially in tissue structure—that is, the equilibrium bound $H_2O \rightleftharpoons$ free H_2O must have been materially disturbed. The skin offers strong resistance to further binding of water when placed in soak water. It is quite possible that, once a certain amount of the bound water has been removed, normal hydration is decidedly decreased. The treatment of dry skins in the beam house is much more strenuous than that of salt-cured skins, and it is quite possible that this resistance to hydration is one of the underlying causes.

Dry-cured skins are often soaked for 24 hours in a 10 to 15 per cent salt solution and then for an additional 24 hours in water. Skins soaked in this manner showed a maximum hydration of 2.6 per cent the first 24 hours and about 5.5 per cent during the second 24 hours, whereas skins soaked in water alone showed a maximum hydration during the first 24 hours of 10 per cent and during the second 24 hours of 11 per cent (Figure 5). On the other hand, the skins which were soaked in water alone showed a distinct tendency toward degeneration, as evidenced by the upward trend of the curves, within about 30 hours, while those soaked first in brine did not show degeneration until after 45 hours.

Prevention of Dehydration by Antiseptic Solutions

In all the work on hydration as measured by the volume-change method, it has been shown that when pure water is used as the hydrating medium, we first have a net contraction in volume of the system, due to the compression of the water within the tissue. This contraction is certainly a measure of the hydration of the skin. After a certain interval the hydration curve apparently approaches an equilibrium, which is maintained only for a short time, when an expansion of the system occurs. Since a net contraction of the system has been said to represent hydration, an expansion must be expressed as a dehydration. In all the previous work it has been assumed that this expansion in volume represents bacterial-enzymatic activity, the bacteria acting upon the skin in such a way that the skin loses its hydration capacity.

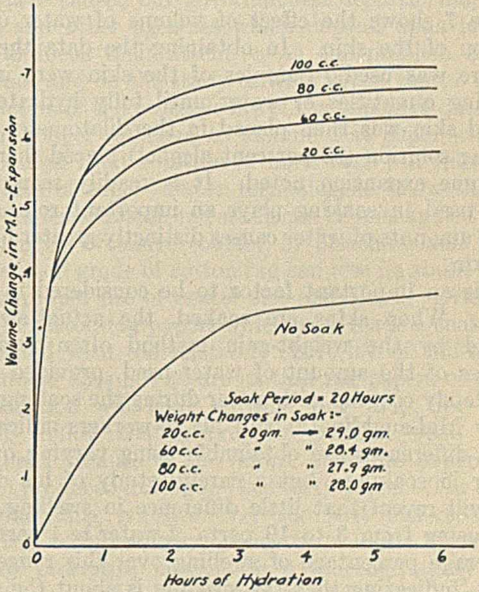

Figure 6—Dehydration of 20 Grams of Calfskin Soaked in Different Amounts of Water, Using 95 Per Cent Alcohol

It has also been postulated that the hydration curve (contraction in volume) represents the bacterial lag period, while the dehydration curve (expansion in volume) represents the period of bacterial logarithmic increase. If such a theory is correct, then by adding certain antiseptic chemicals to the water we should check the bacterial activity and thus prevent the dehydration caused thereby.

Figure 6 shows the hydration of calfskin when various antiseptic solutions are used. Water shows a distinct upward trend at a definite time, whereas solutions containing thymol, formaldehyde, bichloride of mercury, chloroform, and toluene show no such trend. This substantiates the contention that the expansion in volume, for the system skin-water, is due to bacterial-enzymatic activity, since when antiseptics are used no such volume expansion occurs. All the antiseptics except naphthalene check the bacterial activity, but naphthalene seems to be a little better than water alone. It is readily seen that the addition of the antiseptics actively retards the ultimate hydration of the skin.

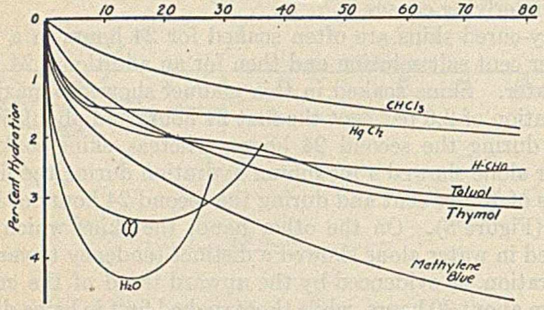

Figure 7—Effect of Antiseptics upon Hydration

Effect of Volume of Water on Hydration

Figure 7 shows the effect of volume of water upon the hydration of the skin. In obtaining the data the reverse procedure was used. Samples of the skin were immersed in varying quantities of water until fully hydrated. The hydrated skin was then placed in the dilatometer, the dehydrating solution (95 per cent alcohol) placed therein, and the volume expansion noted. It is readily seen that the volume used in soaking plays an important role, since increasing amounts of water causes distinctly greater hydration of the skin.

This is an important factor to be considered in tannery practice. When skins are soaked, the actual swelling as measured by the weight-gain method often varies little regardless of the amount of water used, provided the skin is completely covered with water during the soaking. Work done by McLaughlin (*2*) and his co-workers indicates that swelling differences are obtainable using varying quantities of water in soaking; but a careful study of his data and charts will reveal that little difference in swelling was obtained, using from 3 to 10 parts of water to 1 part of skin. The average percentage of swelling over this range was 25 per cent, indicating that the swelling is about the same regardless of the amount of water used. It is to be stressed at this point that, whereas water ratio makes little difference in the swelling of animal skin, it makes a decided difference in the hydration of the skin.

Effect of Temperature on Hydration

As has been previously pointed out (*6*), the swelling of hydrophilic protein materials such as gelatin and animal skin increases with increasing temperature while hydration of such material decreases as the temperature increases. The first must be true if the major portion of swelling is attributed to osmotic effects as shown in the Procter-Wilson theory, since osmotic pressure increases regularly with increasing temperature. On the other hand, hydration is a phenomenon of the adsorption type, consisting in the compression of the medium (water) by the hydrating material, and since the effect is exothermic, thermodynamic reasoning indicates that all types of adsorption must decrease with increasing temperature. Experiments on the hydration of gelatin, animal skin, and silk all show a decrease in hydration with increasing temperature.

Figure 8 shows the effect of temperature upon the hydration of salt-cured calfskins. Here again it is seen that an increase in temperature causes a lessened hydration. Not only does the hydration decrease, but the curves for the higher temperatures (above 20° C.) show an upward trend at an earlier period which is dependent upon the temperature maintained. This fact strengthens the writers' contention that bacterial-enzymatic activity is responsible for this upward trend in the hydration curve.

Measurement of Hydration by Specific Gravity Method

If a piece of skin is immersed in water and at the same time suspended from the beam of an analytical balance, the specific gravity (by displacement method) can be accurately determined. If water merely enters the skin or tissue in the same manner as that of entering a sponge, the specific gravity should not change, but if the water is taken up by the tissue and placed under compression, then the specific gravity of the system should change continually during the hydration period. On experimentation it was found that the specific gravity of the system did change—it became heavier during its immersion in the water, and as it hydrated over a period of time it continued to become heavier. This experiment shows in another manner that hydration is more than mere swelling and that there is a distinct reaction between the tissue and the hydrating medium. This work is being extended and will be reported at some later date.

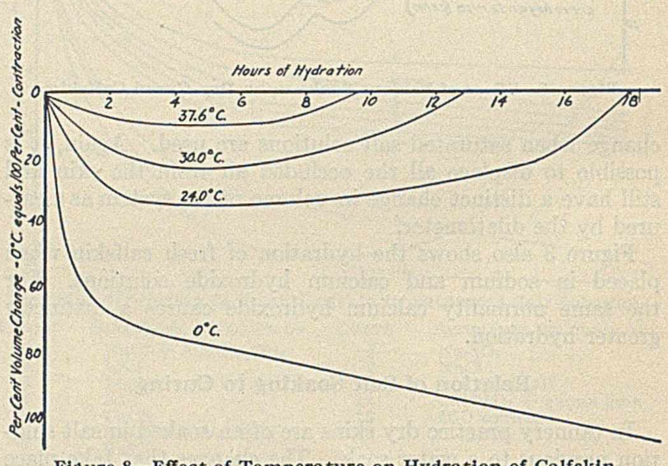

Figure 8—Effect of Temperature on Hydration of Calfskin

Acknowledgment

This work is part of the research program on leather technology of Barrett and Co., Newark, N. J., whose financial support and encouragement made such a program possible. The writers wish to thank the company for permission to publish the results of the investigation.

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Durability of Purified Wood Fibers[1]

Accelerated Aging Tests of Various Types of Paper-Making Fibers

Geo. A. Richter

BROWN COMPANY, BERLIN, N. H.

This paper is the third of a series on purified wood fiber (*10, 11*) and deals with its relative permanence.

The durability of paper is undoubtedly related to the purity of the fiber from which it has been fabricated and to the non-cellulosic materials that are added to impart desired characteristics. Properly prepared rag and linen papers have endured over long periods of time, whereas the ordinary impure wood fibers have suffered degradation in a relatively short time. The present study was conducted with an object of comparing the relative stability of the purified wood fibers with rag stocks and with impure wood fiber.

Deterioration of paper may be attributed mostly to oxidation and hydrolysis. The chemical changes may be accelerated and the degradation can be used as a means of comparing the relative stability of paper. Several artificial aging procedures were investigated. Experimental data confirm the belief that atmospheric oxygen is actively potent in its attack on paper and that the presence of moisture can under some conditions exaggerate the effect of oxidation. The trials included exposures of various papers in air at 100° C. and in oxygen under pressure at lower temperatures. The results with both methods appear concordant and show that papers that are most resistant to oxidation and physical injury are consistently high in alpha-cellulose. The purified-wood-fiber papers rank with the better grades of rag sheets and both are distinctly superior to the sulfite papers.

Acids that are present as residues in the papers or as impurities in the surrounding atmosphere cause hydrolysis of the cellulose. When the hydrolysis is intensified by increase in temperature or by increase in concentration of acid reagent, the deterioration proceeds rapidly and severe embrittlement occurs. The experimental data thus far do not point to greater resistance to hydrolysis of the high-alpha-cellulose cotton or wood fiber. All papers appear equally affected by exposures to sulfur dioxide gases, although more trials are in order before final conclusions can be drawn.

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PAPER may be classified in many ways depending upon the purposes for which it is intended. If we ignore for the time such minor requirements as color, finish, pattern, and texture, we find by careful study that paper is generally valued in terms of:

(1) Physical strength and resistance to disintegration by forces which act when the sheet is punctured, torn, pulled, or folded.

(2) A retention of physical strength and chemical properties when the paper is exposed to the various agents that are encountered when the paper is filed or stored for record purposes. This measure of inertness is sometimes designated as the relative permanence of the paper.

It is evident that none of these requirements is of great importance in the case of many of the cheaper papers which serve temporary requirements and which outlive their usefulness in a short time. For such papers it is sufficient that they possess enough strength to allow their passage through rapid printing presses and that they have a certain degree of opaqueness and printing quality.

There is, however, an ever growing mass of evidence which emphasizes the need of a more careful selection of paper for the transcription of literature and records which are of a semi-permanent or permanent nature and which may or may not require frequent handling. A paper record which is well supported and properly bound and which is consulted only occasionally need not possess extremely high initial physical strength, but it must be capable of withstanding chemical changes that would lead to ultimate disintegration or excessive physical weakness. On the other hand, paper which is to be subjected to frequent use over long periods of time—i. e., ledger stock, maps, and various sensitized papers—demands both a high initial strength and the ability to retain such strength over long periods of time.

There have been many instances of the instability of paper where a high degree of permanence had been expected. These failures have caused our governmental departments, library bureaus, and other agencies which depend upon long-time records to focus their attention on the problem of paper permanence and on the study of tests which can be used for the prediction of the probable life of the papers in question.

It is no longer sufficient to assume that paper which has been produced from a cotton or linen base will endure over long periods of time. Paper technologists know that even the best grades of cotton-rag stuffs can be mishandled in their purification by excessive cooking or bleaching and that an otherwise good grade of cotton rag can lose its stable properties by improper use of beater size and alum. Evidence of long life of cotton-rag papers which were made a century ago as contrasted with the relatively short life of sulfite-wood-fiber products does not assure us that rag papers of present-day fabrication will have equally long life; nor does it necessarily follow that a properly purified wood fiber is impermanent because of the failure of sulfite papers which have been produced during the last forty years. The changes in manufacturing practice over the past half-century, as well as the technical improvements in both the rag and wood-fiber processes, necessitate a thorough study with a hope that there may result sufficient data to answer the questions which are facing the printer and the keeper of records.

A first important question relates to the factors which determine the degree of permanence of a paper. This study must include a survey of the prior history of the paper, inasmuch as treatments in the purification process may possibly affect cellulose stability without its being evident by an examination of the initial physical and chemical tests. It is also essential that the investigation attempt to identify the constituents which make for stability and those which cause an accelerated decomposition. Furthermore, the problem will not have been completed until it is known to what degree the various atmospheric agencies affect cellulose and until there is more information concerning

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[1] Received February 24, 1931.

the effect of adventitious mineral residues which remain with the cellulose. It is evident that the conditions under which paper is stored may affect the paper in different ways. Among those agents which are undoubtedly of major importance may be listed oxygen, moisture, light, carbon dioxide, sulfur dioxide, and warmth.

Table I—Effect of Exposing Loosely Felted Fiber to 100° C. for 72 Hours

KIND OF FIBER	ALPHA-CELLULOSE		VISCOSITY		COLOR	
	Original	Final	Original	Final	Original	Final
New rag pulp:						
A	98.3	97.7	24.0	18.0	White	Very little change
B	97.6	97.2	14.0	10.0	White	Very little change
Old rag pulp	88.5	85.4	2.0	0.5	Cream	Appreciable change to cream
Sulfite pulp:						
A	85.3	82.1	2.1	0.8	White	Appreciable change to cream
B	86.4	83.1	6.2	2.0	White	Cream
Purified wood fiber:						
A	94.6	94.0	12.0	10.0	White	No appreciable change
B	94.9	94.2	20.0	17.5	White	No appreciable change

Because of the many ramifications and the multiplicity of factors which play a part in the investigation suggested in the previous paragraph, and by reason of new principles and practices which will undoubtedly enter the pulp and paper industries, it is evident that this program of research will require years of work to complete. So that the makers and users of paper may, in the meantime, be guided in their use of material and in their procedures, it is essential that the durability of papers may be judged by accelerated aging tests which will be formulated to measure the chemical inertness of the paper in the presence of the known chemically reactive reagents. An accelerated test of this type will help to establish positive relationships between the composition of paper and its relative permanence when it is exposed to the ordinary weathering elements.

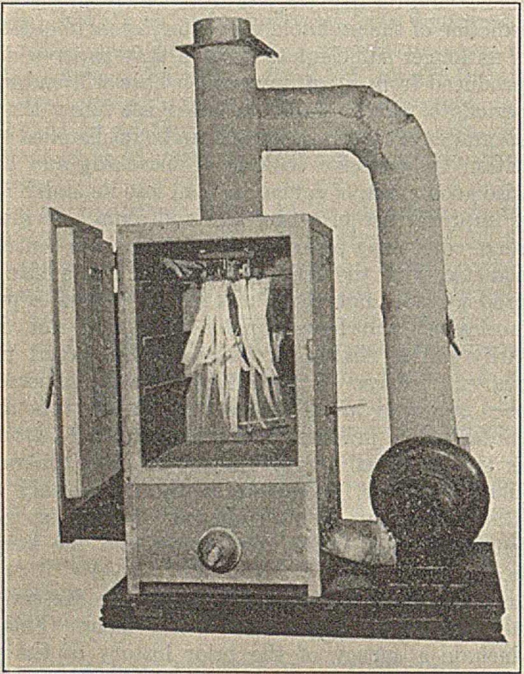

Figure 1—Apparatus for 100° C. Permanence Tests

Many investigators have published their findings in this important field of research (*1* to *8*, *12* to *14*). Much of the work has been concerned with specific phases of the entire problem. The color changes which occur when paper is aged have often been looked upon as evidence of decomposition and have demanded the attention of a number of men. Hall has found relationships (*2*) between alpha-cellulose content of paper and its corresponding permanence. Rasch (*9*) has reported an extended investigation in which there appears testimony that a wood fiber which has been carefully purified and which contains 93 to 95 per cent alpha-cellulose is as stable as a high-quality rag paper, and that both of these products are superior to sulfite papers when all are exposed to accelerated aging tests which were used in his study.

The Research Laboratories of the Brown Company have conducted an independent investigation to study the existing methods for determining the relative permanence of paper and to supplement the work with other procedures which appeared pertinent. These various procedures were applied in the examination of papers that are ordinarily accepted as possessing a high degree of permanence and also those known to be perishable. The behavior of these two distinct types of paper presented background against which new fiber compositions could be measured and judged.

The experimental trials were made with a number of different cellulose pulps and papers. The samples were characterized by both physical and chemical tests. Samples were again tested after they had been subjected to the accelerated aging treatments and an effort was made to correlate the chemical composition and the physical changes in the several types of paper.

The fact that increased temperatures accelerate chemical reactions and the precedent which has been established in parallel cases, such as the use of higher temperatures and oxygen pressures in the artificial aging of rubber, suggest the value of a permanence test in which the cellulose material is heated in a current of air for a suitable period of time (*9*). Preliminary trials in the laboratory led to the adoption of standard conditions in which the cellulose sheets are exposed to a current of moving air at 100° C. for a 72-hour period. The apparatus is similar to that used by Rasch at the Bureau of Standards and is shown in Figure 1. The change in appearance of the fiber, as well as in physical and chemical characteristics, constitutes a measure of the stability of the paper tested. Other means of measuring stability have corroborated the findings of the above procedure and indicate that oxidation plays a major part in the natural disintegration of papers. Color changes alone are not necessarily accompanied by a serious loss of physical strength, although it was found that they parallel physical changes in the case of cellulose that is free of disturbing ingredients such as dyestuff, rosin, glue, and gums.

The effect of artificial aging of paper on its physical characteristics has been determined in many ways. The trials have included a study of the change which takes place in pop test and tearing resistance, as well as the loss in folding endurance (*11*). The entire investigation points out the greater sensitivity of the folding test than any of the other common methods of measuring degradation. This fact is confirmed by an inspection of naturally aged papers, which take on a brittle condition as time goes on.

Heat Treatments of Loose Fiber

The effect of aging loose or thickly sheeted unbeaten fiber is manifested by changes in color, alpha-cellulose, and viscosity of a cuprammonium solution of the cellulose (*10*). When there is no added chemical such as rosin or dyestuff present, a sacrifice in degree of whiteness connotes instability of cellulose. The percentage drop in alpha-cellulose content and the decrease in the viscosity of a cuprammonium solution of the cellulose present additional evidence of relative permanence of fiber. The experimental results in Table I confirm in some respects the data published by the Bureau of Standards two years ago (*9*). A maximum percentage decrease of cuprammonium viscosity, alpha-cellulose, and color is shown in the case of those fibers which in subsequent series appear least permanent in paper form.

In a single experiment a purified wood fiber was subjected to a temperature of 120° C. for 24 hours. The alpha-cellulose value of 93.5 per cent remained unchanged, although the viscosity of the cuprammonium solution was decreased from 5.3 to 2.7.

Effect of Acids on Color Reversion

The presence of acid reagents does not necessarily affect the color of a pulp which in the absence of acid does not change in appearance when subjected to the 72-hour heat test. A set of experiments included the exposure of samples of a purified wood fiber which had been treated with distilled water, 0.25 per cent aluminum sulfate solution, and 0.25 per cent boric acid solution. Table II summarizes the results.

Table II—Effect of Reagents Added to Purified Wood Fiber Exposed in Air at 100° C. for 72 Hours

Expt.	Reagent Added to Fiber	Strength of Soln.	pH of Dried Sheets	pH of Heated Sheets	Color Change
		%			
1	Distilled water	..	5.0	4.2	None
2	Alum solution	0.25	2.4	2.4	None
3	Boric acid	0.25	4.4	4.4	None

Humid heat at 95° C. is much more drastic in its effect on the various typical pulp fibers. A 2-hour exposure in steam at atmospheric pressure caused color changes which were as marked as after a 72-hour exposure in dry air at 100° C. The several pulp stocks reverted in the same order as did those in Table I.

Exposure to ultra-violet light or sunlight causes similar but less rapid changes in the pulp sheets. When the sheet is held 20 inches from a 1500-candlepower quartz-mercury light the color reverts more slowly than when heated in air at 100° C. This observation does not hold in the case of most commercial papers, which contain dyestuffs that are quickly affected by the mercury light. This entire field deserves more attention and is being investigated more fully.

Physical Deterioration of Waterleaf Papers

Inasmuch as so-called "waterleaf" papers automatically eliminate many of the complications that arise when commercial papers are examined for relative permanence, much of the preliminary work was carried out with paper made from beaten fiber containing no rosin, starch, alum, glue, color, or other ingredients which usually appear in a bond or ledger sheet. When such papers are exposed to the various stability tests, it is possible to supplement the usual observations on color and chemical changes by a measure of the physical deterioration. As with natural aging, the folding endurance or flexibility appears to be affected more quickly than the tearing resistance or tensile strength. Many of the experimental series include both tearing values and folding endurance, but less can be concluded from the changes which take place in tearing resistance. The aging process appears to affect the bonding gel which forms when the fiber is hydrated and which is partly responsible for the folding properties of the dried paper. The physical character of this cellulose gel and its stability when aged are undoubtedly related to the chemical composition of the fiber from which it is made. Table III includes results obtained with a number of unsized waterleaf papers.

In the absence of added reagents which often cause secondary effects, the high-alpha-cellulose cotton and wood-fiber products resist the action of the 72-hour heat test surprisingly well. The sulfite papers become brittle when aged by this treatment.

In order to study the effect of increased hydration on the permanence as measured by the 72-hour heat test, additional experiments were made with a sulfite pulp and with a purified wood fiber. In both cases the fiber was beaten according to a standard procedure in a mill hollander having a capacity

Table III—Heat Tests with Waterleaf Papers[a]
(Treatments made at 100° C. in air for 72 hours; tests made at 45 per cent relative humidity)

Kind of Paper	Basis Weight	Bursting Strength	Tearing Resistance				Tear Retention	Folding Endurance				Fold Retention	Alpha-Cellulose	pH
			Original		After heat			Original		After heat				
			With	Across	With[b]	Across		With	Across	With	Across			
							%					%	%	
Rag acetylation	42	42						12	40	8	27	67	97.0	5.2
Rag nitration	13.5	87						0	44	0	37	84	96.0	4.2
Whatman's rag filter	50.4	28						6	6	7	7	100	..	5.4
Special rag[c] .	47.5	81	281	303	256	276	87.7	2247	2795	1751	2356	80	..	..
Sulfite:														
1	70		156		116		74	545		209		38.4	..	..
2	44	60	110	115	90	106	89	210	212	98	69	39.9	..	..
Soda pulp	70		96		90		96	148		69		46.6	..	..
Purified wood fiber:														
1	27.5	49						6	22	6	22	100	94.5	4.4
2	40.7	91						578	347	473	273	80.5	..	..
3	46.0	93	154	165	140	158	93.6	1248	1403	1131	1221	88.5	..	5.6
4	47.1	89	163	176	166	166	98.2	924	1317	1017	1280	103	..	5.7
5	48.0	85	...	...	...	...	..	1593	1489	1481	1279	89.7	..	..
6	70	137	288		269		93.3	2124	3107	2064	2472	86.8	..	..
7	46.0	90	172	173	155	145	87.2	1186	1393	1116	1319	94	..	..
8	46.0	94	141	138	140	133	98.5	1481	1593	1279	1489	93.5	..	..
9	44	90	185	185	180	186	99.0	1758	1761	1499	1564	87	..	..
10	44.2	95	224	195	198	192	92.8	1550	1551	1548	1372	94	..	..

[a] Waterleaf papers comprise the beaten fiber alone and contain no sizing agent. Significance of and procedure for basis weight, bursting strength, tearing resistance, and folding endurance are discussed in a previous article (*10*).

[b] "With" direction means that the specimen is torn so that the tear takes place in the direction in which the paper-machine wire is traveling when the paper is formed.

[c] Special rag paper was produced by a 24-hour beating of a linen and cotton rag mixture. The stock was kept "long" to emphasize a high tearing strength.

Table IV—Permanence Tests on Waterleaf Papers Sampled and Tested at Different Stages of Beating Operation

(Permanence work conducted with 72 hours, 100° C., air test)

BEATING TIME	SLOWNESS	STRENGTH	TEAR (AVERAGE)		TEAR RETENTION	FOLDING ENDURANCE				FOLD RETENTION	COLOR CHANGE
						ORIGINAL		AFTER HEAT			
			Original	After heat		With	Across	With	Across		
Hours					%					%	
PURIFIED WOOD FIBER											
1/2	1.85	59	273	233	85.4	17	18	17	19	100	Inappreciable
1	1.99	61	261	254	97.3	29	29	29	23	89.7	Inappreciable
2	2.11	68	291	272	93.5	49	45	48	42	96.7	Inappreciable
4	2.66	76	328	287	87.5	74	74	74	69	93.0	Inappreciable
10	4.66	91	369	333	90.2	275	437	299	309	89.2	Inappreciable
12	7.51	104	363	306	84.3	558	1100	541	763	83.2	Inappreciable
16	12.28	111	340	304	89.4	1440	1570	1188	1533	90.1	Inappreciable
24	42.75	121	333	294	88.2	1429	2062	1426	1966	97.6	Inappreciable
32	102.0	135	319	269	84.3	2185	3812	2124	3473	94.2	Inappreciable
40	285.0	134	290	250	86.2	1609	3764	1741	3563	100.0	Inappreciable
48	790.0	137	288	269	93.3	2124	3107	2064	2472	86.8	Inappreciable
NORMAL BLEACHED SULFITE PULP											
0	1.40	59	213	202	94.6	52	49	35	35	69	Distinctly darker than original
1/2	1.60	74	222	191	86.0	81	124	60	75	66	Distinctly darker than original
1	2.41	85	210	178	84.8	209	235	124	112	53	Cream
2	3.96	88	194	178	91.8	301	436	227	235	63	Cream
4	15.08	110	161	138	85.6	436	824	148	376	42	Cream
6	34.8	110	161	128	79.5	605	777	233	457	50	Cream
8	75.0	110	147	122	83.0	464	816	214	400	48	Cream
10	158.0	107	125	107	85.6	472	721	177	217	33	Cream

Table V—Purified-Wood-Fiber Hydration in Stone Roll Beater

(Alpha-cellulose content, 94.0 per cent)

BEATING TIME	FREENESS[a]	TEMP. IN BEATER	TEARING RESISTANCE (Av.)		BURSTING STRENGTH		FOLDING ENDURANCE				STRENGTH RETENTION	TEAR RETENTION	FOLD RETENTION
							BEFORE HEAT		AFTER HEAT				
			Before heat	After heat	Before heat	After heat	With	Across	With	Across			
Hours	Cc.	° C.									%	%	%
0	...	12	185	186	42	42	4	4	3.9	3.8	100	100	96
1	...	13	360	338	81	75	299	326	318	319	92.5	93.8	98
2	108	17	290	259	109	105	1274	1875	1274	1632	96.3	89.2	94
3	62	22	256	229	123	123	1995	2463	1555	2411	100.0	89.2	88
4	43	25	206	196	119	116	1842	1622	1962	1324	97.3	95.0	94
5	32	29	175	154	113	111	1737 (av.)		1307 (av.)		98.0	88.0	75
8	21	38	125	107	138	99	647 (av.)		461 (av.)		91.7	85.5	71

[a] "Freeness" test is used for severely hydrated cellulose. It is expressed in cubic centimeters of water that can drain from the hydrated fiber suspension when the cellulose is retained on a silk cloth and standard testing conditions are maintained. The values are relative.

of 500 pounds of fiber. The action was continued until the respective stocks had attained degrees of "slowness" (*11*) far beyond what is ordinarily employed in making paper. The charge was sampled at intervals during the experiment. Each sample was identified by a slowness determination. Hand sheets were prepared at each sampling point. These sheets were characterized by tearing resistance and fold endurance and were then subjected to the standard 72-hour, 100° C. test. Both tear and fold retentions were measured. The data are summarized in Table IV and charted in Figures 2 and 3.

Table VI—Heat Treatments (100° C. for 72 Hours) of Various Severely Hydrated Pulps

ORIGINAL FOLDING ENDURANCE (Av.)	FOLDING ENDURANCE AFTER 72-HOUR HEAT TEST (Av.)	pH VALUE	RETENTION OF FOLD	HISTORY
			%	
SULFITE PULP				
346	65	4.8	18.8	Beaten to fiberless gel and sheeted
36	10	...	26.3	Commercial glassine paper made from severely beaten fiber
175	11	...	6.3	Commercial glassine paper made from severely beaten fiber
98	26	...	27.0	Commercial glassine paper made from severely beaten fiber
PURIFIED WOOD FIBER				
373	270	5.0	72.3	Beaten to fiberless gel and sheeted
1960	1575	4.6	80.7	A 50% mixture of a nearly fiberless gel from a purified wood fiber and a normally beaten fiber from the same source

These data show clearly that a high-alpha-cellulose fiber continues to maintain a very high retention of tearing resistance and folding endurance as the hydration is brought to increasing degrees of slowness. The sulfite pulp, on the other hand, is better able to withstand the heat test at the lower stages of slowness and loses an increasing percentage of its initial folding strength as the gel content of the stock is increased by further hydration. This indicates the hydrated cellulose bond of a sulfite sheet is quite easily attacked by oxygen and temperature. The relatively fair fold retention of the lightly beaten sulfite fiber probably explains the occasional examples of sulfite papers that have a very low original folding endurance but which retain 50 to 60 per cent of this fold when artificially aged.

To explore further the effect of extreme hydration on permanence of a purified wood fiber, some of this 94 per cent alpha-cellulose fiber was beaten in a 1000-pound hollander which was equipped with a lava roll and a stone bedplate. With stone equipment of this type it is possible to secure degrees of hydration which are practically impossible to reach with the metal fly bars. The beaten fiber at the end of the hydration period had lost practically all fiber structure and was converted into sheets of exceptional transparency. The usual slowness method does not suffice for such overbeaten fiber. The units that are used are on an entirely different scale and indicate increasing degrees of hydration as the "freeness" value decreases numerically. Table V and Figure 4 include the data obtained in this experiment. It is evident that even at extreme degrees of hydration the purified wood fibers continue to retain their ability to withstand the decrease in flexibility that is caused by aging

Table VII—Aging Tests with Oxygen

KIND OF PAPER[a]	BASIS WEIGHT	BURSTING STRENGTH		FOLDING ENDURANCE				BURSTING STRENGTH RETENTION	AV. FOLD RETENTION	CIRCULATING GAS
				ORIGINAL		AFTER HEAT TEST				
		Before heat	After heat	With	Across	With	Across			
								%	%	
Sulfite	35.4	66	61	66	130	10	55	92.4	28.7	Air
	35.4	66	56	40	132	1	12	85.0	9.1	Oxygen
Purified wood fiber	45.4	103	99	676	773	524	422	96.0	66.1	Air
	45.5	99	91	564	713	279	383	93.0	51.6	Oxygen
Rag bond	81.2	127	114	441	667	147	322	89.7	40.8	Air
	81.1	117	105	333	725	58	101	89.7	15.7	Oxygen
Purified wood fiber	32.9	109	104	246	513	229	471	95.5	92.5	Air
	32.2	104	97	203	671	174	470	93.3	77.9	Oxygen

[a] All papers were sized; the rag and purified-wood-fiber samples were glue-sized.

Table VIII—Aging Tests (72 Hours, 100° C.) of Rosin-Sized Papers

SPECIMEN[a]	BASIS WEIGHT	BURSTING STRENGTH	ORIGINAL TEARING RESISTANCE		TEAR RETENTION	FOLDING ENDURANCE				FOLD RETENTION	pH	ROSIN
						ORIGINAL		AFTER AGING				
			With	Across		With	Across	With	Across			
					%					%		%
1	47.1	82	174	178	86.5	820	863	825	803	84.5	4.5	..
2	44.9	73	185	203	88	343	786	250	607	75.0	4.5	1.5
3	46.0	90	188	195	92	890	1040	..	..	68.0	4.2	1.75
4	46.4	84	175	160	83.6	1533	1028	1211	847	80.7	5.4	2
5	47.5	83	154	149	95.7	1403	1263	1201	843	76.2	5.6	1.9
6	46.4	84	175	160	83.6	1533	1028	1211	847	80.7	5.4	2.0
7	46.3	110	187	197	89.9	917	1071	774	801	84.5	4.6	1.8
8	45.0	117	184	211	92.7	1090	1674	874	1479	84.2	5.0	1.5
9	49.9	120	181	190	97.4	1480	1658	1241	1541	88.5	5.2	1.5
10	45.8	109	199	210	98.0	1457	1391	1332	1324	93.4	4.5	1.0
11	49.3	129	180	202	96.5	2084	1825	1723	1584	84.8	5.2	1.0
12	54.6	96	135	112	..	825	1167	777	902	80	...	1.5

[a] All specimens were made from purified wood fiber of about 94 per cent alpha-cellulose content.

treatments. The retention of tearing resistance and pop-test strength are high and give additional evidence that extreme hydration of high-alpha-cellulose fiber does not influence the aging properties of the resulting papers.

The effect of overhydration of cellulose on the corresponding fold retention is further illustrated by subjecting several samples of highly hydrated fiber to the 72-hour heat test. Table VI confirms the idea that overhydrated sulfite stocks are particularly sensitive to the aging test.

Effect of Oxygen in 72-Hour Aging Test

It was assumed that the injury which occurred when the paper samples were exposed to the 72-hour heat test was largely the effect of an accelerated oxidation of the cellulose which comprised the samples. A few additional experiments were made to determine whether the loss in physical strength could be exaggerated by using oxygen in place of air in the heating oven. In this experiment there was probably some leakage of air, but during the entire 72-hour period the oxygen content of the circulating gas ranged well over 95 per cent. Table VII testifies that the increased oxygen concentration caused an added deterioration of paper, and suggests that oxidation of less resistant cellulose is reflected in sacrifice of folding endurance of the paper in question.

Aging Tests with Sized Papers

Although there are occasional exceptions which can be partly explained by the presence of excessive residues of acid salts, the data secured when various grades of commercial and machine-made papers were exposed to the 72-hour heat test parallel results obtained with waterleaf papers of corresponding fiber furnish. Several sets of data have been selected to illustrate the behavior of respective papers which were exposed to the accelerated aging test.

Physical identification of the original and the heat-treated, rosin-sized, purified-wood-fiber papers are given in Table VIII. None of these papers was coated with glue. The retention of tearing resistance is consistently high in all cases and suggests that the presence of rosin or alum residues does not change the findings which were made with the waterleaf papers. It is possibly significant that the two samples having the lowest retention of folding endurance were also more acidic as is evident by the pH values. The flexibility of the various papers was, however, well retained by the samples that had undergone the heat treatment and shows that the purified wood fiber is not unduly sensitive to the usual rosin and alum residues which appear in this type of paper.

Table IX compares the stability of several samples of purified-wood-fiber paper before and after the rosin-sized paper was treated with glue. It had been expected that the glue-sized sheets would lose a greater percentage of their original folding strength, but this did not occur. Probably higher percentages of glue in the finished sheet would have meant a greater sacrifice of initial folding endurance, since other investigators have found that when the folding strength of papers is artificially raised by use of large amounts of glue the added folds are relatively impermanent. The papers listed in Table IX do not show an abnormally great increase in folding strength by the addition of glue.

The relative permanence of other glue-sized purified-wood-fiber papers was studied, and such values are given in Table X. The results are very similar to those given in Tables VIII and IX and again indicate that the high alpha-cellulose wood fiber retains its stable character in the presence of reasonable amounts of sizing agents. The papers which have lower pH values again appear to suffer somewhat greater deterioration than do the sheets which are less acid.

A large number of commercial 100 per cent rag papers were also identified and then subjected to the 72-hour heat

Table IX—Effect of Glue Size on Stability of Purified-Wood-Fiber Papers Aged 72 Hours at 100° C.

Sample	Size	Basis Weight	Bursting Strength	Original Tearing Resistance		Tear Retention	Folding Endurance				Fold Retention	pH	Rosin	Glue	Color Change
							Original		After aging						
				With	Across		With	Across	With	Across					
						%					%		%	%	
1	Rosin	44	112	138	166	96.4	600	1140	422	1005	79.1	5.2	0.46	None	Very slight
	Glue	49.6	129	116	136	94.8	939	1003	766	764	79.9	5.2	0.46	3.1	Very slight
2	Rosin	44.2	115	193	209	76.4	418	817	349	488	71.5	5.0	1.98	None	Slight
	Glue	46.4	130	156	155	88.8	599	873	445	729	79.0	5.0	1.98	2.8	Slight
3	Rosin	44.0	100	200	210	90	1410	1222	1250	1080	88.6	5.1	1.50	None	Very slight
	Glue	46.0	110	190	185	85	1620	1433	1280	1135	79.5	5.2	1.50	3.2	Slight
4	Rosin	44.5	92	188	204	86.5	313	791	200	526	65	5.4	2.40	None	Slight
	Glue	44.5	112	151	169	85.8	452	618	328	480	75.1	5.6	2.40	3.4	Slight

Table X—Aging Tests (100° C., 72 Hours) of Glue-Sized Purified-Wood-Fiber Papers

Specimen	Basis Weight	Bursting Strength	Original Tearing Resistance		Tear Retention	Folding Endurance				Fold Retention	pH
						Original		After aging			
			With	Across		With	Across	With	Across		
					%					%	
1	44.0	116	...	...	..	650	796	497	552	71	4.4
2	57.2	87	...	...	..	2464	1558	1636	1171	71.2	4.4
3	45.3	92	...	...	..	480	395	325	264	82	5.0
4	46.0	110	195	205	82	1214	1312	1080	1165	88.8	4.8
5	47.7	94	179	182	..	1135	1107	877	844	81	5.2
6	47.4	90	168	187	..	1247	1131	1072	787	83.0	5.2
7	48.0	85	179	193	..	1240	1021	1133	915	91.0	5.2
8	50.0	85	189	185	..	1060	1144	944	936	86.0	5.2
9	34.0	117	125	124	..	651	884	631	726	90.0	...

Table XI—Aging Tests (100° C., 72 Hours) of 100 Per Cent Rag Papers (Glue-Sized)

Specimen	Basis Weight	Bursting Strength	Original Tearing Resistance		Tear Retention	Folding Endurance				Fold Retention	pH	Color Change	Glue
						Original		After aging					
			With	Across		With	Across	With	Across				
					%					%			%
1	52.3	137	...	...	..	1355	1475	863	718	56	5.0	Slight	..
2	79.0	113	...	...	..	2312	2286	2157	1641	83	5.2	Slight	3.1
3	42.3	110	...	...	..	700	1114	302	332	37	4.5	Slight	..
4	43.6	106	...	...	..	619	1046	372	433	52	4.8	Moderate	4.9
5	43.6	113	...	...	..	1201	1561	864	1272	78	5.0	Slight	..
6	34.9	129	...	...	..	854	1110	589	867	72	4.8	Very slight	3.4
7	58.5	121	173	179	..	861	1024	558	719	67.5	...	Slight	..
8	42.6	122	192	211	91	933	1360	553	1012	67	4.8	Slight	4.1
9	43.4	116	181	182	91.5	721	1022	602	721	76.9	5.0	Slight	..
10	43.6	138	210	218	88.8	1563	2108	1410	1472	80.0	5.0	Slight	3.0
11	43.2	115	148	156	87.6	594	999	256	502	46.7	5.0	Very slight	..
12	44.3	130	175	195	93.0	1417	1334	839	887	62.8	5.4	Moderate	4.8
13	34.2	138	220	234	79.1	1259	1563	871	983	65.7	5.0	Slight	2.74
14	43.7	126	186	234	85.3	614	1742	490	986	68.5	5.2	Slight	4.2
15	46.7	119	133	156	93.2	676	941	456	670	69.5	...	Slight	..
16	44.8	132	140	148	94.3	999	897	731	723	76.9	...	Slight	..
17	20.6	104	141	216	98.8	279	1476	185	1396	79.2	5.0	Slight	..

test. Table XI includes a number of results which typify similar data on a great many more brands of rag paper. These specimens are evidently of a wide variety and include some of the most highly reputed papers and some which, although they contain 100 per cent rag fiber, were evidently made from an inferior grade. It must also be noted that some of the relatively low fold retentions may possibly be due to the high glue content which, as has previously been suggested, permits of an abnormal increase in folding test of an impermanent character. The pH value of 4.5 in the case of the third sample is probably responsible for the very low retention of fold in that case. Again the loss in tearing resistance is not serious and does not parallel the corresponding sacrifice in folding strength of the respective papers.

Table XII gives data on tests carried out on several grades of rag papers containing less than 100 per cent of cotton. The initial tearing resistance and folding endurance of these papers is markedly lower than in the better grades of all-rag papers. The retention of folding strength is lower than with most 100 per cent rag papers, although the 80 to 90 per cent rag sheets are for the most part quite stable. The change in color when such sheets are exposed to the 72-hour test is more evident than in the case of the purified-wood-fiber papers or the all-rag papers. Whether part of this difference can be attributed to less stable dyestuffs which may be used in their manufacture is a debatable point.

It is a recognized fact that the sulfite papers are decidedly less stable than the rag or purified-wood-fiber papers, and such knowledge is confirmed by the results of the heat treatments which are given in Table XIII. None of these papers was glue-sized. The fact that sulfite papers are not glue-sized and consequently demand a greater usage of alum to produce a water-resistant sheet may explain the tendency for the pH values to be low. The higher acidity than that found in glue-sized papers may also explain the greater difference in stability of the waterleaf and the sized sulfite papers. The presence of starch as a part sizing agent does not appear to influence the durability of the paper. Sulfite

Table XII—Aging Tests (100° C., 72 Hours) of Part-Rag Papers (Glue-Sized)

SPECIMEN	BASIS WEIGHT	RAG CONTENT	BURSTING STRENGTH	ORIGINAL TEARING RESISTANCE		TEAR RETENTION	FOLDING ENDURANCE				FOLD RETENTION	pH	COLOR CHANGE	ROSIN CONTENT	GLUE CONTENT
							ORIGINAL		AFTER AGING						
				With	Across		With	Across	With	Across					
		%				%					%			%	%
1	42.0	75	101	...	...	..	622	769	319	532	59	4.4	Moderate	..	..
2	42.8	..	71	...	...	..	36	52	10	9	25	4.4	Moderate	..	..
3	42.6	60	91	...	...	..	378	752	291	457	67	...	Moderate	..	3.4
4	45.3	30	85	...	...	..	60	78	3	15	12	4.4	Marked	..	..
5	42.6	35	96	96	115	87	159	227	61	66	33.5	...	Marked	..	..
6	42.4	70	97	113	123	85	75	137	31	70	46	...	Moderate	..	..
7	44.4	90	110	139	144	86	419	461	227	265	56	...	Slight	..	4.1
8	45.8	68	109	160	169	91.1	585	711	416	433	66	5.0	Moderate	..	..
9	43.0	88	117	194	200	83.4	392	893	326	462	68.7	5.0	Moderate	2.48	3.84
10	43.7	75	101	137	143	98.4	614	445	377	292	64.0	...	Moderate	1.15	7.4
11	44.8	80	110	127	134	93.8	681	636	414	403	62.0	5.0	Moderate	..	..
12	46.8	80	97	128	145	94.6	249	301	121	122	44.6	4.4	Moderate	..	..

Table XIII—Aging Tests (100° C., 72 Hours) with 100 Per Cent Sulfite Papers (No Glue Size)

SPECIMEN	BASIS WEIGHT	BURSTING STRENGTH	ORIGINAL TEARING RESISTANCE		TEAR RETENTION	FOLDING ENDURANCE				FOLD RETENTION	pH	STARCH PRESENT
						ORIGINAL		AFTER AGING				
			With	Across		With	Across	With	Across			
					%					%		
1	51.2	52.0	...	...	..	51	5	2	0	4	4.4	Yes
2	45.4	47.0	...	...	..	8	3	1	1	23	4.2	No
3	43.8	58	...	...	..	34	118	5	19	15	4.3	Yes
4	42.1	62	...	...	..	28	29	7	3	30	4.6	Yes
5	35.4	66	...	...	..	66	130	10	55	28.7	...	Yes
6	45.9	66	81	92	81.5	9	13	1.3	1.5	13	...	No
7	43.1	69	74	97	82.5	14	20	2	5	20	4.6	No
8	45.2	68	110	105	88.0	180	192	62	68	35	4.8	Yes

Table XIV—Pressure Aging Tests at Temperatures Lower than 100° C. under Various Conditions

SAMPLE	FIBER COMPOSITION[a]	BASIS WEIGHT	STRENGTH	ORIGINAL TEARING RESISTANCE		TEAR RETENTION	ORIGINAL FOLDING ENDURANCE		FOLD RETENTION	CONDITIONS OF TREATMENT			
				With	Across		With	Across		Temp.	Time	Pressure	Oxygen
						%			%	° C.	*Hrs.*	*Lbs./sq. in.*	
A	100% rag	44.0	128	199	227	98.1	1184	1384	95	50	6	200	Dry
A	100% rag	44.0	128	200	216	100	1003	1344	100	50	6	200	Wet
B	Purified wood fiber	53.2	104	168	145	100	814	437	100				
C	Sulfite	45.3	70	108	106	100	134	90	95				
A	100% rag	44.0	128	217	238	100	1393	1433	85	70	6	200	Wet
B	Purified wood fiber	53.2	106	160	168	100	1025	576	99.8				
C	Sulfite	45.3	76	117	109	100	111	100	79.3				
A	100% rag	44.0	125	192	212	94	1214	1181	83.0	60	100	200	Dry
B	Purified wood fiber	53.2	104	165	150	94	1063	731	84.0				
C	Sulfite	45.3	73	116	112	94	113	81	62.0				
A	100% rag	44.0	125	202	199	99.0	1484	1333	86.5	60	100	200	Wet
B	Purified wood fiber	53.2	104	165	150	96.2	1063	735	85.7				
C	Sulfite	42.6	78	66	55	96.7	86	83	49.4				

[a] The rag and the purified-wood-fiber papers were rosin- and glue-sized. The sulfite paper was rosin- and starch-sized.

Table XV—Pressure Aging Tests. 60° C. for 240 Hours, 200 Pounds Pressure, and Water-Saturated Oxygen

SAMPLE	BASIS WEIGHT	BURSTING STRENGH	ORIGINAL TEARING RESISTANCE		TEAR RETENTION	ORIGINAL FOLDING ENDURANCE		FOLD RETENTION
			With	Across		With	Across	
					%			%
100% rag:								
1	44.0	125	202	199	92.2	1484	1333	59.9
2	43.9	142	220	212	96.0	1354	1495	62.8
Purified wood fiber:								
1	53.2	102	165	165	94.5	1063	735	63.8
2	36.3	120	137	141	94	1241	644	76.3
Sulfite paper:								
1	45.2	75	103	114	80	128	102	37.2
2	42.6	78	65	55	89.5	63	37	23.5
3	43.7	81	110	126	80.8	268	200	33.0

paper has a very much lower original strength than the high-alpha-cellulose wood-fiber papers and the rag-content papers, particularly in respect to folding endurance and tearing resistance. This initial low strength, together with the greater embrittlement on aging, results in a condition which does not allow appreciable handling of the sheet without rapid disintegration.

Aging Tests at Temperatures Lower than 100° C.

Some investigators have suggested that the 72-hour heat test at 100° C. may cause changes in paper which would not occur in a natural aging process. It is conceivable that certain types of paper may be peculiarly sensitive to temperature and may, therefore, undergo decomposition which would not take place at lower temperatures. In order to investigate this criticism the work was extended to include exposures of various papers at appreciably lower temperatures. Inasmuch as oxygen appears to play a part in the decomposition of cellulose, and in order to accelerate the test as much as possible, the treatments were made under 200 pounds per square inch gage pressure. The samples were cut into suitable dimensions, suspended on a rack to avoid contact as much as possible, and hung in a chrome-steel pressure container, which was partly submerged in an oil bath. A thermostat regulated the oil-bath temperature to give the desired temperature within the pressure apparatus. Figure 5 shows this apparatus. Pressure was applied by a direct connection with a cylinder of the gas which was selected for use. No difficulty was experienced in holding a fairly constant pressure by occasional manipulation of the cylinder valves. The atmosphere within the pressure unit was kept dry or saturated with moisture as desired. This apparatus was used in many ways, in order to establish conditions under which the most durable paper would show some deterioration. When this preliminary work had been completed, the most suitable treating conditions were chosen and employed in the study of the stability of various grades of paper.

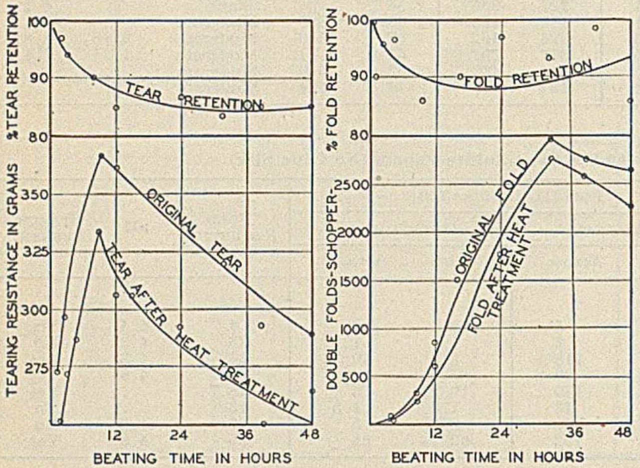

Figure 2—Effect of Progressive Hydration on Aging of Purified Wood Fiber

Table XIV summarizes results from a number of preliminary trials which were made to determine the most suitable temperature and time of treatment. The same papers were used in the several series. The differences recorded in physical tests illustrate the differences in tests from sheet to sheet and demonstrate the necessity of retesting each new portion which is to be aged. These preliminary data suggest that it is necessary to extend the pressure treatment for more than 100 hours if a temperature of 60° C. is not to be exceeded. It was arbitrarily decided to adopt a treating time of 240 hours in order to exaggerate differences in the behaviors of the papers to be investigated.

An extended series of tests was made under such conditions. Table XV includes data secured in a first 10-day test in which all the papers in question were exposed at one time. The results parallel those of the 72-hour, 100° C. tests, and give further testimony that the purified-wood-fiber papers are greatly superior to the sulfite sheets in stability and possess permanence qualities equal to the rag specimens.

It was thought of sufficient interest to investigate further the influence of moisture on the fold retention of various grades of paper when such papers are subjected to the 200-pound pressure test at 60° C. Two sets of paper sampled from the same respective original lots were exposed at 60° C. and 200 pounds oxygen pressure for 240 hours. In one experiment a dry atmosphere was maintained. In the second experiment the oxygen was kept saturated by placing a pool of water within the pressure container.

Table XVI indicates strongly that moisture accelerates the deterioration, thus substantiating the results of the steam tests which were made with various pulps and which were reported in an earlier portion of this paper. The data deserve further attention and more extended experiments should be planned to determine whether the effect of moisture is in turn influenced by the temperature under which the tests are made. Some investigators have been of the opinion that in the usual 72-hour, 100° C. permanence test the absence of moisture is responsible for most of the physical injury of the fiber.

Table XVI—Effect of Moisture on Pressure Aging Tests

Series I—60° C., 240 hours, 200 pounds pressure, dry oxygen
Series II—60° C., 240 hours, 200 pounds pressure, water-saturated oxygen

SAMPLE	BASIS WEIGHT	BURSTING STRENGTH	ORIGINAL TEARING RESISTANCE		ORIGINAL FOLDING ENDURANCE		FOLD RETENTION	pH	SERIES
			With	Across	With	Across			
							%		
A	43.5	121	222	224	1249	1542	84	4.8	I
	43.5	121	222	224	1262	1492	62	4.8	II
B	45.7	82	117	140	174	157	61	5.0	I
	45.7	82	117	140	175	119	57	5.0	II
C	55.1	84	181	173	845	914	83	4.4	I
	55.1	84	181	173	828	804	70	4.4	II
D	49.1	79	150	177	746	895	85	4.6	I
	49.1	79	150	177	723	782	75	4.6	II
E	30.0	39	223	203	4	11	80	5.0	I
	30.0	39	223	203	2	9	77	5.0	II
F	44.8	85	103	105	111	88	65	4.2	I
	44.8	85	103	105	102	66	32	4.2	II
G	45.1	60	125	123	91	135	63	4.6	I
	45.1	60	125	123	65	106	37	4.6	II

A—High-grade, glue-sized paper made from new white rags.
B—Contains 50% rag and 50% sulfite.
C and D—Glue-sized purified-wood-fiber papers.
E—A waterleaf purified-wood-fiber paper; contains no rosin or glue; lightly beaten to preserve absorbency properties.
F and G—Commercial rosin-sized sulfite papers.

Decomposition of Paper by Bacteria and by Acids

Although oxidation plays a major role in the deterioration of paper, decomposition may also be produced by other agencies. Bacterial effects are sometimes manifest, particularly when paper is stored in damp vaults or when it is exposed in the hot, humid climate of tropical countries. Heavily sized papers usually contain antiseptics which are used to preserve the gelatin coating—i. e., formaldehyde and alum—and are therefore less liable to suffer such destruction. It is probably safe to state that bacterial injury of present-day papers is of minor importance in temperate zones, and that it may be minimized by the use of suitable bactericides in tropical regions.

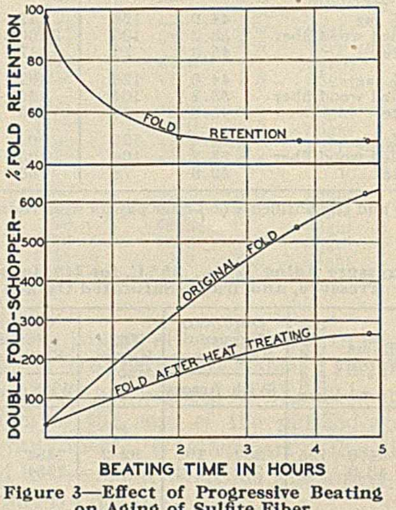

Figure 3—Effect of Progressive Beating on Aging of Sulfite Fiber

A far more serious cause of the deterioration of paper, as well as other cellulose products, is the embrittlement which takes place when acid reagents act upon cellulose. The effect of acid hydrolysis upon cellulose is well recognized. This sensitivity to acids has often resulted in serious objection to the use of cellulose for other purposes. The hydrolysis may take place in the presence of all acids and, in fact, with water alone, although some of the less ionized acids and water act slowly except at elevated temperatures. It is probable that the carbon dioxide present in the atmosphere will slowly hydrolyze cellulose and cause progressive decay of paper. The high vapor pressure of carbonic acid and its inability to accumulate ordinarily in substantial concentrations would lead one to conclude that in itself it is not of major importance in the physical degradation of paper on aging.

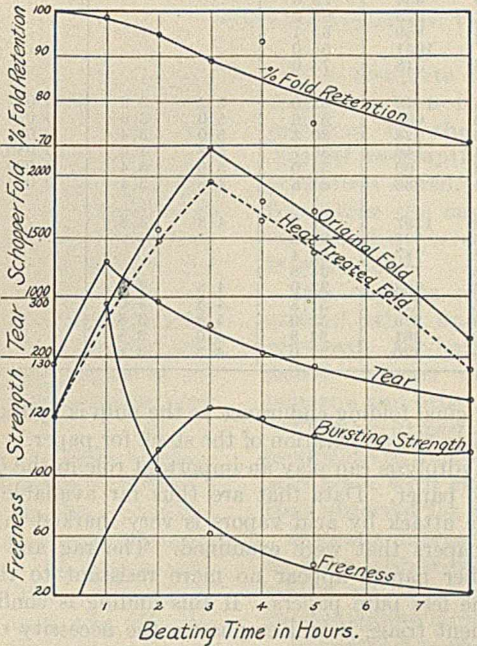

Figure 4—Aging Tests of Purified Wood Fiber Beaten in Stone Roll Beater

There is no question, however, that acidic sulfur oxides are often largely responsible for the decomposition of paper that has been kept in communities in which there is such atmospheric contamination. Sulfur dioxide oxidizes readily and is adsorbed progressively to form sulfuric acid, which produces hydrolytic effects even at ordinary temperatures. There are many analytical findings to confirm the fact that the sulfur content of all paper publications is very appreciable and that the increased concentration in the exposed edges of paper is accompanied by a higher degree of physical degradation.

Preliminary tests were made to determine the sensitivity of several types of paper on exposure to appreciable concentrations of wet sulfur dioxide vapors at room temperature. The paper strips were hung freely in an atmosphere which contained the desired percentage of sulfur dioxide. The system was kept saturated by means of a pool of sulfurous acid solution which was at equilibrium with the gas above it. In this way various concentrations of sulfur dioxide could be maintained in the vapor phase by suitable adjustment of the concentration of the solution. The closed system was maintained at about 20° C. In each series the entire set of samples was exposed simultaneously and therefore slight variations in control did not interfere with a direct comparison of results. The work included a preliminary experiment in which the papers were exposed to a saturated atmosphere which contained no sulfur dioxide. In this acid-free atmosphere there was no evidence of a sacrifice in physical strength.

Table XVII summarizes the data thus far obtained. The results suggest that all the papers are seriously affected when exposed to sulfur dioxide gases. It is very probable that even at lower concentrations of sulfur dioxide all cellulose is attacked. The experiments are being extended to determine whether the high-alpha-cellulose papers are more resistant than the less pure fibers when the exposure is made in lower concentrations of acid gas.

The papers that were exposed to the sulfur dioxide gases became distinctly acidic and analysis showed substantial quantities of sulfur in the treated samples. This is no doubt due to a transfer of gaseous sulfur dioxide to the paper and a progressive oxidation of the adsorbed gas to sulfuric acid.

Other aging experiments are in progress and include the following investigations:

(1) A study of the effect of long-time exposure of various types of paper in sunlight and air in the warm climate of Florida.

(2) A study of the combined effect of successive steps of folding and aging. The papers are to be folded to a point short of ultimate failure and then exposed to the accelerated aging tests, in order to determine the effect of oxygen when the surface coating of size has been broken.

(3) A study of dehydration of papers at room temperature. This work will add to our present knowledge of permanent changes which may be realized by such a procedure, and will be of assistance in determining whether partial dehydration of paper at elevated temperatures causes changes which are not ordinarily experienced in the normal aging process.

(4) A study of the effect of heat on pulps and papers in the absence of oxygen.

Conclusions

1—Sulfite papers which are generally recognized as impermanent suffer appreciable deterioration when subjected to an artificial aging test, which is made in air at 100° C. for a 72-hour period. High-quality rag papers which are considered relatively permanent retain much of their original physical strength when subjected to the same accelerated aging test. Purified wood fibers which are high in alpha-cellulose are also very resistant to the high-temperature exposure. Mixtures of rag stock and sulfite pulp occupy intermediate positions on the permanence scale as determined by the 100° C. test.

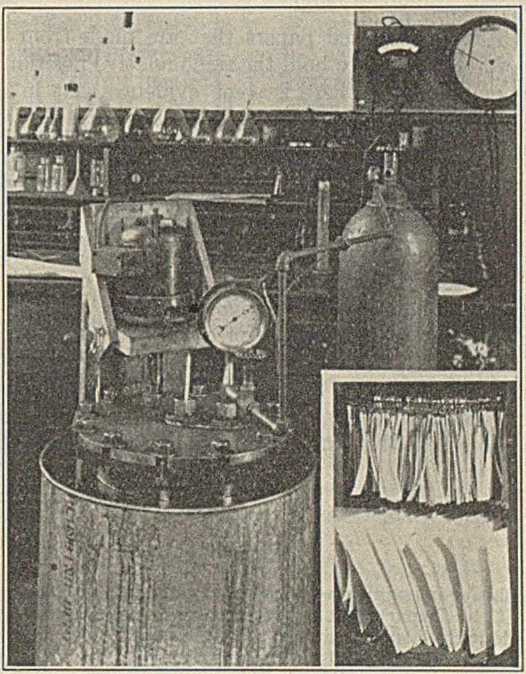

Figure 5—Apparatus for Aging Papers at 60° C. and 200 Pounds per Square Inch Pressure

2—Oxygen is an important element in the decomposition of paper that is aged. Oxidation can be hastened by increased temperature or by increased pressure. At 60° C. and with an oxygen pressure of 200 pounds per square inch

Table XVII—Exposure of Papers to Sulfur Dioxide Gas

(All exposures at room temperature: all papers conditioned at 45 per cent relative humidity before final pH or final sulfur content was determined)

Specimen	Basis Weight	Bursting Strength	Original Tearing Resistance		Tear Retention	Original Folding Endurance		Fold Retention	pH		Total Sulfur Content	
			With	Across		With	Across		Original	Final	Original	Final
					%			%			%	%
1% SO_2, 10 days												
Rag bond	44.0	125	200	223	98.7	1222	1364	70	...	...	..	..
Purified wood fiber	53.2	104	166	146	99.6	759	454	78.5	...	...	..	..
Purified wood fiber	47.8	110	179	210	99.4	661	925	66.2	...	...	..	..
Purified wood fiber	46.7	100	172	196	98.6	344	880	64.1	...	...	..	..
Purified wood fiber	46.5	115	158	179	100.0	767	1051	55.0	...	...	..	..
Sulfite	36.3	89	113	143	97.2	118	318	73.0	...	...	..	..
2% SO_2, 6 days												
Rag bond	44.0	125	187	216	100.0	1181	1419	32.0	5.2	3.6	0.077	0.26
Purified wood fiber	53.2	104	152	161	100.0	846	639	52.6	5.0	3.6	0.073	0.24
Purified wood fiber	46.3	107	182	178	100.0	956	828	30.3	5.0	3.4	0.008	0.15
Sulfite	46.2	87	114	135	100.0	204	146	36.7	5.8	4.0	0.040	0.18
Sulfite	44.0	65	100	101	99.0	34	60	52.0	5.0	3.4	0.030	0.15
Kraft	40.0	115	208	186	100.0	1014	965	64.6	4.8	3.4	0.091	0.33
5% SO_2, 10 days											..	
Rag bond	44.0	125	192	212	100.0	1248	1297	37.2	4.8	3.8	..	..
Rag bond	43.4	116	162	170	99.0	725	934	37.2	...	...	..	..
Rag bond	43.2	115	159	170	100.0	662	747	52.4	...	...	..	..
Purified wood fiber	48.8	115	173	189	...	668	775	34.8	...	...	..	..
Purified wood fiber	48.8	116	170	189	97.3	756	908	37.0	4.8	4.0	..	..
Purified wood fiber	46.0	90	179	199	99.2	615	813	51.8	4.8	4.0	..	..
Purified wood fiber	46.6	117	161	166	92.3	593	879	52.9	4.8	3.8	..	..
Sulfite	44.8	87	129	142	100.0	193	261	52.8	4.0	3.8	..	..
Sulfite	43.6	62	110	120	99.0	110	120	32.0	4.3	3.8	..	..

various papers deteriorate to different degrees. The loss in flexibility parallels the results which were obtained when the tests were made at 100° C. and at atmospheric pressure, in that the best rag papers and the purified-wood-fiber sheets are less affected and the sulfite papers are more severely attacked.

3—Preliminary work indicates that the presence of moisture in the pressure test accelerates the decomposition of paper.

4—Unsized and sized papers that are made from various types of fiber appear to hold the same relative position in the permanence scale. There is some evidence that in general sized papers sacrifice a greater percentage of their original folding endurance when they are aged, but the use of size does not disturb the relative permanence of the high-alpha-cellulose fiber as compared with the less pure stocks.

5—The effect of light at room temperature is less severe in its action on cellulose than the action of oxygen at somewhat elevated temperatures. The influence of light in the absence of oxygen should be investigated.

6—The degree of hydration of a purified wood fiber does not influence the retention of flexibility of paper that is artificially aged, even when the fiber has been drastically beaten. Sulfite papers, on the other hand, are rendered much more sensitive and sacrifice increasing percentages of their original folding endurance as the pulp is hydrated more severely in the preparation of the stock for paper.

7—Hydrolysis can play an important role in the decomposition of paper. Data that are thus far available indicate that the attack by acid vapors is very marked in the case of all papers that were examined. The rag and purified-wood-fiber papers appear no more resistant to the action than the less pure papers. If this finding is confirmed by subsequent trials, it will emphasize the necessity of storing permanent documents in acid-free atmospheres.

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Added Funds to Aid in Enforcing Food and Drugs Act

Legislative recognition of the continuing need for additional funds, if the Department of Agriculture is to maintain a reasonably adequate control, under the pure food laws, of a rapidly expanding traffic in foods and drugs designed for the American consumer, is seen by W. G. Campbell, director of regulatory work of the department, in the recent grant by Congress of an additional $181,973 for the Federal Food and Drug Administration for the fiscal year 1932. Mr. Campbell commented in part as follows upon these additional funds:

> The increased appropriations will vitalize substantially the administration's regulatory work under the Federal Food and Drugs Act. The administration for many years has felt an urgent need to increase the personnel and facilities at the larger seaports for examining foods and drugs offered for entry into the United States. Additional means for the routine interstate inspection and analysis of staple food products are also needed. As much of the increased appropriations as can be spared will be used to extend and improve control over this commerce.
>
> The administration has for years been handicapped by lack of equipment and personnel sufficient for adequate biological testing of potent drugs. Many of the more important drug products, such as aconite, cannabis indica digitalis, ergot, and the like, must be tested for potency under the direction of pharmacologists, and most of these tests have become official and compulsory within the last few years. Today there is also a rapidly expanding trade in fraudulent glandular preparations. The administration will set aside about one-sixth of the additional appropriations to increase facilities for this work.
>
> Another sixth will be used in the control of commerce in other drug products and medicines. Recent surveys by the administration have shown that some drugs prescribed by physicians in the most serious diseases are much below or much above standard. Either extreme is dangerous. Proprietary medicines that are practically worthless are still being sold. Work on these preparations, as well as on worthless antiseptics and similar products, will be extended.
>
> In recent years falsely labeled vitamin preparations have appeared on the American market. Approximately one-sixth of the increase in funds will be used to establish a vitamin-testing laboratory.
>
> It is planned to add to the administration staff several medical officers, chemists, pharmacologists, veterinarians, inspectors, scientific aids, and other trained workers. The increase in funds will also make possible the acquisition of badly needed laboratory equipment in Washington and in the field.

Some Copper Mercaptides and Their Reaction with Carbon Disulfide[1]

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The complete series of copper mercaptides from methyl to *n*-nonyl and *sec*-propyl to *sec*-nonyl are prepared by the interaction with copper acetate. Typical mercaptides are analyzed and some of the properties noted. In all cases during the mercaptide formation the cupric salt is reduced to the cuprous state and a corresponding amount of alkyl disulfide is obtained.

The cuprous mercaptides are insoluble in water, alcohol, ether, and benzene, with the exception of the *sec*-amyl, *sec*-hexyl, *sec*-heptyl, *sec*-octyl, and *sec*-nonyl cuprous mercaptides, which are soluble in benzene and ether.

They are at first light yellow and show decomposition analogous to that observed for lead mercaptides. They also react with elementary sulfur in a way similar to that observed for the lead salts.

Cuprous mercaptides add carbon disulfide readily to form red-brown alkyl cuprous trithiocarbonates, which are more soluble in organic solvents than the corresponding cuprous mercaptides.

In contrast to the behavior observed for lead, there is no indication of the formation of basic copper mercaptides. Also hydrolysis of the mercaptides is not marked.

Copper mercaptides are formed by the action of mercaptans in benzene solution on copper metal, copper sulfide, and copper oxide, also by reaction with butyl copper phthalate. In this connection some peculiarities observed during the removal of mercaptans by the above reagents are further explained.

THE literature concerning copper mercaptides is scanty. Zeise, who discovered mercaptans, mentions the formation of a light yellow copper mercaptide as a precipitate on mixing a solution of copper sulfate and ethyl mercaptan. The formula was given as $Cu(SC_2H_5)_2$ until Klason (*4*) showed that cuprous mercaptide is obtained according to the reaction:

$$2CuSO_4 + 4C_2H_5SH = 2CuSC_2H_5 + (C_2H_5S)_2 + 2H_2SO_4$$

However, he gave no detailed proof of this reaction and no analysis of the copper mercaptide. The only analysis is given by Kohler (*5*), who obtained $CuSC_2H_5$ in the reaction between copper acetoacetic ester and ethyl sulfocyanate:

$$4(CH_3COCHCO.OC_2H_5)_2Cu + 4C_2H_5SCN = 2(CH_3COC(CN)CO.OC_2H_5)_2Cu + 4CH_3COCH_2CO.OC_2H_5 + (C_2H_5S)_2 + 2C_2H_5S.Cu$$

An instance of the oxidation of mercaptans to disulfides by cupric salts is given by Drummond and Gibson (*1*), who used cupric chloride for the oxidation of thiol camphor to the disulfide.

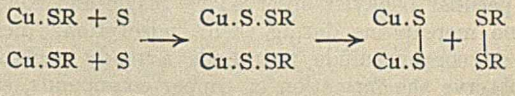
The present study was undertaken to obtain a more exact knowledge of copper mercaptides. The primary and secondary mercaptans up to nonyl[5] were used. It was of interest to find whether basic as well as neutral copper mercaptides are formed, as was found to be the case with lead (*8*). Some light on the peculiar solutions obtained by treating copper or copper sulfide with a solution of a higher secondary mercaptan was considered particularly desirable (*10*). It has been found that both primary and secondary mercaptans in benzene solution react with a water solution of cupric acetate to give cuprous mercaptides.

The cuprous derivatives of ethyl, *n*-propyl, *n*-butyl, *n*-hexyl, *n*-nonyl, isopropyl, *sec*-butyl, *sec*-amyl, *sec*-hexyl, and *sec*-nonyl mercaptans have been prepared and analyzed. All these compounds are pale yellow when first formed but turn darker on standing even out of contact with air. The derivatives of the secondary mercaptans seem to be affected by light whereas those of the primary mercaptans are not. All are insoluble in water and alcohol. The derivatives of the normal mercaptans and of isopropyl and *sec*-butyl are insoluble in benzene and ether, but those of the higher secondary mercaptans are soluble. The insoluble mercaptides separate as precipitates, the *n*-hexyl and *n*-nonyl being fibrous. The soluble derivatives of the higher secondary mercaptans are obtained by evaporating the benzene solutions. This leaves the mercaptides mixed with the slightly volatile alkyl disulfides, which can be removed by extraction with alcohol. If the disulfide is not volatile, analysis of this mixture gives results corresponding to those calculated for cupric mercaptide. That the copper derivatives are cuprous was proved quantitatively by analysis and qualitatively by dissolving specimens in concentrated hydrochloric acid and adding excess of caustic soda which precipitated the yellow cuprous hydroxide. The color deepened but slightly on boiling, which showed the absence of cupric compounds.

The formation of the alkyl disulfide was qualitatively proved in the case of ethyl and quantitatively for *sec*-hexyl and *sec*-nonyl. Hence the reaction takes place as postulated by Klason.

No evidence could be found for the formation of basic copper mercaptides, though the conditions known to give basic lead mercaptides were simulated.

The cuprous mercaptides react with sulfur, as do the lead mercaptides, but more slowly. In the case of *sec*-hexyl mercaptide the dark brown reaction product was analyzed, though it did not appear to be entirely uniform and was found to approximate cupric sulfide in composition, but from its formation it should be cuprous disulfide. The reaction might be (compare *9*):



$$\begin{array}{l} Cu.SR + S \\ Cu.SR + S \end{array} \longrightarrow \begin{array}{l} Cu.S.SR \\ Cu.S.SR \end{array} \longrightarrow \begin{array}{c} Cu.S \\ | \\ Cu.S \end{array} + \begin{array}{c} SR \\ | \\ SR \end{array}$$

When the soluble secondary copper mercaptides are left standing in benzene solution, the originally yellow solutions become deeper and deeper colored regardless of the presence of light, and eventually turn deep brown. A sealed sample

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[5] Prepared by L. M. Ellis, Jr., as part of A. P. I. Project 28.

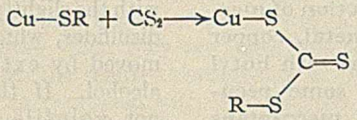
of *sec*-hexyl mercaptide solution which was left standing for more than 6 weeks yielded, after evaporation and treatment with alcohol, a small amount of a dark brown precipitate which gives a red-brown solution in benzene. This contained 56.16 per cent copper ($Cu.SC_6H_{13}$ = 35.17 per cent Cu; CuS = 66.47% Cu). Nothing definite can therefore be said about the reaction as yet, but evidently a marked change in composition has occurred.

Reaction of Carbon Disulfide with Cuprous Mercaptides

It has long been known that carbon disulfide combines with sodium mercaptides to form sodium alkyl trithiocarbonates. Thus Mylius (*7*) prepared sodium butyl trithiocarbonate and Holmberg (*3*) the corresponding potassium ethyl salt. From these the heavy-metal salts were obtained by double decomposition. The copper salt was described as a reddish brown precipitate, but neither it nor other salts of its kind have been thoroughly studied.

The present writers have found that the cuprous mercaptides combine with carbon disulfide readily to form reddish brown products which are considerably more soluble in benzene–carbon disulfide mixtures than the mercaptides are in benzene. The higher members of the normal and secondary series are quite soluble in benzene and only the methyl and ethyl compounds are insoluble. In the normal series from amyl mercaptan upward the solutions often thicken to jellies upon standing. This is not so likely to occur in the secondary series, but has been observed for *sec*-amyl after prolonged standing. The reaction products are still more soluble in carbon disulfide.

The investigation of these products leaves no doubt that they are the alkyl cuprous thiocarbonates formed according to the reaction:



The *n*-butyl cuprous trithiocarbonate was prepared in this way and also by precipitation from an aqueous solution of sodium *n*-butyl trithiocarbonate and cupric acetate. Both preparations were alike in color, solubility, and general behavior. Analysis showed them to have approximately the same composition, though both were low in sulfur. They are not so stable as the sodium alkyl trithiocarbonates are reputed to be. They decompose slowly on standing; one sample contained 36.49 per cent sulfur when first analyzed and only 35.19 per cent 2 days later. Although a cupric salt was used in its precipitation, the salt obtained is cuprous butyl trithiocarbonate. This does not seem to have been noted previously, but it is well known that cuprous xanthate is similarly formed.

The butyl cuprous thiocarbonate becomes soluble in alcohol when butyl sodium thiocarbonate is added, probably owing to formation of a complex $CuRCS_3.NaRCS_3$. Addition of copper acetate will again precipitate out the previous product. A similar observation has been made for cellulose xanthate (*6*), where it was found that the deep red-brown copper salt became very soluble when an excess of the sodium salt was added.

The peculiar behavior observed by Slagle and Reid (*10*) for some mercaptans during their "adsorption" measurements on copper sulfide now finds a ready explanation. They observe the formation of copper compounds, soluble in benzene, which were suspected to be the mercaptides, exactly in the cases where we find the cuprous mercaptides to be soluble. If to such a solution carbon disulfide is added the color changes to a red-brown, as was found to be typical for the cuprous mercaptides. Also the darkening of the benzene solution by itself upon standing is characteristic.

Experimental

ANALYTICAL PROCEDURE—The sulfur was determined with the Parr bomb, by the same procedure as described in a previous article (*8*).

The copper was determined electrolytically by the method of Hillebrand and Lundell (*2*). Special pains were taken to decompose the compound entirely and to boil off all mercaptan.

PREPARATION OF COPPER MERCAPTIDES—The mercaptides were usually prepared by shaking 0.3 *N* aqueous copper acetate solution with a dilute solution of the desired mercaptan in benzene, washing the precipitate thoroughly with different solvents, and drying in high vacuum. However, the mercaptides can also be obtained by the interaction of mercaptans with copper butyl phthalate solutions.

Usually the first method was employed, but in the case of ethyl mercaptan several different methods were used giving essentially the same results, as may be seen from the following analyses:

CUPROUS ETHYL MERCAPTIDE	COPPER		SULFUR		Cu:S
	Obsd.	Calcd.	Obsd.	Calcd.	
	%	%	%	%	
A	49.29	50.99	25.36	25.72	1:1.02
B	48.28	50.99	25.23	25.72	1:1.04
C	48.03	50.99	24.90	25.72	1:1.03
D	49.84	50.99	25.94	25.72	1:1.03
E	50.34	50.99	...	25.72	....

Sample A. The benzene solution was shaken with excess of copper acetate solution, copper acetate solution drained off, precipitate plus benzene shaken with water and water drained off; repeated three times. The precipitate was filtered off, washed with benzene, 95 per cent alcohol, and ether, and desiccated to constant weight in vacuum (10 minutes).

Sample B. The two solutions were shaken as before, same volume of alcohol added; precipitate filtered off, washed with benzene, alcohol, and ether, and dried as before.

Sample C. The mercaptan solution was added to a very slight excess of copper butyl phthalate in benzene. The gelatinous precipitate was washed well with benzene and dried. This sample darkened more than the others.

Samples D and E. A 100-cc. solution of C_2H_5SH (2 cc. C_2H_5SH) was shaken with 75 cc. 0.3 *N* copper acetate solution. The separated benzene layer plus precipitate was shaken with 3 portions of water (100 cc. each), alcohol added, and filtered. The precipitate was washed with benzene, alcohol, water, alcohol, ether, and dried as before.

The Cu:S ratio is very nearly the same in all cases, which shows that hydrolysis is not important as was previously assumed. This behavior differs, therefore, from that of the lead mercaptides. The color observed is light yellow only at first and rapidly changes to a light orange-brown.

OTHER INSOLUBLE COPPER MERCAPTIDES—All the other insoluble copper mercaptides were prepared essentially according to the procedure for samples D and E. Often free mercaptan was added to the wash water to check possible hydrolysis. The desiccation was often prolonged for higher mercaptides. In the case of *sec*-amyl mercaptan part of the mercaptide remained dissolved and only part formed a precipitate. The precipitated fraction alone was analyzed.

sec-HEXYL AND *sec*-NONYL COPPER MERCAPTIDES WITH REMOVAL OF ALKYL DISULFIDE—These mercaptides, which are very soluble in benzene, had to be prepared in a different manner. A solution of 2 cc. of the mercaptan in 50 cc. of benzene was shaken with 50 cc. of copper acetate solution; the benzene layer was separated, filtered, and evaporated with dry air down to about 10 cc. The addition of 75 cc. of alcohol (95 per cent) caused the formation of a fine precipitate, which was filtered off, washed well with alcohol, and dried as usual.

The mercaptides prepared and their analyses are given in the following table:

Mercaptide	Copper Obsd. %	Copper Calcd. %	Sulfur Obsd. %	Sulfur Calcd. %	Cu:S	Color
			Normal series			
Ethyl	49.84	50.99	25.94	25.72	1:1.03	Light orange-brown
Propyl	45.60	45.84	22.77	23.12	1:0.99	Deep yellow
Butyl	41.00	41.63	20.92	21.00	1:1.01	Nearly white
Hexyl	35.60	35.17	17.57	17.74	1:0.98	Yellow-white
Nonyl	28.96	28.53	14.45	14.39	1:0.99	Light yellow
			Secondary series			
Propyl	45.40	45.84	22.56	23.12	1:0.99	Light yellow
Butyl	40.93	41.63	20.79	21.00	1:1.01	Nearly white
Amyl	37.85	38.13	18.84	19.23	1:0.99	Yellow-white
Hexyl	35.14	35.17	17.70	17.74	1:1.00	Light yellow
Nonyl	28.61	28.53	14.57	14.39	1:1.01	Amber

Reaction Products from *sec*-Hexyl and *sec*-Nonyl Mercaptans without Removal of Disulfides—In the case of *sec*-hexyl mercaptan, where the corresponding disulfide is non-volatile at moderate temperatures, the benzene solution was evaporated to dryness. The residue, which was a mixture of 2 molecules of cuprous mercaptide with 1 of the disulfide, gave analytical results corresponding to cupric mercaptide as shown by the analyses below.

Sample 1 was prepared by shaking the benzene solution of the mercaptan with cupric acetate.

Sample 2 was prepared under conditions which should have given a basic mercaptide, were the formation of such possible. The benzene solution of the mercaptan was shaken with a suspension of cupric hydroxide in 4 *N* caustic soda. In both cases the resulting benzene solution was separated, filtered, and two equal portions were evaporated with dry air, for the copper and sulfur determinations. The analyses show that no basic copper mercaptide was formed and that there is no hydrolysis of the salt.

Sample	Found Cu %	Found S %	Ratio Cu:S	Calcd. for $CuS_2C_{12}H_{26}$ Cu %	Calcd. for $CuS_2C_{12}H_{26}$ S %
1	20.53	20.96	1:2.02	21.34	21.53
2	20.67	21.48	1:2.06	21.34	21.53

Analysis of the mixed reaction product from *sec*-nonyl mercaptan, prepared as sample 1, gave 16.60 per cent copper, calcd. 16.64 for $CuS_2C_{18}H_{38}$. In all these cases the cuprous mercaptides could be obtained from the mixtures by washing out the disulfides with alcohol.

Proof of Presence of Ethyl Disulfide—A benzene solution of ethyl mercaptan was shaken with cupric acetate, then several times with water, separated, and filtered to get rid of the insoluble cuprous ethyl mercaptide. The clear benzene solution was shown to be free of mercaptan by the doctor test. This solution was refluxed with zinc dust and acetic acid for 2 hours and then gave all the tests for the mercaptan. This shows that ethyl disulfide had been formed in the original reaction.

Reaction of Sulfur with a Copper Mercaptide—A solution of 1 cc. *sec*-hexyl mercaptan in benzene was shaken with 50 cc. of 4 *N* caustic soda solution containing an excess of suspended copper hydroxide, separated, filtered, and 100 cc. of saturated benzene solution of sulfur added. After 30 minutes the precipitate was filtered off, washed carefully with benzene, and dried to constant weight.

Analysis: 59.58 per cent Cu; 35.37 per cent S; Cu:S = 1:1.17. $CuSC_6H_{13}$ gives 35.17 per cent Cu; CuS gives 66.47 per cent Cu.

The analysis shows that essentially copper sulfide is present; contaminated, however, with higher polysulfides as well as with some of the alkyl residue (incomplete splitting off of the alkyl disulfide).

Preparation of *n*-Butyl Cuprous Thiocarbonate—Solid cuprous *n*-butyl mercaptide shaken with excess of carbon disulfide gave a reddish brown solution containing some suspended solid. After an hour this was filtered and the filtrate evaporated to dryness under vacuum in a desiccator. The analysis of the dark red-brown product is given below.

Preparation from sodium salt. A solution of the *n*-butyl sodium thiocarbonate was obtained by dissolving 3.6 grams of sodium hydroxide in 100 cc. of absolute alcohol, adding 10 cc. of *n*-butyl mercaptan and then 6 cc. of carbon disulfide. To this solution aqueous copper acetate solution was added in excess to yield a heavy red-brown precipitate of butyl cuprous thiocarbonate. The precipitate was filtered off, washed well with alcohol, dried as before in vacuum, and analyzed. The dark red-brown powder was soluble in benzene and carbon disulfide, but very slightly so in ether.

Preparation	Copper Obsd. %	Copper Calcd. %	Sulfur Obsd. %	Sulfur Calcd. %	Ratio Cu:S Obsd.	Ratio Cu:S Calcd.
$CuS(C_4H_9) + CS_2$	27.10	27.78	38.97	42.04	1:2.85	1:3
$Na(C_4H_9)CS_3 + Cu(C_2H_3O_2)_2$	27.77	27.78	36.49	42.04	1:2.61	1:3

Ethyl Cuprous Thiocarbonate—The ethyl cuprous thiocarbonate (obtained by addition of carbon disulfide to the mercaptide) was of brick-red color, nearly insoluble in carbon disulfide. It was considerably less stable than the butyl product, which is in agreement with the similar observation for the alkali salts. It readily lost carbon disulfide, so that the Cu:S ratio was low. The following were observed for different preparations: Cu:S + 1:2.5; 1:2.14; calcd. 1:3.

Addition of Carbon Disulfide to Mixture of Cuprous Mercaptide and Alkyl Disulfide—A benzene solution of *sec*-hexyl mercaptan was shaken with copper acetate solution, separated, and evaporated to dryness in vacuum. The residue, which contained 2 molecules of cuprous *sec*-hexyl mercaptide to 1 of *sec*-hexyl disulfide, was dissolved in a large excess of carbon disulfide, which gave a dark red solution. This was evaporated in vacuum and the residue analyzed.

Sample	Copper %	Sulfur %	Cu:S
1	19.21	26.32	1:2.72
2	19.10	25.87	1:2.69
3	19.14	26.20	1:2.71

These results indicate the composition $6CuSR.3(SR)_2.2CS_2$, which requires 19.66 per cent copper, 26.45 per cent sulfur, and Cu:S ratio of 1:2.67. The presence of the disulfide seems to alter the ratio in which the carbon disulfide combines with the cuprous mercaptide.

Addition Compound of Cuprous and Sodium Alkyl Trithiocarbonates—To determine the composition of the addition compound between butyl cuprous thiocarbonate and butyl sodium thiocarbonate, varying amounts of an alcohol solution of the sodium salt were added to the solid copper salt. When the molar ratio of Cu:Na was 1:1, practically a clear solution was obtained with a very small residue. When this ratio was 2:1, approximately half the copper salt remained undissolved. Thus there must be an addition product of the composition $Cu(C_4H_9)CS_3.Na(C_4H_9)CS_3$. When the dark-brown solution is left standing for a day, a dark precipitate is formed and the solution becomes yellow; addition of further copper acetate will not give any precipitation.

The butyl copper thiocarbonate is but slowly attacked by concentrated hydrochloric acid and remains distinctly red-brown, but the fresh solution of the above sodium-copper addition product gives, upon addition of hydrochloric acid, a brilliant scarlet-red precipitate, presumably the free acid of the complex.

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Equilibrium in the Iron-Oxygen-Hydrogen System at Temperatures above 1000° C.[1]

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A method for the determination of the iron-iron oxide-hydrogen-water vapor equilibrium at various temperatures has been developed in which a gaseous mixture of hydrogen and water vapor is allowed to flow past a sample of metallic iron. The ratio of hydrogen to water vapor in the inlet gases is controlled so that the mixture will be either oxidizing or non-oxidizing to the iron and at any temperature the true equilibrium ratio will lie between the closest oxidizing and non-oxidizing points.

By this method the equilibrium range has been determined at various temperatures between 1097° and 1427° C. The points obtained are in line with those obtained by Emmett and Schultz below this temperature.

The equilibrium data when plotted show a break in the curves at about 1357° C. which may be taken as the melting point of the ferrous oxide. The heat of fusion of ferrous oxide as determined from these data is +29,000 ± 5000 calories per gram-mol.

THE results presented in this paper were obtained as part of an investigation of the scaling of steel at forging temperatures. This study of the scaling of steel in turn was one of a series of investigations concerned with the application of heat to forging conducted during the past four years at the Engineering Research Laboratories of the University of Michigan for the committee on Industrial Gas Research of the American Association. A method of test and equipment were developed which made possible the determination of the rate of scaling of steel at temperatures up to 1427° C. It was suggested that this equipment and method of test might be used to determine the equilibria for the system iron-iron oxide-hydrogen-water vapor, and that in this manner an independent check might be obtained of the position of the iron-iron oxide line. Further, since by this method tests could be made up to 1427° C., it would be possible to check the melting point of ferrous oxide and to calculate its heat of fusion.

Inasmuch as this information was desired in the study of scaling, it was decided to make such an investigation. The method of test consisted in passing mixtures of hydrogen and water vapor over a sample of electrolytic iron at a given temperature and then determining whether the iron was oxidized in the particular mixture of gases. This method of test and the equipment used have already been described by the authors (*10*). While the tests with the hydrogen-water vapor mixtures were in progress, a paper on the same subject using a similar method was published by Emmett and Schultz (*5*). This excellent paper showed the position of the iron-iron oxide line at 1000° C. and temperatures below. Since the work of the present writers was all conducted at temperatures above 1097° C. and especially since at 1371° and 1427° C. the ferrous oxide is liquid, it was believed worth while to finish the work.

Previous Investigations

In 1870 Henry Deville (*2*) published the results of the pioneer research on the iron-oxygen-hydrogen system. The method used served as a model for all subsequent investigations except those of Ferguson (*6*), and of Emmett and Schultz (*5*), and thus was the basis for the work of Preuner (*13*), Chaudron (*1*), Wohler and his co-workers (*16*), Schreiner and Grimmes (*14*), and Eastman and Evans (*4*).

The method employed by Deville and the later investigators consisted essentially in heating iron or iron-iron oxide mixtures to a constant temperature in a porcelain tube and permitting water vapor to react with the iron in a sealed system until equilibrium was reached. Before admitting the water vapor, the tube containing the iron was evacuated and the water vapor was introduced by having one end of the sealed tube connected with a water reservoir held at a constant temperature. Owing to the reaction of the water vapor on the iron, hydrogen was formed, which caused an increase in pressure. This pressure was carefully observed by means of a manometer. When the pressure became constant, equilibrium was considered to have been established. By subtracting the pressure of the water vapor from that of the manometer reading, it was possible to obtain the pressure of hydrogen. Sufficient analyses were made of the solid phase to insure the presence of both iron and iron oxide at the time equilibrium was established.

Eastman (*3*), in 1922, very ably reviewed the available literature on this system. He noted that in general the results of preceding investigations fell into two groups differing by about 50 per cent, and there seemed to be no reason for choosing one set in preference to the other on the basis of experimental procedure, though there is logically some question concerning the data of Preuner and of Schreiner and Grimmes because neither seemed to present definite assurance of the presence of both solid phases. The results of Preuner, Chaudron, and some of Deville's fall in the group showing lower values of the equilibrium constant, while those of Wohler and his co-workers, and of Schreiner and Grimmes, fall in the group showing higher values. Consideration of this system and the iron-oxygen-carbon system led Eastman to postulate the existence of solid solutions instead of definite, constant solid phases as an explanation of the discrepancies existing between the two groups of data. Later his investigation with Evans (*4*) seemed to confirm the higher group and, as was the case in other researches, there is no apparent fault in his excellent work. Consideration of his data at 772° C. seemed to offer substantial proof of various ranges of solid solutions of iron

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[1] Received February 2, 1931.

oxide in iron from 0 to 5 per cent oxygen and from 20 to 24 per cent oxygen. The apparent reliability of his results with the iron-oxygen-hydrogen system led to questions concerning the reliability of the accepted constants for the water-gas reaction as determined by Haber (*7*), Hahn (*8*), and others when his data were combined with data on the iron-carbon-oxygen system in the indirect calculation of these constants. Ferguson's work in 1923, in which he used a flow method, was intermediate between the two groups and could not serve to settle the discrepancy.

Neumann and Kohler (*12*) in 1928, in a careful and thorough research on the direct determination of the water-gas equilibrium, determined the constants of that reaction with considerable precision and agreed substantially with the previous direct determinations by Haber and Hahn and others. The results of the indirect calculation from the iron-carbon-oxygen and iron-oxygen-hydrogen systems pointed to weaknesses in the iron-oxygen-hydrogen determinations. Krings and Kempkens (*11*) in 1929 published data which definitely limited the solid solubility of iron oxide in iron to approximately 0.1 per cent of oxygen. The researches of Tritton and Hanson (*15*) and of Herty (*9*) have seemed to indicate that the solubility of iron in iron oxide is certainly not greater than 1 per cent at the melting point of the oxide, and is doubtless even lower at the temperatures involved in previous investigations. Krings and Kempkens, Tritton and Hanson, and Herty appear to have set aside the supposed possibility of the existence of solid solutions as an explanation of the discrepancies existing in the iron-oxygen-hydrogen system.

Emmett and Schultz (*5*) used a method similar to that of Ferguson. Their method consisted in passing steam-hydrogen mixtures over iron–iron oxide mixtures, collecting the effluent gases over a certain period of time, and then determining the relative quantities of each. The analyses were repeated many times at each temperature starting with steam-hydrogen mixtures for both reducing and oxidizing conditions, and thus insured a high degree of accuracy. The excellent agreement of their results with Neumann and Kohler's direct determinations when combined with data on the iron-carbon-oxygen system in indirect calculation of the water-gas constants seems to the authors to be substantial proof of the validity of their work.

In none of this previous work, however, is there any reliable information concerning the reaction above 1000° C. which leaves unknown the equilibria above the melting point of the oxide. Such information is particularly needed in the application of physical chemistry to steel making.

Experimental Method

The method of test was similar to that used by the authors in the investigation of scaling. The gas mixture of hydrogen and water vapor was passed over electrolytic iron for about 30 minutes, at the end of which exposure the iron was quenched into distilled water to stop the reaction. By means of the analytical method employed in the previous work on scaling it was possible to determine whether the sample had been oxidized by the exposure to the gas mixture.

The electrolytic iron used was obtained in sheets about 0.8 mm. ($^1/_{32}$ inch) thick and was annealed for 3 hours at 1000° C. in moist hydrogen to decrease the carbon content. After annealing, the analysis of the iron was found to be:

	%
Carbon	0.012
Manganese	0.008
Sulfur	0.007
Phosphorus	0.002
Silicon	0.001

To make the test sample the iron was polished bright and then bent into the shape of a tube 20.6 mm. ($^{13}/_{16}$ inch) outside diameter and 25.4 mm. (1 inch) long. Each sample was then numbered, washed in ether, weighed, and kept in a desiccator until placed in the furnace, care being taken not to touch it with bare hands after the polishing operation.

The desired ratio of hydrogen to water vapor was maintained by passing the hydrogen through water held at a predetermined temperature. To do this a large glass container was filled with water which could be maintained at any desired temperature by means of an electric heater and pump. In this water bath were placed five glass bottles connected by glass tubes. Four of the bottles were filled with distilled water. The bottles and connecting tubes were sealed and entirely immersed in the water of the container. The hydrogen to be saturated was then passed through the four bottles of distilled water and finally through the empty bottle to remove entrained water. The equipment was then calibrated to determine the percentage of water in the hydrogen at temperatures from 70° to 80° C. The values thus found correspond to the percentage of water required for saturation at the particular temperature.

The glass tubing which conducted the water-hydrogen mixture to the furnace was heated by means of an electric coil in order to avoid any precipitation of moisture from the hydrogen. The furnace tube consisted of a porcelain tube glazed on the outside and mounted inside of a Carborundum muffle. The porcelain tube extended out 12 inches (30 cm.) beyond the furnace at one end so that it could be closed with a rubber stopper. The furnace was heated with gas. The thermocouple, which was platinum, platinum-rhodium, was so mounted that the bead of the thermocouple was about $^1/_4$ inch (6 mm.) away from the center of the test sample. Readings were taken each minute that the sample was in the furnace and the temperature was maintained within ±3° C. It is, of course, appreciated that at the higher ranges the accuracy of the thermocouple is only ±5° C.

To make a test, the gas mixture was passed through the tube for about 20 minutes at a velocity of about 9.2 meters (30 feet) per minute to purge the tube, and at the same time the temperature was adjusted. A small positive pressure was maintained in the tube at all times by keeping the specified rate of flow. The rubber stopper was then removed from the cold end of the tube and the sample, previously mounted on a wire boat so that it could not touch the refractory tube, was placed in the tube and pushed into the hot zone directly under the bead of the thermocouple. After remaining in the furnace for 30 minutes, the sample was pulled out of the the tube and allowed to fall from the edge of the tube into cold distilled water. The sample was weighed before and after exposure. A loss in weight indicated that scale was split off by the sudden cooling in the distilled water. The scale that still remained on the piece was removed by the electrolytic pickling method used by the authors in their previous investigation.

The experimental procedure permitted the immediate stopping of the reaction, but caused a small amount of scale to form on the iron both from contact with the air for about a second and from reaction with the cooling water. The loss in weight produced by this reaction of unoxidized iron with water and air was approximately constant for any given initial temperature of the iron and was in all cases much smaller in amount than that formed during heating in oxidizing atmospheres. It was found that the method made it possible to observe the effect of a change of 0.5 per cent of water vapor in the gas mixture at the point of change from non-scaling to scaling, since at the temperatures used in this investigation there was a decidedly sharp increase in the scaling when the water vapor was increased slightly above the equilibrium percentage. For instance, at 1260° C., using a mixture of hydrogen and water vapor containing 44.2 per cent of the latter, there was a loss in weight of 0.127 gram per 100 sq. cm. of surface, whereas with 44.6 per cent water vapor there was a loss of 0.96 gram per 100 sq. cm. With atmospheres containing less than 44.2 per cent moisture, the loss was approximately the same as at 44.2, while atmospheres containing more than 44.6 per cent moisture caused consistent increases in loss in weight. The true equilibrium composition was thus fixed at 1260° C. between 44.2 and 44.6 per cent moisture.

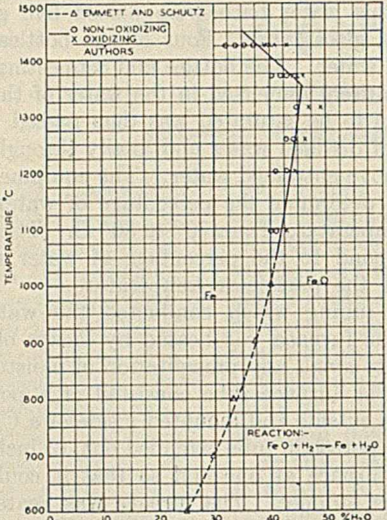

Figure 1—Equilibrium of Iron-Oxygen-Hydrogen System at Temperatures up to 1427° C. Plotted against Gas Composition

At the temperatures at which the scale was liquid—that is, at 1371° and 1427° C.—it was not possible to use a wire boat to mount the sample. Accordingly, a boat was made from Chrom-patch cement in the shape of a segment of a cylinder about 25 mm. (1 inch) longer than the iron sample and 38 mm. (1.5 inches) wide. Small sillimanite cross bars were cemented onto the boat and the iron samples were placed across these bars so that they touched at only two points. At these higher temperatures the point where scaling just commences is easily found, since with an increase of only 0.5 per cent in water-vapor content above this point blisters are formed on the steel as a result of the coagulation of liquid iron oxide.

Results

Tests were made at 1097°, 1204°, 1260°, 1316°, 1372°, and 1427° C. The results are given in Table I and Figure 1. The curve in this figure was drawn so that at all temperatures it was between the lowest point at which scaling occured and the highest point at which scaling did not occur. The lower part of the curve is drawn from data taken from the work of Emmett and Schultz, whose values are in line with those obtained by the authors.

In attempting to find the approximate location of the equilibrium at 1260° C., an extrapolation of the curve of Eastman and Evans was used. It was found that the water-hydrogen ratio indicated by this extrapolation produced decided oxidation at this temperature and that the point at which oxidation was just eliminated corresponded to a water-hydrogen ratio of 0.792. From this it appeared that the extrapolation of the curve of Eastman and Evans could not be used in obtaining the approximate location of the equilibrium to be used as a guide in the preliminary tests. The curve shows that less hydrogen is required to stop scaling at 1316° C. than at 1097° C. This, of course, might have been expected from the results of previous investigations. The change in direction of the curve above 1357° C., however, could not have been predicted. It is due to the fact that ferrous oxide is molten above this temperature.

Table I—Experimental Data from Scaling Tests

Run	Temp. ° C.	H_2O %	Scaling	Temp. ° K.	$\frac{1000}{\text{Temp. (° K.)}}$	*K*	−Log *K*
12	1088	42.9	Yes	1360	0.735	0.7500	0.12494
13	1091	41.1	Yes	1363	0.733	0.6983	0.15595
14	1091	41.0	No	1363	0.733	0.6962	0.15730
15	1094	40.0	No	1366	0.732	0.6654	0.17692
5	1205	44.3	Slightly	1480	0.675	0.7964	0.09887
9	1204	42.9	No	1480	0.675	0.7493	0.12535
6	1204	40.8	No	1480	0.675	0.6887	0.16195
2	1259	46.1	Yes	1533	0.652	0.8566	0.06720
16	1262	44.7	Yes	1533	0.652	0.8078	0.09269
18	1259	44.6	Yes	1533	0.652	0.8052	0.09410
3	1260	44.2	No	1533	0.652	0.7921	0.10123
4	1260	42.9	No	1533	0.652	0.7505	0.12464
19	1256	42.9	No	1539	0.654	0.7500	0.12497
7	1316	49.0	Yes	1590	0.630	0.9617	0.01697
8	1316	46.7	Yes	1590	0.630	0.8765	0.05725
11	1315	44.7	No	1590	0.630	0.8067	0.09330
20	1371	46.4	Yes	1645	0.609	0.8670	0.06196
21	1372	44.6	Yes	1645	0.609	0.8047	0.09437
1R	1371	43.9	Yes	1645	0.609	0.7836	0.10590
22	1372	42.9	No	1646	0.609	0.7505	0.12467
8R	1371	42.8	No	1645	0.609	0.7498	0.12505
27	1371	41.8	No	1645	0.609	0.7196	0.14293
26	1371	40.1	No	1645	0.609	0.6684	0.17497
23	1427	43.0	Yes	1700	0.589	0.7533	0.12301
24	1427	40.7	Yes	1700	0.589	0.6852	0.16418
7R	1427	39.9	Yes	1700	0.589	0.6646	0.17742
25	1427	39.2	Yes	1700	0.589	0.6443	0.19090
12R	1427	39.0	Yes	1700	0.589	0.6399	0.19391
31	1426	36.9	No	1699	0.589	0.5849	0.23292
28	1427	35.3	No	1700	0.589	0.5449	0.26368
29	1425	33.6	No	1698	0.589	0.5060	0.29589
30	1424	32.0	No	1698	0.589	0.4713	0.32674

Figure 2 was plotted from data also presented in Table I and data given by Emmett and Schultz. The points at 1000° C. and below are those of Emmett and Schultz. This curve was drawn by plotting log *K* as ordinates and 1000/*T* as abscissas where *K* is the ratio P_{H_2O}/P_{H_2} and *T* is degree absolute. At all temperatures the curve lies between the closest scaling and non-scaling points. It will be noted that there is a sharp change in direction of slope where 1000/*T* has a value of 0.613, corresponding to a temperature of 1357° C. The change in slope is due to the melting of ferrous oxide, and the point at which the break occurs agrees quite well with Herty's range of 1355–1377° C. for the melting point of ferrous oxide. From the slope of the two branches of this curve the heat of fusion of FeO was calculated from the equation

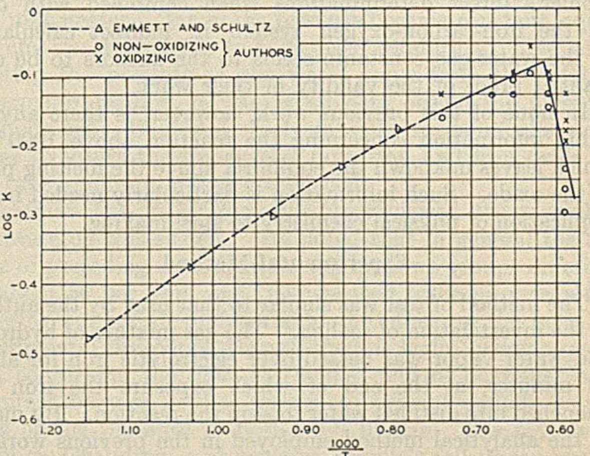

Figure 2—Equilibrium Constants of Iron-Oxygen-Hydrogen System at Temperatures up to 1427° C.

$$\frac{\Delta H}{RT^2} = \frac{d \ln K}{dT}$$

in which ΔH is the heat of reaction, *R* is the gas constant (1.998), *T* is absolute temperature, and *K* is the ratio $P_{H_2O}/$-

P_{H_2}. This calculation shows the heat of fusion to be +29,000 calories per gram-mol. Since the heat of fusion depends so greatly on the slopes of the two branches of the curve, and since even the melting point of ferrous oxide is not accurately known, the authors believe that the value of +29,000 is only approximately correct. The probable error in the curve below the melting point is estimated at 1.0 per cent, but above the melting point, because of the few temperatures used and experimental limitations, the error may be 2 or 3 per cent. In view of these errors and the possibility of drawing several curves through the points above the melting point of the oxide, it is found that there is a possible variation of ± 5000 calories.

Acknowledgment

The authors are indebted to the Committee on Industrial Gas Research of the American Gas Association, and to John Chipman, whose advice and coöperation were extremely helpful in the preparation and reviewing of this paper.

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Decomposition of Rotenone in Solution[1]

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THE use of rotenone, obtained from derris and cube roots, as an insecticide may soon be on a commercial basis. Various organic solvents will play an important part in its extraction from the root and in the application of the material as an insecticide. For this reason the question of the stability of rotenone in solution is of considerable commercial interest.

In the course of previous work on the solubility of rotenone *(3)*, it was noted that solutions made with many of the solvents changed from colorless to various shades of yellow on standing. This change, which occurred very rapidly in some solvents (e. g., pyridine) and very slowly in others (e. g., acetone, benzene), was accompanied by a change in optical rotation. A loss in toxicity of rotenone to both insects *(1)* and fish *(2)* was also found to occur in these solutions. For this reason a more thorough study of the changes involved has been made.

From experiments conducted principally with pyridine solutions, it was found that this decomposition of rotenone is accelerated by access of air, but apparently is unaffected by differences in amount of light or by the presence of water. When a pyridine solution was kept for several days in an atmosphere of nitrogen, no change in color occurred, whereas a similar solution in air darkened to an amber color within an hour. Yellow needle-like crystals form in pyridine solutions of rotenone after it has stood for several days, and similar yellow crystals have been obtained from acetone, amylene, dichloride, chloroform, diacetone alcohol, and ethyl formate. Crystals of the same general appearance had been previously reported by Tattersfield and Roach *(4)* as separating from boiling alcoholic solutions of rotenone. Chemical investigations by H. L. Haller of this division, to be reported in detail in the near future, have shown that the crystals obtained from pyridine solutions are mixtures of dehydrorotenone and rotenonone, both oxidation products of rotenone. From these considerations it appears certain that the change occurring in solution is an oxidation of the rotenone, forming various yellow products.

Dry rotenone shows no decomposition on standing over long periods of time. Thus a sample of pure rotenone prepared from derris root in July, 1929, and tested at that time for melting point, optical activity, and for toxicity against fish showed the same melting point, optical rotation, and piscacidal effect when again tested in October, 1930.

By noting the rate of change of color an idea of the comparative rates of decomposition in various solvents was obtained. Two per cent solutions (solution was not complete in the cases of alcohol, water, and kerosene) in various solvents, made at the same time, were allowed to stand in flasks capped with cheesecloth and shaken at intervals to insure access of air. Of these the pyridine solution was found to decompose most rapidly, becoming deep amber within a few days, and a solution made with 72–25 pyridine and water decomposed at the same rate. A solution in acetone containing tannic acid (used in making spraying suspensions) also decomposed very rapidly. Chloroform and ethylene dichloride solutions darkened slowly at first, but after a few days showed fairly rapid decomposition. Acetone, diacetone alcohol, and dichlorobenzene (technical mixture of ortho and para) solutions showed a comparatively slow decomposition. Of the solvents in which the rotenone was completely soluble, benzene gave the least decomposition. The mixture in alcohol showed only slight coloration at the end of one month, and the mixtures in water and in kerosene showed no coloration whatever after standing several months.

The decomposition varies also with the concentration of the solution, solutions of the lower concentrations, in pyridine, changing color more rapidly.

As has been mentioned, the change is accompanied by a change in optical rotation. Inasmuch as a number of different decomposition products having different optical rotations are formed, this phenomenon could not be used as an accurate measure of the decomposition. A 5 per cent solution in pyridine changes in specific rotation from about −109 degrees to −96 degrees in 1 week, to −77 degrees in 1 month, and to −66 degrees in 3 months. On the other hand, a 4 per cent solution of rotenone in acetone changed only from −106 degrees to −100 degrees in 4 months, indicating again that the change in acetone takes place very slowly.

[1] Received February 7, 1931.

Entomological tests (*1*) also indicate that the decomposition occurs very rapidly in pyridine, but less rapidly in acetone and other solvents.

Conclusions

It is therefore seen that care must be exercised in the making and keeping of solutions of rotenone. Benzene may prove particularly valuable as a solvent because of its high solvent power and the fact that with it no appreciable decomposition of rotenone occurs. When a water-soluble solvent is desired, acetone may be used.

Solutions of rotenone should be freshly made, but if solutions are required to stand over a long period of time they should be kept in air-tight containers.

Rotenone should be stored and shipped in the dry condition whenever possible, since dry rotenone undergoes no decomposition.

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Free Energy of Some Copper Compounds[1]

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The chief obstacles faced today by practical metallurgists, when called upon to solve their problems by the use of thermodynamics, are the lack of data from which to start and the difficulty of finding and appraising such data when they do exist. An examination of the available information, collected, sifted, and organized into a unified group by a competent authority, permits one to use what is set down therein with confidence.

The previous tables of free energy by Lewis and Randall were limited to a study of the non-metallic elements. This is the first extensive review consistent with those data of the equilibria of a metallic element. Most of the nineteen substances whose free energies are tabulated are important compounds in the metallurgy of copper. The equilibria deal especially with the high-temperature reactions of copper. The present values are consistent with the previously published free energies.

THE following review[2] of the equilibria in various reactions of copper compounds is presented, in the hope that it will greatly assist those who are interested in the metallurgy of copper. It has not been possible to include all the compounds of copper for which data are available. An effort has been made to present a partial table of free-energy values which are reasonably consistent among themselves and with those of Lewis and Randall (*42*). The agreement of the individual determinations and the accuracy of the equations which have been derived may be judged from the constancy of the values of the constant *I*, which we have given in all cases. The method of treatment will follow that of Lewis and Randall.

Elementary Copper

Standard Condition of Copper. Unstrained electrolytic copper crystals, produced by the method of Lewis (*40*) and of Lewis and Lacey (*41*) are taken as the standard condition of copper. We shall probably ultimately adopt the single crystal as the standard condition.

Heat Capacity and Entropy of Solid Copper. The specific-heat measurements of the various investigators indicate that only one form of solid copper exists. The older work on the specific heat of copper has been summarized by Harper (*25*), from which we have $C_{p273\cdot1} = 5.73$, and $C_{p298\cdot1} = 5.83$ calories per mol per degree. We have plotted these values and those of Nernst and Lindemann (*55*), Nernst (*54*), Keesom and Onnes (*34*), and Griffiths and Griffiths (*24*) against log T in the conventional way (*42*). The curve extends to such low values of C_p that the uncertainty (*34*) in extrapolation by means of the Debye temperature cube law is very small. Summing the areas, we find

$$\text{Cu(s)};\ S^\circ_{273\cdot1} = 7.30;\ S^\circ_{298\cdot1} = 7.815 \text{ calories per degree} \quad (1)$$

For the algebraic heat-capacity curve above 298.1° we mention the determinations of Umino (*93*), Klinkhardt (*35*), Wüst, Meuthen, and Durrer (*102*), Naccari (*53*), Schübel (*84*), Magnus (*47*), and Doerinckel and Werner (*13*). For comparison, their results were converted into heat content per gram atom above 273.1° and plotted against the temperature. It was at once apparent that the heat content corresponding to the solid at the melting point (1083° C.) was about 7260 calories for all the investigators except Umino, who gave 7720 calories. Fortunately both Umino (*93*) and White (*98*) determined the heat capacity of nickel. Umino (*93*) obtained 0.1294 and White (*98*) 0.134 for the mean specific heat of nickel between 0° and 1452° C., or White's result is 3.5 per cent higher than Umino's. Umino gives 70.4 and White 73 calories per gram for the heat of fusion of nickel, again 3.7 per cent lower. White has the reputation for exceedingly careful work and we are thus led to the conclusion that the heat capacity of copper is at least as high as that given by Umino and is perhaps a few per cent higher. Taking Umino's results we find:

$$\text{Cu(s)};\ C_p = 4.91 + 0.003\,22\,T - 0.000\,000\,54\,T^2 \quad (2)$$

Maier (*49*) recently used an equation based upon these same results which does not differ greatly from Equation 2, but the coefficient of our T^2 term is more convenient and the agreement near room temperatures is better with Equation 2 than with Maier's equation.

Liquid Copper. For the heat capacity of liquid copper we have only the measurements of Wüst, Meuthen, and Durrer (*102*), and of Umino (*93*). The former measurements 7.65 calories per degree for the mean heat capacity between 1083° and 1300° C. agree in magnitude with the latter but

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[2] The preliminary review was made in 1925 by Randall and Nielsen, whose results appear in the Free Energy Section, Vol. VII, International Critical Tables. The present publication includes supplemental work by Randall and West.

give an unreasonable temperature coefficient, while those of Umino give:

$$\text{Cu(l)};\ C_p = 7.75 \text{ calories per degree} \qquad (3)$$

We shall accept this latter result for, although we should expect the heat capacity to decrease slightly just above the melting point, there should be a small positive temperature coefficient at the higher temperatures. Umino's result, which gives a constant value between 1360° and 1780° K., is probably slightly low at the higher temperatures.

Cu(s) = Cu(l). For the heat of fusion Glaser (*22*) found ΔH = 2650 calories; Richards (*70*) found 2750 calories; Wüst, Meuthen, and Durrer (*102*) give 2610 calories, but their value should be 3240 calories owing to a typographical error; Umino's measurements (*93*) give 3210 calories, which we shall use. Honda and Ishigaki (*30*) studied the lowering of the freezing point in metallic systems and found about 2540 calories, but this value varies with the solute metal, and must be given little weight.

The melting point of copper is (*93a*) 1083° C. or (1356.1° K). From the above data we may therefore write

$$\text{Cu(s)} = \text{Cu(l)};\ \Delta F^\circ = 1871 - 2.84\,T \ln T + 0.001\,61\,T^2 - 0.000\,000\,09\,T^3 + 17.086\,T;\ \Delta H^\circ_{298\cdot 1} = 2580;\ \Delta S^\circ_{298\cdot 1} = 1.000;\ \Delta F^\circ_{298\cdot 1} = 2282 \qquad (4)$$

Gaseous Copper. Cu(l) = Cu(g). Von Wartenberg (*95*) measured the vapor density of a number of metals and found that most metallic vapors are monatomic. We may therefore assume copper vapor to be monatomic, take its heat capacity as constant, and write

$$\text{Cu(g)};\ C_p = 4.97 \text{ calories per mol} \qquad (5)$$

The critical temperature of copper vapor is very high. For copper vapor in the presence of no other vapor the saturated vapor is more perfect at lower temperatures than at high temperatures, especially above the boiling point. For the vapor in the presence of nitrogen or other gas at atmospheric pressure the vapor of copper is probably far from perfect.

For the entropy of copper vapor we have, from the Sackur equation (*78, 91, 43*)

$$\text{Cu(g)};\ S^\circ_{298\cdot 1} = 3/2\,R \ln 63.57 + 26.03 = 38.41 \text{ calories per degree} \qquad (6)$$

Entropy and Heat Capacity of Diatomic Gaseous Copper. Although we will assume that copper vapor exists principally as monatomic vapor, it is desirable to consider the properties of diatomic copper vapor. These following calculations are estimates based upon spectroscopic data for various substances (*44, 7, 31, 87*). We write[3]

$$\text{Cu}_2\text{(g)};\ S^\circ_{298\cdot 1} = 3/2\,R \ln \text{w} + 5/2\,R \ln T - R \ln P - 2.30 + R \ln 8\pi^2 I\,k\,T/h^2 - R \ln 2 + R + S_E = 40.48 + 15.98 + 1.42 = 58.88 \text{ calories per degree} \qquad (7)$$

where the sum of the first four terms represents the entropy of translation, of the fifth, sixth, and seventh, the entropy of rotation (*79, 91, 14*) of a symmetrical molecule (symmetry reduces the entropy of rotation by $R \ln 2$), and the last the entropy of vibration (*15, 16, 83*). In Equation 7 w is the molal weight, I the moment of inertia, k the Boltzmann constant (*7*), 1.372×10^{-16}, h is Planck's constant (*7*), 6.554×10^{-27}, and S_E is the entropy of vibration (*15, 16, 83*). The moment of inertia was estimated to be about 500×10^{-40} by assuming that the distance between the centers of the copper atoms was twice the difference between the distance for normal CuH gas and one-half that between the hydrogen atoms in normal hydrogen gas (*31*). The characteristic frequency in the Einstein function was estimated $\nu = 9 \times 10^{12}$, whence $\beta\nu/298.1 = h\nu/k\,298.1 = 1.442$, and S_E (single degree of freedom) = $^1/_3\,S_E$ for solids as given in the tables (*87*) = 1.42.

The value of $\beta\nu/T$ becomes unity at about 430° K., at which temperature the heat capacity of Cu_2(g) has almost reached (*31*) the limiting value of $9/2\,R$ or about 9 calories per degree. Thus at high temperature the heat capacity does not differ greatly from that of 2Cu(g).

Vapor Pressure of Liquid Copper. Cu(l) = Cu(g). The vapor pressure of liquid copper has been measured by Fery (*17*), Greenwood (*23*), Harteck (*26*), Jones, Langmuir, and Mackay (*33*), Ruff and Bergdahl (*74*), Ruff and Konschak (*75*), and Ruff and Mugden (*76*). The data are given in Table I.

Using the specific heat equations of the previous paragraphs, we may write

$$\text{Cu(l)} = \text{Cu(g)};\ \Delta F^\circ = \Delta H^\circ_0 + 2.78 \ln T + IT \qquad (8)$$

We may rearrange the general free-energy equation of Lewis and Randall,

$$\Delta F^\circ/T = -R \ln P = \Delta H^\circ_0/T + 2.78 \ln T + \text{I} \qquad (9)$$

and for convenience group the terms,

$$\Sigma = -R \ln P - 2.78 \ln T = \Delta H^\circ_0/T + I \qquad (10)$$

If Σ is plotted, as in Figure 1, against the reciprocal of the absolute temperature, we should be able to draw a straight line, the slope of which will be ΔH°_0. With the exception of the points of Fery (*17*), of Greenwood (*23*) at 2253° K., and of Jones, Langmuir, and Mackay (*33*), they seem to fall upon the line whose slope gives ΔH°_0 = 88,500 calories.

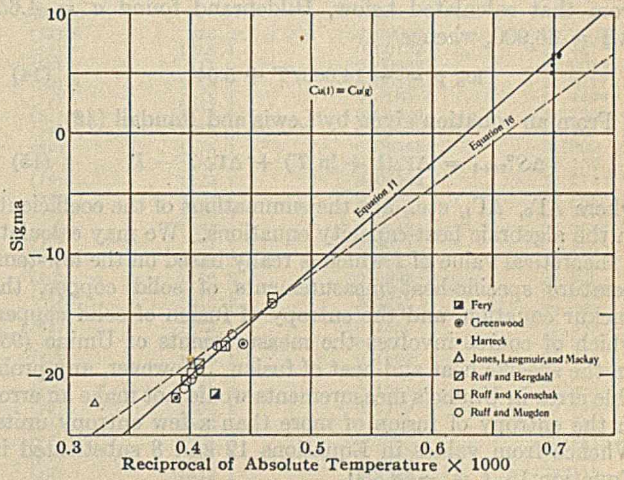

Figure 1—Sigma Plot for Cu (l) = Cu (g)

The values of I obtained by subtracting $\Delta H^\circ_0/T = 88{,}500/T$ from Σ are given in column 6. Omitting the three very divergent starred points, the average value of I is −55.531. Column 7 gives the deviation from the mean, omitting the starred values, the average deviation being ±0.304. From which we find

$$\text{Cu(l)} = \text{Cu(g)};\ \Delta F^\circ = 88{,}500 + 2.78\,T \ln T - 55.531\,T;\ \Delta H^\circ_{298\cdot 1} = 87{,}672;\ \Delta S^\circ_{298\cdot 1} = 36.912;\ \Delta F^\circ_{298\cdot 1} = 76{,}662 \qquad (11)$$

The average deviation of the value of I is only 0.304 entropy units. Considering the experiments as a whole, this would seem quite satisfactory. However, combining Equations 1, 4, and 6, we find

$$\text{Cu(l)} = \text{Cu(g)};\ \Delta S^\circ_{298\cdot 1} = 29.595 \text{ (prelim.)} \qquad (12)$$

There is a discrepancy of 7.317 entropy units between Equations 11 and 12. This difference could arise in a systematic

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[3] We wish to thank Prof. W. F. Giauque for suggestions in making this calculation.

Table I—Cu(l) = Cu(g)

Ref.	T, ° K.	log $P_{\text{atm.}}$	$1/T \times 10^4$	Σ	1 (Eq. 11)	Dev. from Mean	ΔH° (Eq. 16)	I (Eq. 19)
(26)	1419	−5.839	7.0472	6.5604	−55.807	−0.276	77,726	−88.723
(26)	1420	−5.816	7.0423	6.4521	−55.872	−0.341	77,628	−88.815
(26)	1421	−5.839	7.0373	6.5565	−55.723	−0.192	77,831	−88.636
(26)	1430	−5.839	6.9930	6.5392	−55.349	0.182	78,299	−88.241
(26)	1445	−5.780	6.9204	6.2395	−55.007	0.524	78,687	−87.874
(26)	1449	−5.669	6.9013	5.7200	−55.356	0.175	78,152	−88.208
(26)	1463	−5.538	6.8353	5.0976	−55.394	0.137	77,997	−88.223
(75)	2138	−1.677	4.6773	−13.6389	−55.033	0.498	73,924	−87.945
(76)	2148	−1.580	4.6555	−14.0954	−55.296	0.235	73,289	−88.203
(23)	2253	−0.881	4.4385	−17.4281	−56.709*	−1.178*	69,363*	−89.591
(76)	2301	−1.066	4.3459	−16.6402	−55.101	0.430	72,653	−87.974
(75)	2328	−0.856	4.2955	−17.6357	−55.651	−0.120	71,189	−88.519
(75)	2348	−0.868	4.2589	−17.6022	−55.351	0.180	71,879	−88.161
(76)	2368	−0.871	4.2230	−17.6131	−54.987	0.544	72,465	−87.831
(17)	2373	0.000	4.2123	−21.6060	−58.885*	−3.354*	63,143*	−91.748
(74)	2448	−0.561	4.0850	−19.1260	−55.278	0.253	71,210	−88.135
(23)	2453	−0.471	4.0766	−19.5415	−55.620	−0.089	70,336	−88.477
(74)	2488	−0.404	4.0193	−19.8898	−55.461	0.070	70,473	−88.317
(76)	2493	−0.296	4.0112	−20.3886	−55.888	−0.357	69,371	−88.745
(74)	2518	−0.274	3.9714	−20.5156	−55.663	−0.132	69,748	−88.521
(76)	2531	−0.136	3.9510	−21.1634	−56.129	−0.598	68,467	−88.986
(74)	2573	−0.0052	3.8865	−21.8069	−56.203	−0.672	67,948	−89.064
(23)	2583	0.000	3.8715	−21.8415	−56.105	−0.574	68,123	−88.967
(75)	2643	+0.0034	3.7836	−21.9211	−55.406	0.125	69,495	−88.276
(33)	3110	0.000	3.2154	−22.3581	−50.814*	4.717*	80,415*	−83.749

error or a trend in the vapor-pressure measurements, thus giving a value of ΔH which is too large. We may compare the value of ΔH (column 8) calculated on the basis of Equations 12 and 16 with the value to be expected on the basis of Hildebrand's formula (*28*) for the vapor pressure of copper.

$$\log p_{(\text{atm.})} = -3140\,a/T + 4.97 + \log a \qquad (13)$$

The equation of Hildebrand presupposes a constant value of ΔH (ΔC_p = 0). The single constant a, which is characteristic of each metal, and the constant 4.97 were determined by a consideration of the vapor-pressure curves of mercury, cadmium, zinc, lead, and thallium. For copper, using Greenwood's (*23*) value of the boiling point, which is not far from that calculated below, Hildebrand found a = 4.65, ΔH = 66,900, whence

$$\log p = -14{,}600/T + 5.64 \qquad (14)$$

From an equation given by Lewis and Randall (*42*),

$$\Delta S^\circ_{298\cdot 1} = \Delta\Gamma_0(1 + \ln T) + \Delta\Gamma_1\, T - I \qquad (15)$$

where ΔΓ₀, ΔΓ₁, etc., are the summations of the coefficients in the algebraic heat-capacity equations. We may calculate a theoretical value of I which is really based on the low-temperature specific-heat measurements of solid copper, the Sackur equation, and the entropy of fusion of solid copper, which of course involves the measurements of Umino (*93*) on the specific heat and heat of fusion. However, any probable error in Umino's measurements would not make an error in the entropy of fusion of more than a few entropy units. Whence from values in Equations 12 and 8 substituted in Equation 15, I = −48.380.

Now, using the values of Σ in Table I and I = −48.380, we may calculate a value of ΔH_0/T based upon each of the pressure measurements of Table I. Giving equal weight to all the experiments, we find an average value, ΔH_0 = 73,040. On the basis of the entropy calculation of I and the measured values of the pressure, we have the equation

$$\text{Cu(l)} = \text{Cu(g)};\ \Delta F^\circ = 73{,}040 + 2.78\,T \ln T - 48.215\,T;\ \Delta H^\circ_{298\cdot 1} = 72{,}211;\ \Delta S^\circ_{298\cdot 1} = 29.595;\ \Delta F^\circ_{298\cdot 1} = 63{,}386\ \text{(prelim.)} \qquad (16)$$

We may easily calculate the pressure corresponding to this equation by means of the above equation, which gives 2792° K. for the boiling point. The values of ΔH corresponding to Equation 16 are given as the dotted curve of Figure 1. Solving Equation 11 for ΔF° = 0, by the method of approximations we find for the boiling point of copper, 2632° K. Equation 14 gives 2588° K. as compared with 3110° K. as calculated by Jones, Langmuir, and Mackay (*33*).

Vapor Pressure of Solid Copper. Cu(s) = Cu(g). The vapor pressure of solid copper has been measured by Langmuir and Mackay (*38*), Mack, Osterhof, and Kraner (*46*), and by Rosenhain and Ewen (*72*). The last-mentioned investigators measured the rate of evaporation in a vacuum, but we have reduced their measurements by means of an equation given by Langmuir (*37*). The results are given in Table II, where the columns designate the same quantities as in Table I. The result at 1273° K. by Mack, Osterhof, and Kraner (*46*) is given as the vapor pressure of CuO(s), but seems to be rather that of Cu(s).

Table II—Cu(s) = Cu(g)

Ref.	T	log $p_{\text{atm.}}$	Σ	I (Eq. 17)	I (Eq. 20)
(46)	1083	−9.158	40.715	−42.723	−59.631
(46)	1273	−6.946	30.330	−40.661	−56.302
(38)	1186	−8.546	37.769	−38.429	−55.132
(38)	1298	−7.371	32.244	−37.379	−53.620
(72)	1288	−7.814	35.779	−34.385	−52.146
(72)	1288	−7.634	34.952	−35.212	−52.973
(72)	1288	−7.621	34.892	−35.272	−53.053
(72)	1288	−7.527	34.462	−35.702	−53.462

The values of Σ are plotted against $1/T$ in Figure 2. Curve 17 corresponds to Equation 17, which is the sum of Equations 4 and 11. Curve 18 corresponds to Equation 18, which is the sum of Equations 4 and 16.

$$\text{Cu(s)} = \text{Cu(g)};\ \Delta F^\circ = 90{,}371 - 0.06\,T \ln T + 0.001\,61\,T^2 - 0.000\,000\,09\,T^3 - 38.445\,T;\ \Delta H^\circ_{298\cdot 1} = 90{,}251;\ \Delta S^\circ_{298\cdot 1} = 37.912;\ \Delta F^\circ_{298\cdot 1} = 78{,}944 \qquad (17)$$

$$\text{Cu(s)} = \text{Cu(g)};\ \Delta F^\circ = 74{,}911 - 0.06\,T \ln T + 0.001\,61\,T^2 - 0.000\,000\,09\,T^3 - 31.129\,T;\ \Delta H^\circ_{298\cdot 1} = 74{,}791;\ \Delta S^\circ_{298\cdot 1} = 30.595;\ \Delta F^\circ_{298\cdot 1} = 65{,}668\ \text{(prelim.)} \qquad (18)$$

The two points of Langmuir and Mackay give Δ$H°_0$ = 75,945, which agrees very well with the value calculated from Equation 12, but their pressure is tenfold too large. It is not easy to account for these differences, for some unpublished calculations by Randall and others show that the entropies of vaporization of mercury, cadmium, zinc, and thallium are in excellent agreement with such calculations as were made in Equations 16 and 18. We prefer to use Equations 11 and 17 since, although the entropy is not properly accounted for, these equations will reproduce the average of the experimental measurements of the vapor pressure.

Evidence for Existence of Cu₂(g). We shall not give any detailed calculations, but we wish to point out that if the formula of copper vapor is Cu_2 rather than Cu, then we must reduce Harteck's calculated log P by ¹/₂ log 2. Recalculating the data of Table I, we find

$$2\text{Cu(l)} = \text{Cu}_2\text{(g)};\ \Delta F^\circ = 97{,}880 + 6.5\,T \ln T - 88.410\,T;\ \Delta H^\circ_{298\cdot 1} = 95{,}942;\ \Delta S^\circ_{298\cdot 1} = 44.874;\ \Delta F^\circ_{298\cdot 1} = 82{,}565 \qquad (19)$$

The individual values of I (Equation 19) are given in the last column of Table I. Combining Equations 1, 4, and 7, we calculate the entropy of vaporization of liquid copper to diatomic copper vapor to be 41.25 entropy units. The difference between this value and that of Equation 19 is only 3.63 entropy units, a better agreement than that obtained on the assumption of monatomic copper vapor.

Combining Equations 4 and 19, we find

$$2Cu(s) = Cu_2(g);\ \Delta F^\circ = 101{,}622 + 0.82\ T \ln T + 0.003\ 22\ T^2 - 0.000\ 000\ 18\ T^3 - 54.238\ T;\ \Delta H^\circ_{298\cdot1} = 101{,}102;\ \Delta S^\circ_{298\cdot1} = 46.874;\ \Delta F^\circ_{298\cdot1} = 87{,}129 \qquad (20)$$

We reduce log P found by Mack, Osterhof, and Kraner (*46*) by log 2 and by the others (*38, 72*) by $^1/_2$ log 2, whence we find the values of I (Equation 20) given in the last column of Table II. The value of I calculated from the entropy ($\Delta S^\circ_{298\cdot1}$ calcd. = 43.25) is −50.614. We see that the agreement is again better when we assume copper vapor to consist largely of Cu_2 molecules.

Copper Amalgam. The difference in potential between metallic copper and copper amalgam has been found by several investigators (*11, 60, 59, 57*) to vary from 0.0001 to 0.005 volt. We shall make no large error in provisionally assuming that the difference in free energy is negligible.

Oxides of Copper

$2CuO(s) = Cu_2O(s) + {^1/_2}O_2(g)$. The dissociation pressures of cupric oxide have been carefully studied by Smyth and Roberts (*89*) and Roberts and Smyth (*71*), who showed that up to the eutectic point, 1080.2° C., cupric oxide and cuprous oxide do not form solid solutions. They thus confirm the earlier results of Foote and Smith (*19*) and contradict the still earlier results of Wöhler and Foss (*101*), who claimed different dissociation pressures for different mixtures of cupric and cuprous oxides. Roberts and Smyth (*71*) found that false equilibria in these systems were common. The early measurements of Debray and Joannis (*12*) are also in fair agreement with the results of Foote and Smith (*19*) and Smyth and Roberts (*89*). Measurements by Moles and Payá (*52*) and Ruer and Nakamoto (*73*) are also given.

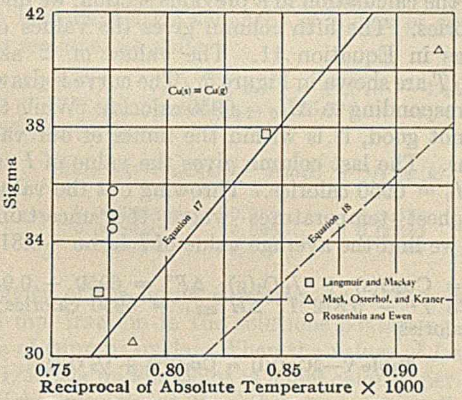

Figure 2—Sigma Plot for Cu(s) = Cu(g)

The heat capacity of cuprous oxide was studied by Magnus (*48*), who found the mean heat capacity to be 16.41 between 17° and 100° C. and 17.78 calories per degree between 18° and 541° C. Neuman (*49*) gives 15.3 for the heat capacity at 291° K., while Millar (*51*) has found accurate values at low temperatures. Maier (*49*) used the equation $Cu_2O(s)$; $C_p = 11.75 + 0.01\ T$ based upon Millar's low-temperature results and Magnus' measurements at higher temperatures, but his equation gives values at high temperature which are much too high. We prefer to use a linear equation passing through the mean of Magnus' points, and this equation again gives a slope which must be a little too large:

$$Cu_2O(s);\ C_p = 14.34 + 0.0062\ T \qquad (21)$$

The heat of formation of cuprous oxide is found by Thomsen (*92*) to be 40,810 at 291° K., from which we have the value $Cu_2O(s)$; $\Delta H^\circ_0 = -41{,}166$ calories as given in Equation 30.

The heat capacity of cupric oxide from the data of Magnus (*48*) is

$$CuO(s);\ C_p = 8.32 + 0.0071\ T \qquad (22)$$

Millar (*51*) also gives accurate values at low temperatures in essential agreement with those of Magnus at high temperatures.

The heat of formation of cupric oxide from Thomsen (*92*) is $\Delta H^\circ_{291} = 37{,}160$, whence we find $\Delta H^\circ_0 = -37{,}353$ calories as given in Equation 96.

For oxygen gas we have

$$O_2(g);\ C_p = 6.50 + 0.001\ T \qquad (23)$$

from Lewis and Randall (*42*).

The data are given in Table III. The value of ΔH°_0 found by plotting $\Sigma\ (-R \ln P^{1/2} + 0.95 \ln T - 0.00375\ T)$ against $1/T$ is 34,500 calories, in fair agreement with ΔH°_0 = 33,550 calories, calculated from Thomsen's data, which give 33,490 calories at room temperature. We have adopted the calorimetric value of ΔH°_0. In calculating the average value of I we have omitted the starred values. Whence,

$$2CuO(s) = Cu_2O(s) + {^1/_2}O_2(g);\ \Delta F^\circ = 33{,}550 - 0.95\ T \ln T + 0.00375\ T^2 - 22.340\ T;\ \Delta H^\circ_{298\cdot1} = 33{,}490 \text{ calories};\ \Delta F^\circ_{298\cdot1} = 25{,}610 \text{ calories} \qquad (24)$$

Table III—$2CuO(s) = Cu_2O(s) + {^1/_2}O_2(g)$

Ref.	T, ° K.	$p$atm.	I
(*52*) [a]	823.1	0.00026	−29.250*
(*52*) [a]	1058.1	0.00132	−22.467*
(*89*)	111.9	0.00608	−22.601*
(*52*) [a]	1118.1	0.00322	−21.821*
(*52*) [b]	1118.1	0.0165	−23.449*
(*52*) [a]	1173.1	0.01026	−21.731*
(*19*)	1173.1	0.02078	−22.432
(*89*)	1178.1	0.01963	−22.269
(*89*)	1188.7	0.02263	−22.180
(*19*)	1223.1	0.04932	−22.271
(*89*)	1229.2	0.0539	−22.245
(*52*) [a]	1233.1	0.0339	−21.727*
(*52*) [b]	1233.1	0.0643	−22.363*
(*12*)	1234.1	0.0671	−22.366
(*101*)	1234.1	0.0671	−22.366
(*89*)	1256.5	0.0922	−22.270
(*52*) [a]	1273.1	0.0875	−21.925*
(*19*)	1273.1	0.1303	−22.308
(*101*)	1273.1	0.1355	−22.345
(*89*)	1273.7	0.1272	−22.275
(*19*)	1283.1	0.1592	−22.334
(*89*)	1290.8	0.1782	−22.310
(*19*)	1293.1	0.1881	−22.326
(*19*)	1303.1	0.2250	−22.336
(*101*)	1303.1	0.2328	−22.367
(*73*)	1304.1	0.208	−22.241*
(*89*)	1311.9	0.2566	−22.321
(*19*)	1313.1	0.2683	−22.345
(*89*)	1316.2	0.2830	−22.345
(*19*)	1323.1	0.3144	−22.341
(*89*)	1332.2	0.3673	−22.349
(*101*)	1333.1	0.3813	−22.373
(*71*)	1344.4	0.4650	−22.393
(*71*)	1348.1	0.4905	−22.383
(*71*)	1349.8	0.5023	−22.388
(*71*)	1350.5	0.5093	−22.387
(*71*)	1351.0	0.5120	−22.385
(*71*)	1353.2	0.5300	−22.387
(*71*)	1353.3 [e]	0.5291	−22.383
(*71*)	1353.8 [m]	0.5347	−22.387
(*71*)	1354.6 [m]	0.5420	−22.387
(*71*)	1358.1 [m]	0.5721	−22.389
(*73*)	1378.1 [m]	1.00	−22.686*

[a] 40 per cent CuO, 60 per cent Cu_2O
[b] Pure(?) CuO
[e] Eutectic point
[m] Metastable

Temperature-Composition Diagram of Copper–Cuprous Oxide–Cupric Oxide System. The melting points of various mixtures of copper and cuprous oxide have been studied by Heyn (*27*), by Slade and Farrow (*88*), by Smyth and Roberts (*89*), by Roberts and Smyth (*71*), and Vogel and Pocher (*94*). Heyn (*27*) studied the copper–cuprous oxide eutectic and the compositions varying between 0 and 12 per cent cuprous oxide. Slade and Farrow (*88*) showed that two liquid phases were formed by mixtures of copper and cuprous oxide containing between 20 and 96 per cent of cuprous oxide above 1195° C., and Smyth and Roberts (*89*) studied the cupric oxide–cuprous oxide system. All these authors state that there is no evidence of solid solutions in these systems. The results for the copper–cuprous oxide system are shown in Figure 3 and those for the cuprous oxide–cupric oxide system in Figure 4. Figure 3 shows that the copper-rich phase in contact with a mixture of cuprous oxide and copper is a solid solution containing not more (*94*) than 0.9 mol per cent of Cu_2O. The dotted curve in Figure 4 shows the theoretical freezing point of cuprous oxide if its melting point is 1236° C. and the heat of fusion is 18,400 calories as determined in the following section. The flatness of the curve for compositions near pure cuprous oxide indicates that the cuprous oxide in the liquid phase is largely dissociated. If we assume Raoult's law and use average values of the melting points of mixtures containing solid cupric oxide (points on the curve, $N_2(CuO) = 0.652$ at 1200° C. and $N_2 = 0.436$ at 1186° C.), then the heat of fusion of cupric oxide is 13,300 calories. The projection of the average curve (broken curve) gives the melting point of cupric oxide as 1393° C., whereas the melting point calculated in a later section is 1336° C.

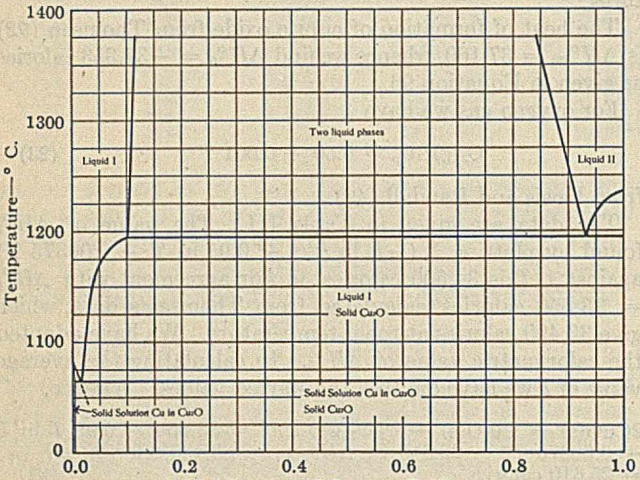

Figure 3—Phase Diagram of the System Copper–Cuprous Oxide

$2CuO(s) = Cu_2O(l) + {}^1/_2O_2(g)$. Smyth and Roberts (*89*) determined the pressure of oxygen over this system. Their pressures are shown in the second column of Table IV. The third column shows the activity of $Cu_2O(l)$ if we assume that its activity is proportional to its mol fraction. The mol fractions of cuprous oxide in the liquid at the various equilibrium pressures were read from the curve of Figure 4. The fourth column gives the value of $K\ [= N(Cu_2O).p^{1/2}\ (O_2)]$. In the absence of any data we shall assume that the specific heat of liquid cuprous oxide is the same as that of solid cuprous oxide, whence we write:

$2CuO(s) = Cu_2O(l) + {}^1/_2\,O_2(g);\ \Delta F° = 51{,}950 - 0.95\ T \ln T + 0.00375\ T^2 - 34.533\ T;\ \Delta H°_{298\cdot1} = 51{,}900$ calories; $\Delta F°_{298\cdot1} = 40{,}410$ calories (25)

The value of ΔH_0 (51,950) was found by plotting Σ against $1/T$ as in Equation 11. The average value of I as found in the usual way was -34.738, corresponding to $\Delta F°_{298\cdot1} = 40{,}345$ calories, but we have adopted the value $I = -34.533$, obtained by adding Equations 24 and 26, in order to obtain consistent results. The difference is due in part to erroneous assumptions respecting specific heats and to errors in taking the average slope in calculating ΔH_0 and in averaging the value of I.

Table IV—$2CuO(s) = Cu_2O(l) + {}^1/_2O_2(g)$

T	p	N	K	I
1356.9	0.592	0.533	0.410	−34.739
1361.8	0.674	0.524	0.430	−34.711
1365.7	0.791	0.520	0.463	−34.761
1369.5	0.883	0.515	0.484	−34.755
1370.3	0.950	0.513	0.504	−34.816
1378.1[a]	1.000	...	...	....
1378.8	1.235	0.502	0.557	−34.808
1392.1	1.655	0.482	0.620	−34.700
1403.1	2.257	0.465	0.698	−34.678
1408.9	2.657	0.456	0.744	−34.670
1444.1	8.82	0.400	1.188	−34.811
1477.5	21.18	0.341	1.567	−34.552
1483.7	31.80	0.330	1.862	−34.866
1505.6	58.85	0.282	2.163	−34.724

[a] Ruer and Nakamoto (*73*). The amount of liquid phase was probably very small.

$Cu_2O(s) = Cu_2O(l)$. The melting point of cuprous oxide was found to be 1236° C. by Smyth and Roberts (*89*). By subtracting Equations 24 and 25, we find $\Delta H_0 = 18{,}400$ calories. Whence,

$Cu_2O(s) = Cu_2O(l);\ \Delta F° = 18{,}400 - 12.193\ T;\ \Delta H°_{298\cdot1} = 18{,}400$ calories; $\Delta F°_{298\cdot1} = 14{,}760$ calories (26)

$2CuO(l) = Cu_2O(s) + {}^1/_2\,O_2\,(g)$. Roberts and Smyth (*71*) measured the vapor pressure in this system. Their pressures are given in the second column of Table V, the third showing the mol fraction of the cupric oxide at the temperatures shown in the first column and read from the curve in Figure 4. Assuming that the activity of the cupric oxide is equal to its mol fraction, we have the values of K equal to $p^{1/2}\,(O_2)/N^2(CuO)$ given in the fourth column. Assuming, as in the case of liquid cuprous oxide, that the specific heats of solid and liquid cupric oxide are identical, and assuming that the heat of fusion of cupric oxide is 13,300 calories, as given by the calculation in a previous section, we find $\Delta H_0 = 6950$ calories. The fifth column gives the values of Σ calculated as in Equation 11. The values of Σ as plotted against $1/T$ are shown in Figure 5. The curve is drawn with a slope corresponding to $\Delta H_0 = 6950$ calories. While the agreement is not good, it is within the limits of our various assumptions. The last column gives the value of I calculated using $\Delta H_0 = 6950$ calories. Throwing out the values at the three highest temperatures where the uncertainties are greatest, we find the average value of I to be -5.812, and

$2CuO(l) = Cu_2O(s) + {}^1/_2\,O_2(g);\ \Delta F° = 6950 - 0.95\ T \ln T + 0.00375\ T^2 - 5.812\ T;\ \Delta H°_{298\cdot1} = 6950$ calories; $\Delta F°_{298\cdot1} = 3938$ calories (27)

Table V—$2CuO(l) = Cu_2O(s) + {}^1/_2\ O_2(g)$

T	p	N	K	Σ	I
1357.3	0.4913	0.428	3.827	−0.897	−6.017
1358.4	0.4751	0.427	3.830	−0.901	−6.017
1358.6	0.517	0.427	3.833	−0.904	−6.019
1361.6	0.465	0.424	3.848	−0.919	−6.022
1363.2	0.5100	0.423	3.990	−0.997	−6.095
1365.0	0.414	0.421	3.628	−0.814	−5.906
1369.6	0.414	0.417	3.696	−0.864	−5.938
1373.4	0.3974	0.414	3.672	−0.863	−5.923
1382.3	0.3382	0.405	3.548	−0.822	−5.850
1396.1	0.2705	0.388	3.455	−0.812	−5.790
1404.4	0.289	0.376	3.802	−1.028	−5.976
1407.9	0.2067	0.370	3.322	−0.770	−5.706
1413.0	0.2205	0.362	3.548	−0.916	−5.835
1417.8	0.1672	0.354	3.262	−0.765	−5.667
1423.1	0.1520	0.346	3.259	−0.780	−5.664
1426.4	0.1172	0.340	2.960	−0.598	−5.470
1427.5	0.121	0.337	3.063	−0.670	−5.538
1448.2	0.0755	0.292	3.224	−0.837	−5.636
1458.5	0.0434	0.264	2.992	−0.717	−5.482
1470.0	0.0292	0.228	3.288	−0.943	−5.670
1473.9	0.0217	0.215	3.190	−0.894	−5.611
1484.8	0.0129	0.176	3.665	−1.204	−5.885
1494.9	0.00461	0.134	3.780	−1.296	−5.948
1503.2	0.00135	0.090	4.54	−1.687	−6.310
1504.4	0.00125	0.080	5.53	−2.084	−6.703
1506.9	0.00202	0.060	1.25	0.867	−3.745

$CuO(s) = CuO(l)$. Combining Equations 24 and 28, we find

$CuO(s) = CuO(l);\ \Delta F° = 13{,}300 - 8.264\ T;\ \Delta H°_{298\cdot1} = 13{,}300$ calories; $\Delta F°_{298\cdot1} = 10{,}836$ calories (28)

Calculating the point at which $\Delta F° = 0$, or the melting point, we find it to be 1609° K. or 1336° C., the value given in the preceding section. Although this calculation is subject to numerous errors, the result is quite reasonable.

$Cu_2O(s) = 2Cu(l) + {}^1/_2O_2(g)$. Roberts and Smyth (*71*) made three measurements of the pressure of oxygen over the system containing solid cuprous oxide and liquid copper. Their pressures are shown in the second column of Table VI, the third showing the mol fraction of the copper as read from the curve of Figure 3. The fourth column gives the value of $K[= N^2(Cu).p^{1/2}(O_2)]$. Taking the heat of formation of cuprous oxide from Thomsen as $\Delta H_{291} = 40{,}810$ calories and the heat capacities and heat of fusion of copper from previous sections, we write

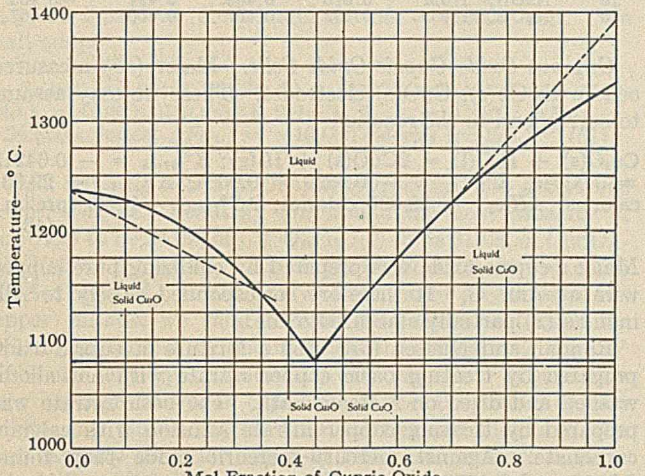

Figure 4—Phase Diagram of the System Cuprous Oxide–Cupric Oxide

$Cu_2O(s) = 2Cu(l) + {}^1/_2O_2(g)$; $\Delta F° = 44{,}618 - 4.41\,T\ln T - 0.002\,85\,T + 6.422\,T$; $\Delta H°_{298.1} = 45{,}970$ calories; $\Delta F°_{298.1} = 39{,}576$ calories (prelim.) (29)

Table VI—$Cu_2O(s) = 2Cu(l) + {}^1/_2O_2(g)$

T	*p*	N	*K*	*I*
1392.3	0.0000368	0.975	0.00577	10.502
1423.5	0.0000460	0.965	0.00632	11.089
1457.7	0.0000540	0.953	0.00666	11.832

The activity of the liquid copper is probably a little larger than its mol fraction in the solutions containing the larger amounts of cuprous oxide. When the values of *I* are plotted against $1/T$, the middle point is 0.009 calories per degree off the straight line joining the other two points, the slope of which gives $\Delta H° = 3650$ calories less than the calorimetric value. Adopting the calorimetric value and taking the average value of *I* as 11.141, we have the equations given above. The discrepancy in the calorimetric and calculated value of $\Delta H°$ throws considerable doubt on the accuracy of the assumptions made in the above calculations.

$Cu_2O(s) = 2Cu(s) + {}^1/_2O_2(g)$. Adding Equations 4 and 29, we have

$Cu_2O(s) = 2Cu(s) + {}^1/_2O_2(g)$; $\Delta F° = 41{,}166 + 1.27\,T\ln T - 0.00037\,T^2 + 0.000\,000\,18\,T^3 - 27.750\,T$; $\Delta H°_{298.1} = 40{,}810$ calories; $\Delta F°_{298.1} = 35{,}012$ calories (prelim.) (30)

In Equation 30 we have used the heat capacities of solid copper and cuprous oxide and the heat of formation of cuprous oxide from the preceding sections, in order to insure greater accuracy in the terms.

$Cu_2O(s) + H_2(g) = 2Cu(s) + H_2O(g)$. The reduction of cuprous oxide by hydrogen was studied by Wöhler and Balz (*100*) and by Maier (*49*).

The values of their equilibrium constants and the values of *I* calculated from Equation 31 are given in Table VII.

Table VII—$Cu_2O(s) + H_2(g) = 2Cu(s) + H_2O(g)$

Ref.	*T*	log *K*	*I*	Mean *I*
(*100*)	723.2	1.223	1.419	....
(*100*)	723.2	1.279	1.162	1.291
(*49*)	1173	4.70	−24.752	....
(*49*)	1223	4.54	−24.741	....
(*49*)	1273	4.40	−24.771	....
(*49*)	1323	4.27	−24.806	−24.768

The two series of measurements are in entire disagreement. The measurements of Maier (*49*) give $\Delta H°_0 = -15{,}720$ calories, which is in fair agreement with the value calculated from thermal data or −16,260.

$Cu_2O(s) + H_2(g) = 2Cu(s) + H_2O(g)$; $\Delta F° = -16{,}260 + 2.21\,T\ln T + 0.001\,28\,T + 0.000\,000\,38\,T^3 - 24.768\,T$ (Maier); $\Delta H°_{298.1} = -17{,}023$; $\Delta F°_{298.1} = -21{,}610$ (Maier) $= -12{,}011$ (Wöhler and Balz) (prelim.) (31)

The value of Maier (*49*) leads to −32,897 and of Wöhler and Balz (*100*) to −42,496 for the free energy of formation of cuprous oxide. Our accepted value is −35,000 which indicates that the preliminary measurements of Maier (*49*) are the more accurate.

$2CuO(s) + H_2(g) = Cu_2O(s) + H_2O(g)$. Wöhler and Balz (*100*) found log $K = 1.420$ and 1.492 at 723.2° K. These values give $I = 23.060$ and 22.731, mean 22.896, when substituted in Equation 32.

$2CuO(s) + H_2(g) = Cu_2O(s) + H_2O(g)$; $\Delta F° = -24{,}000 - 0.01\,T\ln T + 0.0054\,T^2 - 0.000\,000\,37\,T^3 + 22.896$; $\Delta H°_{298.1} = -23{,}543$; $\Delta F°_{298.1} = -16{,}720$ (prelim.) (32)

Combined with the accepted free energies of cuprous oxide and water vapor, this value leads to −36,388 calories for the free energy of formation of cupric oxide as against the accepted value of −30,300 calories.

Copper–Cuprous Oxide Cells. Maier (*50*) measured the cell

$Cu(s), Cu_2O(s), Ba(OH)_2\ (aq.), HgO(s), Hg(l)$ (33)

using cuprous oxide prepared by the dissociation in silica of a specially prepared pure cupric oxide, and a platinum spiral electrode upon which was plated electrolytically a dense, coherent, and non-crystalline copper deposit. He gives as the mean of five cells [$Ba(OH)_2$, 0.0426–0.2130*M*] at 24.83°, E = 0.45210 ± 0.00050 volt. The authors prefer

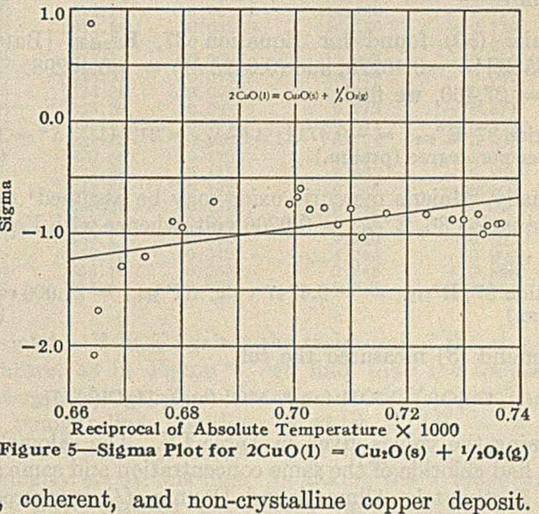

Figure 5—Sigma Plot for $2CuO(l) = Cu_2O(s) + {}^1/_2O_2(g)$

$2Cu(s) + HgO(s) = Cu_2O(s) + Hg(l)$; $E°_{298.1} = 0.4519$; $\Delta F°_{298.1} = -20{,}854$ (prelim.) (34)

Randall and Nielsen (*67*, *56*) in some preliminary experiments used finely divided copper prepared by electrolysis from aqueous copper sulfate, as recommended by Lewis (*40*) and by Lewis and Lacey (*41*).

Different samples of copper prepared at different current densities gave the same potentials with copper sulfate as electrolyte. They prepared cuprous oxide by the reduction of Fehling's solution with glucose. The oxide was washed and dried on a steam bath. With concentrated barium hydroxide the potential of two cells, Equations 33 and 34, was 0.5097 and 0.5098 volt. With 0.5 *M* potassium hydroxide as electrolyte the potential was 0.4788 and 0.4789 volt. With fifth molal potassium hydroxide the potential was 0.5028 volt.

Ishakawa and Kimura (*32*) used copper prepared by reducing powdered copper oxide with hydrogen. Their cuprous oxide was prepared by reducing a warm Fehling's solution with cane or grape sugar. After washing, it was dried over calcium chloride in a vacuum desiccator. The water used was boiled and cooled in a current of hydrogen. With 1.027 *N* sodium hydroxide and red mercuric oxide prepared by carefully heating mercurous or mercuric nitrate, they found the mean values (eight cells) given in the second column of Table VIII.

Cell of Equation 33; $\mathrm{E} = 0.4617 + 0.000\,144\,(t - 25) + 0.000\,000\,14\,(t - 25)^2$ (35)

Ishakawa and Kimura (*32*) standardized their mercuric oxide by measuring the cell

$\mathrm{H_2(g) + HgO(s) = Hg(l) + H_2O(l)};\ \mathrm{E}° = 0.92565 - 0.000\,2948\,(t - 25) + 0.000\,000\,4991\,(t - 25)^2$ (36)

as given in the third column of Table VIII.

Table VIII—Potential of Some Cells (*32*)

t	Eq. 35	Eq. 36	Eq. 37
0	0.4582	0.93332	−0.47510
15	0.4602	0.92870	−0.46850
25	0.4617	0.92565	−0.46395
35	0.4632	0.92275	−0.45955
45	0.4646	0.91995	−0.45544

Subtracting Equation 35 from Equation 36, we find the values given in the fourth column of Table VIII.

$\mathrm{2Cu(s) + H_2O(l) = Cu_2O(s) + H_2(g)};\ \mathrm{E}° = -0.463\,95 + 0.000\,4388\,(t - 25) - 0.000\,000\,3591\,(t - 25)^2;\ \Delta F°_{298\cdot1} = 21{,}410;\ \Delta S°_{298\cdot1} = 20.25$ calories per degree; $\Delta H°_{298\cdot1} = 27{,}447$ (prelim.) (37)

Maier (*50*) found for Equation 37, $\mathrm{E}°_{318\cdot02}$ [$\mathrm{Ba(OH)_2}$, 0.1065 *M*] = −0.46270, and (0.0426 *M*) = −0.46298. Using $\Delta H = 27{,}460$, we find

Reaction 37; $\mathrm{E}°_{298\cdot1} = -0.4711;\ \Delta F°_{298\cdot1} = 21{,}741;\ \Delta S° = 19{,}184$ calories per degree (prelim.) (38)

Finally, Maier's mercuric oxide may be assumed[4] to give for Equation 36, $\mathrm{E}°_{298\cdot1} = 0.9266$ volt, whence with Equation 34,

Reaction 37; $\mathrm{E}°_{298\cdot1} = -0.4747$ volt; $\Delta F°_{298\cdot1} = 21{,}906$ calories (prelim.) (39)

Allmand (*3*) measured the cell

Cu(s), $\mathrm{Cu_2O}$(s), MOH (aq.), MCl (aq.), HgCl(s), Hg (40)

obtaining the values given in Table IX. The calomel electrode had chloride of the same concentration and same metal ion. Fortunately Allmand and Donnan (*4*) measured the cell

Hg(l), HgO(s), MOH (aq.), MCl (aq.), HgCl(s), Hg(l) (41)

with the same concentration of electrolytes. Combining the values of cells 40 and 41, we obtain the values corresponding to Equation 33, which corrected to 298.1 gives the values in column 5 (mean, 0.457 volt or −21,090 calories). Finally, by combination with $\mathrm{E}°_{298\cdot1} = 0.9266$ volt, we obtain the values of Equation 42.

Reaction 37; $\mathrm{E}°_{298\cdot1} = -0.470;\ \Delta F°_{298\cdot1} = 21{,}671$ (42)

Table IX—Some Copper–Cuprous Oxide Cells (Allmand)

t	Electrolyte	E(40)	E(33)$_t$	E(33)$_{298.1}$	E(37)
17	NaOH, 0.1*M*	0.598	0.452	0.453	−0.474
17	NaOH, 0.1*M*	0.601	0.455	0.456	−0.471
17	(2)KOH, 0.1*M*	0.605	0.451	0.452	−0.475
17	NaOH, 1.0*M*	0.604	0.456	0.457	−0.470
17	NaOH, 1.0*M*	0.606	0.458	0.459	−0.468
17	KOH, 1.0*M*	0.613	0.457	0.458	−0.469
16	NaOH, 1.0*M*	0.610	0.463	0.464	−0.463
0	NaOH, 1.0*M*	0.592	0.457	0.460	−0.467

Cuprous Oxide–Cupric Oxide Cells. Maier (*50*) measured cells with Cu(s), CuO(s) electrodes. These we may assume to correspond to the reaction

$\mathrm{Cu_2O(s) + H_2O(l) = 2CuO(s) + H_2(g)};\ \mathrm{E}°_{297\cdot98} = -0.64213 \pm 0.00046;\ \mathrm{E}°_{318\cdot02} = -0.6369 \pm 0.0004;\ \Delta F°_{298\cdot1} = 29{,}631$ calories; $\Delta H_{298\cdot1} = 29{,}995$ calories; $\Delta S°_{298\cdot1} = 1.222$ (prelim.) (43)

Maier's cupric oxide was prepared by oxidizing pure copper wire at 700° C. It therefore corresponded closely to Allmand's (*2*) partially stabilized oxide.

Randall and Nielsen (*67*) used a mixture of cupric oxide prepared by treating basic copper nitrate with hot alkali, washed and dried on a steam bath. The basic nitrate was prepared by treating copper nitrate solution with calcium carbonate. Against mercury–mercuric oxide they found 0.2530 and 0.2272 volt in preliminary experiments, but the last cell was unstable. For Reaction 43 their values are −0.6730 and −0.6994 volt, respectively.

Allmand (*2*) measured various stable cupric hydroxides against calomel. Combined with Allmand and Donnan's (*4*) mercuric oxide–calomel cells they give **E** = 0.181 to 0.189 volt at 17° C., or

$\mathrm{Cu_2O(s) + 2H_2O(l) = Cu(OH)_2(s) + H_2(g)};\ \Delta F°_{290} = 34{,}344$ (approx.) (44)

Entropy of Cuprous and Cupric Oxides. Millar (*51*) measured the heat capacity of the oxides from the temperature of liquid air to room temperature. He gives

$\mathrm{Cu_2O(s)};\ S°_{298\cdot1} = 21.7 \pm 1.0$ calorie per degree (45)

$\mathrm{CuO(s)};\ S°_{298\cdot1} = 9.75 \pm 0.05$ calorie per degree (46)

$\mathrm{O_2(g)};\ S°_{298\cdot1} = 49.03$ (*21*) (47)

Combined with Equation 1 and our adopted heats of formation, we have

$\mathrm{Cu_2O(s)};\ \Delta S°_{298\cdot1} = -18.445$ calories per degree; $\Delta H_{298\cdot1} = -40{,}810;\ \Delta F°_{298\cdot1} = -35{,}312$ (prelim.) (48)

$\mathrm{CuO(s)};\ \Delta S°_{298\cdot1} = -22.580$ calories per degree, $\Delta H_{298\cdot1} = -37{,}150;\ \Delta F°_{298\cdot1} = -30{,}419$ (prelim.) (49)

$\mathrm{Cu_2O(s)} + {}^1/_2\,\mathrm{O_2(g) = 2CuO(s)};\ \Delta S°_{298\cdot1} = -26.715$ calories per degree; $\Delta H_{298\cdot1} = -33{,}490;\ \Delta F°_{298\cdot1} = -25{,}526$ (prelim.) (50)

We will postpone a choice of final values for the oxides until we have discussed the sulfates and sulfides.

Copper Sulfate

Cu (in satd. amalg.) + $\mathrm{Hg_2SO_4(s) + 5H_2O}$ *(in satd.* $\mathrm{CuSO_4.5H_2O}$ *soln.) =* $\mathrm{CuSO_4.5H_2O(s) + 2Hg(l)}$. Cohen, Chattaway, and Tombrock (*11*) measured this cell with amalgams containing 1, 2, 4, 8, and 16 per cent of copper, and obtained 0.3472 volt as the average electromotive force of all cells containing more than 2 per cent of copper in the amalgams. The cell with 1 per cent amalgam gave an electromotive force of 0.3474 volt. This cell was later studied more carefully

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[4] Ishakawa and Kimura (*32*) found different potentials for different samples of mercuric oxide. Buehrer (*9*), and Randall and Frandsen (*66*), give E° = 0.9266 for both yellow and red mercuric oxide in Reaction 36. Maier (*50*) used the technic of this laboratory.

by Öholm (*60*) and by Obata (*59*). Öholm, using a two-phase amalgam containing 12 per cent of copper, found the electromotive force of the copper standard cell, which corresponds to this reaction, to be 0.3500 volt at 20° C. or 0.3467 volt at 25° C., as the mean of five closely agreeing cells. From the mean temperature coefficient of two cells Öholm found $\Delta H = -24{,}860$ calories. In a similar cell Obata found $\mathbf{E} = 0.34979$ volt at 20° C. and $\mathbf{E}_t = \mathbf{E}_{20} - 0.000635\ (t - 20) - 0.0000024\ (t - 20)^2$, or $\mathbf{E}_{298\cdot1} = 0.3466$ volt. From the temperature coefficient Obata finds $\Delta H = -24{,}710$ calories. Nielsen and Brown (*57*) also found $\mathbf{E}_{298\cdot1} = 0.3467 \pm 0.0001$ and 0.3468 ± 0.0001 volt. We shall adopt

Cu (in het. amalg.) + Hg_2SO_4(s) + $5H_2O$ (in satd. $CuSO_4 = .5H_2O$ soln.) = $CuSO_4.5H_2O$(s) + 2Hg(l); $E_{298\cdot1} = 0.3467$; $\Delta H_{298\cdot1} = -24{,}860$ calories; $\Delta F_{298\cdot1} = -16{,}000$ calories (prelim.) (51)

Heat Capacity and Heat Content of Hydrated and Anhydrous Copper Sulfate. Schottky (*82*) found the heat capacity of $CuSO_4$(s) to be 24.09, of $CuSO_4.H_2O$(s) to be 31.08, of $CuSO_4.3H_2O$(s) to be 48.88, and of $CuSO_4.5H_2O$(s) to be 67.15 calories per mol. In the study of the vapor pressures of the copper sulfates we shall assume that their heat capacity will change in such a manner that the terms in T and T^2 of the ordinary equation for ΔC_p will disappear. The difference between the heat capacity of the anhydrous copper sulfate and $CuSO_4.H_2O$ is 6.99 calories per mol, and the heat capacity of water vapor at room temperature is 8.43. We shall arbitrarily assume $\Delta\Gamma_0 = 1.5$ calories per mol. The difference in heat capacity of $CuSO_4.H_2O$ and $CuSO_4.3H_2O$ is 17.80, and of $CuSO_4.3H_2O$ and $CuSO_4.5H_2O$ is 18.27. The heat capacity of 2 mols of gaseous water is 16.86, and we shall assume in both these cases $\Delta\Gamma_0 = 0$.

Thomsen found the difference between the heat of solution of anhydrous copper sulfate and copper sulfate monohydrate in the same large volume of water to be 6470 calories. Schottky (*82*) found this difference at 18° C. to be 6600 calories, and Siggel (*86*) found as a mean of two closely agreeing experiments, 6590 calories. We shall take the latter value and write

$CuSO_4.H_2O$(s) = $CuSO_4$(s) + H_2O (in dilute $CuSO_4$); $\Delta H_{298\cdot1}$ = 6590 calories (52)

We may take the heat content of the water in a dilute copper sulfate solution as nearly equal to that of pure water, and $H_2O(l) = H_2O(g)$; $\Delta H^\circ_{298\cdot1} = 10{,}450$ calories (*42*). Using the above value of $\Delta\Gamma_0$, we find

$CuSO_4.H_2O$(s) = $CuSO_4$(s) + H_2O(g); $\Delta H^\circ_0 = 16{,}590$ calories (53)

In a later section we shall find, by an indirect method, $\Delta H^\circ_0 = 16{,}550$ calories. We shall use the calorimetric value.

Thomsen found the difference between the heat of solution of copper sulfate monohydrate and of copper sulfate trihydrate to be 6520 calories, and between copper sulfate trihydrate and pentahydrate to be 5560 calories, or, adding, between copper sulfate monohydrate and copper sulfate pentahydrate, 11,080 calories. Making the same assumptions as above as to the heat content of liquid water, we may write

$CuSO_4.3H_2O$(s) = $CuSO_4.H_2O$(s) + $2H_2O$(g); $\Delta H^\circ_{298\cdot1} = 27{,}420$ calories (54)

and

$CuSO_4.5H_2O$(s) = $CuSO_4.3H_2O$(s) + $2H_2O$(g); $\Delta H^\circ_{298\cdot1}$ = 26,460 calories (prelim.) (55)

By indirect methods in later sections we shall find for these two values ($\Delta\Gamma_0 = 0$ in both cases), $\Delta H^\circ = 26{,}530$ and 26,550 calories, respectively. We shall adopt the calorimetric value, $\Delta H^\circ_0 = 27{,}420$ calories, for the dissociation of Equation 54 and the indirect value, $\Delta H^\circ_0 = 26{,}550$ calories, for the dissociation of Equation 55.

$CuSO_4.5H_2O$(s) = $CuSO_4.3H_2O$(s) + $2H_2O$(g). The equilibrium pressures of water vapor over a mixture of copper sulfate pentahydrate and copper sulfate trihydrate have been carefully determined by Lescoeur (*39*) and by Carpenter and Jette (*10*), who used a tensimeter, by Frowein (*20*), by Hollmann (*29*), and by Wilson (*99*), who compared the vapor pressure with that of sulfuric acid, by Noyes and Westbrook (*58*) and by Foote and Scholes (*18*), who brought the two solids into equilibrium with aqueous alcohol, by Linebarger (*45*), who brought the two solids into equilibrium with an aqueous solution of ether, by Partington (*61*), by Partington and Huntingford (*62*), and by Schumb (*85*), who used the air-stream method. The results of all these investigators are summarized in Table X. The values of I were calculated by assuming $\Delta H_0 = 26{,}550$ calories. We have not made a correction for the fact that the activity of the water vapor is slightly greater than the pressure, but the error is small and will affect the value of ΔH more than the value of ΔF°.

Table X—$CuSO_4.5H_2O$(s) = $CuSO_4.3H_2O$(s) + $2H_2O$(g)

Ref.	T	p	$-R \ln K$	I
(*39*)	283.1	0.00368	22.302	−71.515*
(*20*)	287.05	0.003933	22.026	−70.466*
(*29*)	293.1	0.00763	19.391	−71.192*
(*20*)	293.56	0.00666	19.932	−70.513*
(*85*)	298.1	0.01023	18.224	−70.841†
(*10*)	298.1	0.01026	18.213	−70.852†
(*58*)	298.1	0.01026	18.213	−70.852†
(*99*)	298.1	0.01026	18.213	−70.852†
(*62*)	298.1	0.01042	18.151	−70.914
(*18*)	298.1	0.00921	18.642	−70.423*
(*20*)	299.40	0.01062	18.076	−70.601
(*62*)	303.1	0.01545	16.585	−71.009
(*39*)	303.1	0.01645	17.723	−69.900*
(*10*)	303.27	0.01527	16.631	−70.912
(*20*)	303.30	0.01435	16.878	−70.660
(*45*)	307.3	0.01987	15.584	−70.812
(*20*)	307.83	0.02015	15.528	−70.722
(*62*)	308.1	0.02237	15.113	−71.299*
(*10*)	308.23	0.02172	15.230	−70.906
(*10*)	309.75	0.02433	14.779	−70.935
(*20*)	312.65	0.02823	14.188	−70.732
(*20*)	312.80	0.02858	14.139	−70.739
(*10*)	313.22	0.03052	13.877	−70.887
(*39*)	318.1	0.0395	12.837	−70.655
(*10*)	318.17	0.04317	12.498	−70.949
(*10*)	323.26	0.05971	11.208	−70.951
(*10*)	328.39	0.08133	9.979	−70.871
(*39*)	333.1	0.0948	9.371	−70.359*
(*10*)	333.28	0.1102	8.771	−70.892
(*10*)	333.56	0.1126	8.685	−70.912
(*10*)	338.26	0.1482	7.593	−70.897
(*10*)	342.88	0.1939	6.524	−70.909
(*10*)	343.26	0.1978	6.445	−70.900
(*39*)	351.1	0.308	4.679	−70.962
(*39*)	353.1	0.346	4.220	−70.993
(*10*)	353.23	0.3422	4.265	−70.901
(*10*)	363.14	0.5690	2.245	−70.868
(*39*)	373.1	0.878	0.517	−70.664

If we plot $-\mathrm{R} \ln K$ against the reciprocal of the absolute temperature, as in Figure 6, we find that the values of Carpenter and Jette (*10*) are the only ones that do not deviate from a straight line, the slope of which is $\Delta H_0 = 26{,}550$ calories. The points of Lescoeur and the other investigators lie irregularly about this line. In taking the average value of I, we have omitted the starred values, which are obviously largely divergent, and we have given triple weight to the closely agreeing values at 25° C. which are marked with †. We shall adopt the average value, −70.876, and write:

$CuSO_4.5H_2O$(s) = $CuSO_4.3H_2O$(s) + $2H_2O$(g); $\Delta F^\circ = 26{,}550 - 70.876\ T$; $\Delta H^\circ_{298\cdot1} = 26{,}550$ calories; $\Delta F^\circ_{298\cdot1} = 5420$ calories (56)

$CuSO_4.3H_2O$(s) = $CuSO_4.H_2O$(s) + $2H_2O$(g). The vapor pressures in the system containing both the mono- and tri-

hydrates were determined by Lescoeur (*39*), Carpenter and Jette (*10*), and Frowein (*20*), by the methods given in the preceding section. The data are given in Table XI.

Table XI—$CuSO_4.3H_2O(s) = CuSO_4.H_2O(s) + 2H_2O(g)$

Ref.	T	p	I	Ref.	T	p	I
(*20*)	298.1	0.006184	−71.741	(*39*)	333.1	0.0592	−71.11
(*10*)	298.1	0.007368	−72.438	(*10*)	338.22	0.10224	−72.014
(*39*)	303.1	0.00658	−70.51	(*39*)	351.1	0.1908	−71.53
(*10*)	308.23	0.015526	−72.285	(*39*)	353.1	0.2210	−71.67
(*39*)	318.1	0.01644	−69.89	(*10*)	353.16	0.2412	−71.970
(*10*)	318.27	0.02908	−72.358	(*39*)	373.1	0.691	−72.04
(*10*)	323.33	0.04066	−72.074				

Since the difference in the specific heat of the tri- and monohydrate is almost exactly that of 2 molecules of gaseous water, we shall call $\Delta\Gamma$ zero and write

$CuSO_4.3H_2O(s) = CuSO_4.H_2O(s) + 2H_2O(g)$; $\Delta F^\circ = 27{,}420 - 72.190\,T$; $\Delta H^\circ_{298\cdot1} = 27{,}420$ calories; $\Delta F^\circ_{298\cdot1} = 5900$ calories (57)

where $\Delta H^\circ_{298\cdot1}$ ($= \Delta H^\circ_0$) is the calorimetric value. Lescoeur's (*39*) values give $\Delta H^\circ = 30{,}000$ calories and the values of Carpenter and Jette (*10*) give $\Delta H^\circ = 25{,}530$ calories. Since the values of Carpenter and Jette for the tri-pentahydrate system are extraordinarily concordant, we shall use their values in calculating I. Whence we find $I = -72.190$.

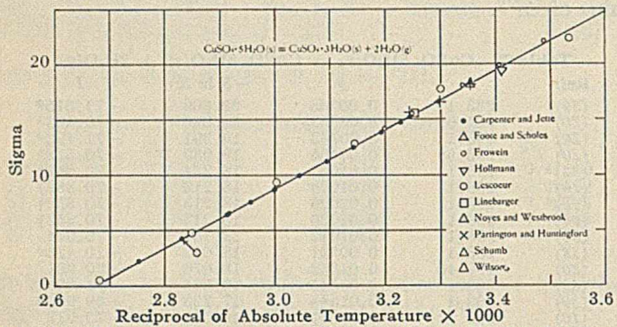

Figure 6—Sigma Plot for $CuSO_4\cdot5H_2O(s) = CuSO\cdot3H_2O(s) + 2H_2O(g)$

$CuSO_4.H_2O(s) = CuSO_4(s) + H_2O(g)$. The vapor pressures in this system have been determined by Lescoeur (*39*), Siggel (*86*), and Schottky (*82*), all of whom used tensimeters, and by Foote and Scholes (*18*), who brought the two solids into equilibrium with aqueous alcohol. Their results are shown in Table XII. Adopting the calorimetric values of a previous section, we shall take $\Delta H_0 = 16{,}590$ calories and $\Delta\Gamma_0 = 1.5$. The results of Lescoeur (*39*) and of Foote and Scholes (*18*) are in entire disagreement with those of Siggel (*86*) and Schottky (*82*). We shall, however, use only the values of Siggel in calculating I, since the value of ΔH°_0 calculated from Siggel's results is in good agreement with the calorimetric value. Whence

$CuSO_4.H_2O(s) = CuSO_4(s) + H_2O(g)$; $\Delta F^\circ = 16{,}590 - 1.5\,T \ln T - 26.126\,T$; $\Delta H^\circ_{298\cdot1} = 17{,}040$ calories; $\Delta F^\circ_{298\cdot1} = 6255$ calories (58)

Table XII—$CuSO_4.H_2O(s) = CuSO_4(s) + H_2O(g)$

Ref.	T	p	I	Ref.	T	p	I
(*18*)	298.1	0.00105	−33.468	(*86*)	420.4	0.1190	−26.168
(*82*)	351.1	0.00329	−27.091	(*39*)	436.1	0.0145	−20.503
(*86*)	372.1	0.0079	−26.081	(*39*)	459.6	0.0578	−21.234
(*86*)	383.3	0.0158	−26.112	(*39*)	479.1	0.188	−22.048
(*86*)	403.9	0.0503	−26.128	(*39*)	493.1	0.876	−24.081
(*86*)	410.2	0.0704	−26.142				

$3Cu(s) + CuSO_4(s) = 2Cu_2O(s) + SO_2(g)$. Schenck and Hempelmann (*81*) measured the pressure of $SO_2(g)$ over this system, two series of measurements being taken. Their pressures are given in the third column of Table XIII, the second of which gives the absolute temperatures. The first column shows from which series the pressures were taken. We take Thomsen's value of 182,600 calories for the heat of formation of copper sulfate at room temperature and use the heat capacities at room temperature of the substances involved, with the values for sulfur dioxide from Lewis and Randall (*42*).

$SO_2(g)$; $C_p = 7.0 + 0.0071\,T - 0.000\,001\,86\,T^2$; $\Delta H^\circ = -67{,}966$ calories (59)

In taking the average value of I, we have omitted the starred values, which are largely divergent. Whence we may write

$3Cu(s) + CuSO_4(s) = 2Cu_2O(s) + SO_2(g)$; $\Delta F^\circ = 32{,}480 + 3.14\,T \ln T - 0.00492\,T^2 + 0.000\,000\,04\,T^3 - 70.977\,T$; $\Delta H^\circ_{298\cdot1} = 31{,}980$ calories; $\Delta F^\circ_{298\cdot1} = 16{,}218$ calories (prelim.) (60)

We have plotted the values of $-R \ln P$ against $1/T$ in Figure 7. The authors themselves thought that measurements above 300° C. represented a different reaction. We shall return to these measurements in connection with our discussion of Equation 83.

Table XIII—$3Cu(s) + CuSO_4(s) = 2Cu_2O(s) + SO_2(g)$

T	P	I	T	P	I
525.1^a	0.0868	−74.078	585.1^c	0.4158	−70.933
534.1^a	0.0973	−73.271	587.1^d	0.5380	−71.186
552.1^a	0.1302	−71.885	588.1^b	0.4615	−70.820
557.1^a	0.1328	−71.398	588.1^d	0.5420	−71.153
557.1^b	0.1224	−71.252	597.1^d	0.7723	−71.030
566.1^a	0.1710	−70.971	601.1^a	0.9436	−71.073
569.1^a	0.1974	−71.032	601.1^d	0.9565	−71.100
574.1^c	0.2408	−70.838	603.1^a	0.9710	−70.950
575.1^c	0.2592	−70.911	603.1^b	1.000	−71.033
576.1^b	0.2579	−70.803	606.1^c	1.067	−70.867
578.1^b	0.2921	−70.861	608.1^{b,c}	1.136	−70.806
578.1^d	0.4315	−71.552			

^{a} Direct, rising temperature.
^{b} Second series, same as ^{a}.
^{c} Third series, same as ^{a}.
^{d} Reverse, falling temperature.

$CuO.CuSO_4(s) + Cu_2O(s) = 4CuO(s) + SO_2(g)$. Reinders and Goudriaan (*69*) made two series of determinations of the vapor pressures over this system. In Table XIV the first column gives the series, the second the absolute temperature, and the third the pressure of $SO_2(g)$ in atmospheres. To find the heat of formation of $CuO.CuSO_4(s)$, we have plotted Σ against $1/T$ for this and the three following reactions and have taken the average, omitting the value obtained from the reaction $4CuSO_4(s) + Cu_2O(s) = 3CuO.CuSO_4(s) + SO_2(g)$, since this curve was rather difficult to draw. This average gives

$2Cu(s) + S\text{ (rhomb.)} + 2^1/_2O_2(g) = CuO.CuSO_4(s)$; $\Delta H^\circ_0 = -219{,}090$ calories (61)

We have used Equation 61 and have assumed that the change in the heat capacity in this and the three following reactions is negligible. These assumptions give $\Delta\Gamma_0 = 0$ and $\Delta H^\circ_0 = 43{,}020$ calories for the present reaction. We have averaged all the values of I in Table XIV and may therefore write

$CuO.CuSO_4(s) + Cu_2O(s) = 4CuO(s) + SO_2(g)$; $\Delta F^\circ = 43{,}020 - 40.676\,T$; $\Delta H^\circ_{298\cdot1} = 43{,}020$ calories; $\Delta F^\circ_{298\cdot1} = 30{,}895$ calories (prelim.) (62)

Table XIV—$CuO.CuSO_4(s) + Cu_2O(s) = 4CuO(s) + SO_2(g)$

Series	T	p	I	Series	T	p	I
1	917.1	0.0520	−41.029	2	978.1	0.1750	−40.515
2	928.1	0.0710	−41.093	2	996.1	0.2700	−40.584
1	939.1	0.0684	−40.476	1	998.1	0.2850	−40.605
2	952.1	0.1000	−40.605	1	1009.1	0.3842	−40.730
1	957.1	0.1132	−40.616	2	1022.1	0.5080	−40.743
2	972.1	0.1513	−40.500	1	1027.1	0.5513	−40.701
1	976.1	0.1731	−40.586				

$4CuSO_4(s) + Cu_2O(s) = 3CuO.CuSO_4(s) + SO_2(g)$. The heat capacities and heat contents given in previous sections give $\Delta H^\circ_0 = 45{,}240$ calories and $\Delta\Gamma_0 = 0$ for this reaction. The data as determined by Reinders and Goudriaan (*69*), and the values of I are given in Table XV, all of which were averaged in obtaining the equations

$4CuSO_4(s) + Cu_2O(s) = 3CuO.CuSO_4(s) + SO_2(g)$; $\Delta F^\circ = 45{,}240 - 48.673\,T$; $\Delta H^\circ_{298\cdot1} = 45{,}240$ calories; $\Delta F^\circ_{298\cdot1} = 30{,}730$ calories (prelim.) (63)

Table XV—$4CuSO_4(s) + Cu_2O(s) = 3CuO.CuSO_4(s) + SO_2(g)$

T	p	I
825.1	0.0632	−49.338
846.1	0.0934	−48.755
855.1	0.1144	−48.594
865.1	0.1500	−48.522
877.1	0.2210	−48.577
898.1	0.417	−48.634
921.1	0.661	−48.292

$2CuSO_4(s) = CuO.CuSO_4(s) + SO_3(g)$. Using the heat contents and heat capacities of previous sections, taking the heat capacity of $SO_3(g)$ as equal to that of $SO_2(g) + {}^1/_2O_2(g)$, and writing $SO_2(g) + {}^1/_2O_2(g) = SO_3(g)$; $\Delta H°_0 = -22{,}600$ calories, from Lewis and Randall (*42*), we obtain $\Delta\Gamma_0 = -1.25$ and $\Delta H°_0 = 55{,}080$ calories for the above reaction. In calculating the partial pressure of $SO_3(g)$, we have used the equation

$$SO_2(g) + {}^1/_2O_2(g) = SO_3(g);\quad \Delta F° = -22{,}600 + 21.36\ T;\quad \Delta H°_{298\cdot1} = -22{,}600 \text{ calories};\quad \Delta F°_{298\cdot1} = -16{,}230 \text{ calories} \tag{64}$$

from Lewis and Randall. The data are given in Table XVI. The total pressures over the system in atmosphere were those determined by Reinders and Goudriaan (*69*), and the values of K are the partial pressures of sulfur trioxide. The average of I is −58.546. We may therefore write

$$2CuSO_4(s) = CuO.CuSO_4(s) + SO_3(g);\quad \Delta F° = 55{,}080 + 1.25\ T \ln T - 58.546\ T;\quad \Delta H°_{298\cdot1} = 55{,}120 \text{ calories};\quad \Delta F°_{298\cdot1} = 39{,}750 \text{ calories} \tag{65}$$

Table XVI—$2CuSO_4(s) = CuO.CuSO_4(s) + SO_3(g)$

Series	T	p	K	I
1	953.1	0.04475	0.0198	−58.566
2	955.1	0.04865	0.02166	−58.626
1	983.1	0.1000	0.0450	−58.472
2	984.1	0.1052	0.0476	−58.529
1	1003.1	0.1724	0.0791	−58.503
2	1005.1	0.1868	0.0862	−58.567
1	1013.1	0.2223	0.1026	−58.491
2	1023.1	0.3092	0.1463	−58.677
1	1033.1	0.3777	0.1780	−58.558
2	1043.1	0.488	0.2324	−58.590
1	1053.1	0.5815	0.2748	−58.432

$CuO.CuSO_4(s) = 2CuO(s) + SO_3(g)$. The calculations for this reaction have been made like those of the preceding paragraph. Here $\Delta\Gamma_0 = -1.25$ and $\Delta H°_0 = 53{,}970$ calories. The data are given in Table XVII, the measurements being those of Reinders and Goudriaan (*69*). The average value of I is −54.617 and we may therefore write

$$CuO.CuSO_4(s) = 2CuO(s) + SO_3(g);\quad \Delta F° = 53{,}970 + 1.25\ T \ln T - 54.617\ T;\quad \Delta H°_{298\cdot1} = 54{,}010 \text{ calories};\quad \Delta F°_{298\cdot1} = 39{,}810 \text{ calories (prelim.)} \tag{66}$$

Table XVII—$CuO.CuSO_4(s) = 2CuO(s) + SO_3(g)$

T	p	K	I
1013.1	0.0803	0.0289	−54.876
1033.1	0.1105	0.0386	−54.445
1053.1	0.1895	0.0683	−54.611
1073.1	0.295	0.1075	−54.581
1083.1	0.374	0.1377	−54.621
1093.1	0.454	0.1674	−54.565

Sulfides of Copper

Heat Capacity and Heat of Transition of Cuprous Sulfides. There appears to be much confusion in the literature regarding the forms of cuprous sulfide and their heat capacities. Bellati and Lussana (*6*) found a transition at 103° C. and gave formulas for the specific heat above and below the transition point and up to 190° C. Posnjak, Allen, and Merwin (*63*) studied this transition carefully and concluded that the real transition point was at 91° C. on the basis of powdered material. Schad and Bornemann (*80*) reported other transitions between 200° and 300° C. Regnault (*68*) (molten cuprous sulfide, probably artificial) and Kopp (*36*) measured the heat capacity of chalcocite, which was presumably mineral and which in the light of the experiments of Posnjak, Allen, and Merwin (*63*) would not be transformed at the upper temperature reached in their determinations. Bornemann and Hengstenberg (*8*) have measured the heat capacity of cuprous sulfide up to 1100° C. These last measurements are not easily explained. We have taken on the basis of our studies of these data

$$Cu_2S(\beta);\ C_p = 18.20 + 0.0022\ T \tag{67}$$

based largely upon the data from the higher temperatures. We have, then, on the basis of the measurements of Regnault (*68*) [C_p (mean 7–97°) = 19.29] and of Kopp (*36*) [C_p (mean 19–52°) = 19.10] and the slope of the $Cu_2S(\beta)$ curve, taken

$$Cu_2S(\alpha);\ C_p = 18.63 + 0.0022\ T \tag{68}$$

We have also postulated a transition from $Cu_2S(\alpha')$ to $Cu_2S(\beta)$ at 250° C. and have arbitrarily taken the heat capacity of $Cu_2S(\alpha')$ equal to that of $Cu_2S(\beta)$.

Now, assuming that Bellati and Lussana (*6*) were dealing with a delayed transition, we have taken $\Delta H_{463} = 896$ calories, calculated from their heat-capacity curves and their heat of transition at 103° C. This combined with the heat capacity curves we have assumed gives for the transition

$$Cu_2S(\alpha) = Cu_2S(\alpha');\ \Delta H_{364\cdot1} = 1313 \tag{69}$$

Further, assuming that the total heat at high temperatures measured by Bornemann and Hengstenberg (*8*) is given by the heat capacities of the various forms of the sulfide, the heat of the transition of $Cu_2S(\alpha)$ to $Cu_2S(\alpha')$, and a heat of transition from $Cu_2S(\alpha')$ to $Cu_2S(\beta)$ at 250° C., we find

$$Cu_2S(\alpha') = Cu_2S(\beta);\ \Delta H_{523\cdot1} = 1046 \tag{70}$$

Free Energy of Transition of the Cuprous Sulfides. Using the data of the previous section we find

$$Cu_2S(\alpha) = Cu_2S(\alpha');\ \Delta F° = 1477 + 0.45\ T \ln T - 6.709\ T;\ \Delta H°_{298\cdot1} = 1343;\ \Delta F°_{298\cdot1} = 262 \text{ calories} \tag{71}$$

$$Cu_2S(\alpha') = Cu_2S(\beta);\ \Delta F° = 1046 - 2.000\ T;\ \Delta H°_{298\cdot1} = 1046;\ \Delta F°_{298\cdot1} = 450 \text{ calories} \tag{72}$$

Heat Capacity of Cupric Sulfide. From measurements by Russell (*77*) at low and room temperatures on material prepared by Wasjuchnowa (*97*), we estimate

$$CuS(s);\ C_p = 11.2 + 0.0038\ T \tag{73}$$

Heat Content of Copper Sulfides. The best measurements of the heats of formation of the copper sulfides seem to be those of von Wartenberg (*96*). He gives as the mean of a number of measurements

$$2Cu(s) + S \text{ (rhomb.)} = Cu_2S(\alpha);\ \Delta H°_{298\cdot1} = -18{,}970 \text{ calories} \tag{74}$$

Whence with Equations 71 and 72,

$$Cu_2S(\beta);\ \Delta H°_{298\cdot1} = -16{,}580 \text{ calories} \tag{75}$$

$$Cu(S) + S \text{ (rhomb.)} = CuS(s);\ \Delta H°_{298\cdot1} = -11{,}610 \text{ calories} \tag{76}$$

$Cu(s) + S$ (rhomb.) $= CuS(s)$. A preliminary value of the entropy of cupric sulfide is (*5*)

$$CuS(s);\ S°_{298\cdot1} = 15.93 \text{ calories per degree (prelim.)} \tag{77}$$

We may combine this value with 7.6 calories per degree for the entropy of rhombic sulfur (*42*) and Equation 1; whence,

$$Cu(s) + S \text{ (rhomb.)} = CuS(s);\ \Delta S°_{298\cdot1} = 0.485 \text{ calorie per degree};\ \Delta F°_{298\cdot1} = -11{,}755 \text{ calories} \tag{78}$$

$4CuS(s) = 2Cu_2S(\beta) + S_2(g)$. The total pressure of sulfur vapor over this system was measured by Wasjuchnowa (*97*), who swept out the sulfur vapor with a stream of nitrogen

and gave her results in terms of grams of sulfur per liter of nitrogen under standard conditions. In recalculating her data to total pressures of sulfur vapor in atmospheres, we have assumed that the total pressure in the reaction chamber was 1 atmosphere and have used the values of Preuner and Schupp (*65*) for the average molecular weight of sulfur vapor at various pressures and temperatures. The pressure of sulfur vapor in the same system was also measured by Preuner and Brockmöller (*64*), who used a spiral manometer, and by Allen and Lombard (*1*), who compared the pressure over this system with that over liquid sulfur. We have calculated the partial pressures of S_2(g) by employing the tables of Preuner and Schupp (*65*). The data are given in Table XVIII. The values of I were calculated by assuming $\Delta H°_0 = 43,100$ calories and $\Delta C_p = -1.9 - 0.0098\ T$. The values of Preuner and Brockmöller ($I = -63.244$, $\Delta F°_{298 \cdot 1} = 27,910$ calories) are in entire disagreement with those of Wasjuchnowa (*97*) and of Allen and Lombard (*1*), and we have therefore omitted the values of Preuner and Brockmöller (*64*) in calculating the average value of I. Whence we may write

$4CuS(s) = 2Cu_2S(\beta) + S_2(g)$; $\Delta F° = 43,100 + 1.9\ T \ln T + 0.0049\ T^2 - 67.056\ T$; $\Delta H°_{298 \cdot 1} = 42,970$ calories; $\Delta F°_{298 \cdot 1} = 26,773$ calories (prelim.) (79)

Table XVIII—$4CuS(s) = 2Cu_2S(\beta) + S_2(g)$

Ref.	T	p(mm.)	K	I
(*97*)	666.5	0.6	0.00066	−65.747
(*1*)	673.1	1.5	0.00133	−66.535
(*97*)	678.9	1.6	0.00145	−66.192
(*1*)	683.1	2.7	0.00158	−66.013
(*97*)	694.6	5.3	0.00303	−66.347
(*1*)	706.8	11.2	0.00632	−66.827
(*97*)	709.3	14.0	0.00777	−67.040
(*97*)	720.5	29.0	0.0126	−67.150
(*64*)	723.1	80	0.0191	−63.185
(*1*)	723.1	31	0.0144	−67.215
(*1*)	733.1	55	0.0200	−67.140
(*97*)	740.4	110	0.0305	−67.443
(*1*)	741.1	93	0.0290	−67.292
(*64*)	743.1	200	0.00394	−63.176
(*64*)	748.1	250	0.00480	−63.221
(*1*)	748.1	170	0.0415	−67.521
(*64*)	753.1	313	0.00579	−63.245
(*1*)	755.1	320	0.0599	−67.758
(*97*)	756.9	295	0.0612	−67.679
(*1*)	758.1	393	0.0671	−67.786
(*1*)	763.1	510	0.0796	−67.788
(*64*)	773.1	980	0.0121	−63.393
(*97*)	775.4	595	0.1042	−67.527

$2Cu_2O(s) + Cu_2S(\beta) = 6Cu(s) + SO_2(g)$. Reinders and Goudriaan (*69*), Schenck and Hempelmann (*81*), and Stubbs (*90*) measured the pressure of sulfur dioxide over this system, Schenck and Hempelmann making two series. From previous sections we find $\Delta H°_0 = 31,826$ calories and $\Delta C_p = -10.42\ T + 0.011\ 82\ T^2 - 0.000\ 005\ 10\ T^2$. The data are given in Table XIX. The values of I do not vary much, and we have taken the average to obtain the equation

$2Cu_2O(s) + Cu_2S(\beta) = 6Cu(s) + SO_2(g)$; $\Delta F° = 31,826 + 10.42\ T \ln T - 0.00591\ T^2 + 0.000\ 000\ 85\ T^3 - 98.820\ T$; $\Delta H°_{298 \cdot 1} = 29,200$ calories; $\Delta F°_{298\ 1} = 19,563$ calories (80)

$3CuS(s) + CuSO_4(s) = 2Cu_2S(\beta) + 2SO_2(g)$. Reinders and Goudriaan (*69*) made three measurements of the pressure of sulfur dioxide over this system. The pressures are given in Table XX, and we have taken the mean of the last two values of I, calculated by assuming $\Delta H°_0 = 46,063$ calories.

$3CuS(s) + CuSO_4 = 2Cu_2S(\beta) + 2SO_2(g)$; $\Delta F° = 46,063 + 7.29\ T \ln T - 0.0036\ T^2 + 0.000\ 000\ 62\ T^3 - 146.416\ T$; $\Delta H°_{298 \cdot 1} = 44,176$ calories; $\Delta F°_{298 \cdot 1} = 14,494$ calories (prelim.) (81)

Table XX—$3CuS(s) + CuSO_4(s) = 2Cu_2S(\beta) + 2SO_2(g)$

T	$K^{1/2}$	I
368.1	0.2368	−161.262
394.1	0.3238	−154.642
432.1	0.5825	−147.252
448.1	0.943	−145.578

$3CuS(s) + CuSO_4(s) = 2Cu_2S(\alpha') + 2SO_2(g)$. Reinders and Goudriaan (*69*) found the pressure of sulfur dioxide to be 0.2368 atmosphere over this system at 368.1° K. Assuming $\Delta H°_0 = 46,940$ calories we find

$3CuS(s) + CuSO_4 = 2Cu_2S(\alpha') + 2SO_2(g)$; $\Delta F° = 43,109 + 6.39\ T \ln T - 0.0036\ T^2 + 0.000\ 000\ 62\ T^3 - 147.910\ T$; $\Delta H°_{298 \cdot 1} = 41,490$ calories; $\Delta F°_{298 \cdot 1} = 9569$ calories (prelim.) (82)

The value of $\Delta F°_{298 \cdot 1}$ is certainly erroneous, since the free energy of transition of cuprous sulfide is only 450 calories at 25° C., according to Equation 72, while combining Equations 81 and 82 we obtain about 2963 for the free energy of transition. No doubt the desired equilibrium was not reached at the low temperature of this pressure measurement, as was the case with a large number of the measurements over similar systems made at comparatively low temperatures.

If we assume that the cuprous sulfide was in the β form then we have the values in the first row of Table XX.

$2CuSO_4(s) + Cu_2S(\beta) = 2Cu_2O(s) + 3SO_2(g)$. The pressure of sulfur dioxide over this system was measured by Schenck and Hempelmann (*81*); and by Reinders and Goudriaan (*69*), each making two series of measurements. The data are given in Table XXI. From previous calorimetric data we have $\Delta H°_0 = 96,789$ and $\Delta \Gamma = -16.70 + 0.0315\ T - 0.000\ 005\ 58\ T^2$. The data of the above authors which were definitely attributed to this reaction are plotted in Figure 7. The values of $-R \ln P$ or $-{}^1/_3\ R \ln K$ are plotted against

Table XIX—$2Cu_2O(s) + Cu_2S(\beta) = 6Cu(s) + SO_2(g)$

Ref.	Series	T	p	I
(*81*)	2	781.1	0.0447	− 99.871
(*81*)	1	789.1	0.0474	− 99.646
(*81*)	1	799.1	0.0724	−100.068
(*81*)	1	803.1	0.0816	−100.144
(*81*)	2	809.1	0.0578	− 99.030
(*81*)	1	812.1	0.1131	−100.428
(*81*)	2	813.1	0.0658	− 99.310
(*81*)	2	820.1	0.0788	− 99.396
(*81*)	2	823.1	0.0960	− 99.668
(*81*)	2	824.1	0.0934	− 99.577
(*81*)	2	834.1	0.0947	− 99.219
(*81*)	2	836.1	0.0961	− 99.173
(*81*)	1	849.1	0.1237	− 99.195
(*81*)	1	853.1	0.1442	− 99.355
(*69*)		859.1	0.0961	− 98.332
(*81*)	1	863.1	0.1802	− 99.444
(*81*)	1	864.1	0.1567	− 99.132
(*81*)	2	864.1	0.1565	− 99.219
(*81*)	1	867.1	0.1711	− 99.203
(*81*)	1	870.1	0.1710	− 99.097
(*81*)	1	878.1	0.2067	− 99.197
(*69*)		880.1	0.1579	− 98.595
(*81*)	2	887.1	0.2105	− 98.935
(*81*)	2	888.1	0.2303	− 99.081
(*81*)	1	889.1	0.2210	− 98.966
(*81*)	1	896.1	0.2448	− 98.942
(*81*)	1	898.1	0.2503	− 98.920
(*81*)	1	899.1	0.2580	− 98.847
(*81*)	2	902.1	0.2700	− 98.942
(*81*)	1	903.1	0.2738	− 98.937
(*81*)	2	906.1	0.2923	− 98.970
(*81*)	1	909.1	0.2975	− 98.913
(*81*)	1	910.1	0.3186	− 99.019
(*81*)	1	915.1	0.3265	− 98.912
(*81*)	1	918.1	0.3395	− 98.896
(*69*)		923.1	0.2922	− 98.474
(*81*)	2	926.1	0.3750	− 98.822
(*81*)	2	930.1	0.415	− 98.931
(*81*)	1	933.1	0.4220	− 98.868
(*81*)	1	934.1	0.4355	− 98.987
(*81*)	1	935.1	0.4315	− 98.861
(*81*)	2	936.1	0.453	− 98.927
(*81*)	1	937.1	0.451	− 98.890
(*69*)		942.1	0.3802	− 98.404
(*81*)	2	946.1	0.500	− 98.832
(*81*)	1	947.1	0.5108	− 98.466
(*81*)	2	958.1	0.544	− 98.646
(*69*)		964.1	0.5135	− 98.376
(*81*)	2	966.1	0.607	− 98.652
(*81*)	2	971.1	0.655	− 98.669
(*81*)	2	975.1	0.728	− 98.767
(*81*)	2	977.1	0.744	− 98.725
(*69*)		983.1	0.642	− 98.305
(*81*)	2	995.1	0.893	− 98.647
(*90*)		999.7	0.908	− 98.650
(*81*)	2	1003.1	1.007	− 98.677
(*69*)		1003.1	0.788	− 98.189
(*90*)		1041.1	1.451	− 98.236
(*90*)		1083.6	2.170	− 98.320
(*90*)		1124.6	3.032	− 98.133
(*90*)		1166.1	4.015	− 97.898
(*90*)		1204.6	4.960	− 97.636
(*90*)		1246.6	5.73	− 97.230
(*90*)		1285.6	6.27	− 96.808
(*90*)		1324.6	6.46	− 96.316

the reciprocal of the absolute temperature. We also show in Figure 7 the values of $-R \ln P$ for the reaction of Equation 60 and Table XIII. The line to the right corresponds to Equation 60. It is seen that the six lowest points of the first series of Schenck and Hempelmann for $3Cu(s) + CuSO_4(s) = 2Cu_2O(s) + SO_2(g)$ fall closely upon the broken curve ($\Delta H = 9835$) characteristic of many of Reinders and Goudriaan's points and the lowest points of Schenck and Hempelmann for the reaction of Table XXI. Likewise two of Schenck and Hempelmann fall upon a curve ($\Delta H = 15{,}860$), which also passes through some of the points taken by reversing the reaction of Equation 60. These considerations make it impossible to attempt to assign an equation from these data alone.

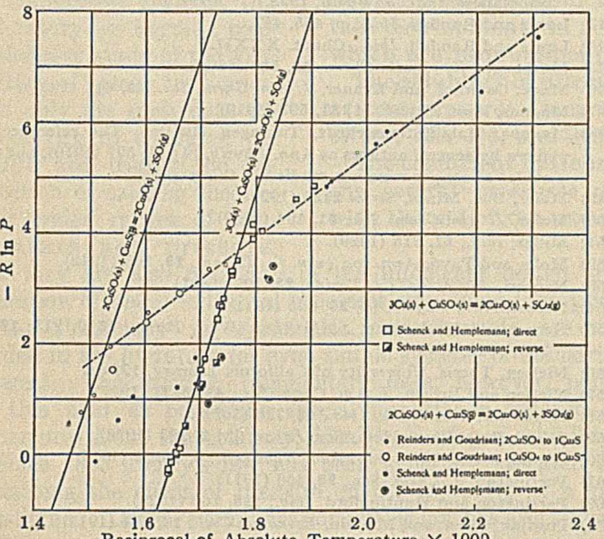

Figure 7—Reactions $2CuSO_4(s) + Cu_2S(\beta) = 2Cu_2O(s) + 3SO_2(g)$ and $CuSO_4(s) + 3Cu(s) = 2Cu_2O(s) + SO_2(g)$

However, by combining Equations 60 and 80, we find $\Delta F^\circ_{298.1} = 51{,}948$ calories or

$2CuSO_4(s) + Cu_2S(\beta) = 2Cu_2O(s) \pm 3SO_2(g)$; $\Delta F^\circ = 96{,}789 + 16.70\ T \ln T - 0.01575\ T^2 + 0.000\,000\,93\ T^3 - 240.774\ T$; $\Delta F^\circ_{298.1} = 52{,}000$ (prelim.) (83)

The curve to the left in Figure 8 represents this synthetic equation and shows that at the highest temperatures the measurements of Reinders and Goudriaan (*69*) really corresponded to the assumed reaction.

Table XXI—$2CuSO_4(s) + Cu_2S(\beta) = 2Cu_2O(s) + 3SO_2(g)$

Ref.	T	p
(*81*)^{a,b}	433.1	0.0224
(*81*)^{a,b}	453.1	0.0369
(*81*)^{a,b}	491.1	0.0526
(*81*)^{a,b}	496.1	0.0592
(*81*)^{a,b}	516.1	0.0829
(*81*)^{c,d}	546.1	0.1803
(*81*)^{c,d}	548.1	0.2026
(*81*)^{a,b}	550.1	0.1987
(*69*)	573.1	0.1776
(*81*)^{c,d}	575.1	0.4093
(*69*)	583.1	0.1947
(*81*)^{c,d}	583.1	0.6276
(*81*)^{a,b,e}	591.1	0.522
(*81*)^{a,b,f}	591.1	0.413
(*69*)	600.1	0.2302
(*81*)^{a,b,e}	603.1	0.921
(*81*)^{f}	604.1	0.537
(*81*)^{b,c}	608.1	1.180
(*69*)	623.1	0.2762
(*69*)	624.1	0.300
(*69*)	633.1	0.3224
(*81*)^{a,b,e}	633.1	0.537
(*81*)^{a,b,e}	644.1	0.726
(*69*)	648.1	0.4605
(*69*)	650.6	0.3750
(*81*)^{a,b,e}	661.1	1.0789
(*69*)	663.1	0.5828
(*69*)	673.1	0.681

[a] Direct reaction
[b] Temperature rising
[c] Reverse reaction
[d] Temperature falling
[e] Maximum value
[f] End value

Entropy and Free Energy of Cuprous Sulfide. The preliminary value of the entropy of cuprous sulfide by Mr. Anderson (*5*) is

$Cu_2S(\alpha)$; $S^\circ_{298.1} = 28.9$; $\Delta S^\circ_{298.1} = 5.67$ calories per degree (84)

It is assumed that this is the value for what we have called the alpha form. We thus have, with Equation 74,

$2Cu(s) + S\ (rhomb.) = Cu_2S(\alpha)$; $\Delta F^\circ_{298.1} = -20{,}660$ (prelim.) (85)

Combining the Equations—Summary

In the previous sections we have not attempted to make a critical selection of final values, owing to the uncertainties in the data and to the many approximations which we were forced to make in the reduction of data to standard forms. With all the experimental data before us, we shall attempt to select the most probable values of the free energies of formation of the several compounds. We also give several equations from Lewis and Randall (*42*) which are needed in the combinations.

$H_2O(g)$; $\Delta H^\circ_{298.1} = -57{,}820$; $\Delta F^\circ_{298.1} = -54{,}507$ (86)

$H_2O(l)$; $\Delta F^\circ_{298.1} = -56{,}560$ (87)

$H_2O(g) = H_2O$ (l, in satd. $CuSO_4.5H_2O$); $\Delta F^\circ_{298.1} = -2063$ (88)

$SO_2(g)$; $\Delta H^\circ_{298.1} = -69{,}000$; $\Delta F^\circ_{298.1} = -69{,}660$ (89)

$SO_3(g)$; $\Delta F^\circ_{298.1} = -85{,}890$ (90)

SO_4^{--}; $\Delta F^\circ_{298.1} = -176{,}500$ (91)

$S_2(g)$; $\Delta F^\circ_{298.1} = 18{,}280$ (92)

It is obvious that there are many ways of combining these equations. It is also obvious that not all the combinations are independent; that is, they involve some sort of choice or averaging of other data in which some of the same equations have been used. The final values of I and of ΔF° for the various preliminary equations can be found by summing the various final equations for the free energy of formation given in Table XXII. The final equations and the combinations which we have chosen to make are indicated below. The numbers in parenthesis refer to the equations of this paper. We have used the results of Table XXI as a check on other equations.

Table XXII—Summary of Combinations of Data

REACTIONS AND COMBINATIONS	$\Delta F^\circ_{298.1}$	
$2CuO(s) = Cu_2O(s) + \frac{1}{2}O_2(g)$ (final)	25,610	(94)
Direct by (24)	25,610	
Direct to Cu_2O (l) by (25) − fusion of Cu_2O (s) (26)	25,650	
Reduction $CuO(s)$ by $H_2(g)$ (32) − $H_2O(g)$ (86)	37,787	
$Cu_2O(s)$, $CuO(s)$ cells (43) − $H_2O(l)$ (87)	26,929	
Entropy (50)	25,526	
$-\frac{1}{4}[3(62) + (63)]$ − $CuSO_4(s)$ (101) − $CuO(s)$ (96) + $SO_2(g)$ (89)	25,756	
Ditto but with final $CuSO_4(s)$ (100)	25,386	
$\frac{1}{2}[(65) + (66)] - \frac{1}{4}[3(62) + (63)] - (64)$	25,156	
$2Cu(s) + \frac{1}{2}O_2(g) = Cu_2O(s)$; $\Delta F^\circ = -41{,}166 - 1.27\ T \ln T + 0.00037\ T^2 - 0.000\,000\,18\ T^3 + 27.881\ T$; $\Delta H^\circ_{298.1} = -40{,}810$; $\Delta S^\circ_{298.1} = -20.718$; $\Delta F^\circ_{298.1}$ (final) =	−34,990	(95)
Direct from Cu(l) by (3) + fusion 2Cu(l)2 (4)	−35,012	
Reduction by $H_2(g)$; − (31, Maier) + $H_2O(g)$ (86)	−32,897^a	
Ditto; − (31, W and B) + $H_2O(g)$ (86)	−42,496^a	
$Cu(s)$, $Cu_2O(s)$ cells, I and K; (37) + $H_2O(l)$ (87)	−35,150	
Ditto, Maier $H_2(g)$; (38) + $H_2O(l)$ (87)	−34,819	
Ditto, Maier $HgO(s)$; (39) + $H_2O(l)$ (87)	−34,654	
Ditto, Allmand; (42) + $H_2O(l)$ (87)	−34,889	
Entropy; (48)	−35,312	
$\frac{1}{2}[(60) + CuSO_4(s)\ (101) - SO_2(g)\ (89)]$	−35,466	
$-\frac{1}{3}\{\frac{1}{4}[(62) + (63)] - (60)\} - CuO(s)$ (96)	−35,180	
$-\frac{1}{2}[(80) + SO_2(g)\ (89) - Cu_2(\beta)\ (85)]$	−34,638	
$-\frac{1}{2}\{(80) + SO_2(g) - \frac{1}{2}[(79) - S_2(g)\ (92) - 4CuS(s)\ 4\ (78)]\}$	−34,980	
$Cu(s) + \frac{1}{2}O_2(g) = CuO(s)$; $\Delta F^\circ = -37{,}353 - 0.16\ T \ln T - 0.001\,69\ T^2 - 0.000\,000\,09\ T^3 + 25.082\ T$; $\Delta H_{298.1} = -37{,}150$; $\Delta S^\circ_{298} = -22.979$ (final) $\Delta F^\circ_{298.1}$	−30,300	(96)

Dissociation; − $^1/_2$[(94) − (95)]	−30,300	
Entropy; (49)	−30,419	
$^1/_2$[(65) + (66)] + $CuSO_4$(s) (100) − SO_3(g) (89)	−30,530	
$^1/_3$ {$^1/_4$[(62) + (63)] − SO_2(g) (88) + Cu_2O(s) (93) + $CuSO_4$(s) (100)}	−30,225	
$^1/_2$[(65) + (66)] − (60) + Cu_2O(s) (93)	−30,111	
CuO(l); (96) + (28) (final)	−19,464	(97)
Cu_2O(l); (95) + (26) (final)	−20,230	(98)
$Cu(OH)_2$(s); (44) + Cu_2O(s) (93) + $2H_2O$(l) 2 (87) (approx. final)	−113,766	(99)
Cu(s) + S (rhomb.) + $2O_2$(g) = $CuSO_4$(s) (final)	−156,200	(100)
By e. m. f. through hydrates; (51) + (56) + (57) + (58) + (93) + SO_4^{--} (91) + 5 (88)	−156,570	(101)
−(60) + Cu_2O(s) (95) + SO_2(g) (89)	−155,858	
−$^1/_4$[3 (62) + (63)] − Cu_2O(s) (95) + 3CuO(s) 3 (96) + SO_3(g) (89)	−156,424	
−$^1/_2$[(65) + (66)] + CuO(s) (96) + SO_3(g) (90)	−155,965	
$CuSO_4.H_2O$(s); (100) − (58) + H_2O(g) (86) (final)	−216,962	(102)
$CuSO_4.3H_2O$(s); (100) − (58) − (57) + $3H_2O$(g) 3 (86) (final)	−331,876	(103)
$CuSO_4.5H_2O$(s); (100) − (58) − (57) − (56) + $5H_2O$(g) 5 (86); (final)	−446,310	(104)
2Cu(s) + S (rhomb.) + $2^1/_2O_2$(g) = $CuO.CuSO_4$(s) (final)	−186,570	(105)
−(62) − Cu_2O(s) (95) + 4CuO(s) 4 (96) + SO_2(g) (89)	−186,765	
$^1/_3$[(63) + Cu_2O(s) (95) + $4CuSO_4$(s) (100) − SO_2(g) (89)	−186,467	
(65) + $2CuSO_4$(s) 2 (100) − SO_3(g) (90)	−186,760	
−(66) + 2CuO(s) 2 (96) + SO_3(g) (90)	−186,300	
2Cu(s) + S (rhomb.) = $Cu_2S(\beta)$ (final)	−19,243	(106)
Entropy $Cu_2S(\alpha)$ (85) + (71) + (72)	−19,948	
$^1/_2$[(79) − S_2(g) (92) + 4CuS(s) 4 (78)]	−19,264	
−80 + SO_2(g) (89) − $2Cu_2O$(s) 2 (95)	−19,243	
Cu(s) + S (rhomb.) = CuS(s); (final)	−11,755	(78)
Entropy; (78)	−11,755	
−$^1/_4$[(79) + $2Cu_2S(\beta)$ 2 (85) + S_2(g) (92)]	−12,097	
$Cu_2S(\alpha)$; (106) − (72) − (71)	−19,955	(107)
$Cu_2(\alpha')$; (106) − (72)	−19,693	(108)

Table XXIII—Free Energies of Some Copper Compounds

Substance	$\Delta F^\circ_{298.1}$	Equation	Substance	$\Delta F^\circ_{298.1}$	Equation
Cu(g)	78,944	17	$CuSO_4$(s)	−156,200	100
Cu(l)	2,282	4	$CuSO_4.H_2O$(s)	−216,962	102
Cu(s)	0		$CuSO_4.3H_2O$(s)	−331,876	103
Cu (in satd. amalg.)	0		$CuSO_4.5H_2O$(s)	−446,310	104
			Cu_2O(l)	− 20,230	98
Cu_2(g)	82,565	19	Cu_2O(s)	− 34,990	95
CuO(l)	− 19,469	95	$Cu_2S(\alpha)$	− 19,155	107
CuO(s)	− 30,300	97	$Cu_2S(\alpha')$	− 19,693	108
$Cu(OH)_2$(s)	−113,766	99	$Cu_2S(\beta)$	− 19,243	106
CuS(s)	− 11,755	78	Cu_2SO_4(s)	−186,570	105

The melting point of pure cupric oxide to form pure liquid cupric oxide is calculated to be 1336° C.

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Solubility of Nitrogen in Water at High Pressures and Temperatures[1]

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A high-pressure gas-solubility apparatus has been developed which is suitable for the determination of gas solubilities at ordinary and elevated temperatures, and at pressures from 100 to 1000 atmospheres. Certain developments in solubility technic are presented, which are improvements over previous methods.

The solubility of nitrogen in water has been measured at temperatures from 0° to 170° C. and at pressures of 100, 125, 200, and 300 atmospheres.

The coefficient in Henry's law has been calculated for the several pressures and solubility theories tested with the aid of the new data.

As part of the program for the collection of fundamental data on compressed systems, this laboratory has begun a comprehensive study of the solubilities of gases in liquids. Not only are such data interesting in enlarging the scope and testing the application of existing theories over wider ranges of temperature and pressure, but they are also necessary in the intelligent design and operation of many industrial processes employing high pressures. Practically no systematic measurements are recorded in the literature for even simple systems of industrial interest. The existing, fragmentary data, however, point to this field as possessing special importance because of departures from the ordinary, ideal laws of gas solubility.

Since 1803 Henry's law has been generally accepted as describing the effect of pressure on the solubility of a gas in a liquid. Dalton's amplification of this law has also served well for many purposes, although the number of exceptions seems to grow as more measurements are reported. Certainly as "ideal" laws, useful in cases where polarity, association, chemical combination, and deviations from the perfect gas laws do not enter, they will continue to find a place in textbooks.

The effect of temperature on gas solubility is usually connected with the thermal changes involved by means of the Clausius-Clapeyron relation in such cases where it is considered valid. Below the critical temperature of the gas, therefore, this always indicates diminishing gas solubility with increasing temperature. For gases above their critical temperature no satisfactory generalizations are available, although it is customary to reach the conclusion just stated for such cases also. Travers (*10*) makes the statement:

> The curves representing the change of solubility with temperature, for gases under constant pressure, appear to indicate that for each gas there exists a point of minimum solubility and that the temperature corresponding to this is in some way related to the critical point for the gas.

Very few data are offered to support this astonishing conclusion, and none involve common solvents such as water or gases considerably above their critical temperatures. It is not generally recognized that the existence of minimum solubility points is common. The logical interpretation of the phenomenon is difficult and will be discussed subsequently. For examples of systems showing radical departures from accepted theory, reference to Figure 1 is invited. Neon in water and nitrogen-hydrogen mixtures in liquid ammonia show increasing solubility with temperature. Helium in water exhibits a minimum solubility between 25° and 30° C. at 1 atmosphere, and hydrogen in water shows not only a minimum at 25° C. but a very unusual relationship with temperature.

These facts are sufficient to call for further investigation from a theoretical viewpoint at least. The development of high-pressure synthesis of ammonia and methanol and other processes where products are separated by condensation under pressure furnishes further pressing needs of solubility data. The volume of gas dissolved in such condensed products is often very large. Most efficient operation calls for an exact knowledge of such data.

Previous Work

Investigation of the literature has shown the previous published work on pressure solubilities to be very meager, although many investigations have been carried out to test the validity of Henry's law. The systems considered usually were treated at low temperatures and at but small temperature intervals. The pressures were low and seldom exceeding a few atmospheres.

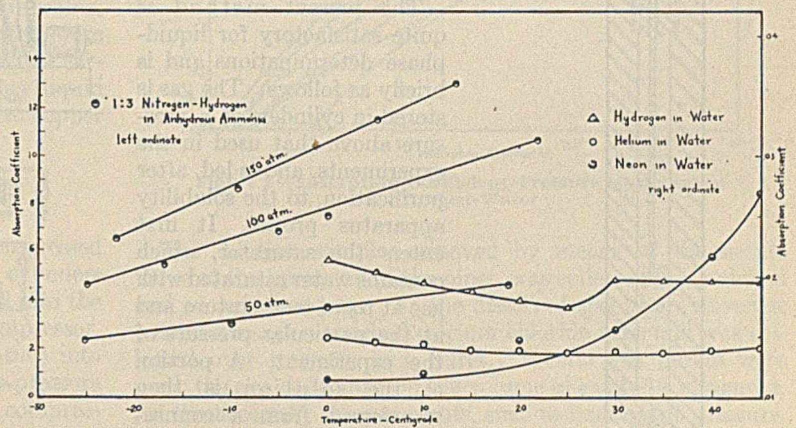

Figure 1—Positive Temperature Coefficients of Solubility

The solubility characteristics have been determined for a number of the inactive gases at ordinary pressures by numerous investigators. Just (*5*) determined the solubility of nitrogen and other gases in aqueous and non-aqueous solvents. Bohr and Bock (*2*) have shown data on the solubility of nitrogen, oxygen, hydrogen, and carbon dioxide in water at temperatures from 0° to 100° C. Besides the work of Estreicher (*4*) and Von Antropoff (*1*) on the solubilities of helium, neon, and argon at atmospheric pressure, there exist many notations of repeated work on nitrogen in water and in non-aqueous solvents.

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[2] Submitted in partial fulfilment of the requirements for the degree of doctor of philosophy in chemistry in the Graduate School of the University of Illinois.

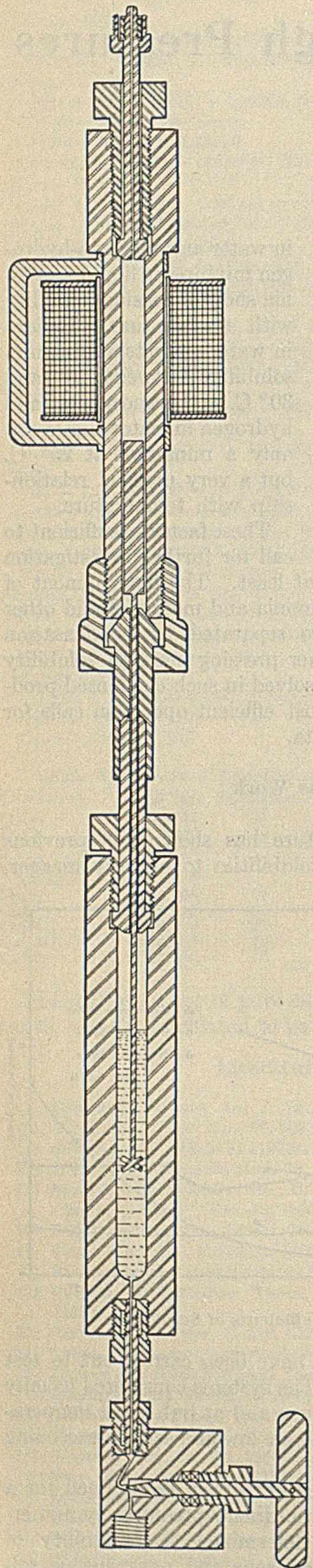

Figure 2—Solubility Pipet

Comprehensive solubility measurements at higher pressures are likewise lacking. The solubility measurements of Larsen and Black (*7*) on the system nitrogen-hydrogen-liquid ammonia are the only instances of recent determinations of high-pressure solubility. These data, while at rather low temperatures, included pressures up to 150 atmospheres. The work of Cassuto (*3*) includes the solubility measurements of nitrogen in water at pressures up to 10 atmospheres along with solubility determinations of hydrogen, oxygen, and carbon monoxide in water. In the consideration of solubility measurements at higher pressures, the work of Sander (*9*) on carbon dioxide in water might also be included. This work embraced measurements taken up to 170 atmospheres. Von Wroblewski (*12*), in his determination of the hydrates of carbon dioxide, took measurements up to 60 atmospheres.

Experimental Method

The present method is quite satisfactory for liquid-phase determinations and is briefly as follows: The gas is stored in cylinders at a pressure above that used in the experiments, and is led, after purification, to the solubility apparatus proper. It first enters the saturator, which contains water saturated with gas at room temperature and at the particular pressure of the experiment. A portion of the solution is then transferred from a connection in the bottom of the saturator to the solubility pipet, which is surrounded by either a copper thermostat for high temperatures or an ice thermostat. While in the solubility pipet, the liquid solution is stirred by means of a magnetic stirrer, at the same time being subjected to the desired pressure. After sufficient time has elapsed to bring the solution to equilibrium, a sample is removed by means of a needle valve at the bottom of the solubility pipet. The sample removed is separated by means of a cooled trap into the gaseous and liquid constituents. The usual corrections for gas volume are applied to reduce the results to standard conditions. A satisfactory apparatus has been developed which permits the use of this procedure in determining gas solubilities in water up to 1000 atmospheres pressure and from 0° to 170° C.

Solubility Apparatus

The main portion of the apparatus is, of course, the solubility pipet (Figure 2). This was constructed of chrome-vanadium steel with a liquid chamber $^1/_2$ inch (1.3 cm.) in diameter and $5^1/_2$ inches (14 cm.) long, the capacity being about 19 cc. The whole pipet was machined to a smooth finish and then completely copper-plated inside and out. The inner surface of the chamber was further plated with silver. These protective coatings were used in order to reduce corrosion and to prevent contamination of the solutions with iron.

The magnetic stirrer was placed on top of the solubility pipet. The present design of this stirring device is unique as applied in this problem, although the original idea was derived from an all-glass gas-circulating pump described by Porter, Bardwell, and Lind (*8*). The cylinder of the stirrer was constructed from a bar of nichrome IV; this alloy was chosen after experience with a manganese-bronze alloy showed that electrolytic corrosion in this section was serious. In the cylinder there was placed a piston of soft iron carefully turned but fitting somewhat loosely, there being about $^1/_{32}$-inch (0.8-mm.) clearance. To insure free passage of the gas past the piston, two longitudinal grooves were cut in the piston; these grooves also permitted any liquid carried up into the stirrer from the lower section of the pipet to drain down again. At the lower end of the piston was attached a small bronze rod, which passed through the connecting nipple between the stirrer and the solubility pipet. At its lower end two small paddles were attached to induce circulation of the liquid in the pipet as the piston was drawn up into the cylinder. To actuate the magnetic stirrer a motor-driven interrupter was designed.

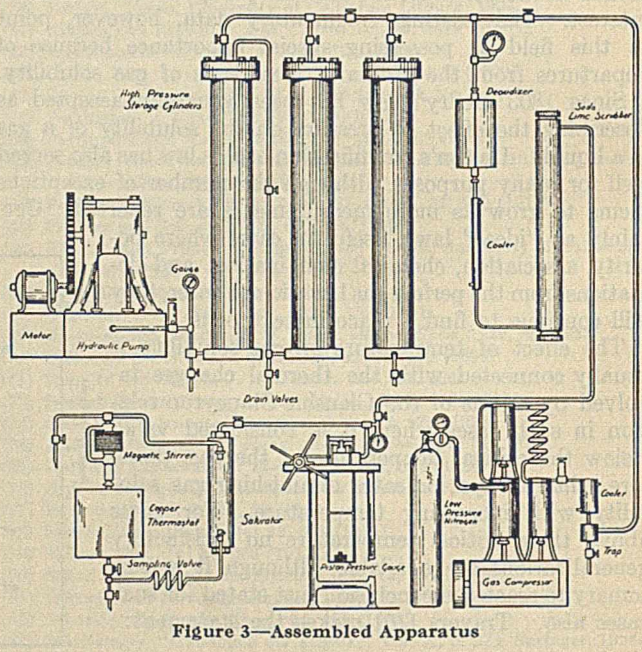

Figure 3—Assembled Apparatus

In this work it was noted that measurements at the higher temperatures were considerably affected by temperature changes. The operation of a high-temperature thermostat is often troublesome, for hot-oil, molten-salt, or metal baths are a considerable hazard. To remove entirely the hazards and to improve further the temperature control, a copper thermostat was used. The authors have used this style of thermostat in previous problems and found it completely satisfactory. The present thermostat was a cast block of copper 5 by 6 by 7 inches (12.7 by 15.2 by 17.8 cm.). Three holes were bored through the block to accommodate the solubility pipet, the electrical heating unit, and the thermometer. The mass of copper left after the necessary holes were bored was approximately 40 pounds (18.2 kg.). For measurements at 0° C. an ice thermostat was used. It was simply a large galvanized iron container, heavily lagged with hair felt and filled with cracked ice and water.

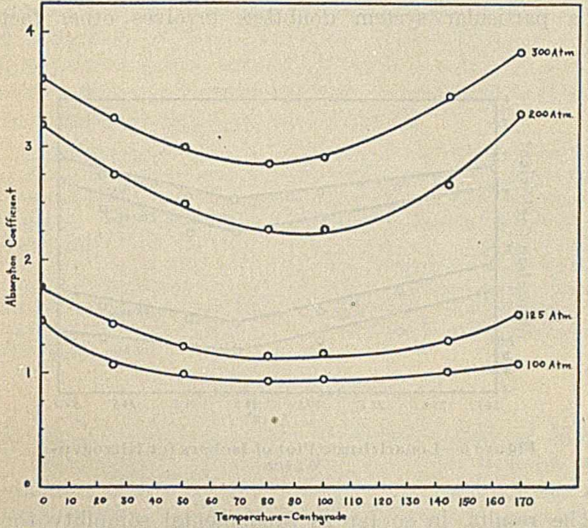

Figure 4—Absorption Coefficient–Temperature Isobars for Nitrogen-Water

The sampling valve connected to the bottom of the solubility pipet was of the usual design of high-pressure valve. The exposed interior sections of the valve body and stem were plated as much as was possible with copper to reduce corrosion. All the high-pressure tubing carrying either liquid solutions or gas was of chrome-molybdenum steel with copper lining.

Auxiliary Apparatus

Figure 3 shows all necessary apparatus. Compressed nitrogen was expanded from the commercial gas cylinders down to about 5 pounds (0.35 atm.) pressure and led into the first stage of a Rix three-stage, water-cooled compressor, in which it was compressed to 4000 pounds (272 atm.) into the low-pressure storage cylinders or into the low-pressure cylinder of the high-pressure storage system. The compression was continued in the high-pressure storage cylinders using a water piston and hydraulic pump. These cylinders were used to store the compressed nitrogen at a pressure always above that used in the experiments.

The connecting tubing used in the system is all of chrome-molybdenum alloy steel, copper-lined. All gages used were calibrated against the laboratory piston gage taken as a standard. Ordinary hydraulic gages calibrated up to 10,000 pounds per square inch (680 atm.) were used for all low-pressure readings.

The gas was purified as it was drawn out of the high-pressure cylinders by passing over heated copper wire at 450° C. It was then cooled by passing through a water-jacketed tube before entering the purifying tower. The absorbent used with nitrogen was soda lime, because this material removes any water in the gas as well as small traces of carbon dioxide.

A line from the high-pressure storage system ran to the solubility apparatus. By means of a needle valve any desired quantity of gas could be admitted to the saturator. This was a steel cylinder 2 feet (61 cm.) long, $2^1/_2$ inches (6.3 cm.) inside diameter, with a wall thickness of 1 inch (2.5 cm.). The solubility operations were facilitated by filling this vessel with about 1.5 liters of distilled water and then bubbling nitrogen through this liquid at a higher pressure than at which the experiments were to be run. This gave a saturated solution of nitrogen in water at room temperature. When this solution was run into the solubility pipet, it simply remained to add or remove nitrogen in solution to correspond to the temperature of the experiment. This presaturating of the solution shortened the time of stirring in the pipet.

The pressure on the solubility apparatus was indicated by a calibrated Bourdon tube gage. Although constant-reading, the Bourdon gage was not sufficiently accurate for measuring the pressures. The actual total pressures were measured by means of the dead-weight piston gage which was connected into the pressure line when so desired. This piston gage was of the type developed at the Massachusetts Institute of Technology (*6*).

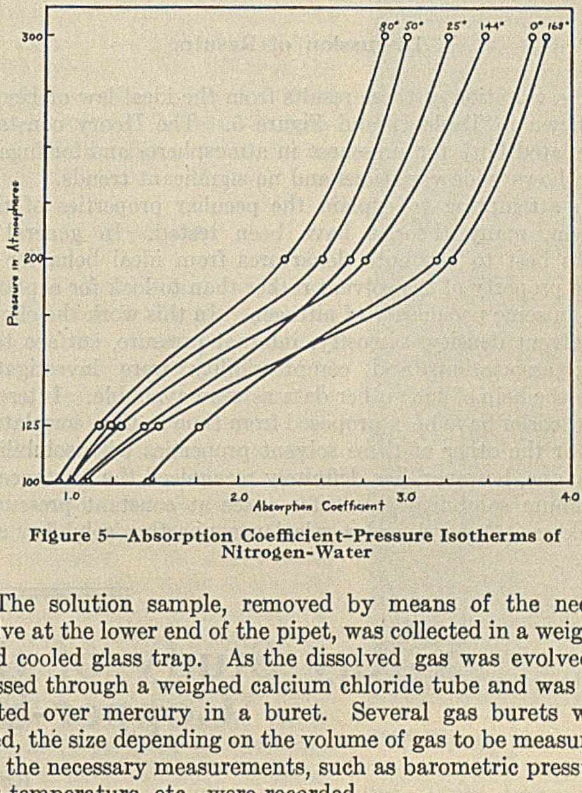

Figure 5—Absorption Coefficient–Pressure Isotherms of Nitrogen-Water

The solution sample, removed by means of the needle valve at the lower end of the pipet, was collected in a weighed and cooled glass trap. As the dissolved gas was evolved it passed through a weighed calcium chloride tube and was collected over mercury in a buret. Several gas burets were used, the size depending on the volume of gas to be measured. All the necessary measurements, such as barometric pressure, gas temperature, etc., were recorded.

Results

The experimental results, showing the solubility of nitrogen in water at 100, 125, 200, and 300 atmospheres and at temperatures up to 169° C., are presented in Table I.

Table I—Solubility of Nitrogen in Water at Various Temperatures

PRESSURE *Atm.*	0° C. *Cc.*	25° C. *Cc.*	50° C. *Cc.*	80° C. *Cc.*	100° C. *Cc.*	144° C. *Cc.*	169° C. *Cc.*
100	1.46	1.07	1.003	0.934	0.954	1.025	1.08
125	1.76	1.44	1.24	1.15	1.17	1.30	1.52
200	3.19	2.76	2.49	2.27	2.25	2.68	3.29
300	3.60	3.25	2.99	2.86	2.91	3.46	3.83
$1/T$, °K.	0.00366	0.00336	0.0031	0.00283	0.00268	0.0024	0.00226

The data are shown graphically in Figure 4, where the absorption coefficient, cubic centimeters of gas at standard conditions per gram of water, is plotted against temperature. Figure 5 presents the solubility isotherms at several temperatures. Figure 6 is the usual representation of the thermal characteristics by plotting the logarithm of the solubility coefficient against the reciprocal of the absolute temperature.

Table II—Henry's Law Constant

Temp.	Pressure	Absorption Coefficient	K_p	Fugacity	K_f
° C.	Atm.			Atm.	
0	100	1.46	0.0146	97.43	0.0150
	200	3.19	0.0160	195.4	0.0163
	300	3.60	0.0120	302.6	0.0119
50	100	1.003	0.0100	101.0	0.0099
	200	2.49	0.0125	207.0	0.0120
	300	2.99	0.0150	326.5	0.0092
80	100	0.934	0.00934	102.0	0.00915
	200	2.27	0.0114	212.5	0.0107
	300	2.86	0.0143	334.1	0.0086
100	100	0.954	0.00954	102.8	0.0094
	200	2.25	0.0113	214.3	0.0105
	300	2.91	0.0145	338.7	0.0086
169	100	1.08	0.0108	104	0.0104
	200	3.29	0.0185	217.8	0.0151
	300	3.83	0.0128	344.0	0.0111

Discussion of Results

The variation of these results from the ideal law of Henry is shown in Table II and Figure 5. The Henry constant calculated both for pressures in atmospheres and for fugacities shows wide variations and no significant trends.

In attempting to explain the peculiar properties of this system, many theories have been tested. In general it seems best to attribute departures from ideal behavior to some property of the solvent rather than to look for explanation in some peculiarity of nitrogen. In this work the effects of solvent density, viscosity, internal pressure, surface tension, association, and compressibility were investigated with the help of such other data as were available. Interesting theories have been proposed from time to time correlating one or the other of these solvent properties with solubility. Only one, however, has definitely recognized the existence of minimum solubility points for gases at constant pressures. Winkler (*11*) developed a relation connecting solubility and viscosity and suggested also that the thermal expansion of the solvent as measured by its specific volume change with temperature was a factor opposite in effect to viscosity. As a result these opposing factors at some point neutralized each other and a minimum solubility point resulted. Careful study of these properties has convinced us that, while qualitatively the idea seems sound, the quantitative application to a particular system doubtless involves other factors also.

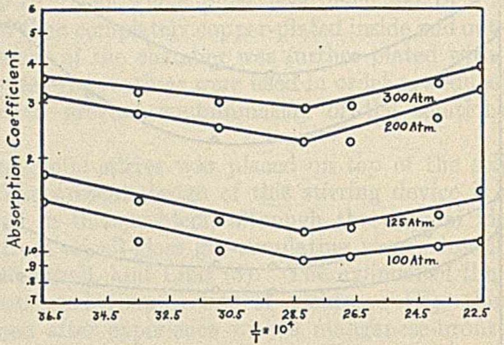

Figure 6—Logarithmic Plot of Isobars for Nitrogen-Water

The results, in so far as fundamental solubility theory is concerned, lead one inevitably to the conclusion that many more data are necessary for complete understanding of these compressed systems.

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X-Ray Study of the Copper End of the Copper-Silver System[1]

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During an x-ray investigation of the plastic deformation of copper, it was noticed that both the Hull and the Laue types of spectra contained lines other than those of copper. Upon analysis these were found to be lines from the silver spectrum. Inasmuch as the copper under investigation did not contain enough silver to be beyond the accepted solid-solution range for silver in copper, the appearance of the silver lines seemed quite worthy of investigation.

Constitution diagrams (*3*, *4*) of the copper-silver system all show that silver is soluble in copper up to about 5 per cent by weight. The diagram in the International Critical Tables has the silver-in-copper solubility line dotted from the eutectic temperature, 778° C., down to room temperature, indicating that such solubility is questionable.

It is generally accepted that there are two types of solid solution. In the most common type the solute atoms replace the solvent atoms on the lattice of the solvent. Opinions differ as to whether the replacement is statistical or random, but whichever condition obtains the resulting solid solution is of the substitutional type. For a continuous series of solid solutions it is necessary that the two pure components A and B crystallize on the same type of lattice. According to the additive law of Vegard (*1*) the lattice constant changes linearly with the composition in atomic per cent between the limiting values of the pure components.

Copper and silver both crystallize on the face-centered

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cubic lattice; consequently, if silver were at all soluble in copper, the solid solution would be of the substitutional type. Weinbaum (*6*) notes that in the formation of solid solutions in the copper-silver system of alloys the lattice constant on the copper end of the series increases up to a silver content of 3 per cent and on the silver end the lattice constant decreases up to a copper content of 5 per cent by weight. In the work done in the preparation of this paper, no increase was noticed in the lattice constant of the copper spectrum, but the silver lattice had an apparent decrease of approximately 0.5 per cent. This change in the silver parameter is in agreement with Weinbaum's results.

Note—Weinbaum used a back-reflection method, all his results being obtained in the 90–180 degree quadrant, taking the zero beam as 0 degree. He made no reference to the presence of spectral lines other than the dominant phase. This is quite as would be expected, because even in the first quadrant, where the planes of lower indices are defined, the intensity maxima due to their reflections are weak. To obtain any indication, in the second quadrant, of the presence of a phase of such low concentration as the silver would necessarily be, would require a prohibitively long exposure. This probably explains why Weinbaum made no mention of the presence of a second phase.

Experimental Procedure

In the investigation at the Michigan College of Mining and Technology a great number of copper samples were examined. These samples included cast lake copper, cast western copper, cold-worked copper, copper annealed at and quenched from 850° C., native copper, float copper, commercial copper wires, deoxidized copper, high arsenic and low arsenic coppers, and a spectroscopically silver-free sample prepared by fractional electrolysis of a copper sulfate solution. Other than this last, the samples examined varied in silver content from 0.003 to 1 per cent by weight. Most of the samples assayed in the neighborhood of 0.2 per cent silver. The general detection of phases of such low concentration is worthy of consideration.

The spectra were all obtained on a General Electric unit, using molybdenum $K\alpha$ radiation for the Hull type and general radiation for the pinhole type of spectra. Some samples were in the form of powders and some were wires. The time of exposure varied from 900 to 3000 milliampere-hours, most of the samples receiving in the neighborhood of 1800. The work was all conducted under ordinary room temperature and pressure.

Results

The spectrum of the spectroscopically silver-free copper had no definite indications of silver lines. All the other copper spectra did contain silver lines. Not all possible silver lines were present in all the spectra, but in the spectra of cast copper, filings from cast copper, cold-drawn wire, and annealed wire, the full silver spectrum within the limit of the film was occasionally visible. A sample quenched from 850° C. contained silver lines in its spectrum. This indicates that silver is not soluble at that temperature or that the cooling was not rapid enough to prevent its precipitation. In all of the silver spectra the reflections from the (111) planes were not relatively so intense as was expected. The reason for this peculiarity has not been determined, but possibly the lack of intensity is due to some interference phenomenon or to a preferential precipitation of the silver phase on a certain plane or planes in the copper lattice (*5*).

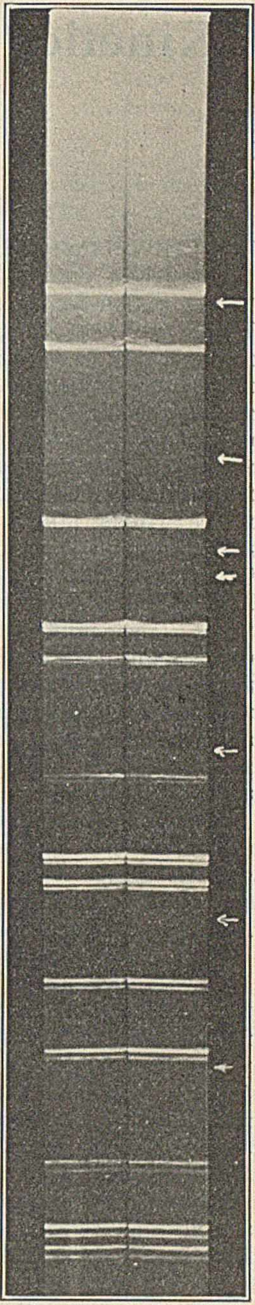
In cutting a billet of cast copper into half-inch slices a small nodule of silver was observed. This billet was obtained from a commercial refinery and assayed less than 50 ounces of silver per ton. This appearance of a nodule of silver under such conditions would indicate the possibility that silver is insoluble in copper.

Samples of silver containing up to 2 per cent copper showed no copper spectral lines. This fact would indicate that copper is soluble in silver, at least up to 2 per cent. The silver lines in the copper spectra were in all probability spectral lines of a high silver–low copper solid-solution phase.

These results, tending to show the insolubility of silver in copper, were substantiated by conductivity determinations performed by the research department of the Calumet and Hecla Copper Company. The conductivities which they obtained of low-silver coppers indicated that the loss in conductivity was due to the presence of a low copper–high silver solid-solution phase disseminated throughout a matrix of copper, and not to a general solid solution of the silver in the copper. Such a general solid solution would decrease the conductivity much more than the results obtained.

Conclusion

All these facts led to the conclusion that in the samples examined the silver was not dissolved in the copper. This might mean that silver is not soluble in copper or that the samples examined had not gone through a treatment which would permit solid solution to occur. But manifestly the latter explanation is untenable. The writer is of the opinion that there is no solid solution formed by silver atoms replacing copper atoms in the copper lattice—that is, under ordinary room conditions silver is not soluble in copper. Work is now in progress to determine whether such solubility occurs at higher temperatures.



Hull Diagram of Copper Wire

Assaying 0.2 per cent silver. Arrows indicate reflections from silver lattices.

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Chilean Sulfur Mines Bought by British

An agreement was recently signed in Antofagasta whereby a large British company acquired from the former Italian owners the Tacora sulfur mines near Arica, at a price said to be 3,500,000 pesos. Modern methods of refining are to be introduced, and the sulfur will be shipped to Europe and to markets on the Atlantic coast of South America, where distributing agencies are said to have been established.

Kinetics of a Type of Heterogeneous Reactions[1]

The Mechanism of Combustion of Pulverized Fuel

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A theory has been presented and developed mathematically to account for the kinetics of a particular type of heterogeneous reaction—namely, a highly exothermic reaction between a finely divided reacting solid suspended in a reacting fluid medium, the products of reaction being totally fluid.

Employing only fundamental physical constants, such as coefficients of thermal conduction and diffusion, this theory of the reaction mechanism has been applied to the combustion of pulverized solid fuel with results which are in striking accord with the available published experimental data.

The effects of numerous variables influencing the combustion of pulverized coal and coke are discussed. Certain theoretical conclusions are drawn respecting the combustion of pulverized fuel in furnaces and kilns which are found to be in accord with the results of modern practice.

IN VIEW of the trend during recent years toward the combustion of solid fuel in pulverized form, the paucity of reliable data on the mechanism of this most important chemical reaction is astonishing. The first noteworthy attempt at a serious investigation which has come to the writers' attention is the recent study by Griffin, Adams, and Smith (*1*), of the United States Bureau of Mines. Their results are in such striking accord with a theory of the kinetics of reactions of this type, conceived several years ago by one of the writers, that the detailed presentation of this theory seems justified.

As an approach to the general problem, the following specific case may be considered: Given a sphere of carbon which is suspended in an atmosphere containing a fixed amount of oxygen kept at a constant temperature, what will be the rate of combustion of the sphere?

Statement of Theory

In the accepted theory of fluid flow and of heat transfer by convection, it has been assumed that a hot body immersed in a cooler fluid is surrounded by a relatively stationary or stagnant fluid film, outside of which turbulent motion is maintained by convection currents (*3*). The extensive work of C. W. Rice (*4*) and others has made it possible to compute the approximate magnitude of the dimensions of such films.

Accordingly, therefore, if a sphere of non-volatile combustible material were immersed in an oxygen-containing atmosphere, and if combustion were proceeding uniformly on the surface of the solid, the formation of a stationary film of the atmosphere around the solid might be expected. If this condition should actually obtain, the combustion of the sphere would then proceed by the diffusion of oxygen through the film to react at the surface of the sphere. If the sphere is composed of carbon, the oxygen might react at its surface to form carbon dioxide, which in turn would diffuse outward through the film to disperse in the turbulent atmosphere at the external boundary of the film. On these assumptions, then, the rate of combustion will be controlled by the rate of diffusion of the oxygen, and of the carbon dioxide through the film, provided the rate of chemical reaction is rapid compared with the rate of diffusion. The heat generated at the solid surface is the heat of reaction at the temperature of the surface, and the energy so liberated tends to raise the temperature of the solid and of the film. Heat is lost, however, by conduction through the film to the turbulent fluid, and by direct radiation to the furnace wall. In the final analysis, therefore, the rate of combustion will be controlled by the composition of the atmosphere; the pressure; the temperatures of the sphere, the ambient fluid, and the furnace walls; the size of the sphere; the thickness of the film; and similar factors. This conception of combustion is diagrammatically illustrated in Figure 1.

Mathematical Development

The following calculations based upon this picture of combustion furnish a mathematical presentation of our theory. The additional assumption is made that the sphere is surrounded with an infinite amount of the oxygen-containing atmosphere or that the atmosphere is constantly renewed, so that the products of combustion do not change the concentration of the oxygen at the external boundary of the stationary film.

The symbols employed are defined as follows:

T_1 = temperature of surface of sphere, ° K.
T_2 = temperature of ambient atmosphere, ° K.
T = temperature at any point in the annular fluid film, ° K.
T_0 = normal temperature, 273° K.
R_1 = initial radius of combustible solid sphere, cm.
R_2 = initial radius to outside of film, cm.
R = final radius of sphere, cm.
r_1 = radius of sphere at any time, cm.
r_2 = radius to outside of film at any time, cm.
r = radial distance to any point, cm.
f = fraction by weight of non-combustible (ash) in carbon
C_0 = concentration of oxygen in ambient atmosphere, grams per cc.
C = concentration of oxygen in film at any point, grams per cc.
M = mass of oxygen consumed per second, grams
ρ = density of sphere, grams per cc.
K = coefficient of heat conduction of the film, cal. per sq. cm. per second per ° C. at any point
K_0 = coefficient of heat conduction of the film at N. T. P.
σ = constant of heat radiation, cal. per sq. cm. per second per $° C.^4$
δ = coefficient of diffusion at any point in film, sq. cm. per second
δ_0 = coefficient of diffusion at N. T. P.
B = $r_2 - r_1$ = thickness of annular fluid film
D = $2r_1$ = diameter of sphere
Q = heat liberated by combustion of 1 gram of oxygen
p = pressure, atmospheres
H_1 = rate of heat transfer from sphere by conduction, cal. per second
H_2 = rate of heat transfer from sphere by radiation, cal. per second
H = rate of heat liberation by chemical reaction (combustion), cal. per second
t = time, seconds

To be specific, the combustion of coal in air will be considered, and therefore the values of K, δ, and C_0 for air will be employed. Thus, since 1 cc. of oxygen at N. T. P. weighs 1.43×10^{-3} grams, and air contains 21 per cent oxygen,

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[1] Received December 27, 1930. Presented before the Division of Gas and Fuel Chemistry at the 79th Meeting of the American Chemical Society, Atlanta, Ga., April 7 to 11, 1930.

$$C_0 = 0.00030\, p\, \frac{T_0}{T_2} \tag{1}$$

The formula adopted by Rice (*4*) for the thermal conductivity of air is

$$K = 0.000053 \left(\frac{T}{T_0}\right)^{0.75} (1 + 0.0002\, T) \tag{2}$$

For the purpose of calculating the heat transfer which takes place from the sphere to the surrounding atmosphere, it is assumed that the temperature gradient across the film is the same as it would be in the steady state of heat transfer. This assumption implies that the rate of change of the temperature of the sphere is slow as compared with the establishment of thermal equilibrium throughout the film. The heat conducted away per second across any spherical surface is equal to the area of the surface times the temperature gradient—i. e.,

$$H_1 = -4\pi K r^2 \frac{\partial T}{\partial r} \tag{3}$$

If the value of K from Equation 2 is substituted in Equation 3 and integrated, it leads to a very complicated expression. The procedure adopted is as follows:

$$\text{Let } K = K_0 T \tag{4}$$

which assumption is quite a close approximation to the relation given in Equation 2. Substitute this value for K in (3) and integrate. The resulting expression is

$$4\pi K_0 \int_{T_1}^{T_2} T\,dT = -H_1 \int_{r_1}^{r_2} \frac{dr}{r^2} \tag{5}$$

or

$$H_1 = \frac{4\pi r_1 r_2 (T_1 - T_2)}{r_2 - r_1} K_0 \frac{T_1 + T_2}{2} \tag{6}$$

On the other hand, had Equation 3 been integrated on the assumption that K was independent of T, then the following result would have been obtained:

$$H_1 = \frac{4\pi r_1 r_2 (T_1 - T_2)}{r_2 - r_1} K \tag{7}$$

On comparison, Equations 6 and 7 are seen to be identical except that in the latter K takes the place of $K_0 \frac{T_1 + T_2}{2}$. To a close approximation, therefore, the heat transferred by conduction from the sphere can be calculated as if the thermal conductivity of the film were constant, provided that the value corresponding to the arithmetical mean of the temperatures of the inside and outside boundaries of the film is adopted. Hence,

$$H_1 = \frac{4\pi r_1 r_2 (T_1 - T_2)}{(r_2 - r_1)} \times 0.000053 \left(\frac{T_1 + T_2}{2T_0}\right)^{0.75} [1 + 0.0001\,(T_1 + T_2)] \tag{8}$$

An additional approximation is tacitly made in the foregoing derivation of the formula for H_1. Oxygen enters the film at temperature T_2 and reaches a temperature T_1 as it diffuses to the sphere. Carbon dioxide leaving the carbon particle reverses this process. Since carbon dioxide has a higher specific heat than oxygen, the heat liberated by carbon dioxide as its temperature is lowered from T_1 to T_2 will not be exactly compensated by the absorption of heat by oxygen.

The temperature at any point in the film may now be readily calculated from Equation 5 if one integrates up to T and r, respectively. From such integration it is found that

$$T = \left[\frac{1}{r}\left(a + br\right)\right]^{1/2} \tag{9}$$

where

$$a = \frac{r_1 r_2 (T_1^2 - T_2^2)}{(r_2 - r_1)} \tag{10}$$

and

$$b = \frac{T_2^2 r_2 - T_1^2 r_1}{(r_2 - r_1)} \tag{11}$$

For calculating the diffusion of oxygen through the film, a device is used similar to that employed for the calculation of the heat lost by conduction. The accepted formula for the coefficient of diffusion of oxygen in air (*2*) is

$$\delta = \frac{0.178}{p} \left(\frac{T}{T_0}\right)^{1.75} \tag{12}$$

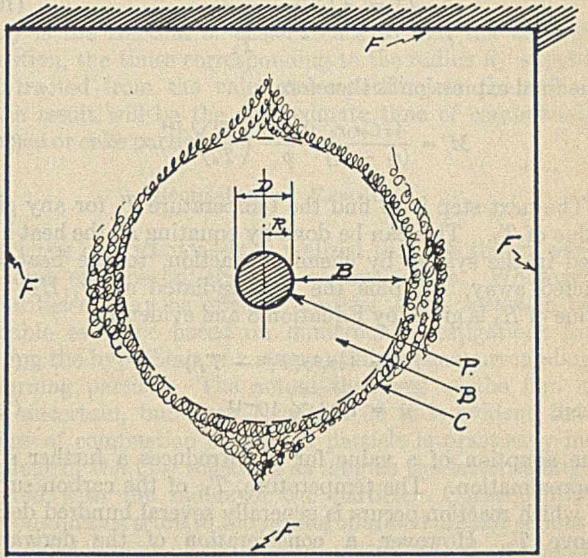

Figure 1—Combustion of Pulverized Fuel

P— Sphere of carbon
B— Stagnant film of gases
C— Air in turbulent motion
F— Furnace walls at temperature, T_2

but instead, the approximate formula

$$\delta = \frac{\delta_0}{p}\left(\frac{T}{T_0}\right)^2 \tag{13}$$

is employed. Now the mass diffusing in unit time across any boundary is equal to the area times the concentration gradient. For a sphere, therefore,

$$M = 4\pi r^2 \delta \frac{\partial C}{\partial r} \tag{14}$$

But according to Equations 9 and 13,

$$\delta = \frac{\delta_0}{pr} \frac{(a + br)}{T_0^2} \tag{15}$$

Substituting this value in (14) and integrating, it is found that:

$$M \int_{r_1}^{r_2} \frac{dr}{r(a + br)} = \frac{4\pi \delta_0 C_0}{p T_0^2} \tag{16}$$

or

$$M = \frac{4\pi C_0 r_1 r_2}{(r_2 - r_1) p T_0^2} \delta_0 \frac{(T_1^2 - T_2^2)}{2 \log \frac{T_1}{T_2}} \tag{17}$$

If (14) had been integrated as if δ were independent of temperature $\left(\delta = \frac{\delta'}{p}\right)$ the following result would have been obtained:

$$M = \frac{4\pi C_0 r_1 r_2}{p(r_2 - r_1)}\,\delta' \qquad (18)$$

Comparing (17) and (18), it is found that δ' takes the place of

$$\delta_0 \frac{(T_1^2 - T_2^2)}{\left(2 \log \frac{T_1}{T_2}\right) T_0^2}$$

As an approximation it may be assumed, therefore, that diffusion occurs as if the coefficient were constant and had a value which is equivalent to the value at the temperature T^1, where

$$T^1 = \sqrt{\frac{T_1^2 - T_2^2)}{2 \log \frac{T_1}{T_2}}} \qquad (19)$$

The final expression is therefore

$$M = \frac{4\pi C_0 r_1 r_2}{(r_2 - r_1)} \frac{0.178}{p} \left(\frac{T^1}{T_0}\right)^{1.754} \qquad (20)$$

The next step is to find the temperature T_1 for any given value of T_2. This can be done by equating H, the heat liberated in the system by chemical reaction, to the heat conducted away, H_1, plus the heat radiated away, H_2. The value of H_1 is given by Equation 8 and evidently

$$H_2 = 4\pi r_1^2 \sigma (T_1^4 - T_2^4) \qquad (21)$$

where

$$\sigma = 1.38 \times 10^{-12} \qquad (22)$$

The adoption of a value for H introduces a further slight approximation. The temperature, T_1, of the carbon surface at which reaction occurs is generally several hundred degrees above T_2. However, a consideration of the derivations made thus far dictates the choice of the fluid temperature, T_2, as that for which the heat of reaction should be taken. The error thus introduced is the energy as sensible heat above T_2 contained in the carbon consumed. This error is slight and is in part compensated for by the increased temperature of the remainder of the carbon sphere (Figure 2).

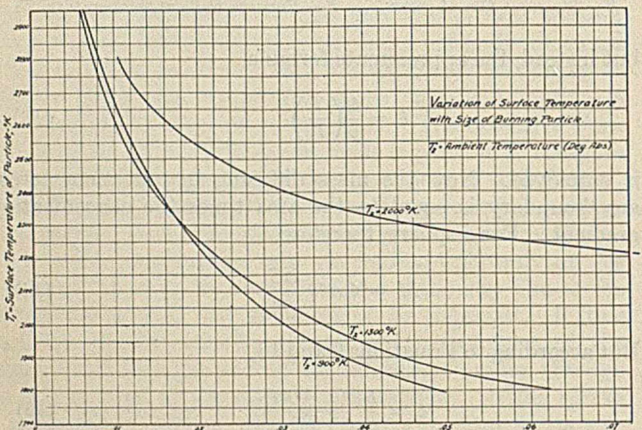

Figure 2—Combustion of Coal Particles

However, for the purpose of further simplifying the formula, we have adopted the value of Q at 15° C. since only a slight additional error is caused thereby. The more correct value at any fluid temperature met in practice can readily be substituted.

The heat liberated by the combustion of 1 mol of carbon at 15° C. is 94,300 calories (*2*).

Hence

$$Q = 2950 \text{ cal.} \qquad (23)$$

and

$$H = QM \qquad (24)$$

It is necessary to find a relation between r_1 and r_2. This fortunately is available from the work of Rice (*4*), who by dimensional analysis has derived the following formula for free convection:

$$\frac{B}{D} = k\left[\frac{\nu}{[\alpha g(T_1 - T_2)]^{1/2} D^{3/2}}\right]^n \left(\frac{k}{\mu C_p}\right)^m$$

where

k, n, m = constants
α = coefficient of density change per ° C.
g = acceleration due to gravity
μ = viscosity of fluid
S = density of fluid
ν = μ/S
C_p = specific heat per gram of fluid at constant pressure

Other symbols are as previously defined.

From experiments on spheres in air, Rice showed that $k = 2.0$, n is $^1/_2$, and m is $^1/_4$, although these values are somewhat uncertain. By proper substitution we find, therefore,

$$r_2 = r_1 + 0.29k\left(\frac{D}{T_1 - T_2}\right)^{1/4} \left(\frac{T_1 + T_2}{2T_0}\right)^{0.88} \frac{1}{p^{1/2}} \qquad (25)$$

whence

$$r = r_1 + 0.75\left(\frac{r_1}{T_1 - T_2}\right)^{1/4} \left(\frac{T_1 + T_2}{2T_0}\right)^{0.88} \frac{1}{p^{1/2}} \qquad (26)$$

Now, putting $H = H_1 + H_2$, the following equation is obtained:

$$\delta C_0 Q = K(T_1 - T_2) + \frac{r_1(r_2 - r_1)}{r^2}\,\sigma(T_1^4 - T_2^4) \qquad (27)$$

If the proper values are substituted from the previous formula, we arrive at a relation between T_1, T_2, and r_1, thus:

$$\frac{(T_1^2 - T_2^2)^{1/8}}{\overline{T_2}\left(\log \frac{T_1}{T_2}\right)^{7/8}} = 3.67 \times 10^{-4}(T_1 - T_2)^{1/4}[1 + 0.0001(T_1 + T_2)] + \frac{3.23 \times 10^{-12}\, r_1^{5/4}\, (T_1 + T_2)^{9/8}\, (T_1^2 + T_2^2)}{r_1 p^{1/2} + 0.75\left(\frac{r_1}{T_1 - T_2}\right)^{1/4}\left(\frac{T_1 + T_2}{2T_0}\right)^{7/8}} \qquad (28)$$

The values of T_1 were calculated from this formula for different values of r_1. This was done for three ambient temperatures, T_2 = 900°, 1300°, and 2000° K., and the results are presented graphically on Figure 2.

It now becomes possible to calculate the total time of combustion of the sphere. Since 2.66 grams of oxygen are required for the combustion of 1 gram of carbon, the mass of oxygen diffusing to the surface of the sphere per second will be equal to 2.66 times the mass of carbon which disappears per second—i. e.,

$$\frac{1}{2.66} M = -\frac{d\left(\frac{4}{3}\pi r_1^3 \rho\right)}{dt} = -4\pi r_1^2 \rho \frac{dr_1}{dt} \qquad (29)$$

or substituting the value for M from Equation 18, we find

$$\frac{C_0 r_2 \delta}{2.66(r_2 - r_1)} = -r_1 \rho \frac{dr_1}{dt} \qquad (30)$$

In this expression both r_2 and δ are such complicated functions of r_1 that the direct integration cannot be performed. However, it is known from the work of Rice and others that the film thickness, $r_2 - r_1$, is fairly constant. The simplifying assumption can therefore be made that $r_2 - r_1$ or B remain constant and also that δ remain constant at some average value. Integrating on this assumption and assuming for the moment that there is no ash and that the sphere thus disappears entirely, we have

$$\int_{R_1}^{0} \frac{r_1 dr_1}{B + r_1} = -\frac{C_0 \delta}{2.66\ B\rho} t$$

or

$$t = \frac{2.66\ B\rho}{\delta C_0}\left[R_1 - B \log\left(1 + \frac{R_1}{B}\right)\right] \qquad (31)$$

Expanding the logarithm by means of the well-known formula,

$$\frac{t}{\rho} = \frac{2.66}{\delta C_0}\left(\frac{R_1^2}{2} - \frac{R_1^3}{3B} + \frac{R_1^4}{4B^2} \cdots\cdots\right) \qquad (32)$$

If R_1 is small compared to B, as will generally be the case in the combustion of pulverized coal or coke, only the first two terms need to be retained.

Substituting the values of δ and C_0 from Equations 12, 14, and 1, the following result is obtained:

$$t/\rho = \frac{3.35 \times 10^6\ T_2}{\left(\frac{\Theta_1^2 - T_2^2}{2 \log \Theta_1/T_2}\right)^{7/8}}\left(\frac{R_1^2}{2} - \frac{R_1^3}{3B}\right) \qquad (33)$$

where Θ_1 has been substituted for T_1, Θ_1 being the average value of T_1 during the time of combustion. The method of calculating Θ_1 which has been adopted depends upon the fact that the time of combustion is roughly proportional to the square of the radius, as will be seen from Equation 33—i. e., $t = cr_1^2$ approximately. Therefore,

$$\Theta_1 = \frac{\int T_1 dt}{\int dt} = \frac{2\int_0^{R_1} T_1 r_1 dr}{R_1^2} \qquad (34)$$

The values of T_1 can be read off from Figure 2 and by means of graphical integration the values of Θ_1 can be found.

The expression for the average value of B is derived from Equation 25, thus:

$$B = 0.75\left(\frac{{}^2/_3\ R_1}{\Theta_1 - T_2}\right)^{1/4}\left(\frac{\Theta_1 + T_2}{2T_0}\right)^{7/}\ \frac{1}{p^{1/2}} \qquad (35)$$

where Θ_1 has been substituted for T_1 and ${}^2/_3\,R_1$ for r_1, since the average value of r_1 during the time of combustion is ${}^2/_3$ R_1, assuming complete combustion (no ash).

Numerical calculation using Equations 33 to 35 leads to the following set of values, the pressure being assumed to be atmospheric:

			T_2 = 900° C.		
R_1 (cm.)	0.01	0.02	0.03	0.04	0.05
Θ_1 (° K.)	2850	2535	2290	2130	2025
B (cm.)	0.174	0.200	0.216	0.227	0.230
t (sec.)	0.296	1.31	3.30	6.15	9.9
			T_2 = 1300° C.		
R_1 (cm.)	0.01	0.02	0.03	0.04	0.05
Θ_1 (° K.)	2830	2525	2320	2180	2095
B (cm.)	0.201	0.238	0.265	0.282	0.297
t (sec.)	0.346	1.54	3.75	6.95	11.10

It is of interest to note that, for coal particles of the sizes usually employed in pulverized coal-fired installations, the film thickness, B, is ten to twenty times as great as the initial radius of the fuel particle, R_1.

The times of combustion of particles of various sizes are shown by the curves in Figure 3. These curves have been constructed for different values of the ambient temperature, T_2. They apply to the combustion of pure carbon, but can also be used to find the approximate time of combustion of coke or coal containing a limited percentage of ash. Bituminous coal particles will very quickly be converted to porous coke in the process of combustion. In general, the surface temperature, T_1, will be above the fusion point of the ash and the molten ash will probably tend to retreat into the pores of the coke. If it is assumed that this actually occurs, then the ash may remain finally as a core of approximately the same density as the original coal or coke. The radius R_1' of the ash core is given by

$$R_1' = R_1 f^{1/3} \qquad (36)$$

where f is the fraction of ash. Hence to find the time of combustion, the times corresponding to the radius R_1' should be subtracted from the value corresponding to the radius R_1; the result will be the approximate time of combustion of the coal or coke particle.

Discussion of Results

Criticism of Theory—It is realized that the theory proposed here may be criticized on various points. Whatever other criticism may be offered, however, there seems to be reasonable evidence based on numerous investigations for accepting the hypothesis of a stagnant film of gas surrounding the burning particle. The actual thickness of the film is rather uncertain, but from Equation 33 it is evident that the time of combustion of a small particle is practically independent of the film thickness as long as the latter is large compared with the radius of the particle. Consequently, objections on this score to the results obtained are not serious. In the development of the theory, mathematical exigencies dictated certain approximations, but it is believed that these approximations do not alter the general magnitude of the calculated results. Naturally, some uncertainty must remain as regards the final values obtained for the time of combustion. This is due in part to the approximations made and perhaps in greater degree to the uncertainty which attaches to the values of the thermal conductivity and the diffusivity of gases at high temperatures.

Once the theory of the stagnant film is accepted, one is led logically to the conclusion that combustion can take place by diffusion only, and thus one is inevitably led to deductions similar to those which have been derived.

Effect of Pressure—From Equation 28 it is evident that the surface temperature, T_1, is practically independent of p, since $p^{1/2}$ occurs in one term only and in such a way that any variation would not greatly affect the result. Again in Equation 33 p is only contained in B, which occurs in the second term of the right-hand expression. This term is small for small particles. To a first approximation it may therefore be concluded that the time of combustion is independent of the pressure.

Effect of Ambient Temperature—From Figure 3 it will be seen that the time of combustion increases as the temperature of the surrounding atmosphere (ambient temperature) is raised. This rather surprising result is due primarily to the fact that the mass of oxygen per cubic centimeter decreases as the temperature rises.

Effect of Density of Particle—From Equation 33 it is evident that the time of combustion is directly proportional to the density of the particle undergoing combustion.

Effect of Enriching Air—Equation 32 indicates that the time of combustion is inversely proportional to C_0, the concentration of O_2 in the ambient atmosphere. Owing to the simultaneous effect that a change in C_0 would have upon T_1, and hence on δ and K and B, this conclusion is not strictly true, but may be accepted as a close approximation.

Effect of Size of Particle—From the curves of Figure 3 it will be found that the time of combustion increases a little more rapidly than the surface area of the particle. As a first approximation it may be accepted that the time of combustion is proportional to the surface area or the square of the initial radius of the particle.

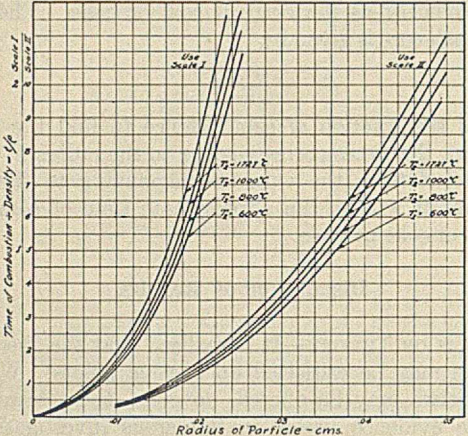

Figure 3—Times of Combustion of Particles of Various Sizes

Effect of Ash—If the ash melts and tends to float the carbon on its surface, the time of combustion will be shortened. A method of calculating its effect has been given above. If the ash does not remain as a core, but drops off in tiny particles during the process of combustion, then its effect will be different. In this case the weight of the ash may be subtracted from the weight of the coal and the corrected density of the coal thus obtained substituted in Equation 33 to find the time of combustion. On the other hand, if the ash tends to coat the surface of the particle, it will lengthen the time of combustion to an indeterminate extent.

Formation of Carbon Monoxide—It was assumed that the oxygen combines directly with the carbon to form carbon dioxide. Obviously this is not strictly true. At any point within the stagnant film there will be a certain concentration of carbon monoxide. As this carbon monoxide diffuses out, it combines with the oxygen diffusing in (assuming thermodynamic equilibrium) so that the final product leaving the film will be practically pure carbon dioxide. Now it can be shown mathematically, in the case of particles of diameter less than 0.5 mm., that the entire process depends hardly at all on what intermediate products are formed, but almost entirely on the final products of combustion. The correction which must be applied to take account of the fact that carbon monoxide is formed as an intermediate product is mainly concerned with the calculation of the temperature variation across the film, since all the chemical heat would not be liberated at the surface of the particle, but might even be entirely released in the film itself. One of the effects of this phenomenon would be a lowering of the surface temperatures as compared with our calculated temperatures.

Reactivity of Carbon—In the discussion it was assumed that the carbon was completely reactive—that is, that every molecule of oxygen striking the surface combined with an atom of carbon. It is of interest to examine what the result would be if complete "reactivity" did not obtain. Let us suppose that only a certain fraction of the collisions between oxygen and carbon lead to reaction, and let:

β = fraction of oxygen collisions which are effective
N_1 = number of oxygen molecules consumed per sq. cm. of surface per second
N_2 = number of oxygen molecules consumed per sq. cm. of surface per second, when the carbon is completely reactive
N = number of molecules in 1 cc. of gas at N. T. P.
S = number of collisions per sq. cm. per second
C_0 = fractional concentration of oxygen outside the film
C_1 = fractional concentration of oxygen at surface of carbon
u = average velocity of gas molecules
B = thickness of stagnant film
δ = coefficient of diffusion

Consider the case of diffusion of oxygen across a film to a plane surface of carbon at N. T. P. If the carbon is not completely reactive, a certain concentration, C_1, will be built up at the surface of the carbon. When the steady state is reached, the concentration gradient will be constant and equal to $\frac{C_0 - C_1}{B}$. The number of oxygen molecules diffusing in per second

$$N_1 = N\frac{C_0 - C_1}{B}\,\delta \qquad (a)$$

Similarly,

$$N_2 = \frac{NC_0\delta}{B} \qquad (b)$$

Now the number of effective collisions must be equal to $SC_1\beta$, and this in turn must be equal to the number of molecules diffusing in—namely, N_1.

Hence

$$N\frac{(C_0 - C_1)}{B}\,\delta = SC_1\beta \qquad (c)$$

But from the kinetic theory of gases it is known that

$$S = N\,{}^{u}/_{4} \qquad (d)$$

and for air at N. T. P.

$$u = 4.88 \times 10^4$$
$$S = 1.22 \times 10^4 N$$

Therefore, from Equation (c),

$$C_1 = \frac{C_0\delta}{\delta + 1.22 \times 10^4\beta B} \qquad (e)$$

Hence from (a) and (b),

$$\frac{N_1}{N_2} = 1 - \frac{C_1}{C_0} = \frac{1.22 \times 10^4\beta B}{\delta + 1.22 \times 10^4\beta B} \qquad (f)$$

N_1/N_2 is the ratio of the rate of reaction when the carbon is only partly reactive to that when it is completely reactive. To estimate the value of this ratio, it is arbitrarily assumed that (Table I)

B = 0.2 cm.
δ = 0.18 sq. cm. per second

and we find that if

β =	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}

then

N_1/N_2 =	0.9993	0.9926	0.931	0.575	0.12

From these results it is seen that there is a decrease of about 7 per cent in the rate of reaction when $\beta = 10^{-3}$—i. e., when one collision in a thousand is effective. If less than one collision in a thousand leads to chemical reaction, then the rate of combustion is retarded quite appreciably.

It has been demonstrated that at a given temperature one type of carbon may be much more reactive than another type. Accordingly, at a given ambient temperature reaction may take place in one case and not in another. When once a sufficiently high temperature has been attained to cause incipient combustion to take place, then the heat developed will probably raise the temperature of the carbon particle to a point where reactivity will become practically complete and combustion will occur uniformly over the entire surface. When this occurs, the rate of combustion depends upon the diffusion alone and not upon the initial reactivity of the carbon. Initial reactivity will primarily influence the minimum ambient temperature at which ignition will occur, and not the time of combustion as such.

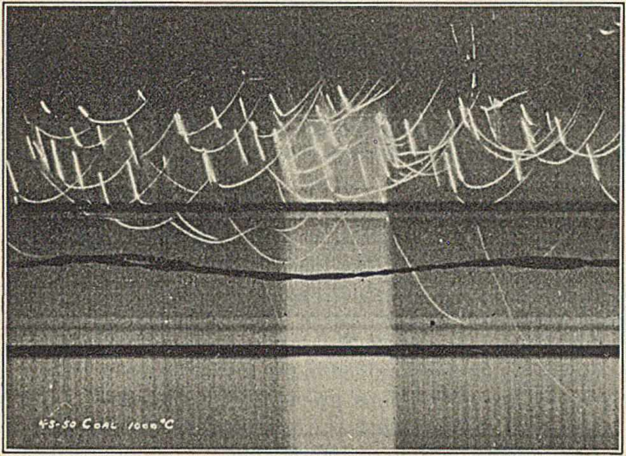

Figure 4

It is evident from the foregoing discussion, however, that the "reactivity" of the particles has a most important influence on the "ignitibility" and the maintenance of a pulverized fuel flame at low furnace temperatures. Beyond the empirical and qualitative knowledge gained in practice with different coals, relatively little appears to be known of the important phenomena associated with the reactivity of solid fuels.

Effect of Volatile Matter—Obviously the ambient temperature of the furnace into which the fuel particles are injected will determine the rate of evolution of the volatile matter and will also determine whether the combustion of the volatile will occur as it distils from the fuel. The thermal ignition of hydrocarbons occurs at temperatures above the coking temperatures of most coals, so that it should be quite possible, when the ambient temperature is low, for most of the volatile matter to be distilled from the fuel before ignition occurs. In any event the coal particle on entering the combustion chamber is first converted to coke, with a consequent loss of weight, decrease in density, and slight change in size. It is with the combustion of the non-volatile residue that this paper deals.

Motion of Fuel Particles during Combustion—A burning particle as dense as coal and larger than 0.01 cm. radius will in general move downward with respect to the ambient atmosphere owing to the action of gravity. During the course of combustion, however, the weight of the diminishing particle rapidly decreases while the volume of the stagnant sphere surrounding it hardly changes. Moreover, the temperature of the stagnant film steadily increases. Consequently, a point is quickly reached at which the buoyant effect of the denser ambient fluid exerts an upward force on the stagnant sphere greater than the force of gravity and the particle rises with respect to the ambient gases. If the ambient gas is stationary, a particle burning in it will first fall and then rise, the stagnant film acting as a tiny balloon. Finally, when combustion is complete, the film disappears and the ash residue falls.

It is of interest to determine approximately the point at which the fuel particle and surrounding film become lighter than the ambient atmosphere. Obviously this is primarily a function of fuel density and the ambient temperature. Sacrificing precision to simplicity, let it be assumed that the fuel has a density of one, that $T_1 = 2800°$ K. and $T_2 = 1300°$ K., and the film thickness, B, is 0.2 cm. (Table I) at the moment the particle rises. It can readily be shown mathematically that in this case the effective temperature of the film determining its density is very nearly 1600° K., and consequently that the fuel particle will rise when its radius is slightly less than 0.008 cm. It is of course evident that, if the initial radius of the particle were large or its ash content high, the ash residue might exceed the weight equivalent to 0.008 cm. radius and consequently the particle would never rise with respect to the ambient gas.

Application of Theory to Other Reactions—It will be evident to the reader that the theory proposed is of wide application and in no way limited to the combustion of fuel particles. It should apply equally well to any highly exothermic reaction between small solid particles and fluids in which the products of reaction are fluid. The reaction between finely divided iron and gaseous chlorine, for example, should be equally amenable to this theoretical treatment.

Comparison with Experimental Results

The theory as developed may now be applied to the experimental results obtained by Griffin, Adams, and Smith (*1*). These authors, in a careful and excellent study, photographed the tracks of burning carbonaceous particles, and obtained their average times of combustion. Two typical pictures are reproduced here. Figure 4 shows 45-50 mesh coal particles at a furnace temperature of 1000° C. and Figure 5 shows 45-50 mesh charcoal at 800° C. It is to be noted that the fuels selected possess widely different "reactivities." The data supplied by these authors concerning the fuels employed can be summarized as follows:

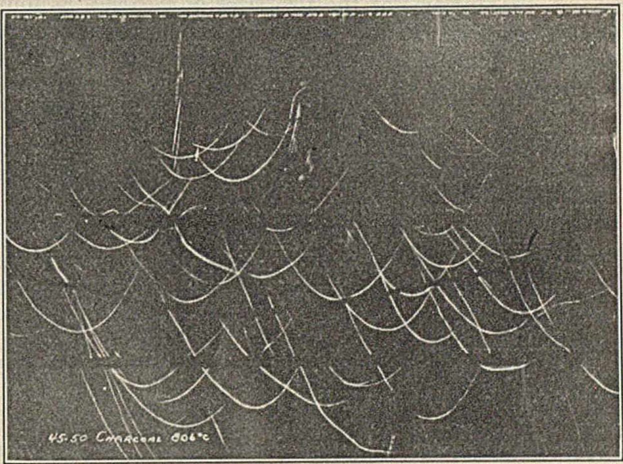

Figure 5

	Coal	Semi-Coke	Beehive Coke	Charcoal
Volatile, %	33.9	15.9	2.1	0
Ash, %	9.8	12.5	11.2	0
$W \times 10^{5}$[a]	2.76	1.41	3.12	1.81

[a] W is the weight of an individual particle in grams.

From the photographs of the tracks of particles of high volatile content, it is evident that the volatile material is ejected from the particle and burns in a very short time compared with that required for the combustion of the residue of carbon. Accordingly, we have subtracted the weight of the volatile matter from the original weight of the particle. The density, ρ, given in the following table, was calculated on the basis of this corrected weight of the particle, assuming that the original density of the coal was equal to 1.3 grams per cubic centimeter. It was further assumed that the particles were sufficiently spherical in shape so that the radius R_1 could be calculated from the relation

$$W = \frac{4}{3}\pi R_1^3\rho$$

To calculate the radius R'_1 of the remaining ash core, it was assumed that the density of the porous ash was equal to unity. If the actual weight of ash in each particle is known, the radius can readily be computed. The results for particles of 45–50 mesh, are listed below:

	COAL	SEMI-COKE	BEEHIVE COKE	CHARCOAL
R_1	0.0172	0.0172	0.0172	0.0172
ρ	0.86	0.56	1.44	0.85
R_1'	0.00875	0.0075	0.00942	0

If R_1, ρ, and R_1' are known, the actual times of combustion can be obtained from the curves in Figure 3, as previously described. In the following table these values are given together with the experimental values. In the case of coal, semi-coke, and charcoal the experimental points are those reported by Griffin and co-workers (*1*), but in the case of beehive coke approximate values were obtained by actually measuring as large a number of tracks as could be distinguished on photographs supplied through the courtesy of D. F. Smith. No photograph was available for 45–50 mesh particles of beehive coke. The time for 80–90 mesh particles at 1000° C. was found from a photograph, and this time was multiplied by a factor 2.7, which is the average ratio, in time of combustion, for the two sizes of particles as found from experiment. In the table below[2] the experimental and theoretical times of combustion for particles of 45–50 mesh are shown:

	T_2 = 800° C.		T_2 = 1000° C.	
MATERIAL	Expt.	Theory	Expt.	Theory
Coal	0.37	0.58	0.58	0.63
Semi-coke	0.31	0.32	0.45	0.38
Beehive coke		1.11	1.35	1.20
Charcoal	0.55	0.82	0.84	0.89

The agreement between the experimental and theoretical values is remarkably good, but must be considered partly fortuitous. The experimental increase in time of combustion with increase in the ambient temperature ("negative temperature coefficient") is greater than that predicted by the theory. This may possibly be due to the fact that the core of ash, being luminous at the higher temperatures, registered on the photographic plate after all the carbon had been consumed. If this is so, the experimental times obtained at the higher temperatures would probably be longer than the actual times of combustion. However, our knowledge of the thermal coefficient of conductivity, diffusion, etc., at these temperatures is so meager that the discrepancy between the experimental and theoretical results indicates no lack of agreement between the two.

Taken as a whole, the experimental results are, in the writers' opinion, strikingly in accord with the proposed theory. The significant points of agreement may be summarized as follows:

(1) The times of combustion calculated from theory, when compared with experimental measurements on a wide variety of fuel particles, not only indicate the correct relative order of rapidity of combustion, and predict the proper magnitude thereof, but actually agree with the measured values well within the unavoidable errors of calculation and experiment.

(2) The effects of all the variables studied experimentally are strictly in accord with the predictions of the theory, especially the rather surprising conclusions concerning reactivity and the negative temperature coefficient.

(3) The peculiar motion of the particles predicted by theory is fully confirmed by the photographic records of the experiments.

Combustion of Pulverized Fuel in Furnaces

Thus far, in calculating the time of combustion of a spherical fuel particle, the ambient temperature and the oxygen concentration have been assumed to be constant. Under these conditions it was possible to calculate the surface temperature and the film thickness with relatively few additional assumptions.

The combustion of pulverized fuel in modern furnaces and kilns is, of course, conducted under conditions which render the assumptions of constant oxygen concentration and constant ambient temperature invalid. The ambient temperature, being determined by the quantity of fuel burnt and by the heat lost through radiation, convection, etc., will vary from point to point in the furnace. The surface temperature of the particle is in turn governed by the ambient temperature and the instantaneous oxygen concentration, as well as by the conditions of radiation and heat transfer. Moreover, as the carbon dioxide concentration in the ambient gases increases, the latter cease to be transparent to radiation, as was assumed in the earlier pages of this paper. However, the conclusions previously reached and presented in Figure 3 indicate that the temperature factors will only slightly affect the time of combustion. The dominant factor controlling the time of combustion is the change in the oxygen concentration.

In the following calculation, therefore, variations in surface and ambient temperatures have been disregarded and only the variation in oxygen concentration has been taken into account.

Let us assume that a perfect mixture of fuel and air is injected into a furnace which is at a constant temperature, T_2. This implies that each fuel particle is surrounded by its aliquot portion of the air supplied.

Let α be the fraction of excess air supplied above that theoretically required for combustion of the fuel. The decrease in oxygen concentration will be directly proportional to the weight of carbon consumed—i. e.,

$$C = P - Q(R_1^3 - r_1^3) \tag{37}$$

where P and Q are constants, R_1 is the initial radius, and r_1 the radius at any instant. The variable C is the concentration of oxygen in the ambient gases at any time after combustion starts

When $r_1 = R_1,\ C = C_0$

Therefore, $P = C_0$

When $r_1 = 0,\ C = \dfrac{\alpha}{1+\alpha}C_0$

Therefore, $\dfrac{\alpha}{1+\alpha}C_0 = C_0 - QR_1^3$

and $Q = C_0\dfrac{1}{(1+\alpha)R_1^3}$

Hence $C = C_0\dfrac{\alpha + \left(\dfrac{r_1}{R_1}\right)}{1+\alpha}$

If this value of C is substituted in Equation 30 and the integration performed, it is found that

$$1 + \alpha \int_{R_1}^{0} \frac{r_1 dr_1}{(B + r_1)\left(\alpha + \frac{r_1}{R_1}\right)^3} = \frac{C_0\delta}{2.66\ B\rho}t \tag{38}$$

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[2] These data were presented at the Columbus Meeting of the American Chemical Society in discussion of the paper by Griffin, Adams, and Smith (*1*).

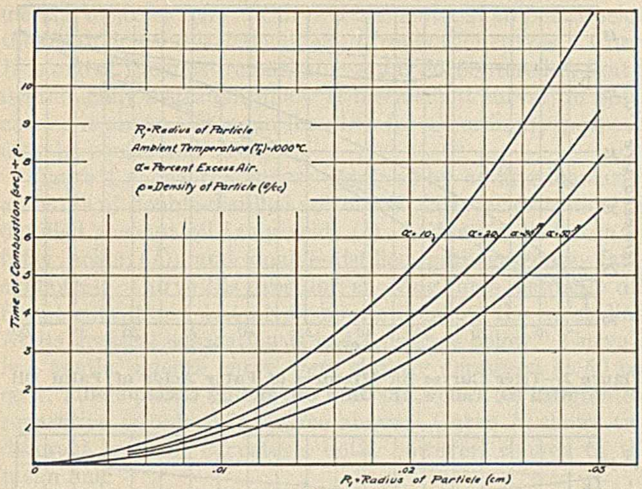

Figure 6—Size of Particles *vs.* Time of Combustion for Various Amounts of Excess Air

This leads to the expression:

$$t/\rho = \frac{2.66\ B\ (1+\alpha)R_1^3}{\delta C_0\ (B^3 - \alpha R_1^3)} \left\{ B \log \frac{B + R_1}{B} - \frac{B}{3} \log \frac{\alpha + 1}{\alpha} + \frac{1}{6}\,\frac{B^2 + R_1^2\alpha^{2/3}}{R_1\alpha^{1/3}} \log \frac{1 + \alpha^{2/3} - \alpha^{1/3}}{(1 + \alpha^{1/3})^2} + \frac{\sqrt{3}}{3}\,\frac{B^2 - R_1^2\alpha^{2/3}}{R_1\alpha^{1/3}} \left[\tan^{-1} \frac{2 - \alpha^{1/3}}{\alpha^{1/3}\sqrt{3}} + \frac{\pi}{6} \right] \right\} \quad (39)$$

From this formula the time of combustion can be calculated for various percentages of excess air. This was done and the results are presented in Figures 6 and 7. From these curves it is seen that the time of combustion at 30 per cent excess air is roughly twice as long as when the oxygen concentration remains undiminished (Figure 3). Furthermore, it is evident that the time of combustion or the length of the flame is not appreciably reduced by supplying more than 30 per cent excess air. Evidently, one way in which the flame-length can be reduced is by decreasing the size of the particles.

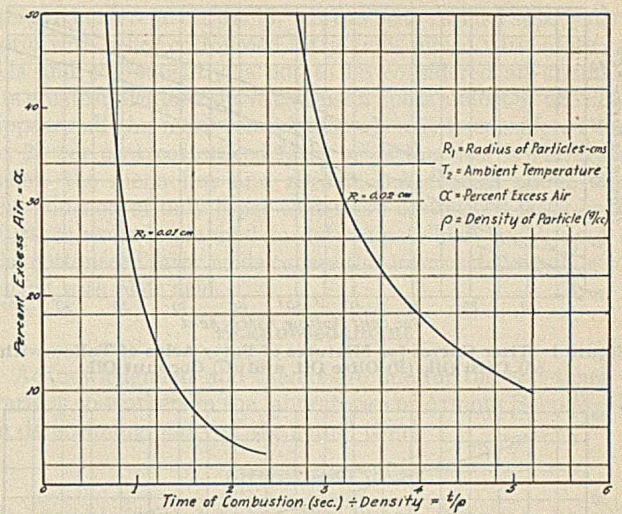

Figure 7—Variation of Time of Combustion with Per Cent of Excess Air

Effect of Turbulence—Assuming that the original mixture of fuel and air was "perfect" as defined, the effect of turbulence in the furnace will be negligible, since it is unlikely that any attainable degree of turbulence will decrease the film thickness to such an extent as to affect the rate of combustion. Obviously, if the original mixture was not "perfect," as is usually the case, some benefit is derived from turbulence in improving the mixture of fuel and air.

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Some Titer Points of Mixed Fatty Acids

I—Mixtures of Commercial Oils, Fats, and Fatty Acids[1]

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The titer points of mixtures of oils and fats and of their fatty acids are important in the manufacture of soap, fatty acids, lubricants, and other products. Soaps for various uses and fatty acids used in the manufacture of lubricating greases are bought on a specified titer basis. The frequent failure of attempts to meet these titer requirements by mixtures of oils and fats calculated simply from their independent titers suggested an investigation of the subject. The results obtained on a number of these mixtures as they occur commonly in commerce are reported in this paper. It is intended to continue this work on the pure fatty acids to determine the cause underlying the apparently erratic results obtained in several cases and to explain the form taken by those curves which are fairly smooth and regular.

The titer point is that temperature in degrees Centigrade which is the highest reached while fatty acids are solidifying from the melted state. While the fatty acids are cooling, the temperature continues to drop until crystals begin to form. Owing to the liberation of the latent heat of fusion of the crystals, the temperature ceases to fall, remains constant for a number of seconds, and then begins to rise. The highest temperature reached before it declines again is called the titer point. In the great majority of cases the temperature, after reaching the peak, continues to drop as long as the air surrounding the fatty acids is colder than the fatty acids, but occasionally a commercial red oil is encountered which will show a second, less well-defined rise in temperature, usually about one degree lower than the first.

Procedure

All titers were determined in accordance with the standard method of the Fat Analysis Committee of the American Chemical Society (*1*), which method, in brief, is conducted as follows: The oil or fat is saponified by a solution of potassium hydroxide in anhydrous glycerol, the fatty acids liberated from the potassium soap by boiling with sulfuric acid, washed with water, filtered, dried, and the titer point determined.

For the work undertaken it was found convenient to pre-

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[1] Received December 4, 1930.

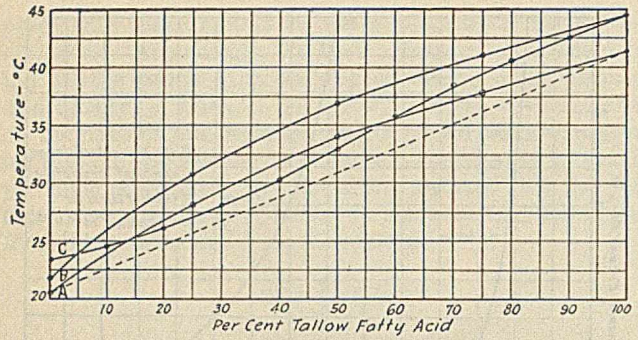

Figure 1—Titer Curves for Mixtures of Fatty Acids of Tallow with (A) Corn Oil, (B) Olive Oil, and (C) Coconut Oil

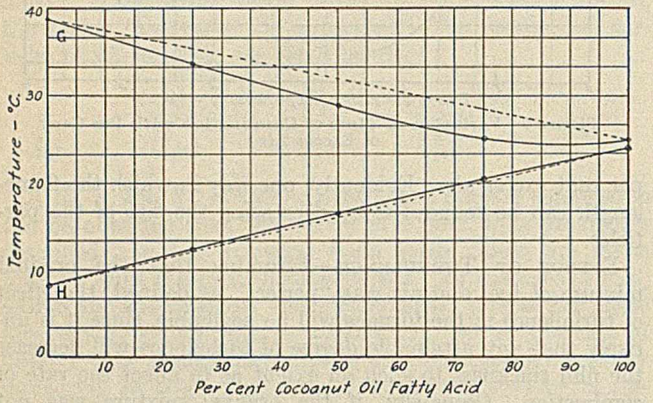

Figure 3—Titer Curves for Mixtures of Fatty Acids of Coconut Oil with (G) Garbage Grease and (H) Commercial Oleic Acid (Red Oil)

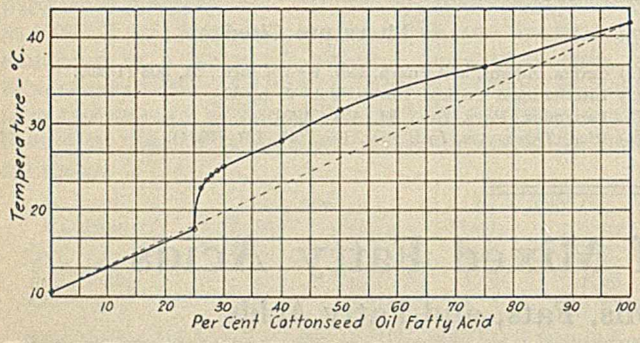

Figure 5—Titer Curve for Mixture of Fatty Acids of Cottonseed Oil and Commercial Oleic Acid (Red Oil)

pare rather large amounts of the mixed fatty acids from each of the oils and fats under examination and to mix small amounts of these acids with each other in the desired proportions just before determining the titer point. The results are reported in the form of curves which are plotted with the titer points as ordinates and the percentage composition of the mixed fatty acids as abscissas. Some of the curves are drawn from figures obtained at each 25 per cent variation in composition of the fatty acids, others from figures obtained at each 10 per cent variation, unless a break appeared, in which case the titers on mixtures varying by 2 per cent were determined. The decision whether to determine the titers at 10 or 25 per cent intervals was based largely on previous experience which had indicated whether or not the curves were regular and smooth. When irregularity was anticipated, the titers were obtained at 10 per cent intervals.

Discussion of Results

The curves in Figures 1 and 2 were determined by mixing varying quantities of the mixed fatty acids obtained from good commercial grades of the oils and fats indicated.

The curves in Figure 1 were obtained by adding increasing amounts of tallow to corn oil (*A*), olive oil (*B*), and coconut oil (*C*). Curves *A* and *B* are smooth and at all points are above the line (not indicated) connecting the titer of the pure oil with that of the pure tallow. For convenience let us call this the "mean line." It really passes through the points of the titers calculated arithmetically from those of the pure oils and tallow, and the separation between this line and the curve indicates the variation obtained in practice from the expected result. Curve *C* is smooth from 0 to 60 per cent of tallow, but below the mean line instead of above. From 60 to 100 per cent of tallow it remains smooth, but reverses its curvature and is above the mean line. The same tallow was used for curves *B* and *C* but not for curve A.

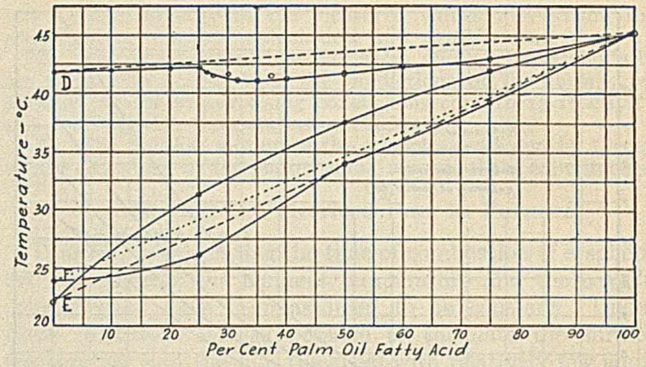

Figure 2—Titer Curves for Mixtures of Fatty Acids of Palm Oil with (D) Tallow, (E) Olive Oil, and (F) Coconut Oil

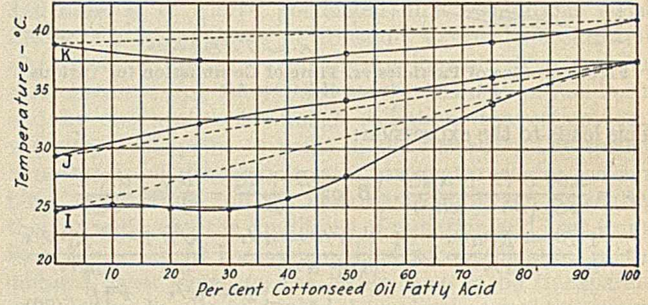

Figure 4—Titer Curves for Mixtures of Fatty Acids of Cottonseed Oil with (I) Coconut Oil, (J) Corn Oil, and (K) Garbage Grease

Figure 2 shows the curves obtained by adding increasing amounts of palm oil to tallow (*D*), olive oil (*E*), and coconut oil (*F*). Curve *D* is below the mean line at all points. Curve *E* is smooth and at all points is above the mean line—about 4 degrees at its greatest divergence. Curve *F* at all points is below the mean line and is fairly smooth. The same palm oil was used for all three curves.

The curves in Figures 3 to 5 were determined on mixtures of commercial fatty acids which had been obtained by twice distilling, on the plant scale, impure fatty acids prepared from low-grade industrial oils and fats. These fatty acids consisted, of course, of all the fatty acids originally present in the oil, together with some impurities. The impurities, amounting to between 2 and 4 per cent in most cases, were mainly unsaponifiable matter (*1*)—that is, cholesterol, phytosterol, or related materials, together with fatty acids oxidized to various compounds by the distillation process. Considering the widely different sources of the waste material from which these fatty acids are prepared, it is surprising how uniform different lots of the same variety of the commercially finished product run. Much of the work here has been checked from time to time with different lots of material and the general forms of the curves shown verified exceptionally well.

Figure 3 shows the curves obtained by adding increasing amounts of double-distilled coconut oil fatty acids to double-distilled garbage-grease fatty acids (*G*) and high-grade commercial oleic acid (*H*). Curve *G* is smooth, at all points below the mean line and is little different from other curves. Curve *H* is one of the most remarkable so far encountered in that it is practically a straight line. It has a slight curvature which carries it above the mean line, but for all ordinary purposes may be considered straight.

Figure 4 shows the curves obtained by adding increasing amounts of double-distilled cottonseed fatty acids to double-distilled coconut oil fatty acids (*I*), double-distilled corn oil fatty acids (*J*), and double-distilled garbage-grease fatty acids (*K*). Curve *I* is irregular, showing three distinctly different curvatures, but at all points is below the mean line. At its greatest separation it is 4.1 degrees below. Curve *J* is a gentle, smooth curve, very slightly depressed at 50 per cent, at all points above the mean line, but at its greatest separation is only 0.75 degree above. Curve *K* shows two different rates of curvature, both, however, convex to the mean line.

Figure 5 shows the curve obtained by adding increasing amounts of double-distilled cottonseed fatty acids to a high-grade commercial oleic acid. It has been verified as to general form with other cottonseed fatty acids mixed with other red oils and consequently is not to be considered an anomaly. Its greatest distance above the mean line is almost 6° C. This appears all the more remarkable when it is considered that at 25 per cent cottonseed fatty acids the titer is 0.5 degree below the mean line and rises to 5.5 degrees above after the addition of only 5 per cent more cottonseed fatty acids. Further work is planned to determine which constituent of the cottonseed fatty acids causes this unexpected result when mixed with oleic acid.

Acknowledgment

Acknowledgment and thanks are due for the assistance of various co-workers in the laboratories of Armour Soap Works in determining many of the actual titers.

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Isolation and Identification of a Polysaccharide from Southern Yellow Pine[1]

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STUDIES of the composition of American woods have been made primarily with the idea of establishing the value of the different species for use in certain industries. In the course of these analyses many interesting observations have been made of products of more or less secondary interest at the present time, but which may later prove to be of significance. One of these is a water-soluble polysaccharide called ϵ-galactan.

This material was first isolated from the western larch by Schorger and Smith (*3*). On the basis of an unusually high yield of purified galactose obtained by hydrolysis of this polysaccharide, these investigators concluded that the polysaccharide contained only this one sugar as its monosaccharide component. The abnormally large amount of furfural formed by distillation of the compound with 12 per cent hydrochloric acid was attributed to a peculiar structure of the galactan molecule rather than to the presence of a pentosan residue. More recently, however, Wise and Peterson (*4*) have definitely shown that the ϵ-galactan yields a pentose constituent which they have identified as arabinose. A series of analyses indicated 11.95 per cent of anhydroarabinose and 84–85 per cent of anhydrogalactose.

Schorger and Smith have also pointed out that most of the coniferae were characterized by the presence of galactans. *Pinus palustris*, *Pinus seratina*, *Pinus heterophylla*, and *Pseudotsuga taxifolia* were found to give mucic acid on oxidation by nitric acid. *Pinus taeda* gave anomalous results—negative with two samples and positive with one. Quantitative determinations were not attempted, as they had already shown that the mucic acid method gave unreliable results when sugars other than galactose were present.

During an investigation of the action of high-pressure steam on southern yellow pine (*Pinus palustris*) now being carried out in this laboratory, it was noted that certain of the concentrated aqueous extracts yielded a polysaccharide material which later proved to contain galactose and arabinose and to resemble the polysaccharide of the western larch.

Isolation of Arabinogalactan from *Pinus Palustris*

The treatment of the wood with high-pressure steam, the Masonite process, has been described (*1*, *2*). The "cyclone condensate" mentioned in this investigation is the aqueous material accumulating in the cyclone separators. Some extraction of the fiber occurs here.

The cyclone condensate was evaporated *in vacuo* to a thin sirup. The sirup was defecated with lead acetate and deleaded with disodium phosphate. The clarified sirup was slowly poured into six volumes of 95 per cent ethyl-alcohol with constant stirring. After the precipitated polysaccharide had settled, the supernatant alcohol was decanted carefully. The polysaccharide was washed by decantation with alcohol until the material was well dehydrated, and then washed several times with ether. The precipitate was filtered onto a Büchner funnel and dried in the vacuum oven at 70° C.

To ascertain whether the substance was formed on exploding the wood or whether it was a natural constituent of the wood, a portion of the wood was extracted. The wood was first extracted with ligroin (b. p. 65–110° C.) in a Soxhlet apparatus for 8 hours. The residue from the ligroin extraction was extracted with water for 40 hours in the apparatus described by Wise and Peterson (*4*). The extract was concentrated and the polysaccharide precipitated exactly as they recommend.

The arabinogalactan as isolated was a white, tasteless powder, readily soluble in water but insoluble in alcohol and ether. The polysaccharide had practically no action on Fehling's solution, but was readily hydrolyzed by heating

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[1] Received February 4, 1931.

with 2 per cent hydrochloric acid for 2 hours at 100° C. The hydrolyzate was strongly reducing.

Hydrolysis of Arabinogalactan Chemical Constituents

Three grams of the dried polysaccharide were dissolved in 150 cc. of 2 per cent sulfuric acid contained in a 250-cc. beaker. The beaker was covered with a watch glass to prevent excessive evaporation and placed in an air bath which was maintained at 100° C. for 8 hours. The solution was cooled and nearly neutralized with a hot aqueous solution of barium hydroxide. The alkali was added slowly and with constant stirring to prevent local overheating. The neutralization was completed with barium carbonate. The neutralized hydrolyzate was evaporated *in vacuo* to a thin sirup.

The sirup was treated with ethyl alcohol to precipitate a small amount of gum which was always present, filtered, and the alcohol removed by evaporation *in vacuo.* The hydrolyzate was then treated with methanol containing a small amount of acetic acid and seeded with a crystal of galactose as described by Wise and Peterson.

When, after standing in the ice box for 3 days, no crystals separated, the methanol was removed by evaporation *in vacuo.* Five grams of diphenylhydrazine dissolved in the least amount of 95 per cent ethyl alcohol were then added and the solution allowed to stand at room temperature for a week.

At the end of this time the crystalline precipitate of mixed diphenylhydrazones was filtered onto a small Büchner funnel and washed several times with ether to remove unchanged diphenylhydrazine. The hydrazones were then fractionally crystallized from 75 per cent alcohol. After three fractionations the less soluble fraction melted at 186–187° C., which was unchanged on recrystallization. The melting point of l-arabinose diphenylhydrazone prepared from Special Chemicals Company l-arabinose melted at 185–186° C. under the same conditions. A mixture of the two melted at 185–186° C. The more soluble fraction melted at 157–158° C. A sample of *d*-galactose diphenylhydrazone melted at 155–156° C. A mixture of the two melted at 156–157° C.

Araban was determined by distillation of the arabinogalactan with 12 per cent hydrochloric acid and precipitation of the furfural as the phloroglucide. The quantity indicated was 12.2 per cent.

The presence of galactose was further established by treatment of the polysaccharide with nitric acid and isolation of mucic acid.

Acknowledgment

The authors wish to thank The Masonite Corporation for furnishing the cyclone condensate and wood chips used in this investigation as well as for the use of their laboratory during a part of this work.

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(2) Kirkpatrick, *Chem. Met. Eng.*, **34**, 342 (1927).
(3) Schorger and Smith, J. Ind. Eng. Chem., **8**, 494 (1916).
(4) Wise and Peterson, *Ibid.*, **22**, 362 (1930).

Dimensional Analysis Applied to the Thermal Conductivity of Liquids[1]

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Assuming that thermal conductivity of liquids is a function of molecular weight, density, specific heat, viscosity, gas constant, thermal expansion, and compressibility, an equation has been derived by dimensional analysis connecting these variables. This equation is:

$$\frac{kK^{1/2}\lambda^{1/8}z^{1/4}}{c^{9/8}\rho^{1/3}m^{5/12}} = \phi\left(\frac{mc}{a}\right)$$

By making certain modifications this equation can be simplified, and a graph is shown connecting $\frac{k}{\sqrt[3]{\rho c}}$ with $\left(\frac{c}{K^2\lambda^{1/3}m^{1/2}z}\right)$. This graph shows a maximum error in thermal conductivity of 4.5 per cent.

FREQUENTLY in research one is confronted with the problem of the determination of a particular property of a fluid or solid. It often happens, also, that this determination is difficult and requires special technic and expensive equipment. In such a case it would be extremely convenient if this property could be calculated from known values of other properties which are more readily obtainable. If, however, it is known that the property wanted is a function of several other properties, it may be a long, tedious process to find the function. The application of dimensional analysis usually simplifies the problem by reducing the number of separate quantities that vary.

Engineers are, in general, not familiar with this subject, so in this article the principle is considered in some detail, avoiding proofs of the theorems. The particular problem is to derive an equation for thermal conductivity of liquids in terms of other properties.

Variables Affecting Thermal Conductivity of Liquids

The first thing to do is to settle which properties affect the thermal conductivity of liquids.

In 1923, Bridgman (*3*) suggested an equation giving thermal conductivity, k, as a function of the gas constant, a, the velocity of sound in the liquid, v, and the mean distance of separation of centers of the molecules, d, assuming an arrangement cubical on the average. The equation is

$$k = \frac{2av}{d^2} \qquad (1)$$

and, of course, it is dimensionally correct.

The arrangement of the variables in the equation could have been determined by dimensional analysis without having the picture portrayed by Bridgman in his derivation provided that k is a function of a, v, and d. The procedure is as follows:

$$k = \phi_1(a, v, d) \text{ or } \phi(k, a, v, d) = 0$$

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[1] Received September 25, 1930.

[2] National Research Fellow, Harvard University Engineering School.

The quantities and their dimensions may be tabulated as follows:

QUANTITY	SYMBOL	DIMENSIONS
Thermal conductivity	k	$ML/T^3\Theta$
Gas constant	a	$ML^2/T^2\Theta$
Velocity of sound in liquid	v	L/T
Mean distance of separation of molecules	d	L

It has been shown (*1*, *4*) that any equation of the type

$$\phi_1(Q_1,\ Q_2,\ Q_3,\ \ldots\ldots Q_n) = 0$$

describing a relation among n different kinds of quantity $Q_1, Q_2 \ldots\ldots Q_n$, is always reducible to the form

$$\phi(\pi_1,\ \pi_2,\ \pi_3,\ \ldots\ldots\ \pi_{n-r}) = 0$$

where each of the variables π represents a dimensionless product of the form $\pi = Q_1^a, Q_2^b, Q_3^c, \ldots Q_n^n$, r is the number of independent fundamental units needed in specifying the units of the n kinds of quantity, and ϕ is an unknown function to be determined by experiment. This is known as the "π theorem."

In the case of thermal conductivity, therefore, $n = 4$ (k, a, v, d) and $r = 4$ (M, L, T, Θ). Thus there appears to be no group involving the four quantities. If, however, we define temperature as the mean energy of the atom, its dimensions are ML^2/T^2 and the gas constant has no dimensions. The new table is as follows:

QUANTITY	SYMBOL	DIMENSIONS
Thermal conductivity	k	$1/LT$
Velocity of sound in liquid	v	L/T
Mean distance of separation of molecules	d	L

In this case $n = 3$, and $r = 2$. Therefore $\phi\ (\pi) = 0$, where $\pi = k^x\, v^y\, d^z$.

It has also been shown (*2*) that, in general, any one of the exponents can be assigned at pleasure. Therefore, since we are interested in k, let us assign the value of 1 to x. Therefore $\pi = k\, v^y\, d^z$.

Apply dimensions:

$$\frac{1}{LT}\left(\frac{L}{T}\right)^y \frac{L^z}{1}$$

From L, $\quad -1 + y + z = 0$

From T, $\quad -1 - y = 0$

Therefore, $\quad y = -1,\ z = 2$

$$\pi = \frac{kd^2}{v} \text{ and } \phi\left(\frac{kd^2}{v}\right) = 0$$

$$\frac{kd^2}{v} = \text{constant } A$$

Therefore, $\quad k = \dfrac{Av}{d^2} \qquad (2)$

which is Bridgman's equation except that the constant A is not explicitly determined. Its value, however, can be found from experiment, and it would be approximately $2a$.

Suppose, not having read Bridgman's paper, we had suspected that thermal conductivity depended not only on the factors v, a, and d, but also on the mass of the molecule, m; then we would have $\phi\ (k, a, v, d, m) = 0$. Giving temperature separate dimensions, and considering the mass of a molecule has dimensions M, we have $n = 5$, and $r = 4$. Therefore, $\phi\ (\pi) = 0$, where $\pi = ka^w\, v^x\, d^y\, m^z$.

Apply dimensions, and we get:

$$\frac{ML}{T^3\Theta}\cdot\frac{M^wL^{2w}}{T^{2w}\,\Theta^w}\cdot\frac{L^x}{T^x}\cdot L^y \,.\, M^z$$

From M, $\quad 1 + w + z = 0$

From L, $\quad 1 + 2w + x + y = 0$

From T, $\quad -3 - 2w - x = 0$

From Θ, $\quad -1 - w = 0$

Solving, $\quad w = -1,\ x = -1,\ y = 2,\ z = 0$

Therefore, $\quad \pi = \dfrac{kd^2}{av}$, or $\dfrac{kd^2}{av}$ = a constant

which is Bridgman's complete equation except that the number 2 is not explicitly determined.

Derivation of Equation

Although this equation is theoretically interesting, results obtained from it are not very accurate. In one instance, that of carbon disulfide, the calculated value is 37 per cent in error, which is perhaps not any closer than one could guess, for after all, outside of water and a few alcohols, thermal conductivities do not vary greatly for liquids. Since, however, this equation gives approximate results, we might forget the physical picture and introduce some other variable and, by dimensional analysis or some other means, create a modifying factor until fairly accurate values of thermal conductivity are obtainable. This method does not appeal to us, however, so we shall try to solve the problem in another way.

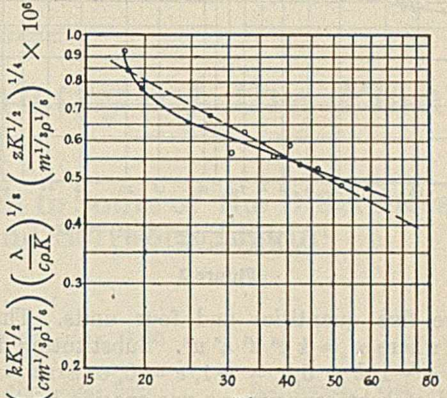

Figure 1

Weber (*6*) suggested the following empirical equation relating thermal conductivity, k, with density, ρ, specific heat, c, and molecular weight, m:

$$k = A\rho c \left(\frac{\rho}{m}\right)^{1/3} \qquad (3)$$

The results obtained from this formula, however, are often considerably in error.

Smith (*5*) proposed an empirical formula for thermal conductivity of liquids in terms of viscosity, z, specific gravity, ρ, specific heat, c, and molecular weight of the liquid, m, which gave very satisfactory results.

Thermal Conductivity Data Determined by Dimensional Analysis

SUBSTANCE	$\frac{kK^{1/2}}{cm^{1/3}\rho^{1/6}}$ × 10^{-6}	mc	$\frac{\lambda}{c\rho K}$	$\frac{zK^{1/2}}{m^{1/3}\rho^{1/6}}$ × 10^{-3}	$\left(\frac{kK^{1/2}}{cm^{1/3}\rho^{1/6}}\right)\left(\frac{\lambda}{c\rho K}\right)^{1/8}\left(\frac{zK^{1/2}}{m^{1/3}\rho^{1/6}}\right)^{1/4}$ × 10^{-6}	$\frac{k}{\sqrt[3]{\rho c}}$ × 10^{-4}	$\frac{c}{K^2\lambda^{1/2}m^{1/2}z}$ × 10^{8}
Water	3.42	18.02	8.0	1.90	0.927	14.44	111.2
Methyl alcohol	2.54	19.70	28.2	1.61	0.773	6.43	7.53
Ethyl alcohol	1.98	27.40	26.5	2.71	0.680	5.55	3.34
Benzene	2.09	32.30	35.5	1.32	0.625	5.17	2.51
Carbon disulfide	3.17	18.50	51.8	0.693	0.843	5.68	3.71
Toluene	1.95	37.44	34.2	1.15	0.558	5.17	2.92
Acetone	2.18	30.30	37.5	0.759	0.568	5.78	6.63
n-Octane	1.72	58.6	24.5	1.23	0.479	4.89	1.62
n-Heptane	1.80	51.9	23.9	1.056	0.483	4.70	1.724
n-Hexane	2.02	46.25	21.8	0.982	0.526	4.66	1.523
n-Pentane	2.36	40.30	18.4	0.905	0.588	4.59	1.203
m-Xylene	1.88	42.5	32.8	1.13	0.533	5.26	2.730

$$\frac{k \times 10^4 \times z^{0 \cdot 12}}{\rho c^{0 \cdot 4}} = 8.1\ (\rho c m^{1/6})^{1 \cdot 15} \qquad (4)$$

Neither of these empirical equations is dimensionally correct. If we apply dimensional analysis, can we get one which is?

Taking Smith's formula, $\phi_1\ (k, z, d, h, w) = 0$.

QUANTITY	SYMBOL	DIMENSIONS
Thermal conductivity	k	$ML/T^3\Theta$
Viscosity	z	M/LT
Density	d	M/L^3
Heat capacity per unit mass	h	$L^2/T^2\Theta$
Mass of a molecule	w	M

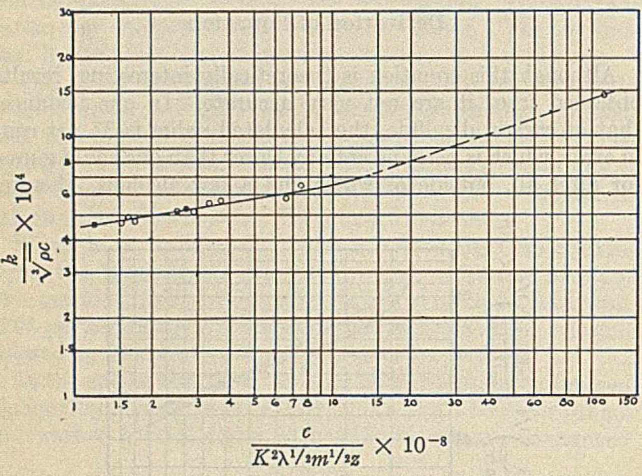

Figure 2

There are five quantities and four units. Therefore, $\phi\ (\pi) = 0$ where $\pi = k\ z^a\ d^b\ h^c\ w^e$. Substituting dimensions we get $a = -1, b = 0, c = -1, e = 0$, or k/zh = constant. If instead of heat capacity we use specific heat, c, we get

$$\frac{k}{cz} = \text{a constant} \qquad (5)$$

It is interesting to note that for all diatomic gases the quantity k/cz is very nearly constant. For liquids, however, it is not so, since there can easily be variations of several thousand to one. It would appear, then, that some modifying factor should be added.

It is known that the thermal conductivity of liquids varies with pressure (*3*) and temperature (*3, 5*), but it is not clear that these should be independent variables in dimensional treatment. For example, as the pressure increases so does the density of the liquid; viscosity also is affected by pressure; so perhaps the changes in these properties (or in others affected) may account for the change in thermal conductivity with pressure. The temperature coefficient may also be due to changes in other properties. It would seem reasonable to replace pressure and temperature as independent variables by compressibility, K, and thermal expansion, λ, respectively. Thus we assume that $\phi_1\ (k, z, d, h, w, K, \lambda, a) = 0$, $n = 8$, and $r = 4$. Therefore, $\phi\ (\pi_1, \pi_2, \pi_3, \pi_4) = 0$, where π_1, π_2, π_3, and π_4 are dimensionless groups.

Now π_1, π_2, π_3, and π_4 can be obtained in several ways. Since, however, we want the other factors in terms of k, then k will enter into only one group—e. g., π_1.

QUANTITY	SYMBOL	DIMENSIONS
Thermal conductivity	k	$ML/T^3\Theta$
Viscosity	z	M/LT
Density	d	M/L^3
Heat capacity per unit mass	h	$L^2/T^2\Theta$
Mass of a molecule	w	M
Thermal expansion per unit volume	λ	$1/\Theta$
Compressibility per unit volume	K	LT^2/M
Gas constant	a	$ML^2/T^2\Theta$

Let us determine one set of groups.

$$\pi_1 = kh^{a_1}w^{b_1}d^{c_1}K^{e_1} \qquad \pi_3 = \alpha\ h^{a_3}w^{b_3}d^{c_3}K^{e_3}$$
$$\pi_2 = zh^{a_2}w^{b_2}d^{c_2}K^{e_2} \qquad \pi_4 = \lambda h^{a_4}w^{b_4}d^{c_4}K^{e_4}$$

Apply dimensions, and we find that

$$\pi_1 = \frac{kK^{1/2}}{hw^{1/3}d^{1/6}} \qquad \pi_2 = \frac{zK^{1/2}}{w^{1/3}d^{1/6}}$$
$$\pi_3 = \frac{wh}{a} \qquad \pi_4 = \frac{\lambda}{hdK}$$

Our equation is therefore:

$$\phi\left[\left(\frac{kK^{1/2}}{hw^{1/3}d^{1/6}}\right)\left(\frac{zK^{1/2}}{w^{1/3}d^{1/6}}\right),\left(\frac{wh}{a}\right)\left(\frac{\lambda}{hdK}\right)\right] = 0 \qquad (6)$$

This is the general equation for thermal conductivity of liquids obtained from dimensional analysis, with the assumed set of variables.

The next difficulty is the determination of the function, and this must be done with reference to experimental observations. In order to plot the various groups on logarithmic paper it has been found advisable to change from heat capacity per unit mass, h, to specific heat per unit mass, c; from mass of a molecule, w, to molecular weight, m; and from density, d, to specific gravity relative to water at 4° C., ρ.

When this has been done, the new groups are:

$$U = \frac{kK^{1/2}}{cm^{1/3}\,\rho^{1/6}},\ V = \frac{zK^{1/2}}{m^{1/3}\,\rho^{1/6}},\ W = \frac{mc}{a},\ X = \frac{\lambda}{c\rho K}$$

Notice that U/V is k/cz, a π already used elsewhere.

Now it is known that, outside of viscosity, none of the properties chosen varies greatly for all liquids, whereas viscosity may vary several thousand fold. Therefore V must enter as one of minor importance.

Plotting U against X yields no obvious regularity. Plotting U against W, we find a semblance of order.

If we plot $(U)\ (X)^{1/8}\ (V)^{1/4}$ against W, we get a good curve.

Since a is a constant, (mc/a) can be replaced by $(mc)/a$, and (mc) used in place of W. This merely changes a dimensionless constant multiplier of (mc/a) to another with the dimensions of $1/a$. Therefore,

$$\left(\frac{kK^{1/2}}{cm^{1/3}\rho^{1/6}}\right)\left(\frac{\lambda}{c\rho K}\right)^{1/8}\left(\frac{zK^{1/2}}{m^{1/3}\rho^{1/6}}\right)^{1/4} = \phi\left(\frac{mc}{a}\right) \qquad (7)$$

is a possible solution, since it agrees with experiment. Reducing this equation we get:

$$\frac{kK^{1/2}\,\lambda^{1/8}\,z^{1/4}}{c^{9/8}\,\rho^{1/3}\,m^{5/12}} = \phi\left(\frac{mc}{a}\right) \qquad (8)$$

which is the end of the dimensional treatment.

Simplification of Equation

It seemed desirable, however, to try to simplify this equation, so a straight line was drawn through the points on the graph (Figure 1). This line did not pass through all of the points, but lay close to them all. The slope of the line is nearly equal to −0.54. Therefore, approximately,

$$\frac{kK^{1/2}\,\lambda^{1/8}\,z^{1/4}}{c^{9/8}\,\rho^{1/3}\,m^{5/12}} = A_1\left(\frac{1}{mc}\right)^{0 \cdot 54} \qquad (9)$$

or

$$\frac{kK^{1/2}\,\lambda^{1/8}\,z^{1/4}\,m^{0 \cdot 124}}{\rho^{1/3}\,c^{0 \cdot 585}} = A_2,\ \text{a constant}$$

or approximately

$$\frac{k}{\sqrt[3]{\rho c}} = A_3\left(\frac{c}{K^2\,\lambda^{1/2}\,m^{1/2}\,z}\right)^{1/4} \qquad (10)$$

Now plotting $k/\sqrt[3]{\rho c}$ against $[c/K^2\lambda^{1/2}m^{1/2}z]$ we get an excellent curve (Figure 2). According to the derivation given it ought to be a straight line, but it is actually slightly curved.

Test for Temperature Coefficient

Let us now test this equation for temperature coefficient. At 60° C. $c/K^2\lambda^{1/2}m^{1/2}z = 130 \times 10^8$, for water and from the graph $k/\sqrt[3]{\rho c}$ for this abscissa is 15.2×10^{-4}. Also $\sqrt[3]{\rho c} = 0.995$. Therefore $k_{60} = 15.1 \times 10^{-4}$, which is exactly Bridgman's value at 60° C. obtained by interpolation between 30° and 75° C.

In calculating the values of the properties at 60° C. care was taken to consider only those values determined by the same observer who obtained those at 30° C.; for there is quite a variation in absolute values among the different observers.

Since the value of k at 30° C. used in this article is 0.00144, it would appear that, for water, the equation derived gives the temperature coefficient accurately. Unfortunately it does not give the temperature coefficient of methanol. Thus it would appear to be accidental that the temperature coefficient of water is determinable by it. On the other hand, the error here may be due to mistakes in the variables at the higher temperature, for if K were 2 per cent higher than that recorded at 60° C. the temperature coefficient of thermal conductivity would be correct for methanol. One observer gives K this higher value at 60° C., but to be consistent the author did not use it. It is unfortunate that K has been determined for very few liquids.

Acknowledgment

The values for the various properties were obtained from the International Critical Tables, Mark's Handbook, Handbook of Chemistry and Physics by Hodgman and Lange, the Smithsonian Tables, and the literature cited.

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Contributions to the Chemistry of the Plant Cell Wall

V—Microscopy of Acid-Treated Sawdust as an Index to Some of the Differences in the Physical Properties of Hardwood and Softwood Lignin[1]

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Most of the methods now in use for separating lignin from wood involve the hydrolysis of the polysaccharides of the cell wall and the retention of an insoluble residue which is designated as lignin. The wood sample is reduced to fine sawdust before treatment, and concentrated sulfuric acid (72 per cent) is commonly employed as the hydrolyzing reagent (*1*, *4*).

During recent quantitative lignin determinations on a number of hardwoods and softwoods, three rather striking differences were noted in the behavior of the diluted wood-acid mixtures during filtration and subsequent drying:

(1) After refluxing, the softwood lignin settled out in a few minutes, leaving a fairly clear, supernatant liquid; in contrast, the hardwood lignin tended to remain in suspension sometimes for an hour or more.

(2) The differences in speed of filtration by suction through a porous alundum crucible were very noticeable; when the crucible was filled with hot wash water, the softwood lignin residue was usually sucked dry in 15 to 30 seconds, while 5 to 15 minutes were required in the case of hardwood lignin. These figures are, of course, only relative and will depend upon the efficiency of the suction pump and also perhaps the porosity of the crucible.

(3) When oven-dry, the softwood lignin appeared rather porous and could be crumbled easily; the hardwood lignin formed a hard, somewhat brittle cake, which fractured rather than crumbled when rubbed between the fingers.

It was thought probable that the differences noted above were in some way related to the microchemistry of the cell wall, and with this in mind a number of woods in the form of fine sawdust (60–100 mesh) were examined with the microscope before and during treatment with concentrated sulfuric acid.

Basswood, *Tilia glabra* Vent.
Beech, *Fagus grandifolia* Ehrh.
Yellow birch, *Betula lutea* Michaux.
Shagbark hickory, *Hicoria ovata* (Mill) Britton
White oak, *Quercus alba* L.
Red alder, *Alnus rubra* Bong
Western yellow pine, *Pinus ponderosa* Laws.
Eastern white pine, *Pinus strobus* L.
Red spruce, *Picea rubra* Link.
White spruce, *Picea glauca* (Moench) Voss
Tamarack, *Larix laricina* (Du Roi) Koch.
Western red cedar, *Thuya plicata* D. Don.

Figures 1 and 3 indicate the general appearance of sawdust when highly magnified; the individual particles are very irregular in shape, and consist of fragmentary groups of cells whose exposed edges are conspicuously ragged. The appearance of sawdust from hardwoods and softwoods, respectively, after treatment with 72 per cent sulfuric acid is shown in Figures 2 and 4. The lignin residue in the first instance consists only of the middle lamella or central layer of the cell wall, while in coniferous woods, not only the middle lamella, but also the much swollen and partially disintegrated secondary layers remain after the removal of the cellulose.

Note—A small amount of amorphous dark brown material appears with both hardwoods and softwoods upon dilution of the acid-wood mixture. This has been termed "cell wall lignin," by Ritter (7) and will be considered in detail from a quantitative standpoint in a subsequent paper.

This is more clearly shown in Figures 5 and 6, and 7 and 8, respectively, which depict thin (20–30μ) transverse sections of the same woods before and after acid hydrolysis.

These experiments with sawdust strongly substantiate previous work with thin sections of wood (*3*), since they offer a means for differentiating sharply between hardwoods and softwoods on the basis of their reaction with sulfuric acid of hydrolyzing strength. Ritter (*8*) is of the opinion that these differences between the two groups of woods are of only minor importance and that they "may be due to some specific properties of the samples" used. He also suggests that the behavior of the softwoods may be explained by assuming that the cellulose is only partially removed. If this view is taken in connection with the present work, the

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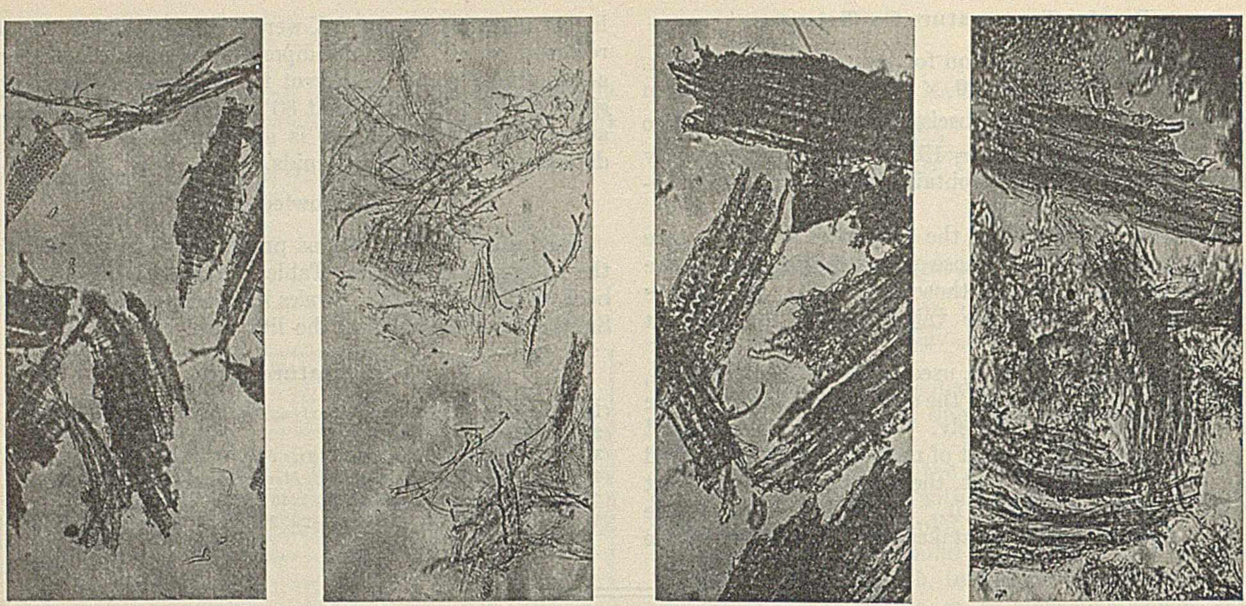
[1] Received January 23, 1931.

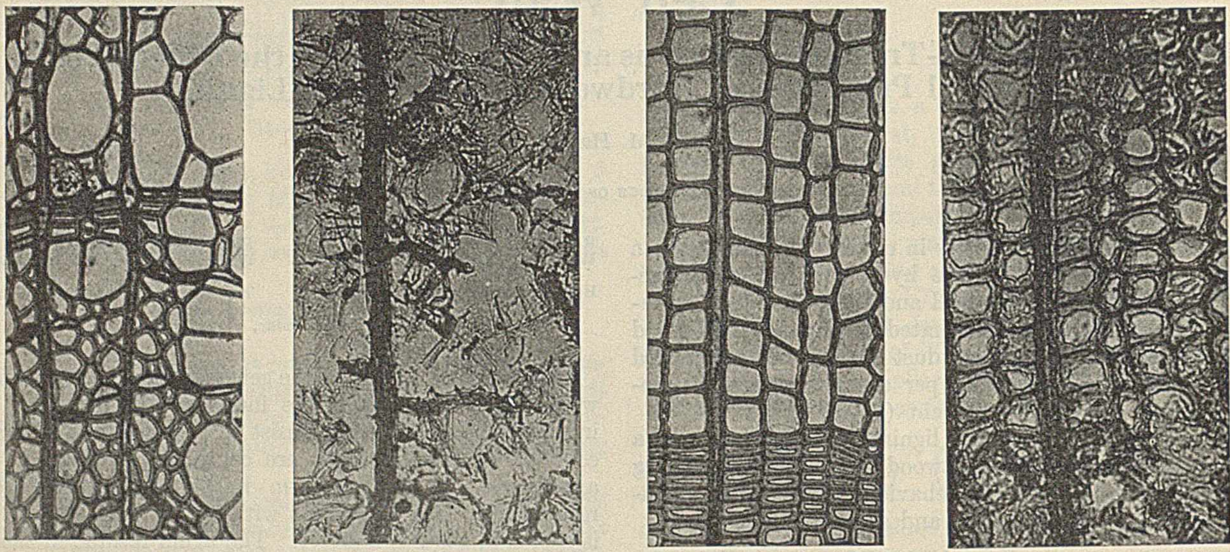


1—Basswood sawdust. × 90

2—Basswood sawdust after treatment with 72 per cent sulfuric acid. × 90

3—Red-spruce sawdust. × 90

4—Red-spruce sawdust after treatment with 72 per cent sulfuric acid. × 90



5—Transverse section of basswood 0.001 inch thick. × 165

6—Same as Figure 5, following treatment with 72 per cent sulfuric acid. × 165

7—Transverse section of red spruce 0.001 inch thick. × 165

8—Same as Figure 7, following treatment with 72 per cent sulfuric acid. × 165

Photomicrographs of Sawdust from Hard and Soft Woods before and after Treatment with Sulfuric Acid

softwood lignin analyses of Klason (*5*), Mahood and Cable (*6*), the Forest Products Laboratory (*4*), and others must all be seriously questioned. This is true since all the samples here used were prepared and treated precisely as in quantitative work; in fact, this paper was in reality a by-product of a number of quantitative lignin analyses of both hardwoods and softwoods.

It may be desirable to compare the thickness of the thin wood sections used in the second part of the experiment with the average size of sawdust particles ordinarily employed in quantitative determinations. The sections of wood were approximately 0.001 inch in thickness and thus considerably thinner than most of the sawdust fragments retained on a sieve of 100 meshes to the inch. The above experiments were, moreover, repeated with sawdust which passed a 200-mesh screen and the results were comparable with those already noted. It may also be observed that thin sections of the softwoods were left in 72 per cent sulfuric acid for 3 to 4 days before subsequent dilution and heating, but in no case were contradictory results obtained. In conclusion, the acid-treated sections failed to transmit polarized light and were apparently completely soluble upon repeated bromination and treatment with ammonia. In view of this experimental evidence, it is highly improbable that the differences noted between hardwoods and softwoods can be explained on the assumption of incomplete removal of the cellulose. This finding has been confirmed to some extent by Freudenberg, Zocher, and Durr (*2*).

In the present instance, the differences in physical properties may be readily explained as follows:

(1) During refluxing, the particles of hardwood sawdust, already deprived of their original topography through acid action, are further broken apart and consist of small, irregular strings or aggregates of the middle lamella, which settle very slowly; the particles of softwood lignin retain the general appearance of the original sawdust and, on account of their size, tend to settle more rapidly.

(2) Speed of filtration is affected by the size and character of the particles which in the case of hardwoods quickly plug the pores of the alundum crucible.

(3) In drying, the hardwood lignin, already closely packed, forms a dense, hard cake at the bottom of the crucible.

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Filterability of Raw Cane Sugars[1]

I—Effect of Various Factors Prior to Pan-Boiling[2]

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It has long been considered desirable to find a method by which sugars can be evaluated as to their filtering properties without making a filtration test. Several methods for colloid determination have been tried, as well as a method for the determination of suspended solids. While in general there was a correlation between the results of some of these methods and filterability of the sugars, none of these tests gave uniformly reliable results.

That suspended material was to some extent responsible for poor filtration tests was shown by the prefiltration of defecated juice. Sirup made from prefiltered defecated juice had a filtration rate twice that not prefiltered. That the presence of suspended solids in the raw sugar affects the filtration rate was demonstrated when pulverizing six representative samples was found to increase the average filterability 54 per cent.

It was found that increasing the P_2O_5 content from 0.016 to 0.027 gram per 100 cc. brought about a 56 per cent increase in the filtration rate of the resulting sirups. On a factory scale over a 4-day period, the addition of P_2O_5 equivalent to 0.008 gram per 100 cc. of juice added to the raw juice materially increased lime consumption. Progressive beneficial effects were immediately apparent throughout the factory and the averages showed an increase of over 100 per cent in the filtration rate of the sirup and approximately 50 per cent in that of the sugar produced.

Analysis of the original juice from this factory showed it to contain 0.028 gram per 100 cc. total P_2O_5, but apparently it was not in available form, since increasing it only slightly allowed the use of considerably more lime. Later laboratory tests on a large number of other juices from which sirups were made clearly indicated that the total P_2O_5 content of the raw juices is not necessarily a criterion of how a juice will defecate. It is very desirable that a method be found to indicate the amount of available P_2O_5 present in raw cane juice.

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THE filterability of raw cane sugars in connection with the refining operation has been given much attention by various investigators during the past few years. Although filterability of the raw sugar is by no means the only index of its quality, it is one of the most tangible and definite criteria, and probably for that reason has been used, often unconsciously and by implication, as an approximate measure of other, less tangible characteristics of quality of raw sugar. It has long been considered desirable to evaluate the filtering properties of raw sugar without an actual filtration test. Moreover, if correlation could be found between filterability and other physical or chemical characteristics, the tracing of the cause or causes of poor filterability would be greatly facilitated. The routine tests ordinarily applied to raw sugar have been found to be in no manner indicative of its filtering qualities.

The significance of colloid content was first considered as it is known that raw sugar contains varying quantities of colloidal material and also that certain colloids may affect filtration rates (*8*, *9*, *10*, *11*, *13*, *14*, *15*). An approximate determination of the content of colloidal material in raw sugar was made, by means of the dye test (*3*, *10*), on a series of selected samples of measured filterability. Ultra-filtration through collodion membranes according to the method of the late L. E. Dawson of this division was also used as a means of approximate quantitative separation of colloids. Although on the whole there was a definite correlation in many instances between filterability and content of colloids as determined by the dye test, especially in sugars from the same factory, yet there were certain exceptions; and it is with these exceptions that this investigation is chiefly concerned.

The weight of suspended material removed by ultra-filtration also was not found to be a satisfactory index of the filterability of raw-sugar solutions, owing, in part at least, to the varying quantities of suspended material removed by filtration prior to ultra-filtration. In addition to determining the approximate percentage of total colloids, their solubility in acetone, alcohol, and water was studied from the standpoint of the presence of cane wax constituents. The results of these tests, however, were in no way enlightening.

Precipitation by alcohol (*2*) with a quantitative separation of the sugar-free precipitate was next considered. A modified method in which tared Gooch crucibles were used to retain the precipitate gave good check results. This alcohol precipitation method was given a thorough trial and found to afford little, if any, correlation with respect to filterability. The ash content of all the raw sugar samples was determined as well as the CaO content of the ash. Neither of these methods gave any conclusive indication of the filtering qualities of raw sugar solutions.

As no definite correlation was found by such methods of

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[2] Contribution No. 103 from Carbohydrate Division, Bureau of Chemistry and Soils, U. S. Department of Agriculture.

examination, the filter cakes resulting from the filtration of various samples—that is, the Hy-Flo Super-Cel with retained suspended material and a portion of the sugar solution—were dried, and the weight of alcohol precipitate obtained from a water dispersion of the cakes was determined. These data were somewhat indicative of the filtering properties of the sugars, but were by no means conclusive.

Pulverization of Raw Sugars

In order to obtain some information as to what effect possible contamination with cane wax (*4*) might have on the rate of filtration, several samples of raw sugar were extracted with pure acetone. Sugars of known filterability were pulverized, dried, and thoroughly mixed with acetone. The acetone was filtered off through filter paper, the sugar was again dried, and the filtration rate determined (*7*). As a control, a portion of the pulverized sample was tested for filterability without treatment with acetone. It was found that pulverizing alone caused a decided improvement in filterability, but the net result of the acetone treatment alone was very slight. Since pulverization produced such an unexpected result, it was repeated with several additional samples of sugar; without exception a decided improvement was noted, the greatest improvement being obtained with the poorer filtering sugars.

Table I—Effect of Pulverizing on Filterability of Raw Sugar

Original Filterability	Filterability after Pulverizing	Increase in Filterability
%	%	%
104.8	133.0	26.9
77.7	113.0	45.4
64.7	99.5	53.8
52.3	79.0	51.0
47.2	82.0	93.6
27.9	55.0	98.5
Av. 62.4	93.6	61.5

All filtration tests were made with the pressure filter designed by L. E. Dawson. The filtration of both sirups and sugars was conducted at 85° C. under 20 pounds (1.5 kg. per sq. cm.) pressure. Hy-Flo Super-Cel was used as a filter medium, 0.25 per cent for sugars and 2.0 per cent for sirups, calculated on the basis of solids. Filtrations were made through a filter leaf of 1 square inch (6.45 sq. cm.) area, a twill filter cloth being used in all tests. All filtrations were made at 50° Brix and extended over 30-minute periods. The filtrate obtained during the first minute was discarded, and the total filtrate of the remaining 29 minutes was weighed. The percentage filterability was calculated from the figure obtained. For sugars, the weight of filtrate in grams obtained in 29 minutes divided by 1100 equals percentage filterability; for sirups, the weight of filtrate in grams for the same period divided by 1500 equals percentage filterability. The results are shown in Table I.

A possible explanation of this phenomenon is that pulverization so changed the physical character of some of the extraneous material in the raw sugar as to allow it to pass through the filter in a much more finely divided condition. This subject is being further investigated.

Determination of Suspended Solids

A study of methods of determination of the suspended solids in a solution of the raw sugar was therefore undertaken. The following method devised by R. T. Balch of this division was adopted: A sample of raw sugar was dissolved in water and diluted to exactly 50° Brix. This solution was filtered through a 250-mesh copper cloth in order to remove coarse suspended material which had been found to have no effect on filtration. Forty grams of this solution, equivalent to 20 grams of solids, were weighed into a tared beaker. Exactly 1 gram of Hy-Flo Super-Cel was added and allowed to stand in the presence of the sugar solution for $^1/_2$ hour before filtering on a tared Gooch crucible. The filter cake in the crucible was then washed with 150 cc. of cold water, care being taken that the cake did not dry at any time during the filtering or washing procedure. The crucible and contents were dried at 105° C. overnight and weighed. Percentage of ash and organic material by difference was obtained. Control tests were made with Hy-Flo Super-Cel and a solution of pure sugar.

The percentage of suspended solids determined by this method on a large number of raw sugars also failed to indicate their filtering qualities. This lack of correlation is apparently due either to inability to separate definitely material which affects filtration from that which does not or to the removal of suspended material upon dilution. When this method was applied to sirups of known filterability, however, the degree of correlation was much better, but even in these cases the differences were not considered sufficiently pronounced to permit evaluation of a sirup with respect to filterability.

Study of Sirups from Various Factory Juices

Since the sirups showed such a difference in filterability, as well as in suspended material, a study was conducted on each of the various juices from which factory sirup is made. In a raw-sugar factory using open defecators the sirup is usually composed of the juice from the defecators, the juice decanted from the mud-resettling tanks, and the filter-press juice. The various juice samples selected were produced under average working conditions. These juices were evaporated at atmospheric pressure for 15 minutes and then concentrated to approximately 60° Brix *in vacuo* in the laboratory. They were all diluted to exactly 50° Brix for the filtration test.

The concentrated defecated juice gave a sirup with a filterability approximately equal to that of the factory sirup; the sirup made from decanted mud-tank juice had a slower filtration rate, whereas that made from filter-press juice had a very good filtration rate. Since the filterability of the sirup from the filter-press juice was so much better than the others it was decided to prefilter defecated and mud-tank juices prior to concentration to determine to what extent the filterability of the resulting sirups would be increased. The prefiltration was conducted at approximately 60° C., with a vacuum leaf and Hy-Flo Super-Cel as a filter medium. The filtrate in all cases was free of visible suspended material. However, in some instances the filtrate was decidedly less brilliant than in others, and this was especially true of mud-tank juices.

Prefiltration of the defecated juices causes a decided improvement (*9*) in the filterability of the resulting sirups, the average filterability being about twice that of sirups made from non-filtered defecated juices. In the mud-tank juices very little improvement resulted from prefiltration. In the defecated juices evidently a large percentage of the detrimental suspended material was removed by Hy-Flo Super-Cel filtration, whereas in the decanted mud-tank juices the flocculated mud particles are probably so disintegrated and dispersed by agitation and reheating that they are not retained by Hy-Flo Super-Cel filtration, thus causing lack of brilliancy in the filtered juices and possibly later flocculation upon concentration.

The sirup made from filter-press juice had a filtration rate about four times that of sirup made from mud-tank juice, owing no doubt to the more thorough removal of suspended material during filtration. A great percentage of the very finely suspended solids which may pass through Hy-Flo Super-Cel in the preliminary filtration as conducted is undoubtedly retained by the mat of cachaza in the filter presses. Since the presence of suspended matter was shown to affect the filterability of sirup, a study of juice defecation was undertaken, in which the filterability of the resulting sirups was used as a criterion of clarification efficiency.

Relation of Added Phosphate to Filterability of Resulting Sirup

It has long been recognized that the presence of phosphoric acid (*1, 5, 6, 8, 11, 12*) in raw juice in available form is an aid to defecation. It would be expected that in the clarified juice of high phosphate content the quantity of suspended material would be less and the filterability of the resulting sirup would consequently be increased. The following experiments were made to determine the effect of phosphate added to the juice on the filterability of the sirup.

A number of samples of juice obtained from sugar canes of known origin as to variety and soil on which they were grown were divided into two portions of 10 gallons (45.4 liters) each and placed in experimental defecators similar in design to those used in factory practice. One portion was limed to pH 8.5; to the other a small amount of phosphate was added in the form of phosphoric acid solution, the acid being thoroughly mixed with the raw juice. This portion also was limed to 8.5 pH. The percentage of phosphate was determined in both the untreated and the treated samples. These two portions were heated simultaneously and brought to the boiling temperature in the same period of time. They were allowed to defecate for 1 hour and 15 minutes, after which the clear, supernatant juice was drawn off each sample and evaporated to sirup in the same manner. The filterability and the CaO content of each of the sirups were determined.

The results of this series of experiments are given in Table II. As will be seen from this table, the filterability of the sirup is increased decidedly by the addition of phosphoric acid, which is what would be expected in view of the comparative brilliancy noted in the respective defecated juices.

Table II—Effect of Adding Phosphoric Acid to Cane Juice on Filterability of the Resulting Sirup

ORIGINAL			SAME PLUS PHOSPHORIC ACID		
JUICE	SIRUP		JUICE	SIRUP	
P_2O_5	Filterability	CaO per 100° Brix	P_2O_5	Filterability	CaO per 100° Brix
Gram/100 cc.	%	*Gram*	*Gram/100 cc.*	%	*Gram*
0.014	29.5	0.2858	0.025	47.6	0.2821
0.022	37.5	0.2858	0.031	51.0	0.2912
0.016	29.9	0.2730	0.024	31.1	0.2912
0.015	22.2	0.3208	0.025	46.2	0.3149
0.014	31.2	0.3532	0.031	53.8	0.3204
0.012	24.2	0.2985	0.027	44.3	0.2912
Av. 0.016	29.1	0.3029	0.027	45.7	0.2985

The net result of the large-scale laboratory experiments was so satisfactory that it was deemed advisable to try addition of phosphate to juice on a factory scale to determine its effect on the filterability of the sugar made. In a factory which was having difficulty in making a good filtering sugar it was found that the sirup was very low in filterability. This factory was grinding a large percentage of Uba cane, and the juice clarification was not satisfactory. After several changes in methods had failed to improve the filterability of the sirup, a 4-day experiment on the effect of adding phosphate to the raw juice was undertaken. A good grade of commercial phosphoric acid was double-diluted, and a 500-cc. portion was added to each tank of raw juice, the whole being thoroughly mixed with air before being limed to a pH of 8.5 when cold. This amount of phosphoric acid was equivalent to approximately 0.008 gram P_2O_5 per 100 cc. of juice. With this increase of P_2O_5 in the raw juice it was necessary to increase materially the amount of 10° Bé. lime in order to maintain the same pH value in the cold-limed juice.

A marked improvement in the general appearance of the defecated juice was noted. The filterability of the sirup and sugar was decidedly improved, as will be seen by the following data showing average filterability for 4-day periods:

	SIRUP	FIRST SUGAR	SECOND SUGAR	TOTAL OUTPUT
	%	%	%	%
Before using P_2O_5	9.9	48.1	38.8	45.2
During use of P_2O_5	20.6	73.5	62.2	68.4

The results of this factory experiment confirmed our laboratory tests and showed clearly that the resulting sugar is likewise benefited by the improved clarification due to the added P_2O_5.

Availability of Phosphate Content of Raw Juice

Because of the great difference in the amount of lime required after the addition of this small percentage of P_2O_5 it was assumed that the phosphate content of the original juice was very low. Analyses of the juice from this factory did not show this to be the case. A 100-cc. portion of the original dilute juice was ashed and found to contain 0.028 gram P_2O_5 per 100 cc. of juice. Since the addition of 0.008 gram of P_2O_5 per 100 cc. necessitated such an increase in lime to maintain the same pH in the cold-limed juice, it would appear that a large percentage of the P_2O_5 in the original juice was not in available form. In previous observations it was noted that, in general, dilute juice from Uba cane is high in phosphate content yet it is very difficult to clarify (*5*). It is not definitely known whether this is a characteristic of the cane variety itself or of the type of soil on which it is grown. Neither can it be definitely stated that the difficulties experienced in defecating juices from Uba canes are due to a lack of available phosphate rather than to the nature of the impurities in the cane itself. However, the results of this experiment strongly indicate that the availability of the phosphate is an important factor.

This was further demonstrated by the data on the sirups made in the laboratory from juices obtained from two widely separated sections of the cane-growing area. As the cane was of the same variety—namely, BH 10–12—apparently the variations in the juice are due to soil or climatic conditions.

Table III gives another illustration of filterability of sirups made from juices of approximately the same total P_2O_5 content.

Table III—Comparative Filtration Rates of Sirups

DENSITY	JUICE		SIRUP	
	Purity	P_2O_5	Filterability	CaO per 100° Brix
° Brix	%	*Gram/100 cc.*	%	*Gram*
GROUP 1				
16.5	84.6	0.014	22.2	0.3208
16.1	86.2	0.011	15.0	0.3168
15.7	90.7	0.009	19.4	0.2394
16.6	84.7	0.024	25.3	0.3249
Av. 16.2	86.6	0.015	20.5	0.3005
GROUP 2				
16.7	84.7	0.012	40.5	0.2821
15.7	84.3	0.014	33.7	0.3685
15.8	82.3	0.015	39.5	0.4296
16.5	86.0	0.022	49.5	0.2985
Av. 16.2	84.3	0.016	40.8	0.3446

This table shows that the two groups have practically the same total phosphate content. Although the juice of group 1 has a higher average purity, the average filterability of the resulting sirup of group 2 is about twice that of group 1.

The same procedure of defecation and evaporation to sirup was followed in each case. In general, the filterability of the sirups made from various areas correlated well with the phosphate content found in the raw juice, but other exceptions noted substantiate the belief that in many cases the phosphate present is not in available form.

The question of the availability of the phosphate present is important, and it is our present plan to continue work on this phase of the problem. It is desirable to use some analytical method by which the amount of available phosphate may be determined, as obviously the total P_2O_5 often gives misleading information. Again, it is important to ascertain how this factor is affected by cane varieties, and soil and climatic conditions, as well as by fertilization.

Conclusion

These data indicate that filterability of sirup and sugars is influenced primarily by finely suspended material, part of which is probably in the upper range of colloid size and the remainder is probably somewhat above the upper limit of colloid dimensions. A large portion of this material may be eliminated by good defecation and proper handling of the muds. That suspended matter is a factor in the filtration rate of sugars was confirmed by the effect of pulverizing. For good defecation it is necessary to have effective manipulation of the proper equipment, and also to have a raw juice containing sufficient available phosphate to form a flocculent precipitate with the lime. The muds should be carefully filtered, and if any juice is decanted from the mud tanks before filter-pressing, this juice should be further treated and not sent direct to the evaporators. However, judging from the good filterability of filter-press juice, it would seem advisable to send this directly to the evaporators whenever good filtration gives a brilliant juice.

The addition of phosphate to the raw juice in the form of phosphoric acid will aid defecation and in turn improve the filterability of the resulting sugar when this constituent is deficient in available form. The advisability of its use from an economic, as well as an operating, standpoint, must be decided by each factory.

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II—Effect of Pan-Boiling Operations[3]

While good filtering sirup is a requisite for the making of good filtering raw sugar, the data clearly show that faulty pan construction and operation may cause poor circulation and be responsible for the production of poor filtering sugar from good filtering sirup. This harmful effect was especially noted in the case of second sugars.

A large sample of sirup was taken from each of five factories and the filtration rate determined. From these sirups strikes were boiled in the laboratory glass vacuum pans under standardized conditions. Two of these factories had poor filtering sirup and were producing sugars with a low filterability; another with a good sirup was producing a good filtering sugar. The remaining factories had good filtering sirups, but the sugar produced had a low filtration rate. In view of the laboratory boiling experiments on sirups, it was strongly indicated that at these factories pan operations were largely at fault.

The filterability of second sugars was investigated at two factories having good filtering sirup, one of which was making good and the other a poor filtering product. The factory making good sugar produced a second sugar with a filtration rate about three times that of the other. Investigation of individual pans at the latter factory showed that, of four pans making second sugar from the same molasses, two of the pans produced a sugar having an average filterability only one-tenth that of the other two.

Although the employment of various boiling systems may influence the filtering quality of the total output of sugar, investigation of the products of individual pans shows that variations in design or method of operation of pans may cause a decided difference in the filtering quality of the resulting sugar. The question of pan circulation, design, and operation should be investigated further from the standpoint, not only of raw-sugar filtration, but of crystallization in general.

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IT HAS long been recognized that good clarification is a prerequisite for making raw sugars of excellent filtering quality. The data obtained in this phase of our investigation clearly confirm the belief (*1*, *2*, *3*, *6* to *12*) that the more brilliant the clarified juice, and the freer it is from finely divided suspended material, the better are the filtering qualities of the resulting factory sirup. Although good filterability of the sirup is essential, our past observation has indicated that it is not the only requisite for the production of raw sugar of satisfactory filtering quality.

During the season of 1930 in Porto Rico, it was decided to consider filterability of raw sugar not only from the standpoint of juice clarification, but also from that of producing sugar from sirup, including the operations of pan-boiling and centrifuging. Two factories grinding similar canes and apparently having good juice clarification were chosen for a study of boiling operations. One factory, hereafter referred to as No. 1, was making a very good filtering raw sugar, whereas the product of the other factory, No. 2, was considerably lower in filterability.

A systematic investigation of the various sugar end products from the two factories was undertaken. Two-day

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[3] Contribution No. 104 from Carbohydrate Division, Bureau of Chemistry and Soils, U. S. Department of Agriculture.

composite samples of first and second sugars were tested for filterability. Also, in order to determine whether or not the wide variation in the filtering quality of the final products was caused by poor clarification at factory No. 2, a 12-hour composite sample and a catch sample of sirup from each factory were examined every other day. This series of samples was studied for a sufficient period to obtain definite information regarding the filtering qualities of the various products. The time required was about one month. During this period consistent results were obtained. All filtration tests were made by the procedure described in Part I (*5*).

Relation of Filterability of Sirup to Corresponding Sugar

The first consideration was the filterability of the factory sirups. It might be expected that the sirup from factory 1 would be of superior filtering quality, as the sugar from this factory was consistently better in this respect than that from factory 2. The results, however, did not show this to be the case. For the duration of these experiments the average filterability of the sirup from factory 2 was 29.3 per cent, whereas that from factory 1 was only 21.2 per cent. If the subsequent procedures of pan-boiling and centrifugal work at the two factories were identical, these results would indicate that the sugar from factory 2 should be better or at least equal in filterability to that from factory 1. Both factories used the same type of three-boiling system, both grained on sirup, and both cut this grain for footings for both second and third sugars.

The average filterabilities of the first and second sugars from the two factories for this period were as follows:

FACTORY	FIRST SUGAR	SECOND SUGAR	WEEKLY COMPOSITE OF OUTPUT
	%	%	%
1	123.9	123.5	118.7
2	88.1	39.0	57.0

These results show clearly that, contrary to what would be expected from the sirup filtration rates, the sugars from factory 2 are decidedly lower in filterability than those from factory 1.

A decided difference may be noted in the filtering quality of the first sugars from the two factories. This variation is attributed to the low filterability of the sugars obtained from strikes to which first molasses had been added. The straight sirup strikes gave for the most part a filterability over 100 per cent. At factory 2 the relative difference in filterability between straight sirup strikes and those to which first molasses had been added was greater than at factory 1 or in the experimental laboratory vacuum pans; in operating the latter sufficient first molasses could be added to lower the purity of the strike three to four points without greatly affecting the filtration quality of the resulting sugar.

The drop in filterability of first sugars from mixed pans was found to be more pronounced when the molasses was added before cutting. It should be noted, however, that in the experimental laboratory pans only virgin molasses from the previous laboratory straight sirup strike was used, and in factory 1 it is a routine procedure to use only virgin molasses for topping off first strikes. It cannot be stated definitely whether this difference in filtering quality of the sugars made from straight sirup strikes as compared with those made from strikes to which molasses had been added is due to the quality of molasses or to the pan work at factory 2. In the second sugars the difference in filterability is much greater than that between first sugars; the filtration rate of second sugar from factory 1 is more than three times that of the second sugar from factory 2.

Boiling Experiments in Laboratory Pans

The foregoing data indicate that either the design or the operation of certain vacuum pans in factory 2 was, in a measure at least, responsible for the poor-filtering sugars. In order to test this conclusion, a series of sugar-boiling experiments was conducted with glass laboratory coil vacuum pans. It was possible in this way to ascertain whether or not poor circulation in the factory pans was a factor in the production of sugar of poor filtering quality.

Several samples of sirup from factory 2 were boiled to massecuite in the laboratory pans. In some instances first molasses from one laboratory strike was used to top off the contents of the next pan. In all cases these massecuites were spun in the laboratory centrifuge, no wash water being used on first sugars. A large sample of sirup was obtained from factory 1, and from it two laboratory strikes were boiled, one being a straight sirup strike and the other topped off with the molasses from the first. In order to check the operation of the pans used for second sugars at factory 2, three samples of factory 2 first molasses were boiled into second strikes in the laboratory pans, sirup being used for footing in each case.

The average filterability of the sugars from the series of laboratory experiments was as follows:

FACTORY	FIRST SUGAR	SECOND SUGAR
	%	%
1	131.4	..
2	123.1	97.5

It will be noted that sirup from factory 1 yielded a first sugar in the laboratory pans that checked very well with the filterability of the factory sugar and that the filterability of the first sugar from factory 2 was somewhat better than that of the corresponding factory sugar. But it should be remembered that the laboratory series contained a greater percentage of straight sirup strikes. The most notable difference, however, is seen in the second sugars of factory 2, since three strikes with an average purity of 70.2 yielded sugar with an average filterability about two and one-half times that of the factory second sugar produced from the same materials during the same period.

Table I—Comparative Filterability of Factory and Laboratory Sugars

FACTORY	FILTERABILITY OF FACTORY SIRUP	FILTERABILITY OF FIRST SUGAR BOILED IN LABORATORY PANS	FILTERABILITY OF FACTORY OUTPUT
	%	%	%
1	26.5	131.4	120.0
2	27.6	125.6	51.2
3	28.5	123.7	62.2
4	17.8	55.9	...
5	15.1	42.6	45.0

As a further study of pan work and its bearing on filterability of the resulting sugar, a large sample of sirup was obtained from each of several factories and boiled in the laboratory pans. The filterability of the sirup was first determined, and then two strikes were boiled from each lot, one being a straight strike and the other being topped off with molasses spun from the preceding strike. The filtration data given in the third column of Table I represent averages for the sugars yielded by these two strikes. The figures given in the fourth column represent the filterability of the sugar produced in each factory during the period when the sirup samples were obtained.

From this table it will be seen that in general the filterability of the sugar increases with the filterability of the sirup from which it is made, assuming that the pan work is equally good in all cases. There is a possibility that a sirup might filter well at a concentration of 50° Brix, for instance, and yet contain very finely divided suspended material which might undergo aggregation and precipitation at higher concentrations, thus affecting the filterability of the resulting sugar, but such cases are believed to be rather exceptional. In factory 1 we have what may be called ideal conditions. The clarification was such as to produce a good filtering sirup, from which, owing to satisfactory pan operation at the factory, a sugar having a high filtration rate was produced. In factories 2 and 3 a good filtering sirup was obtained, from which it was possible to make a good filtering sugar, as can be seen by the results of the laboratory boiling, but owing to faulty pan work the sugar produced by these factories was much lower in filterability than anticipated.

In factories 4 and 5 the sirup was not of good filtering quality, owing no doubt to inferior clarification and, as would be expected, the corresponding factory sugars were lower in filterability. The sugars made in the laboratory pans also had a low filtration rate, showing that in these factories pan operations were not at fault. No filtration rate was determined for the sugar produced at factory 4 at the time of conducting the tests, but it was known to be of inferior filtering quality. In factories 2 and 3 we have an example of unsatisfactory pan-boiling as a cause of poor filtering sugars, and in factories 4 and 5 an example of poor juice clarification as a cause.

Filterability of Second Sugars as Affected by Pan Operation

In the belief that pan operation, particularly circulation in the various pans, was an important factor, a series of filtration tests was made on second sugars at one of these factories, the samples having been spun from strikes boiled in four different factory pans. The results of these tests are shown in Table II. The pans designated as C and D are coil pans; B is a calandria pan with one coil below the calandria and two above it; and E is a calandria pan, a duplicate of the B pan but without coils. The figures were obtained over a period of about 6 weeks and do not necessarily represent consecutive boilings in each pan.

Table II—Filterability of Sugars Boiled in Different Pans

B	C	D	E
%	%	%	%
30.3	40.0	97.8	5.6
20.7	54.4	95.1	2.7
13.1	80.0	147.8	15.7
31.2	74.2	89.0	10.0
22.9	114.4	90.3	7.7
25.0	30.0	...	10.0
36.5	74.1	...	13.4
22.5	55.6	...	9.3
16.7	55.7	...	19.8
16.3	38.2	...	4.0
15.8	...	...	1.6
Av. 22.8	61.7	104.0	9.1

Comparison of the filterabilities of the second sugars produced by boiling in the several pans shows that the coil pans yield a sugar with decidedly superior filterability. The E pan consistently yielded sugars with such low filterability that, since it was used exclusively for second sugars and was in almost constant use, it would appear to be an important factor in the poor filtering quality characteristic of sugar from this factory. The time and amount of water used in purging are dependent very largely on the quality of the massecuite from each individual crystallizer. During these experiments the second molasses produced varied decidedly in purity from one crystallizer to another. It was difficult to determine whether or not this was an inherent quality of a particular strike, as the molasses was often a mixture from one or more crystallizers. Also, the manner in which the massecuites were purged might be partly responsible for these variations.

In order to evaluate the pan operations from several points of view, it was deemed advisable to take samples of massecuites boiled in the various pans as they were being discharged from the crystallizers and purge them under standard conditions in a laboratory centrifuge. In each instance the basket of the centrifuge was filled and allowed to spin for 15 minutes at a definite rate. At the end of the first 5 minutes 100 cc. of water at room temperature were sprayed on the massecuite by means of a small wash bottle. The resulting sugars were polarized, and the filterability was determined. The total molasses was collected, including the quantity resulting from the 100 cc. of wash water; this was thoroughly mixed and the apparent purity was determined. From the apparent purity of the massecuites as obtained by previous analyses and the apparent purity of the run-off molasses, a crystallization factor for each sample was calculated according to the following formula:

$$\frac{100\ (\text{purity of massecuite} - \text{purity of molasses})}{100 - \text{purity of molasses}} = \text{crystallization factor}$$

Table III gives the results of these tests, the massecuites being tabulated according to the pans in which they were boiled.

Table III—Comparative Data on Second Sugars Boiled in Different Pans

(Massecuites taken from crystallizers and spun in laboratory centrifuge under standard conditions, adding 100 cc. wash water)

PAN	APPARENT PURITY Massecuite	APPARENT PURITY Molasses	CRYSTALLIZATION FACTOR	POLARIZATION OF SUGAR	FILTERABILITY OF SUGAR
	%	%	%	° V.	%
B	70.5	50.4	40.5	94.4	3.5
	70.7	49.9	41.3	96.1	8.7
	69.2	49.8	38.6	97.0	21.3
	69.7	47.4	42.2	95.1	2.4
	71.9	52.8	40.5	97.3	9.2
Av.	70.4	50.1	40.6	96.0	9.0
C	68.7	43.5	44.6	96.6	41.5
	70.1	44.7	47.7	96.6	66.2
	69.1	45.3	43.5	96.2	43.9
	68.0	45.0	41.8	97.5	64.4
	67.9	47.4	39.2	97.6	100.0
	70.4	49.4	41.5	97.9	79.6
	69.3	47.4	41.5	97.4	40.7
Av.	69.1	46.1	42.8	97.1	62.3
D	67.9	41.9	44.7	96.7	54.8
	68.5	44.8	42.9	96.5	58.5
	69.5	47.7	41.7	97.0	68.2
	67.5	45.1	40.8	97.0	48.5
	69.7	44.9	45.0	97.2	59.2
	69.7	49.3	40.2	97.5	53.5
	70.8	46.2	45.7	97.7	113.7
	68.8	45.9	42.3	96.4	30.9
Av.	69.1	45.7	43.0	97.0	60.9
E	69.7	50.1	39.3	93.8	3.7
	70.1	49.7	40.4	95.6	4.1
	69.0	48.1	40.6	95.8	4.6
	70.4	50.7	40.0	93.4	1.7
	68.2	50.6	35.8	94.6	3.6
	69.6	48.3	41.2	94.3	8.1
	68.0	52.6	32.5	94.3	0
	69.3	49.8	38.8	95.8	2.6
Av.	69.3	50.0	38.6	94.7	3.6

It will be seen from this table that the coil pans gave decidedly better filtering sugars with higher polarization than either of the calandria pans and, as in the preceding series, the E pan yielded the poorest filtering sugars and likewise sugars of the lowest polarization. In factory practice it would be necessary to use additional wash water in order to increase the polarization of these sugars, thus tending to increase further the purity of the molasses and to lower further the crystallization factor, which is already appreciably below that of products from the coil pans. The results of these experiments are indicative of pan work alone, since the centrifuging operation was standardized, and any slight variations in crystallizer operation would be equalized.

The question naturally presents itself as to whether these pan difficulties are due to methods of operation or to some fault in the construction or heat distribution of the pans themselves. The data and observations are insufficient to vindicate entirely the sugar boilers with respect to the operation of the calandria pans boiling second sugars, since it was possible to make satisfactory grain from sirup in the E pan, this material often being used for footing in other pans yielding a good sugar. This would imply that the circulation of the pan was efficient while sirup was being used. According to the operators, the difficulty was encountered when molasses was added, a false grain appearing unless a high temperature was maintained. However, these sugar boilers stated that at different times they had tried boiling this pan in every possible manner known to them, and they were convinced that the method they employed gave the best results obtainable with this equipment. Also, the sugar boilers were able to make a superior massecuite from the same molasses by using the coil pans. Thus we may assume that, although some improvement might possibly be made in the operation of these pans, the pans themselves are a definite source of the difficulty which is causing poor filtering sugar and deficient crystallization.

Relation between Percentage Crystallization and Filterability

In connection with the average filterability of the raw-sugar outputs from factories 1 and 2 for the season of 1930, which were 112.6 and 48.7 per cent, respectively, it may be of interest to note the various average pan and molasses purities, together with the corresponding calculated crystallization factors. These are shown in Table IV. The purity figures represent crop averages for each factory.

Table IV—Average Purity of Massecuites and Molasses, and Crystallization Factor, Factories 1 and 2, for 1930

FACTORY	PAN	PURITY OF MASSECUITES	PURITY OF MOLASSES	CRYSTALLIZATION FACTOR
		%	%	%
1	1	81.9	62.8	51.4
2		82.4	65.3	49.3
1	2	69.3	44.3	44.9
2		69.2	47.7	41.1
1	3	58.4	28.8	41.6
2		57.1	32.5	36.5

Conclusions

The results of this investigation show that: (1) a good filtering sirup is necessary in order to make a sugar of good filterability; and (2) a poor filtering sugar may result from a good filtering sirup when pan construction or operation is faulty. The effect of inefficient pan work is more pronounced in the case of second sugars. Other investigators (*4*) have found that variations in systems of boiling affect the filterability of the raw sugar produced. This investigation deals, however, with the individual pans.

Although the data given here show that the coil pans which were under observation yielded a decidedly better sugar than that obtained from the calandria pans, this behavior does not necessarily apply to calandria pans in general, as it is very probably due to defects in design or operation of the particular calandria pans investigated. Either of these factors may influence the quality of the resulting sugar, and it is the writers' opinion that the adverse results are largely due to deficient pan circulation. Pan circulation does not refer merely to time of boiling or rate of evaporation but primarily to the manner in which the total mass of crystals is kept in constant motion, bringing individual crystals continually in contact with supersaturated mother liquor and thus producing more complete sucrose crystallization and probably reducing contamination of the sugar crystals. The specific effect that various conditions of boiling may have on the resulting sugar is to be studied further, not only from the standpoint of filterability of raw sugar, but also from the standpoint of crystallization in general.

The results of these experiments on filtration rates show that there are two prevalent and distinct causes of poor filtration of raw cane sugar: one is poor juice clarification and the other is faulty sugar-boiling operations. Each of these in turn involves a number of different factors.

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Heats of Wetting and of Adsorption on Zinc Oxide[1,2]

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ZINC oxide is used extensively in paint as a pigment, in rubber as an activator for organic accelerators and as a reënforcing pigment, in various medicinal preparations, in ceramics, and in numerous other ways. This product exists as a white powder, the particle size varying with the conditions under which it is produced. The average size of the finest oxide is about 0.15 micron, while the coarser oxides may average as high as 0.7 micron. This offers, especially in the finer sizes, an extremely large specific surface, and consequently a fruitful field for adsorption phenomena. Various investigators have observed that the nature of the adsorbed material affects markedly the pigment properties of the oxide when used as a raw material for preparing other substances. For example, when two paints are made up under apparently identical conditions except for humidity, the consistencies of the two paints may show pronounced differences which are due to an adsorbed film of moisture.

The data presented in this article have been accumulated during the investigation of the nature and effect of adsorbed

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[1] Received December 23, 1930. Presented under the title "Heat of Adsorption of Zinc Oxide" before the Division of Physical Chemistry at the 79th Meeting of the American Chemical Society, Atlanta, Ga., April 7 to 11, 1930.

[2] Preliminary work on this problem was carried out at the laboratory of the Research Division, The New Jersey Zinc Co., Palmerton, Pa.

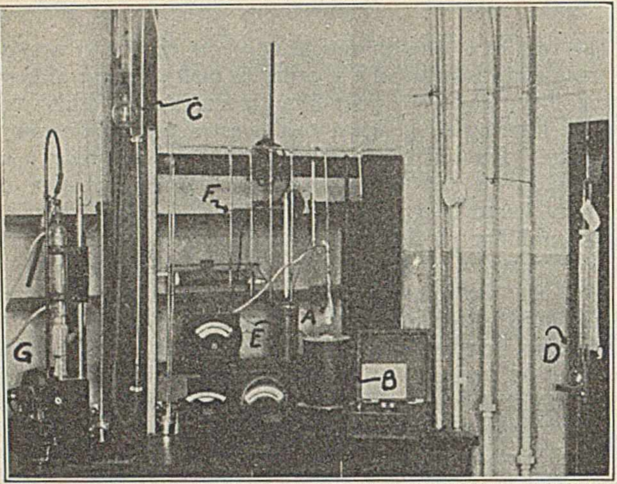


Figure 1—Photograph of Apparatus for Determining Heats of Wetting and Adsorption on Zinc Oxide

materials on zinc oxide. The heats of adsorption of the vapors, carbon dioxide, sulfur dioxide, ammonia, water, benzene, xylene, and pyridine on zinc oxide, and the heats of wetting of the liquids water, benzene, xylene, pyridine, Nujol, linseed oil, and solutions of zinc oleate in benzene and in pyridine have been measured. The effect of particle size of the pigment has also been studied using water vapor as the adsorbed gas.

Experimental Procedure

For most of the measurements U. S. P. zinc oxide was chosen because of its relative chemical purity and uniformity of particle size. This pigment was called sample 1. Sample 2 was a zinc oxide of extremely small particle size used extensively in the rubber industry. Sample 3 was an experimentally prepared oxide having a large particle size.

The liquids and vapors were the ordinary grade of c. p. materials. The pyridine was further purified by fractional distillation. The linseed oil was purified by several methods and contained 0.2 per cent acids.

Figures 1 and 2 show the apparatus used. A 5-gram sample of the zinc oxide was heated to 500° C. in an electric furnace. It was then evacuated at that temperature for 7 hours, the pressure falling off to about 0.00005 mm. Hg. This vacuum either remained constant or improved when the system was closed and the zinc oxide was cooled. The following day the heat of adsorption was determined at 25° C. In measuring heats of adsorption, the calorimeter, *E*, Figure 1, consisting of a Dewar tube containing water, was placed over the bulb of zinc oxide without detaching it from the apparatus. The material to be adsorbed was then admitted. If the material was a vapor, it was admitted by means of device *a*, Figure 2; if a gas, device *b* was used. *H* was an iron rod which could be raised by means of an external permanent magnet. The temperature of the room was maintained at 24° C. in order to prevent distillation of the liquid into the zinc oxide bulb, which was at 25° C.

For the measurement of a heat of wetting, the evacuated sample was sealed off from the apparatus and introduced into the calorimeter, which contained the appropriate wetting liquid, by means of device *c*, Figure 2. Thus the heats of wetting and of adsorption were both obtained directly on the outgassed samples without exposing them to the atmosphere meanwhile. A fresh sample of zinc oxide was used for each determination in order to eliminate the growth of the particle effect which is discussed later.

The data are given in Table I. Usually several determinations were made. Trial 1 and trial 2 are representative determinations recorded merely to illustrate the reproducibility of the method.

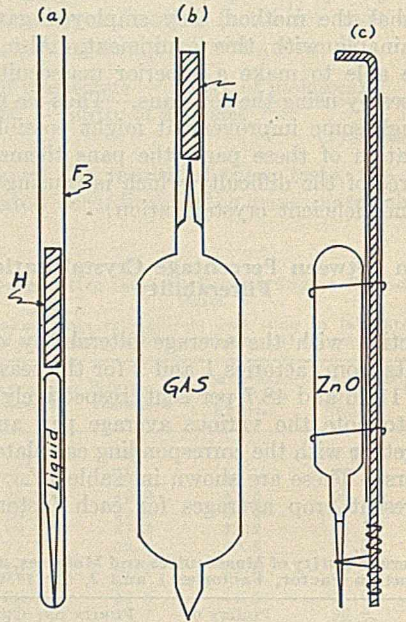


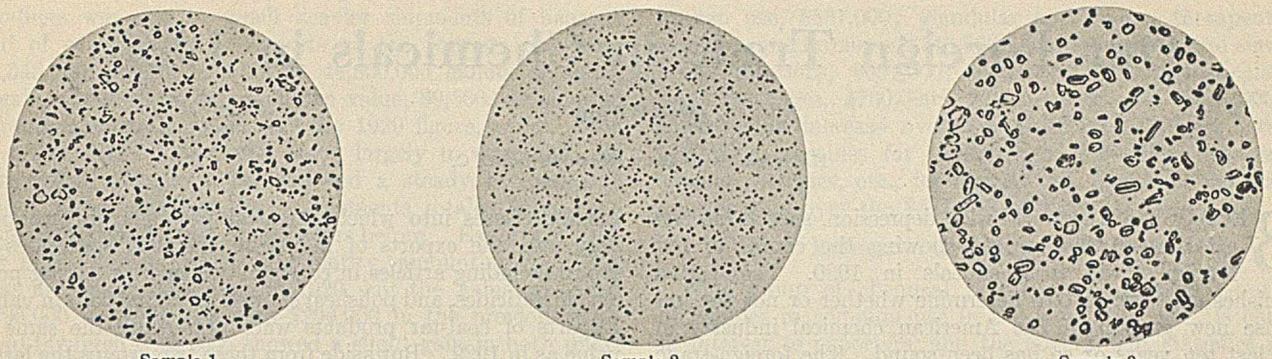
Figure 2—Details of Apparatus
(*a*)—Device for introducing vapor
(*b*)—Device for introducing gas
(*c*)—Device for bringing liquid into contact with zinc oxide in calorimeter

Specific Surface

The specific surface of the oxide was determined by the method suggested by Section 3, Technical Committee 4, of the A. S. T. M. (1930) on size and shape. The following are the essentials of the method: Photomicrographs of the pigment were prepared at a magnification of 1285 × as shown in Figure 3. The diameters of about 500 particles on photomicrographs of each sample were measured with a magnifying glass having a scale with 0.1-mm. divisions. The number of particles, *n*, of each diameter, *d*, was then tabulated and

Table I—Heats of Adsorption and of Wetting

SUBSTANCE	ZnO SAMPLE	d_3	PRESSURE OF GAS	HEATS OF ADSORPTION Trial 1	HEATS OF ADSORPTION Trial 2	HEATS OF ADSORPTION Av.	HEATS OF WETTING Trial 1	HEATS OF WETTING Trial 2	HEATS OF WETTING Av.	SURFACE PER 5 GRAMS	HEAT OF ADSORPTION
		μ	*Mm.*	*Grams-cal. per 5 grams ZnO*			*Gram-cal. per 5 grams ZnO*			*Sq. m.*	*Cal./sq. m.*
Carbon dioxide	1	0.607	49	3.6	3.9	3.7				9	0.4
Ammonia	1	0.607	49	4.7		4.7				9	0.5
Sulfur dioxide	1	0.607	90	7.2	6.9	7.0				9	0.8
Nujol	1	0.607					0.7	1.4	1.0	9	
Benzene	1	0.607	95	1.0	0.0	0.5	2.5	3.0	2.8	9	0.5
Xylene	1	0.607	7	4.3	3.5	3.9	2.5	3.9	3.2	9	0.4
Pyridine	1	0.607	20	3.6	4.5	4.0	3.8	4.4	4.1	9	0.4
Linseed oil	1	0.607					9.0 to	11.0	10.0	9	
1.5% zinc oleate in benzene	1	0.607					6.4		6.4	9	
5% zinc oleate in pyridine	1	0.607					4.5		4.5	9	
Water	1	0.607	23	11 to	13	12.0	4.8 to	6.7	5.6	9	1.3
Water	2	0.374	23	18.7 to	23	21.0				15	1.4
Water	3	0.977	23	3.4 to	4.5	4.0				5.5	0.8



Sample 1 Sample 2 Sample 3

Figure 3—Photomicrographs Used in Measuring Particle Size. × 1285

the specific surface calculated from the equation $S = 6/\rho d_3$, where ρ is the density of the pigment—5.47 grams per cc. (I. C. T.)—and d_3 is the diameter of the particle of average surface. d_3 is equal to $\Sigma nd^3/\Sigma nd^2$.

Although this method is the best available, it must be considered only approximate. There are at least three sources of error in such a method: (1) the error in mechanically measuring the diameters of the irregular particles in the photographs; (2) the assumption of spherical shape; and (3) the possibility that the pigments, especially those like sample 2, contain a considerable number of particles of sizes below the resolving power of the microscope, and are therefore lost in the photograph. The indistinctness of the particles in sample 2 is due to the fact that practically all the particles are approaching this limit. In these measurements all particles that were not resolved were called 0.08 micron.

The experimental values for adsorption phenomena on a substance like zinc oxide must be considered as being only relative and of the correct order of magnitude as to the true value. One reason for this, as discussed above, is that the surface can be measured only approximately. Two other reasons are the growth of the particle on heating and the incompleteness of cleaning up the surface.

Growth of Particle

Zinc oxide at 500° C. has an appreciable vapor pressure. At this temperature the small crystals tend to disappear and the large ones tend to grow larger. For example, an unheated sample had a particle diameter of 0.21 micron and a specific surface of 2.7 square meters per gram. After heating for 24 hours at 500° C., these values were 0.26 micron and 2.5 square meters per gram. Because of the laborious procedure involved, only one particle-size determination on each sample was made in this work. It was assumed that this gave a representative value of the particle size for the given oxide if it was heated a given length of time at a given temperature.

Outgassing

The samples were outgassed for the same length of time. Various factors affect the degree of evacuation which can be obtained in a given time. One of these is the reproducibility of pumping speed. This is quite satisfactory with the combination of a rotary oil pump and a mercury-vapor diffusion pump. The previous history of the sample had a marked effect on the degree of vacuum obtainable. Three instances of this are given: (1) oxides that had been treated with sulfur dioxide or pyridine vapor could not be outgassed again to better than 0.001 mm. of mercury, even with 24 hours of heating at 500° C. and pumping; (2) treatment with carbon dioxide had little effect; (3) treatment with water vapor shortened the time of outgassing, 4 hours sufficing to reëvacuate the samples that had been so treated. There is a further indication that the water vapor may be loosely held. After the heat of adsorption was determined, the pressure of the water vapor was decreased quickly from 23 mm. to 4 mm. either by pumping out the vapor or by chilling the water in *F* with ice, thus condensing the water back into this tube. A negative heat effect amounting to about −2 calories was noted in the calorimeter. This was a reproducible effect. With the permanent gases, lowering the pressure from 90 mm. to 1 mm. had no heat effect.

Conclusions

The heats of wetting by liquids and of adsorption by gases on zinc oxide vary according to the nature of the liquid or gas. The tenacity, as measured by the speed of outgassing with which the adsorbed material is held, also varies according to the nature of the gas. There seems to be no direct relation between the two, water vapor being quickly and sulfur dioxide very slowly removed. Each gives a high heat of adsorption on zinc oxide. Carbon dioxide and pyridine give about the same heats. The former is readily released; the latter is not.

The heat of adsorption of water is greater than its heat of wetting. The difference might be accounted for by assuming that at least part of the adsorption mechanism consists of a condensation of the gas to the liquid state of aggregation. The heat of adsorption then would be made up of the heat of wetting and the heat of condensation.

The heat of adsorption is directly proportional to the surface of the pigment and independent of the size of the particles.

A simple type of calorimeter is sufficiently accurate for this type of work because of inaccuracies inherent in the accompanying procedures. These inaccuracies are due to experimental difficulty in obtaining clean surfaces and in measuring the actual surface.

Soviet Petroleum Sales to South Africa

Negotiations for the large-scale marketing of Russian gasoline and oil in South Africa, with generous financial aid from the Soviet Government, are on the verge of completion, according to current reports in South Africa forwarded to the Department of Commerce.

For some time restricted quantities of these products have been sold in the South African Union. Several years ago a local company, the Atlas Petroleum Products, Ltd., undertook the distribution and sale of Russian goods, operating on a concession granted by the Naphtha Syndicate of Russia. The Atlas has a capitalization of approximately $1,701,000 and has been one of the most important distributors of lubricating oils and gasoline in the Union. However, sufficient money has not been available for this firm to approach the size of several of the better known American and European companies, which have held the greater part of the business of this area. The company now claims that, by virtue of the assistance from Russia, it will be possible to establish bulk storage tanks at Capetown, and depots are to be erected at other ports and the more important inland centers.

Our Foreign Trade in Chemicals in 1930[1]

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BECAUSE of the world-wide depression, special interest attaches to the returns showing the course of our foreign trade in chemicals in 1930. The period furnishes a severe test to determine whether or not the immense new growth of the American chemical industry in the last ten years or so has been sound. The foreign-trade figures provide a good barometer showing how well the industry has weathered this protracted adversity. A brief study indicates that, basically, conditions are wholly encouraging. While the trade in almost all branches of the chemical industry naturally fell off, the decrease was substantially less than the average for the whole foreign trade of the country, and was considerably smaller than that for most other major lines of business.

During the year 1930, while the total imports of all commodities into the United States were registering a decrease of 30 per cent as compared with 1929, those of chemical products fell off only 22.2 per cent. Total exports to foreign countries dropped 27 per cent and those of chemicals, 15.9 per cent. Comparison with other lines of trade shows that our dealers in chemical products have little cause for complaint. In the import trade values in hides and skins fell off 33 per cent; in coffee, 31 per cent; in sugar, 35 per cent; in rubber and manufactures, 42 per cent; in paper and manufactures, 10 per cent; in silk, 38 per cent. In the export trade our sales of automobiles, accessories, and parts to foreign customers were smaller by 49 per cent than in 1929; textiles, 35 per cent; agricultural machinery, 18 per cent; grain and preparations, 33 per cent; meat products, 17 per cent; tobacco and manufactures, 4 per cent; coal and coke, 15 per cent. Chemicals have thus fared comparatively well in the trying times through which the whole world has been passing, and they now occupy a favorable position for taking advantage of the revival to which the business public looks forward.

The considerably smaller decrease of exports than of imports is likewise of significance. To a large extent this may be charged to the higher tariffs which went into effect in June, but it was also in line with the general trend of the trade in the last few years. Until 1927 the balance of trade in chemicals was consistently against the United States. But in three of the last four years exports have exceeded imports in value, and in 1930 the margin was larger than ever before, a clear indication that we are becoming more and more self-sufficient in the chemical industry and are turning out a continually increasing surplus for sale abroad.

Total imports and exports of chemicals and related products in 1930 as compared with the previous year's trade are shown in the following:

Total Foreign Trade in Chemicals and Related Products

	Imports	Exports	Balance of Trade
1929	$144,062,000	$152,109,000	+$8,047,000
1930	112,127,000	127,986,000	+15,859,000

CHEMICALS AND RELATED PRODUCTS

Study of the detailed trade figures shows that the decrease was distributed fairly evenly over the whole field of chemical commodities. There were no precipitous declines in the more important items and no marked gains. Of the greater classes into which chemical products are grouped, only one, the exports of industrial chemical specialties (a group including articles in common use such as baking powder, insecticides, and polishes) showed an actual gain in value. Exports of coal-tar products were practically the same in value as in 1929. But aside from these two groups the larger classes of articles recorded a normal decrease usually of 20 to 30 per cent. The following table shows the trade of the last two years by large groups:

Imports and Exports by Large Groups

Group	Imports		Exports	
	1929	1930	1929	1930
Coal-tar products	$22,824,000	$16,273,000	$18,061,000	$17,876,000
Medicinal and pharmaceutical preparations	6,422,000	4,948,000	21,282,000	17,611,000
Industrial chemicals	30,644,000	23,300,000	28,149,000	23,796,000
Industrial chemical specialties	[a]	[a]	14,457,000	14,808,000
Pigments, paints, and varnishes	3,822,000	3,613,000	29,111,000	21,689,000
Fertilizers and materials	72,340,000	59,122,000	20,441,000	15,284,000
Explosives, fuses, etc.	960,000	911,000	4,549,000	2,950,000
Soap and toilet preparations	6,941,000	4,806,000	16,059,000	13,970,000

[a] Not separately stated.

Coal-Tar Products

The falling-off in imports of coal-tar products was more marked in the case of finished products than in crudes or intermediates. The largest item among coal-tar imports, creosote oil, dropped from a value of $10,119,000 in 1929 to $7,806,000 in 1930, a loss of 23 per cent. But this was due partly to lower prices, since the quantity, 66,922,000 gallons, was only about 16 per cent under that of 1929. The decrease was not due entirely to the general trade depression, but was rather a continuation of a downward tendency which has almost cut the trade in half in the last two years, the value of the 1928 imports having been nearly $14,000,000.

Imports of acids fell off sharply, totaling only about $53,000 in value as against $160,000 in the previous year. Other intermediates were valued at $1,022,000, a decrease of 31 per cent from the 1929 trade.

The drop in imports of finished coal-tar products was marked, even for a year of dull times. For all classes of goods the decrease was just about one-third. The greater part of these products consists of colors, dyes, etc., which dropped 37 per cent in value as compared with 1929. Imports from Switzerland were almost cut in half, in point of value, and those from Germany, the only other important source, were reduced one-third, as shown in the following table:

Imports of Colors, Dyes, Stains, Color Acids, and Color Bases

Country	1929		1930	
	Pounds	*Value*	*Pounds*	*Value*
Belgium	76,000	$96,000	63,000	$81,000
France	108,000	160,000	44,000	57,000
Germany	4,685,000	5,019,000	3,103,000	3,318,000
Italy	14,000	12,000	21,000	25,000
Switzerland	2,563,000	3,000,000	1,557,000	1,637,000
United Kingdom	92,000	101,000	114,000	119,000
Other countries	55,000	60,000	50,000	47,000
Total	7,593,000	8,448,000	4,952,000	5,284,000

Imports of coal-tar medicinals dropped from a value of $332,000 in 1929 to $273,000 in 1930. The decrease in quantity was even more pronounced, the total of 72,000 pounds being less than one-half the trade of the year before.

In the export field the unusually good showing of coal-tar

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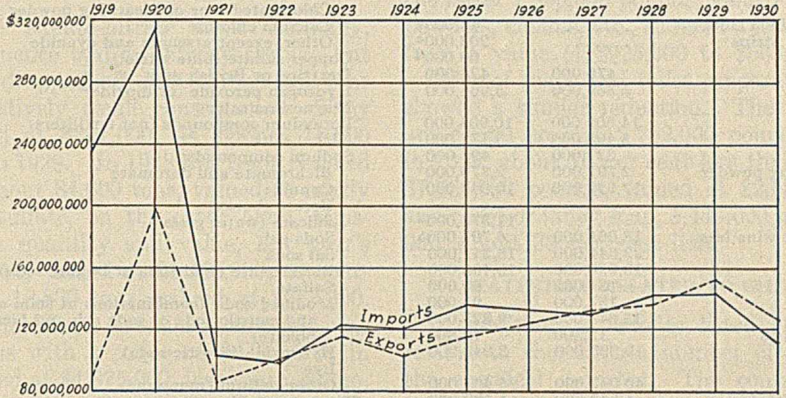
[1] Received March 11, 1931. All figures for 1930 are preliminary, but they may be taken as approximately correct, since the final returns of our foreign trade show few changes from the first-published figures.

products was due to much heavier shipments of benzene and of coal-tar pitch. Exports of the former rose from 33,346,000 gallons in 1929 to 44,600,000 gallons in 1930, a gain of one-third, although the value, $9,566,000, showed a much smaller increase over the 1929 figure, which stood at $8,537,000. This trade, going largely to Germany and the United Kingdom, has enjoyed a steady expansion in recent times, and last year's shipments totaled more than twice as much as those of two years before. Exports of coal-tar pitch almost trebled in quantity, amounting to 27,000 tons as against 9800 tons in 1929, but the value was only $290,000 as compared with $204,000 in the previous year. Coal-tar-pitch coke also showed a slight gain in both quantity and value, the 1930 shipments amounting to 11,900 tons, valued at $89,000, as compared with 11,600 tons, valued at $84,000, in 1929. Crude coal-tar, on the other hand, was sold abroad in considerably reduced quantities, the total of 87,000 barrels, valued at $273,000, being 20 per cent less in quantity and 30 per cent less in value than in 1929. The total value of exports of coal-tar crudes was $10,696,000, a substantial gain over the $9,840,000 of the preceding year.



United States Foreign Trade in Chemicals and Related Products since the War

Exports of intermediates fell off about one-fourth, the total value being $301,000 as against $418,000 in 1929. Finished coal-tar products likewise dropped from a total of $7,803,000 to $6,879,000, the loss being due to lighter shipments of colors, dyes, and stains, which make up nine-tenths of this trade. Coal-tar medicinals, on the other hand, rose in total value, the 1930 figure being $189,000, some 2 per cent more than that of the year before.

Medicinals and Pharmaceuticals

All the leading items in this group shared in the general decline in value, although it is to be noted that menthol, the chief article imported, entered in larger quantities than in 1929, the total trade reaching 308,000 pounds, valued at $1,017,000, as compared with 296,000 pounds, valued at $1,232,000, in the preceding year. This is a growing trade, and last year's gain in quantity was a continuation of an upward tendency already in evidence. Imports of quinine sulfate, on the other hand, were cut in half, the 1930 shipments totaling only 1,253,000 ounces, valued at $449,000, as against 2,472,000 ounces, valued at $855,000, in 1929.

In the export trade proprietary medicines continue to comprise by far the greater part of American medicinals sent abroad. In 1930 their total value reached $9,927,000, a sharp decrease from the large total of $17,557,000 in 1929. Of last year's trade the largest single item was tonics (blood purifiers, appetizers, etc.), which stood at $2,211,000, about one-third less than in 1929, and the second largest item was salves and ointments, $1,976,000, almost as much as in the previous year. For 1930 the government statistics covering medicinals were given in more detail than in previous years, and they show that, aside from proprietary medicines, the more important of the medicinal preparations which we sold to foreign consumers in 1930 included druggists' tablets, pills, and powders, $1,912,000; serums and antitoxins for human use, $861,000; glandular and organo therapeutics, enzymes, and ferments, $746,000; elixirs, cordials, and similar liquid solutions, $691,000; household pharmaceuticals in small packages, $760,000; white mineral oil, $491,000, a considerable increase over the 1929 trade, which totaled $450,000; vaccines for human use, $439,000; antitoxins, serums, vaccines, etc., for animal use, $547,000, likewise a notable gain over the $527,000 of 1929.

Industrial Chemical Specialties

This group of chemical products, comprising a variety of articles in common use in the household, etc., is chiefly of interest to exporters, and the government statistics give the classification only in the export trade. The largest single item in point of both bulk and value is liquid household insecticides and exterminators, of which we sent to foreign lands 11,781,000 pounds in 1930, valued at $3,638,000, a substantial gain over the 1929 trade, which stood at 10,254,000 pounds, valued at $3,054,000. Petroleum jelly was sold abroad to the extent of 11,032,000 pounds, a gain of 54 per cent in quantity over 1929, although the total value, $923,000, was slightly under the figure of the previous year. Baking powder exports, 4,517,000 pounds having a value of $1,434,000, compared with 1929 sales of 5,315,000 pounds valued at $1,730,000. Automobile polishes were one of the few specialties showing an increased exportation, foreign sales amounting to $366,000 as against $345,000 in the preceding year. Nicotine sulfate, valued at $309,000, registered a 42 per cent gain in value while the total quantity, 635,000 pounds, was more than twice as great as that of 1929. Shoe polishes fell from a value of $808,000 to $645,000, with a proportionate decrease in bulk of shipments. Water softeners and purifiers and boiler and feed-water compounds were sold abroad to a value of $416,000, a small increase over 1929, while leather dressings and stains, at a value of $406,000, were only slightly under the figure for the year before.

Industrial Chemicals

This group comprises the articles usually considered as coming under the term "chemicals" used in its more restricted sense. As they enter into most of the so-called chemical industries as basic reagents, it will be interesting to set forth the imports and exports in detail.

In point of value the most important single commodity of this group among the imports continued to be sodium cyanide, the total in 1930 amounting to $2,043,000. This was a sharp decline of one-third from the 1929 trade of $3,199,000, the quantity, 26,401,000 pounds last year, showing about a proportionate falling off. Argols, tartar, or wine lees, while registering almost the same amount with respect to quantity of imports, fell off in value from $2,113,000 in 1929 to $1,836,000 in 1930.

Among the acids, acetic or pyroligneous acid continues to hold first place, the value of the imports in 1930 being $1,498,000, a decline of one-fourth from the total value of the preceding year. Imports of tartaric acid, however, registered a marked increase, the value rising from $689,000

Imports and Exports of Industrial Chemicals

CHEMICAL	1929 Pounds	1930 Pounds
IMPORTS		
Acetylene derivatives	....	15,000[a]
Butylene, ethylene, and propylene derivs.	....	267,000[a]
Acids and anhydrides:		
Acetic or pyroligneous	29,235,000	22,377,000
Arsenious (white arsenic)	26,314,000	21,559,000
Chromic	....	2,000[a]
Formic	1,387,000	510,000
Oxalic	1,346,000	574,000
Sulfuric	16,208,000	918,000
Tartaric	2,220,000	2,912,000
All other	1,800,000	2,328,000
Alcohols, including fusel oil, value	$239,000	$30,000
Ammonium compounds:		
Chloride	9,561,000	6,628,000
Nitrate	9,496,000	8,165,000
All other	974,000	661,000
Barium compounds	8,151,000	6,706,000
Calcium compounds:		
Acetate	....	46,000[a]
Carbide	3,773,000	1,932,000
Cellulose compounds:		
Acetate	....	6,000[a]
All other:		
Sheets, more than 0.003 inch thick	....	45,000[a]
Other sheets, bands, and strips	....	203,000[a]
Other forms	....	99,000[a]
Cobalt oxide	476,000	426,000
Copper sulfate (blue vitriol)	5,389,000	5,964,000
Glycerol:		
Crude	14,602,000	10,906,000
Refined	5,493,000	3,177,000
Iodine	627,000	494,000
Lime, chlorinated, or bleaching powder	2,791,000	2,370,000
Magnesium compounds	17,928,000	10,942,000
Potassium compounds:		
Argols, tartar, and wine lees	....	11,375,000[a]
Bitartrate, crude, argols, or wine lees	18,001,000	6,707,000[b]
Carbonate	22,644,000	18,241,000
Chlorate and perchlorate	13,956,000	15,106,000
Cream of tartar	181,000	60,000
Cyanide	137,000	91,000
Hydroxide (caustic potash)	15,648,000	9,323,000
Nitrite, crude (saltpeter), tons	12,800	12,800
Other potassium compounds	19,393,000	3,943,000
Sodium compounds:		
Cyanide	40,047,000	26,401,000
Ferrocyanide (yellow prussiate)	1,940,000	1,590,000
Nitrite	312,000	61,000
Phosphates (except pyrophosphate)	....	1,445,000[a]
Other sodium compounds, value	$2,987,000	$2,103,000
Radium salts, grains	165	260
Other industrial chemicals, value	$6,912,000	$4,046,000

[a] Beginning June 18, 1930.
[b] Ending June 17, 1930.

CHEMICAL	1929 Pounds	1930 Pounds
EXPORTS		
Acids and anhydrides:		
Sulfuric	6,960,000	5,471,000
Boric	5,204,000	2,804,000
Other	15,254,000	12,126,000
Alcohols:		
Methanol, gallons	498,000	952,000
Glycerol	1,374,000	608,000
Other	2,126,000	3,358,000
Acetone	7,897,000	3,645,000
Other ketones	....	3,000
Formaldehyde (formalin)	2,588,000	3,769,000
Other aldehydes	....	160,000
Ethers and esters	698,000	1,163,000
Nitro or aceto cellulose solutions, collodions, etc.	2,111,000	1,828,000
Ammonium compounds (except sulfate and anhydrous ammonia)	1,746,000	2,365,000
Aluminum sulfate	53,176,000	50,509,000
Other aluminum compounds	549,000	2,018,000
Calcium compounds:		
Acetate of lime	101,000	23,000
Calcium carbide	4,345,000	3,987,000
Chlorinated lime or bleaching powder	5,024,000	2,950,000
Calcium chloride	30,851,000	42,699,000
Other, except arsenate and cyanide	4,145,000	4,969,000
Copper sulfate (blue vitriol)	6,420,000	5,062,000
Dextrine or British gum	20,828,000	17,115,000
Hydrogen peroxide (or dioxide)	2,238,000	1,917,000
Magnesium salts	695,000	601,000
Potassium compounds (not fertilizers)	3,047,000	2,512,000
Nickel salts	42,000	816,000
Sodium compounds:		
Bichromate and chromate	5,855,000	4,933,000
Cyanide	1,816,000	1,242,000
Borate (borax)	159,768,000	165,863,000
Silicate (water glass)	66,735,000	60,494,000
Soda ash	77,985,000	65,873,000
Sal soda	12,419,000	13,073,000
Bicarbonate (acid soda or baking soda)	18,947,000	19,818,000
Sulfate	3,332,000	8,872,000
Modified soda (combinations of soda ash and caustic soda or soda ash and bicarbonate)	14,994,000	207,000
Hydroxide (caustic soda)	121,077,000	126,379,000
Lye	968,000	407,000
Other sodium compounds	221,300,000	51,082,000
Tin compounds	658,000	562,000
Zinc compounds	3,423,000	3,117,000
Gases, compressed and liquefied:		
Ammonia, anhydrous	2,329,000	2,272,000
Chlorine	7,168,000	7,532,000
Oxygen	883,000	495,000
Other	2,254,000	1,874,000
Other industrial chemicals, value	$6,467,000	$4,287,000

in 1929 to $779,000 in 1930. The gain in quantity was still larger. Arsenious acid dropped off by some 22 per cent, the value of last year's trade being $744,000 as against $956,000 in the year before. There were very heavy decreases in shipments of formic and sulfuric acids, the former entering our ports to a total value of only $37,000 as against $109,000 in 1929 and the latter dropping from $97,000 to $6000.

Other leading items in the import trade were iodine, which decreased from a value of $2,249,000 in 1929 to $1,798,000 last year; glycerol, crude, which fell from $847,000 to $633,000; glycerol, refined, the value of which was almost cut in half, amounting to $272,000 as against $501,000 in 1929; caustic potash, which dropped from a value of $1,001,000 to $493,000; potassium carbonate, $1,024,000 in 1929 and $848,000 in 1930; potassium chlorate and perchlorate, which showed a good gain, rising from $498,000 to $541,000; and potassium nitrite, which likewise increased from $546,000 in 1929 to $620,000 in 1930. Of particular interest to those who have been following the ups and downs of the trade in methanol are the figures showing the great falling off in imports of alcohols, which are made up very largely of methanol. These dropped from a value of $239,000 to $30,000, apparently marking the end of serious competition from the synthetic product of Germany.

In the export trade the leading article is sodium hydroxide, or caustic soda, sales of which showed a handsome gain last year. The value rose from $3,516,000 in 1929 to $3,706,000 in 1930. Sales of borax also registered a gain, totaling $3,058,000 as against $2,935,000 in the preceding year. These were the largest single items on the list of industrial chemicals, the only other to pass $1,000,000 being soda ash, the value of which dropped from $1,341,000 in 1929 to $1,139,000 last year. Exports of methanol showed a very large increase in quantity, rising from 498,000 gallons to 952,000 gallons, but much lower prices kept the total value down to $483,000 as against $403,000 in 1929.

Pigments, Paints, and Varnishes

Importations of paints and paint materials were lower all along the line last year. Mineral-earth pigments fell off nearly 40 per cent in value, from $1,616,000 in 1929 to $1,017,000 in 1930. Chemical pigments, valued at $1,494,000 in 1929, dropped to $1,139,000 last year; paints, stains, and enamels fell from $650,000 to $405,000; and varnishes from $61,000 to $51,000. Lithopone and zinc pigments comprise the largest import item of the group in point of value. Shipments in 1930 were 15,042,000 pounds, valued at $670,000, as against 19,578,000 pounds, valued at $957,000, in the year before.

While the larger items in the export trade showed a similar downward tendency, there were increases in several of the smaller export lines. Sales of carbon black to foreign customers fell off from a total of 91,829,000 pounds, valued at $8,271,000, in 1929 to 84,260,000 pounds, valued at $5,789,000, last year; zinc oxide dropped from $2,302,000 to $1,447,000, varnishes from $1,366,000 to $992,000, lacquers from $1,695,000 to $1,462,000, and enamel paints from $1,726,000 to $912,000. But sales of red lead, litharge, and orange mineral jumped from 5,780,000 pounds, valued at $503,000, to 8,255,000 pounds, valued at $590,000; nitrocellulose lacquers from $881,000 to $1,012,000; paste paint from $348,000 to $354,000; and white lead from $922,000 to $923,000. For the export trade in paints, varnishes, and materials as a whole the year was anything but stimulating, the total decrease in value of exports being considerably above the average for chemical lines in general.

Fertilizers and Materials

Drought conditions over large areas of the South and Middle West in 1930 are reflected in the statistics of fertilizer imports, which decreased nearly one-sixth in value.

Particularly noticeable was the slump in imports of Chilean nitrates. They totaled only 568,000 tons in 1930, falling off from 930,000 tons in the year before and more than 1,000,000 tons in 1928. Imports in 1930 were the lowest in fifteen years. Reduction in the total value of these imports was proportionate to that in volume, the average valuation per ton at port of shipment remaining practically the same for the two years ($37.52 in 1929 and $37.71 in 1930).

Imports of ammonium sulfate-nitrate from Germany, which rose to such prominence two or three years ago but greatly declined in 1929, dropped off still further last year and are now of comparatively small consequence. They totaled 8000 tons, valued at $391,000, as against 16,000 tons, valued at $884,000, in 1929. In 1928 this trade reached its peak with a total of about 84,000 tons, valued at nearly $5,000,000. Ammonium sulfate, on the other hand, registered large gains in both quantity and value, last year's total imports of 34,000 tons, valued at $1,160,000, comparing with 1929 imports of 18,800 tons, valued at $763,000. Of the other nitrogenous fertilizers calcium cyanamide was reduced from 184,000 tons with a value of $6,221,000, in 1929 to 145,000 tons, valued at $4,875,000, last year; guano, at 40,000 tons, was 12 per cent under 1929 trade; and calcium nitrate, 44,000 tons, showed a 30 per cent gain.

Phosphate imports dropped from 104,800 tons, valued at $2,149,000, in 1929 to 96,400 tons, valued at $1,909,000, in 1930, a loss of about 8 per cent in quantity.

In the face of much agricultural distress and limited expenditures on our farms, it is somewhat surprising to note that imports of potash showed a handsome gain over 1929. Of the four principal classes of salts making up this trade, only "manure salts" failed to surpass the 1929 figure. Figures for the two years follow:

Potash Imports into the United States

Fertilizer	1929 Tons	1929 Value	1930 Tons	1930 Value
Chloride, crude	231,000	$8,225,000	273,000	$9,928,000
Kainite	76,000	644,000	112,000	981,000
Manure salts	391,000	5,113,000	362,000	5,047,000
Sulfate, crude	80,000	3,648,000	86,000	3,947,000
Other potash-bearing substances	675	9,000	547	5,000

Exports of fertilizer materials, while slightly larger in total volume, had only about three-fourths the value of the preceding year. The gain in quantity was due to a larger trade in phosphates which more than offset a marked decrease in shipments of sulfate of ammonia. Phosphate-rock exports totaled 1,225,000 tons and had a value of $5,628,000. These figures compare with 1,143,000 tons, valued at $5,387,000, for 1929. Acid phosphates likewise gained substantially, attaining a mark of 112,000 tons, valued at $1,598,000, whereas the 1929 trade came to 85,000 tons, with a value of $1,489,000. The heavy decrease in sulfate of ammonia shipments, from 145,000 tons to 82,000 tons and from a value of $6,296,000 to $2,910,000, was due largely to a decline in the trade with the Philippines and Japan, each of which took less than half as much as in 1929.

Explosives, Fuses, etc.

Imports under this heading consisted of only three commodities—powder and other explosives, firecrackers, and fireworks and ammunition. Firecrackers, the chief item, were imported in larger quantity than in 1929, the total of 4,609,000 pounds comparing with 4,023,000 pounds in the previous year. Exports, on the other hand, were considerably reduced. Dynamite was the largest item, the 9,090,000 pounds, with a value of $1,280,000, comparing with 16,277,000, valued at $2,228,000, in 1929.

Soap and Toilet Preparations

Imports in this classification, mostly perfume materials and cosmetics from France, have been steadily declining for several years. Last year furnished no change in this tendency. Perfume materials, the most important item, fell from a total value of $3,296,000 in 1929 to $2,142,000 in 1930. Castile and toilet soaps fell off slightly, the former having a total of 3,664,000 pounds, valued at $347,000, and the latter 1,853,000 pounds, valued at $643,000. Cosmetics, powders, creams, etc., suffered a loss of 40 per cent, dropping from a value of $925,000 to $563,000.

Sales of soaps and toilet preparations to foreign countries showed a similar reduction. The chief items in this trade are dental creams, 2,752,000 pounds, valued at $2,274,000, in 1929, about 10 per cent less than in 1929; laundry soap, 37,866,000 pounds, valued at $2,534,000, 20 per cent less; and toilet or fancy soap, 5,443,000 pounds, valued at $1,235,000, about 38 per cent less.

MATERIALS RELATED TO CHEMICAL INDUSTRIES

In addition to articles listed as chemicals or products related to chemicals a number of others are of interest to the chemical industry. The course of last year's foreign trade in the more important of these commodities is noted below.

Mineral Oils

World conditions of lessened industrial activity cut down the demand for petroleum and its derivatives, and all classes of these oils were sold abroad in reduced quantities in 1930. The totals for the leading classes in the last two years were as follows:

Exports of Mineral Oils

	1929 Barrels	1929 Value	1930 Barrels	1930 Value
Petroleum, crude	26,394,000	$37,800,000	23,704,000	$32,153,000
Gasoline, naphtha and other finished light products	60,007,000	266,904,000	63,197,000	250,653,000
Illuminating oil (kerosene)	19,820,000	83,798,000	16,689,000	63,245,000
Gas and fuel oil	35,715,000	37,200,000	32,378,000	33,220,000
Lubricating oil	10,653,000	102,899,000	9,749,000	88,907,000

Although this trade for the most part followed the usual lines, there were some changes of importance. Almost four times as much crude petroleum was sold to Europe as in 1929, last year's trade totaling 1,152,000 barrels as against 323,000 barrels in the previous year. Japan also took larger quantities, while the trade with Canada fell off somewhat. Sales of gasoline and other light products to several European countries increased, including Belgium, France, Germany, Spain, and the United Kingdom, while shipments to South America declined. In the trade in kerosene the United Kingdom increased its purchases from 2,794,000 barrels in 1929 to 2,946,000 barrels in 1930, but all the other leading buyers took reduced quantities. Trade with China dropped one-fourth, from 4,026,000 barrels to 3,172,000 barrels, and Japan took 1,073,000 barrels in place of 1,304,000 barrels in 1929. Germany increased its purchases of gas and fuel oil from 1,351,000 barrels in 1929 to 2,006,000 barrels in 1930 and increased quantities also went to the Netherlands, Canada, Mexico, and Japan, as well as to smaller buyers, although the gains were more than offset by losses elsewhere.

The United Kingdom, the leading buyer of lubricating oil, took a larger amount last year than in 1929, but trade with nearly all other regular buyers fell off.

In addition to these foreign sales, 50,765,000 barrels of bunker oil were loaded on vessels engaged in foreign trade as compared with 52,278,000 barrels in 1929. Foreign vessels took somewhat more than one-half of this oil.

In the incoming trade the total value of shipments of petroleum and its products showed a small gain, totaling $145,110,000 as against $143,558,000 in 1929. Crude petroleum imports, however, fell off from 78,933,000 barrels in 1929 to 62,129,000 barrels in 1930. Colombia sent 14,204,000 barrels as compared with 12,620,000 barrels in 1929, but all other important sources cut down their shipments to the United States. Imports of gasoline and other light products almost doubled, rising from 8,834,000 barrels to 16,927,000 barrels.

Sulfur

Crude sulfur exports fell from 855,000 tons, valued at $17,629,000, in 1929 to 598,000 tons, valued at $12,526,000, in 1930, a loss of about 30 per cent. The decrease was fairly uniform among all the leading buyers. Canada was our best customer last year, taking 167,000 tons, valued at $3,028,000, followed by Germany, Australia, and France. Sales of crushed, ground, refined, and sublimed sulfur and sulfur in flowers also decreased, the total of 35,870,000 pounds, valued at $556,000, comparing with 39,565,000 pounds, valued at $649,000 in 1929.

Vegetable, Animal, and Essential Oils

In spite of heavy reductions in shipments which cut their total trade down one-third, coconut oil from the Philippines continues to be our leading imported vegetable oil. Last year the trade amounted to 317,919,000 pounds, valued at $19,901,000, as against 411,936,000 pounds, valued at $29,552,000, in 1929. Palm-oil imports reached a total of 287,493,000 pounds, having a value of $16,327,000, the 1929 trade being 261,816,000 pounds, valued at $17,500,000. Tung oil was the third largest import of this class and showed a gain in quantity, 126,323,000 pounds as against 119,678,000 pounds, but a drop in total value from $14,972,000 in 1929 to $12,487,000 in 1930. Inedible olive oil, 62,783,000 pounds, valued at $3,400,000, in 1930, compared with 45,874,000 pounds, valued at $3,128,000, in 1929, but edible olive oil fell from 96,788,000 pounds, valued at $16,408,000, in 1929, to 92,964,000 pounds valued at $11,221,000, last year. The heaviest falling-off was in the trade in palm-kernel oil, imports of which reached only 29,104,000 pounds, valued at $1,771,000, as compared with 69,909,000 pounds, valued at $5,301,000, in 1929.

Exports of cottonseed oil rose from 26,075,000 pounds to 28,297,000 pounds but the total value, $2,396,000, was only slightly more than in 1929. Cuba greatly increased its purchases, taking 6,790,000 pounds in 1930 as against 1,310,000 pounds in 1929.

Imports of essential and distilled oils dropped off 25 per cent in value, the two-years' trade in the leading articles being as follows:

Imports of Essential and Distilled Oils

Oil	1929		1930	
	Pounds	*Value*	*Pounds*	*Value*
Cassia and cinnamon	354,000	$470,000	372,000	$373,000
Geranium	90,000	381,000	189,000	593,000
Otto of roses, ounces	49,000	411,000	18,000	216,000
Bergamot	113,000	481,000	176,000	440,000
Citronella and lemon grass	1,341,000	622,000	1,097,000	542,000
Lavender and spike lavender	381,000	906,000	376,000	722,000
Lemon	345,000	1,096,000	624,000	588,000
Orange	216,000	854,000	166,000	362,000
Sandalwood	29,000	140,000	19,000	80,000
All other	4,239,000	2,215,000	3,064,000	1,727,000
Total		7,576,000		5,643,000

Peppermint oil, the leading essential oil exported, dropped from $795,000 to $700,000 in value, although the volume of shipments, totaling 233,000 pounds, was somewhat above that of 1929, which was 222,000 pounds.

Dyeing and Tanning Materials

Although the total value of imports under this heading fell from $7,939,000 in 1929 to $7,168,000 in 1930 the leading article, quebracho extract, registered a gain in both volume and value, shipments amounting to 87,310,000 pounds, valued at $3,835,000, as compared with 82,377,000 pounds, valued at $3,783,000, in the year before. Quebracho wood dropped from 71,000 tons to 44,000 tons, and from a value of $1,037,000 to $640,000. Valonia, with 1930 imports of 36,096,000 pounds, valued at $454,000, was third in value in the list of imports. The quantity was about twice that of the previous year and the value represented about a 50 per cent gain.

Logwood extract, the leading export item, was only slightly under the 1929 figures, shipments totaling 1,846,000 pounds as compared with 2,025,000 pounds and the value standing at $192,000 as compared with $208,000 in 1929.

Rubber

With the slowing down of automobile manufacture a sharp drop in imports of crude rubber was expected. But the returns show that the heavy decrease was in value rather than in the bulk of shipments. The 1930 imports, amounting to 1,089,830,000 pounds, compared well with those of 1929, which totaled 1,262,939,000 pounds, but the total value was only $140,641,000 as against $240,966,000 in the year before. The decrease was horizontal among the chief rubber-producing countries, and the proportions of the trade supplied by each remained about the same as in 1929. Rather more than three-fourths of the total came from British Malaya.

Naval Stores, Gums, and Resins

Total exports under this classification dropped in value from $30,998,000 in 1929 to $22,688,000 in 1930. Shipments of rosin showed a greater relative decrease than those of turpentine, the former amounting to 1,266,000 barrels, with a value of $14,256,000, as compared with 1,437,000 barrels, valued at $20,442,000, and the latter 15,142,000 gallons, valued at $6,612,000, as against 16,304,000 gallons, having a value of $8,530,000, in 1929. Germany's purchases of rosin fell off about one-third in value and those of the United Kingdom about 22 per cent. In the trade in turpentine the largest changes were in the sales to Germany, whose total value decreased from $1,267,000 to $745,000, and in those to the United Kingdom, the value of which fell from $3,396,000 to $3,030,000. The volume of sales to the latter country, however, rose from 6,892,000 gallons to 7,437,000 gallons. Sales to the Netherlands, 2,040,000 gallons, also represented a slight gain in volume.

Shellac, the most important item in the import trade in gums and resins, registered a steep falling-off in 1930. Imports stood at 18,982,000 pounds, valued at $5,190,000, whereas in 1929 they totaled 33,335,000 pounds, valued at $12,789,000. This was in line with the rest of the trade in these articles. Both natural and synthetic camphor imports were reduced in volume and value, crude natural camphor dropping from 4,024,000 pounds to 1,058,000 pounds, refined from 1,431,000 pounds to 1,031,000 pounds, and synthetic from 3,957,000 pounds to 2,404,000 pounds, all with corresponding decreases in value. Imports of chicle showed a small gain, shipments in 1929 being 13,223,000 pounds, valued at $6,621,000, and in 1930, 13,957,000 pounds, with a value of $7,022,000.

NICHOLS MEDAL AWARD

John Arthur Wilson, of Milwaukee, Wis., was awarded the Nichols Medal for 1931 at the meeting of the New York Section of the American Chemical Society on March 13, 1931, in recognition of his outstanding achievement in colloid chemistry, applied particularly to leather and sanitation. Arthur E. Hill, chairman of the section, presided, and the medal was presented by J. G. Davidson, chairman of the jury of award. D. P. Morgan, Jr., secretary of the section, read an address by Clarke E. Davis on the life of the medalist, and Arthur W. Thomas gave an account of the medalist's scientific accomplishments.

The Nichols Medal is awarded annually by the New York Section to the author of a paper or papers published in any of the Society's journals during the preceding three calendar years which in the judgment of the jury will have an important influence in stimulating original research in chemistry. The complete list of medalists is as follows:

1903	E. B. Voorhees
1905	C. L. Parsons
1906	M. T. Bogert
1907	H. B. Bishop
1908	W. H. Walker
1908	W. A. Noyes and H. C. P. Weber
1909	L. H. Baekeland
1911	M. A. Rosanoff and C. W. Easley
1912	Charles James
1914	Moses Gomberg
1915	Irving Langmuir
1916	C. S. Hudson
1918	T. B. Johnson
1920	Irving Langmuir
1921	G. N. Lewis
1923	Thomas Midgley, Jr.
1924	Charles A. Kraus
1925	E. C. Franklin
1926	Samuel C. Lind
1927	Roger Adams
1928	Hugh S. Taylor
1929	William L. Evans
1930	Samuel E. Sheppard
1931	John Arthur Wilson

……

The Life of the Medalist

Clarke E. Davis

JOHN ARTHUR WILSON was born in Chicago, August 16, 1890, and, after ten years, moved to Milwaukee. In January, 1905, he was graduated from the grammar school there and, somewhat dissatisfied with school, he was desirous of going to work. The laws of the State of Wisconsin at that time permitted a lad of fourteen to go to work if he so desired, and John Arthur so desired.

He started upon a career in the Black Art, becoming first printer's devil in charge of the Hell Box, then nearly everything else in turn, and finally became a journeyman compositor.

During his period of apprenticeship he learned that he did not wish to be a printer, but found that he had an insatiable thirst for alchemy. He would read any book he could acquire that smelled of a laboratory, even though he had no idea what it was all about.

A parson who was a dear friend of the family deplored seeing him a misfit and suggested that, since he was going to live in Baltimore, John Arthur should go with him and enter high school. This was no sooner said than done and he entered the Baltimore City College in September, 1908. The parson, as is the habit of some parsons, was a wanderer, and before Christmas John Arthur found himself attending Central High School in St. Louis. By the next fall he was attending Barringer High School in Newark, N. J. He was graduated there in June, 1911, winning a scholarship at New York University.

During the summer of 1911 he worked as chemist for the Edison Chemical Works at Silver Lake, N. J. He spent only one year at New York University, but dabbled in chemistry courses of the entire curriculum while doing his freshman work. He was elected president of the local chemical society of the university, known as the Radioactive Society.

Being a man of greater powers of emotion than of reasoning, he became a benedict at the end of his freshman year and returned to Milwaukee, securing a job in the tanning business, more from necessity than choice. Being a voracious reader, he soon covered all of the not too voluminous literature on leather and leather chemistry and much of the more elementary literature of chemistry and physiology. Already in 1914 he had made a few rather important discoveries in tanning, interesting his firm so much that it was decided that it might be profitable to send him to Leeds, England. Here he was to work with Professor Procter for two years with the idea of making him chief chemist and assistant production manager upon his return to Milwaukee.

He entered the University of Leeds as a post graduate in October, 1914, and in 1915 was given faculty standing with the title of honorary research assistant of the Procter International Research Laboratory. During this year Procter and Wilson worked out their theories of the gelatin-electrolyte equilibria.

Upon his return, in 1916, he became chief chemist at the Gallun tannery in Milwaukee and soon became inspired to build a real literature of leather chemistry, starting out with about one hundred and fifty papers and culminating with a monograph.

In 1920 he organized the Leather Division of the American Chemical Society and served as its chairman until 1927. He is a past chairman of the Milwaukee Section of the American Chemical Society and past president of the American Leather Chemists Association.

He left the Gallun tannery November 1, 1929, to go into business for himself and to conduct the affairs of International Security Management, of which he was president. He organized the firm of John Arthur Wilson, Inc., Consulting Tanners and Chemists, of which he is president.

This is a remarkable and enviable record for a man who is just past forty.

Scientific Accomplishments of the Medalist

Arthur W. Thomas

JOHN ARTHUR WILSON has published approximately one hundred and fifty papers in the journals of pure and applied chemistry, the first one appearing in 1913; and in all but a half-dozen of these he is the senior author. These contributions involve new theoretical treatments and new experimental data on a wide variety of subjects in the domain of pure and applied colloid chemistry, and more specifically the following categories:

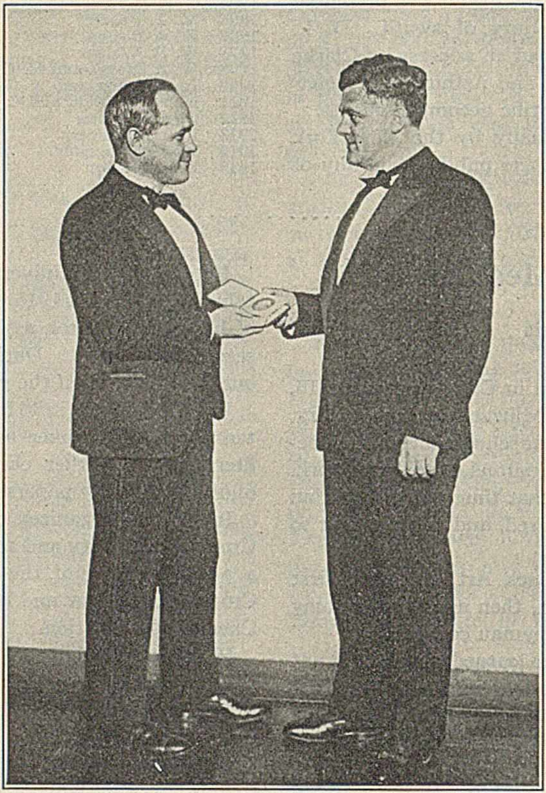
General. Protein swelling, phase boundary equilibria, electrical charge at certain interfaces, neutral salt effects, proteolytic enzyme action, emulsions, and bacteria.

Tanning. Unhairing of hides with alkalies, sulfides, and enzymes, bating with enzymes, hide pickling, chrome, vegetable, and other tannages, fat-liquoring of leather, dyeing and finishing of leather, the chemical and mechanical properties of leathers and analytical methods, particularly a rational method for the determination of vegetable tannin.

Sewage. Mechanism of activated sludge process and the dewatering of the sludge.

Added to this imposing list of journal articles there is his book on "The Chemistry of Leather Manufacture," No. 12 in the American Chemical Society Monograph Series, first published in 1923 as a single volume; In 1928 Volume I of a completely rewritten edition appeared, followed by Volume II in 1929.

From the point of view of the influence upon the broader aspects of chemistry, Doctor Wilson's outstanding papers were upon the swelling of protein jellies, a theory of colloids, and the adsorption formula. His contribution to the swelling of protein jellies, published in 1916, was in collaboration with the late Henry Richardson Procter, professor of leather chemistry at the University of Leeds. This paper accounted for the swelling phenomena of gelatin in the presence of acid and of neutral electrolytes in a quantitative manner. It was the first quantitative explanation of these phenomena and even the first use of the principle of the Donnan equilibrium made outside of Professor Donnan's laboratory.



John Arthur Wilson Receiving the Nichols Medal from J. G. Davidson

The contribution on the theory of colloids (1916) published independently by Doctor Wilson and the paper on "Colloidal Phenomena and the Adsorption Formula" published in collaboration with Mrs. Wilson in 1918, together with the first mentioned, started the line of reasoning which Jacques Loeb developed into his modern theory of the behavior of proteins.

In the field of leather chemistry, his contributions all show the fundamental discipline of the mathematical and quantitative scientific method of attack revealed in his early contributions to general chemical knowledge. In a methodical manner he elucidated and gave freely to the leather industry the reasons and methods for improvements for many complicated operations touching every phase of the tanning process already mentioned in this address. He made extensive additions to the literature of animal skin and its functions, showing the variations in different animals of different ages according to the location on the skin, feeding, and climatic conditions under which they lived. He named the thermostat layer of the skin and demonstrated the part it plays in keeping the body temperature constant, in colds, in making hair straight or curly, and sundry other effects as well as those bearing upon the properties of leather made from the skin. In this work he developed a highly refined technic for making fine sections and photomicrographs of skin.

In 1924 Doctor Wilson started the first comprehensive measurement of the properties of leather. He showed how the area change of leather with relative humidity could be reduced one-third by the proper selection of tanning material. He developed the technic and made the first measurements of the ventilating properties of leather, and showed how leather could be made to allow moisture to pass from the inside of a shoe 80 per cent as fast as from a bare foot and still have the shoe water-repellent from the outside. The relation of strength and stretch of leather to controllable factors was demonstrated by him, as well as new methods for measuring and controlling temper, resilience, porosity, and density of leather.

In the field of sewage disposal he applied himself to the problems involved in the development and operation of the activated-sludge sewage-disposal plant of the City of Milwaukee. The city employed Doctor Wilson as research director in this work from 1920 to 1930. In this capacity he brought into action the fundamental laws of colloid chemistry and the physical chemistry of the proteins with most gratifying results. When his services were enlisted in 1920, the first experimental operating unit of this disposal plant was faced with what appeared to be a hopeless problem. The sludge was a slimy, jelly-like mass, which could not be filtered and from which the removal of water could be accomplished only at prohibitive cost. Doctor Wilson showed that this slimy sludge could be dewatered by a simple chemical treatment followed by vacuum filtration and drying. The chemical treatment suggested by his store of fundamental chemistry just mentioned consisted in adding ferric chloride to reduce the pH of the sludge to its isoelectric point of 3.4. A quadruple reaction was shown to be involved: (1) an oxidation effect, (2) a tanning action on the protein matter, (3) a halogen effect increasing the capacity of the protein matter for iron, and (4) a pH effect reducing the sludge to the isoelectric condition. All four effects contribute to the reduction of the attraction of the solid matter for water.

In this work Doctor Wilson has, with the collaboration of willing assistants, discovered and published new information on many chemical phases of the problems involved in this huge plant, which now separates daily 100 million gallons of sewage into pure water and 100 tons of dry, granular fertilizer which sells at about twenty dollars per ton.

Following the publication of the first edition of his book, "The Chemistry of Leather Manufacture," there appeared in rapid succession translations into German, French, and Russian, a striking proof of the outstanding merit of this treatise on leather chemistry. Now that the second two-volume edition has appeared in English, editions in Italian, Spanish, Bulgarian, and Japanese are being contemplated. I believe that it may properly be said that Doctor Wilson's book has become the world's standard in its field. It is not a collection of recipes and factory methods, but is devoted entirely to a systematic discussion of the chemical fundamentals of the materials and operations involved in the leather-tanning process.

In recognition of his scientific attainments, Doctor Wilson has been invited many times to address various scientific bodies. The University of Chicago appointed him to give a series of lectures in 1925. Columbia University appointed him to lecture on his field in a series on contemporary chemistry in the summer of 1926. He was awarded the Charles Frederick Chandler Medal by Columbia University in 1928. Lehigh University awarded him the honorary degree of doctor of science in 1929, and now the William H. Nichols Medal is added to his trophies.

Surely his is a glorious record of achievement, all accomplished while carrying out the full-time duties of chief chemist in the tannery of the A. F. Gallun & Sons Company, in Milwaukee.

Leather, Sanitation, and Colloid Chemistry

John Arthur Wilson

757 North Broadway, Milwaukee, Wis.

The award this year calls for a lecture upon three subjects—leather, sanitation, and colloid chemistry. Adequate treatment of any one of them would require the production of an encyclopedic work. I may, therefore, be pardoned for offering a sort of medley of special phases of all three.

Practical *vs.* Theoretical Men

The manufacture of leather is an extremely complicated chemical process. Like many other great industries, it was developed by men with no chemical training whatsoever. With the entry of chemists into the leather industry, a sharp conflict arose between the so-called "practical" and "theoretical" minds. The practical man, although possessing no knowledge of chemistry, knew how to make a serviceable and salable piece of leather. The theoretical man, even though he had satisfied his college that he had a good working knowledge of the fundamental principles of chemistry, usually spoiled every lot of leather that he tried to improve. It is but natural, then, that the practical men developed a contempt for the theoretical men, regarding them as ignorant meddlers and their experiments as a waste of time and money.

Chemists would not have been tolerated in the industry at all were it not for the fact that the practical men occasionally got into difficulties which proved very costly and, even after these difficulties were overcome, there was no guarantee that they would not recur. Furthermore, the public taste changes with time, forcing tanners to change their methods. The manufacture of leather involves many extremely complex processes, all of which must be in perfect balance to produce a salable product. If one of these operations is changed in any way, the balance is upset and, unless compensating changes are made in the other operations, the leather may be ruined. The cut-and-try method was usually employed in making these compensating changes and, because of the seemingly infinite number of possible changes, it was a matter of good fortune for the tanner to succeed before the spoilage was so great as to ruin him. For this reason he was loath to throw away any possible chance of assistance, and so he kept his chemist in the hope that he might prove valuable in times of distress, even if only in a small way. Although the chemist might prove a "bull in a china shop" if allowed to meddle with the processes, he often had suggestions which, coupled with the tanner's own knowledge of leather manufacture, got the tanner out of his difficulties.

The university training of the chemist had much to do with this state of affairs. He was taught to study, first of all, only the simplest types of substances and chemical reactions and to proceed logically, step by step, to the more complicated reactions and not to accept the results of a study of the effect of change of one variable factor unless all other variable factors were kept constant or their variations controlled. Were it not for the time required to produce results, this method would seem so logical as to be unquestioned. A chemist might conceivably devote his entire life to a study of the energy relations of protons and electrons and of atom building without ever arriving at a complete understanding of even the simplest electrolytes. In every chemical reaction there are factors involved which are not completely understood, and yet this does not prevent making extremely valuable uses of a study of reactions in which many variable factors are unknown and uncontrolled. Generalizations, with exceptions, are developed and great strides have been made when the chemist can predict that this or that will probably happen under a given set of conditions, even though later tests occasionally prove his guess to be wrong. The generalization suggests the experiment to try, the results of which speak for themselves.

The practical man, experimenting by the cut-and-try method, has probably been of vastly greater benefit to mankind than the scientist, who insists upon a complete solution of the simplest problem before he dares to proceed to the next logical step in the final solution of a bigger problem. If the primary purpose of scientific study is to benefit mankind, then the scientific man cannot ignore the methods of the practical groper, with the probability that the most valuable man will be the one who makes the wisest use of both methods.

Picture a man thoroughly trained in orthodox chemistry entering the leather industry. His raw materials are animal hide, enzymes, vegetable extracts containing tannins and other materials, complex salts of heavy metals of unknown molecular structure, oil emulsions, dyestuffs, complex finishing materials, various kinds of electrolytes, and many other substances of unknown composition or structure. From this confusion of things he is to make a salable product whose properties have not been defined; nor is it easy for him to learn what properties are desired. Is it any wonder that his first attempts are failures and evoke the contempt of the practical man who was told that science would revolutionize the industry?

The Colloid Chemist Offers a Compromise

We can ignore the foolish chemist who dares to predict what will happen when a given change is made in some operation through his knowledge of pure chemistry; his chances of being right are so remote that failure is practically certain. We can ignore also the chemist whose training is insufficient to permit him to do more than follow a routine procedure of empirical analysis laid down by others before him. But let us consider a well-trained chemist of sound judgment. If he is completely imbued with the spirit of purely scientific research, he may decide that so many unknown, important variable factors are involved as to make real progress impossible and leave the industry after his first view of it. But, if he is bold enough to try, he will enter the industry in a spirit of humility as a freshman and spend his time learning the art of the practical tanner and becoming familiar with his difficulties and with the desired properties of the finished product. During his period of training and study of complex materials and their reactions, he will learn, possibly to his surprise, that valuable generalizations can be deduced even though the exact chemical compositions of the substances involved are unknown and many variable factors are uncontrolled. He will have combined the practical with the scientific method. Such men have been of enormous service to the leather industry and to all users of leather.

Men of this type are to be found in nearly all the major industries today. As they lean more towards the practical type of research, they are generally more successful from a standpoint of earnings and of immediate usefulness to the industry. As they lean more towards purely scientific research, they are of greater value to the development of science, but their tendency to follow up every finding suggesting an advance in pure science—called "chasing butterflies"—so greatly prolongs their experiments and the finding of facts of immediate practical value that they tire those who are supporting the research for profit and lose their jobs before they have tasted of large salaries.

It is not necessary to go into the industries to find men of this type and with varying tendencies towards the purely scientific or the practical. They are to be found in abundance in universities and endowed research laboratories working on animal and vegetable tissues, foods, enzymes, and other complex materials.

These men owe their success to the fact that they are bold enough to experiment with systems containing many unknown variable factors. Their method of attack is often very different from that of men working in pure chemistry. Many of their generalizations appear to contradict well-established laws of pure chemistry—only, of course, because of the influence of the unknown variable factors. Nevertheless, their method of research is distinctive and their findings are often so different from those of pure chemistry as to call for a different system of nomenclature. Their special branch of the science is known today as "colloid chemistry." It has been common practice to catalog under this heading much of our knowledge of chemical systems in which important variable factors are still unknown.

Colloidal Phenomena

There has been a suspicion among colloid chemists that a single variable factor may be responsible for a wide variety of apparent deviations from well-established chemical laws. At present many colloidal phenomena are attributed to a great increase in specific surface of one material in contact with another. For example, a sphere of gold weighing one gram shows no tendency to dissolve when placed in water; but when it is dispersed in water to particles having a total surface area millions of times as great, under certain conditions it tends to remain dispersed, as though it had acquired a solubility in water. If the attraction of water for each square centimeter of gold surface remains constant, then the total attraction of the water per gram of gold has been increased millions of times by the dispersion and the tendency for the gold to dissolve is increased accordingly. However, the mere increase in specific surface alone cannot account for the stability of a gold sol, because it has been found that the sol is not stable unless the particles possess an electrical charge of sufficient magnitude. Much light regarding the role played by the electrical charge in colloidal phenomena has been obtained by a study of insoluble protein matter in contact with aqueous solutions.

In the making of leather we have to deal with a hide fiber which is insoluble in the aqueous solutions employed, but which is capable of reacting chemically with substances actually in solution. It is our view that the fiber is built up of a three-dimensional network of atoms with interstices large enough to permit the passage of water and dissolved substances. Thus we have a system of two phases interlocked, both phases being continuous. When a fiber is placed in water, it swells, absorbing water. If acid is added very slowly, the fiber swells still further, absorbing more solution. When a certain concentration is reached a maximum swelling is observed, beyond which concentration the swelling decreases with any further addition of acid. This peculiar behavior has been called a colloidal phenomenon because its cause was not understood.

The same observation was made with sheets of gelatin, which lend themselves more readily to study than hide fibers. It was found possible to examine both the absorbed solution and the external solution. At equilibrium the concentration of acid was always less in the absorbed solution than in the external solution and the total amount of acid in both solutions was always less than that added. The acid not found in either solution was apparently removed from solution by the protein network.

Soluble-Insoluble Ionogens

The swelling was accounted for as follows: When hydrochloric acid was added to water containing a sheet of gelatin, it diffused into the water in the interstices of the gelatin network, where some of the hydrogen ions combined chemically with certain atoms in the network, leaving the corresponding chloride ions remaining in true solution in the interstices. This created what might be called a soluble-insoluble ionogen, one ion being in true solution and the other not in solution at all. The chloride ions, being in true solution, tend to diffuse out of the network into the external solution, but dragging the network with them through the solution. This pull upon the network in all directions results in an increase in volume, according to Hooke's law. Equilibrium is reached when the outward pull is just balanced by the cohesive forces of the gelatin.

Since the water, hydrogen ions, and chloride ions are capable of diffusing freely through the interstices of the gelatin network, the concentrations of hydrogen ions inside and outside of the gelatin must assume a state of equilibrium. The external solution will have equal concentrations of hydrogen ion and chloride ion at equilibrium, but the absorbed solution will contain more chloride ions than hydrogen ions because of the presence of chloride ions balanced only by the electrical charge on the insoluble network. This condition is governed by the principles of the Donnan equilibrium, permitting quantitative treatment of the distribution of ions between the absorbed and external solutions and of the electrical potential difference between the two solutions. The theory has been proved quantitatively for the gelatin-hydrochloric acid equilibrium and is now a part of the literature. We mention it merely as an example of a system in which hydrochloric acid is present in three phases—the insoluble network, the absorbed solution, and the external solution.

By analogy we reason that gold sols have three phases and that failure to recognize this in the past has been responsible for many of the apparent deviations from chemical laws observed in studies of these sols. When gold is dispersed in water, it maintains its apparent solubility only provided minute quantities of certain salts or alkalies are present and the gold particles acquire a negative electrical charge. The greater this charge, the greater the stability of the sol. Apparently anions from the solution have become part of the particles and are removed from true solution. The corresponding cations are still left in true solution. They form a connecting link between water and gold, now having a powerful attraction for each. The cations, being part of the true solution, cause an attraction between gold and solution amounting to a virtual solubility of the gold in the solution as long as the concentration of these cations is sufficiently great relative to the mass of the gold, which is influenced, of course, by the specific surface exposed. The kind of anion which becomes a part of the solid particle is present in the sol in three phases—the insoluble particle, the thin film of solution wetting the particle, which contains the cations balanced by the charge on the particle, and the solution beyond the range of motion of these cations. The stability of the sol appears to be determined, not by the absolute value of the electrical charge on the particle, but by the difference of potential between the two solution phases which may be varied by adding electrolyte to the system without altering the absolute value of the charge on the particle.

Soaps and many other substances fall under the category of soluble-insoluble substances. The fatty acids are insoluble in water, but acquire a solubility when they become part of a highly ionizable salt.

When the effect of greatly increased specific surface, the existence or formation of soluble-insoluble ionogens, and the separation of the system into three phases are recognized and measured, much of the mystery of the colloid chemistry of aqueous systems disappears. This proved particularly true of modern leather chemistry, which had its beginning in a study of the acid-protein equilibrium.

General Tannery Procedure

Although all tanners have their own special methods which differ greatly in detail, most of them follow a common general procedure. After the skins have been washed to remove most of the blood and dirt, they are soaked in cold water to leach out the soluble protein matter and salts and to allow the fibers to absorb water, reassuming their natural size and shape, lost during curing and partial drying. Adhering flesh is removed and the skins are soaked in saturated limewater containing a small amount of sodium sulfide in order to loosen the hair and epidermis, which are composed of epithelial tissue containing the protein keratin. Keratin is much more readily hydrolyzed by alkaline solutions than the protein collagen of the white fibers of connective tissue, which are finally made into leather, whereas in contact with acid solutions the collagen is hydrolyzed more rapidly than the keratin. The use of an alkaline solution thus permits the separation of hair and epidermis before the fibers have been seriously attacked. The addition of a small amount of sulfide has little or no effect upon the hydrolysis of collagen, but greatly accelerates the hydrolysis of keratin, apparently by splitting the cystine linkages at the double-sulfur bond.

When the hair and epidermis have become sufficiently loosened, they are scraped off on an unhairing machine. The grain surface is then scudded, or scraped, by hand or machine to work the dirt out of the surface fibers and hair follicles. The skins are then washed to remove any free lime and bated in a warm infusion of pancreatic enzymes to remove the partially decomposed keratin and sebum still present in the grain, which would otherwise become fixed by the tanning materials used later and spoil the appearance of the leather. The skins thus cleaned and freed from undesirable matters are ready to be tanned.

It will be sufficient to mention very briefly the two methods of tanning most widely used. The first, of ancient origin, is the vegetable tanning process. A tan liquor can easily be prepared in the average kitchen by putting a piece of the bark of a tree through a coffee mill and then through a percolator, as in making coffee. The resulting liquor is capable of tanning. If a piece of bated skin is suspended in it, it will become colored. If, when the color has completely penetrated the skin, it is taken out and dried, it will be found to have become a piece of leather, no longer subject to the tendency to decompose, characteristic of raw skin.

The second method, of recent origin, is the chrome tanning process. An ideal chrome tanning liquor can be prepared by dissolving sodium dichromate in water and adding sulfur dioxide until all the dichromate has been reduced to chromic salt. A piece of bated skin suspended in such a liquor assumes a greenish blue color. When this color has completely penetrated the skin, a small amount of sodium bicarbonate is added to neutralize some of the sulfuric acid present. After a few hours the skin becomes quite resistant to the action of boiling water, whereas raw skin is quickly dissolved, as gelatin, when placed in boiling water. The skin has been converted into leather by the action of the basic chromic sulfate.

In the better tanneries these processes are rigidly controlled as to concentrations of tanning and non-tanning materials, proportion of skin to liquor, temperature, pH value, mechanical agitation, rate of adding neutralizing agent, time of contact, etc. Much of a tanner's success depends upon the delicacy of this control, for slight variations may greatly alter the properties of the finished leather.

The operations following tanning differ according to the kind of leather being made. Sole leather is treated with oil, salts, and sugar, dried, and rolled with heavy pressure to make it firm. Upper leather is colored to the desired shade with aniline dyes, fat-liquored with oil emulsions to make it soft, and finished with waxes, casein, or shellac to give it the desired luster and water-repellence. Many mechanical operations are involved; a skin may be put through dozens of separate operations to give it the properties desired in a given kind of leather.

Principles of Tanning

In chrome tanning, the pH range of the liquors is usually from 2.0 to 3.5; in vegetable tanning from 3.5 to 5.0. In both tannages the active agent is distributed between three phases—the insoluble network making up the fiber, the solution absorbed by the fiber, and the external solution. In practice equilibrium is never reached; the process is stopped when the desired properties are obtained, which in chrome tanning is about 24 hours and in vegetable tanning from 1 to 100 days, depending upon the thickness of the skin and kind of leather being made. Studies made of skin in contact with the same tan liquor for more than a year showed changes still in progress.

This failure to reach equilibrium in reasonable time, the complex anatomical structure of the skin, the difficulty of making a quantitative separation of the external solution held between the fibers from the solution absorbed by the protein jelly of the fibers, and the extreme complexity of the tanning materials themselves make research in tanning difficult to an extreme degree. In spite of these difficulties, however, it has been found possible to do much quantitative work that has proved of great practical value to the tanner and to the ultimate user of leather. The start was made by the quantitative solution of the acid-gelatin equilibrium. Studies were made of colloidal dispersions. Solution of the simpler problems made it possible to do reasoning by analogy, even though a quantitative separation of the phases in a skin could not be made. The accumulation of data from tens of thousands of experiments has made it possible to develop theories of tanning that are comparable in their soundness with many theories in the field of pure chemistry, as, for example, the molecular structure of heavy-metal salts in solution.

Collagen is an ampholyte with an isoelectric point at pH 5. In vegetable tanning it acts as a weak base. The tannins are phenolic substances of weakly acid nature. Many studies of the combination of phenolic substances with simple oxygen and nitrogen bases suggest that the combination of collagen and tannin is quite analogous. The compound formed apparently has an extremely small hydrolysis constant, which accounts for some of the properties of vegetable-tanned leather.

In studying the molecular mechanism of chrome tanning, no progress was made compatible with all the facts known in chrome tanning in practice until Werner's theory of complex salt formation was adopted. Gustavson showed that it is not simply a chromium atom that combines with the protein, becoming part of the insoluble network, but a nucleus in which a central chromium atom is surrounded by an outer shell of six coördinatively bound molecules or equivalents of ions. Depending upon the nature of the coördinatively bound ions, these nuclei may carry either a positive or negative charge and both positively and negatively charged nuclei may be present in the same solution, as shown by simultaneous cathodic and anodic migration of chromium when a chrome liquor is placed in an electrical field. In chrome tanning in practice, three types of combination appear to occur simultaneously, with the first greatly predominating: (1) The acidic groups of the collagen combine with the positively charged chromium nuclei; (2) the basic groups of the collagen combine with the negatively charged chromium nuclei; (3) certain groups of the protein molecule penetrate into the chromium nuclei, becoming coördinatively bound and replacing other groups which pass into solution. The work of Thomas indicates that tanning with salts of iron and aluminum is of similar nature.

Definitions of Leather and Tanning

Many substances are capable of tanning animal skin, including the natural tannins, salts of heavy metals, fish oils, formaldehyde, quinone, silicic acid, and many sulfonic substances. Many kinds of chemical reactions are involved and leathers of very different character are produced. It is, however, possible to formulate simple definitions covering all cases of tanning and all kinds of leather. When proteins are brought into contact with water, they gradually become hydrolyzed. The rate of hydrolysis is greatly increased by the presence of bacteria, enzymes, acids, alkalies, and certain salts. When a protein undergoes chemical change such that its resistance to hydrolysis under a variety of conditions has been increased, it is considered to have been tanned and the agent bringing about the chemical change is classed as a tanning material. Thus, leather may be defined as animal skin whose resistance to hydrolysis has been increased by combination or interaction with any material whatsoever. Any material capable of bringing about this change is a tanning material and the reaction itself is called tanning.

There are different degrees of tanning and of tanning power possessed by different materials. Fish oils increase the resistance of animal skin to hydrolysis, as in the manufacture of chamois leather, but the product becomes hydrolyzed rapidly when placed in water at a temperature above 60° C. Quinone is capable of rendering a skin immune to the action of boiling water. If chrome tanning is stopped when the leather will withstand water at a temperature of 80° C. but no higher, the leather will serve most of the ordinary purposes perfectly. By continuing the tanning operation until more chromium has combined with the collagen, the resistance to hydrolysis is steadily increased until a leather is obtained capable of withstanding steam under pressure.

Properties of Leather

The value of any product lies in its physical and chemical properties. Industries that have made intensive studies of the properties and possible uses of their products have usually prospered greatly. The leather industry has been very weak in this respect, and its present plight may be attributed almost entirely to its failure to make intensive studies of the properties and possible uses of leather. Many tanners cannot even name, let alone give quantitative values for, many of the important properties of the leathers which they make and try to sell. After eleven years of severe depression and the failure of approximately one-third of the tanneries in the country, the industry is gradually beginning to appreciate this unpleasant truth.

In most industries supply and demand are related; if the demand falls off, sooner or later less will be produced. But not so with the leather industry. The supply is determined, not by the demand for leather, but by the demand for meat. Animals are not slaughtered for their hides; the hide is merely a by-product. If there were no demand for leather, the same number of animals would be slaughtered and the same number of hides made available. During the past decade the demand for meat has been relatively greater than the demand for leather and the industry has become very sick. Many tanners have cried out for a curtailment of leather production, apparently being unable to understand that no one is going to throw away good hides that can be made into leather and that every hide taken off will be tanned regardless of the plight of the leather industry. Their only salvation is to find more extended and new uses for leather so that the public will again demand relatively more leather than meat.

The fault does not lie entirely with the tanner. I know of cases where a clever tanner has improved an important property of his leather at the expense of some relatively unimportant property from the standpoint of the ultimate consumer, only to find that he could not sell the improved leather. For example, one tanner made a leather for shoe uppers that was much more serviceable to the wearer of the shoes than the leather that a certain shoe manufacturer was using. It so happened that this leather could not be given quite so high a gloss on the shoes when they left the factory; in every other respect the leather was superior. Even this was not more than a temporary defect, since the shoes could be given as high a gloss as any after the first polishing in actual wear. The shoe manufacturer was apprised of the advantages of the leather and so made up a large lot, which he distributed to many stores. The shoes did not sell nearly so well as those from the poorer leather with the higher initial gloss. The shoe manufacturer claimed that he could not hope to educate the public and that he must order only such leather as appealed most to the average public eye, even though he knew it would not prove so satisfactory in actual service. The tanner had to give up his improvement in order to sell his leather. The public was hardly to blame, either, for its inability to see what was under the initial gloss.

Weather Prophets

Many people have the ability to forecast changes in the weather by the changing degree of pain in their corns, not realizing that the corns are merely responding to a change in size of the shoe. Leather takes up and gives off water with changing relative humidity of the atmosphere, a property common to most organic tissues. With change in water content the dimensions change appreciably. If ordinary chrome upper leather is kept at zero relative humidity, it will lose most of its water. If, now, a piece is cut exactly 1 square foot in area and placed in an atmosphere of 100 per cent relative humidity, the area of the piece will increase to 1.18 square feet. In other words, it will increase 18 per cent in area. With decreasing relative humidity it will shrink again to its original area. When the same test is made with vegetable-tanned leather, the area change is found to be only 6 per cent, or one-third of that found in chrome leather. In actual wearing tests, where chrome leather is worn on one foot and vegetable-tanned leather on the other, this effect is very striking. Only the foot housed in the chrome shoe is capable of forecasting weather changes.

Apparently the basic groups of the protein take up water from the atmosphere more readily than the acidic groups. In chrome leather most of the basic groups are still free; in vegetable-tanned leather the tannin occupies the position that the water would otherwise take, and so the power of the leather to take up water and change in size is correspondingly diminished. The public can have whatever it demands, but it will probably be a long time before it is educated to the point of knowing what is possible to get in the way of foot comfort. Meanwhile the weather prognosticators will be numerous.

Ventilating Power

Few people appreciate that a good shoe-upper leather will permit the water of perspiration to evaporate from 60 to 80 per cent as fast as if the foot were bare, even though the leather is water-repellent. The degree of hydration of leather is a function of the relative humidity of the atmosphere. Inside the shoe, where the perspiration tends to maintain a relative humidity of 100 per cent, the leather continues to take up water of hydration so long as the entire thickness of the leather is not in equilibrium with a saturated atmosphere. On the outside the relative humidity is normally much less than 100 per cent, and so the leather tends to give up its water of hydration as long as it has more than it would have in contact with air of the lower relative humidity. In this way we get a continuous passage of water from the inside to the outside, hydration taking place continuously at the inside surface and dehydration at the outer surface. Measurements made on thousands of samples of leather show that the removal of water from the foot goes on at about 80 per cent of the rate that it would from the bare foot so long as the leather has not been coated with finishing materials.

If we apply to the grain surface of the leather a mixture of carnauba wax, casein hardened with formaldehyde, and shellac, we find that the passage of the water of hydration from the inside is retarded in proportion to the amount of finishing material used. When the grain surface is finished with such a mixture, it becomes water-repellent. When rain falls upon it, the water does not readily wet it, but draws up into tiny globules through the action of surface tension and rolls off from the leather. Unless the leather has become thoroughly wet, this water-repellence appears to be more or less independent of the thickness of the film of finishing material. In fact, it has been found possible to apply such a tiny quantity, still getting the desired gloss and water-repellence, that the decrease in passage of water from the inside out is very small. In this way we obtain a leather which allows the water of perspiration to pass freely from the inside of the shoe to the outside, but repels water striking the outside in liquid form. It should be pointed out, however, that water-repellence does not constitute true waterproofness. If the leather becomes saturated with water on the grain side, the water-repellence is lost and water will then pass from the outside to the inside. Nevertheless, the property described is an extremely valuable one and its proper control in leather manufacture has much to do with the comfort of a shoe.

Wild Grain

We have material enough to fill a large volume on the properties of leather, but can only briefly mention two or three of these properties. Since we described two properties dealing primarily with foot comfort, we might mention one dealing primarily with the appearance of upper leather. A variable number of skins out of each lot show an undesirable network pattern on the grain surface, particularly in the flanks of the skin. This is unsightly and very greatly lowers the selling value of the skin. Close examination shows that the pattern consists of a depression in the skin in the form of a net, but to a depth of less than 0.01 mm., although the pattern itself appears very distinctly.

The cause remained a mystery until we made very thorough microscopic examinations of skins showing it and found it to be the vertical projection of the tiny blood vessels which supply the sebaceous glands. These blood vessels carry a large burden in cold weather and very little in warm weather, which explains why the so-called wild grain is so much more prevalent on winter skins than on summer skins. In the acid or alkaline swelling of a skin, it was found that these blood vessels do not swell so much as the collagen fibers and so any undue swelling caused a tension and strain following the pattern of the network, leaving a permanent depression on the surface. By avoiding excessive swelling it was found possible to reduce the percentage of skins showing wild grain.

Another factor influencing this undesirable pattern is the action of the enzymes in bating. The material removed by bating is more abundant in the spaces inside of the blood-vessel network than it is immediately over them. If the skins are not bated at all, they show very much wild grain. As the bating process progresses, this material is removed and the pattern becomes less pronounced. But when all the material between the network has been removed, the enzymes begin to have a greater effect on the blood vessels themselves and the regions immediately surrounding them and the wild grain becomes more and more pronounced. By carefully controlling the bating process it has been possible to reduce this defect to a small fraction of what it would be otherwise.

Sewage Disposal

Through years of intensive research, involving many applications of colloid chemistry, the City of Milwaukee has built and is now operating what we believe to be the most efficient sewage-disposal plant in the world. It would be going too far afield to give the development of the activated sludge process here, but a brief description of the process as used at Milwaukee may be in order.

When the raw sewage enters the plant, it flows first through coarse bar screens to remove materials that might clog the pumps; then through grit chambers, where the velocity of flow is reduced to permit grit and other heavy materials to settle; and then through fine screens to remove all but the finely divided matter, which constitutes the bulk of the pollution. The screened sewage is mixed with activated sludge returned from the system, the mixture being called mixed liquor. The mixed liquor is allowed to flow through aeration tanks, the bottoms of which are fitted with porous plates through which air is forced and allowed to bubble up through the liquor. It takes about six hours for the mixed liquor to pass through the aeration tanks, during which time a marked change takes place. If a sample is taken in a tall glass cylinder before it enters the aeration tanks and is allowed to stand, the sludge settles but the supernatant liquor remains turbid and foul. If a similar sample is taken at the end of the aeration tanks and is allowed to stand, the sludge settles out quickly and leaves a perfectly clear and sweet supernatant water, from 95 to 99 per cent of the bacteria and polluting materials having been removed.

From the aeration tanks the mixed liquor flows continuously into settling tanks, where the sludge settles and is drawn off continuously from the bottom and the clear, supernatant water flows off continuously into the lake. Part of the sludge drawn off is returned to mix with the incoming raw sewage and part of it is run to the dewatering plant, where it is treated chemically, filtered, dried, and finally sold as the very valuable fertilizer milorganite.

Dewatering Activated Sludge

The first application of colloid chemistry was in the solution of the problem of dewatering the waste sludge. It had been planned to filter-press it, but the sludge refused to be filtered. After a small amount of water was removed, the filter cloths became clogged and would not pass any more water. It was apparent that the process could not be used at Milwaukee unless some practical method for filtering the sludge could be devised, since none was known. Furthermore, no other process of sewage disposal suitable for Milwaukee's conditions was known. One of the commissioners, Victor L. Kadish, being a chemist and knowing of my work in colloid chemistry, asked to have the problem turned over to me, which was done.

The problem resolved itself into decreasing to a minimum the attraction of the sludge for water. It was soon apparent that the sludge was a system containing what we referred to earlier as soluble-insoluble ionogens and that our first step was to reduce it to the isoelectric condition. To our great surprise, we found that the sludge had a constant isoelectric point at pH 3.4 in spite of apparent variations in composition of the raw sewage. The pH value of the sludge coming from the settling tanks was found to be constant at 7.4, identical with that of the blood of a healthy animal. By adding sulfuric acid to bring the pH value down to 3.4, the rate of filtration was increased fivefold, but this was not sufficient to make the process practical.

We knew that a protein at its isoelectric point still has a great attraction for water, but that tanning greatly lessens this attraction; and so various tanning agents were tried, including salts of chromium, aluminum, iron, and other heavy metals, as well as quinone and other organic materials. The material finally adopted as best from the standpoint of efficiency per dollar of cost was ferric chloride, which is added in such quantity as to bring the sludge to its isoelectric point. When this is done, the rate of filtration is increased about fifty fold and the process is made practical. A fourfold action appears to be involved. The ferric chloride exerts a beneficial oxidizing action; it acts as a tanning agent; the chloride ion acts upon the sludge, increasing its capacity to take up iron; and the ferric chloride hydrolyzes, furnishing hydrochloric acid to reduce the sludge to its isoelectric point. Without a solution of the problem of filtering the sludge, the plant could not have been operated.

Principle of Purification

The full story of the application of colloid chemistry to the activated-sludge process will have to be told some other time, but the most recent discovery in the entire research is so fundamental as to warrant special mention at this time. The work was done in collaboration with Robert Cramer, then chief engineer of the Milwaukee Sewerage Commission, and Hilmeyer Cohen, the research chemist. Sanitary engineers and chemists generally have felt that the activated-sludge process was a biological one, even though proof was lacking. I consistently objected to such claims without proof and preferred to consider only the chemical reactions involved until more definite proof was offered. Doctor Cohen's work has furnished the proof.

If sterilized sewage is aerated, no sludge is formed. If bacteria isolated from sewage are added and the aeration is continued, no sludge is formed. But if any one of a number of different types of protozoa is added and aeration is continued, sludge forms and the supernatant water is found to be clear and pure when the sludge is allowed to settle. It was shown also that yeasts are incapable of sludge formation and that algae are not necessary to sludge formation. Purification is effected primarily by the action of protozoa.

Another finding of importance is that sludge formation and purification will take place without aeration if a small amount of sodium chlorate is added and the sewage is allowed to have surface contact with the atmosphere, provided that protozoa are present. Apparently the bacteria utilize the bound oxygen of the sodium chlorate, leaving the dissolved oxygen for the protozoa, which then multiply and destroy the bacteria. It has been known for many years that protozoa are bacteria eaters, but this is the first time, so far as I know, that it has been shown that protozoa are responsible for the purification by the activated-sludge process.

These findings were confirmed by microscopic observation. When samples of mixed liquor were placed under the microscope, the protozoa could be seen feeding on the bacteria and other suspended materials present. The types most abundant were the vorticella, the paramecium, a smaller organism of similar shape, and an unidentified type shaped like a bottle. All seemed to be actively engaged in the purification.

It seems possible that this work may lead to greatly increased capacities for activated-sludge plants. In the testing station units I found that purification was completed in half the time if double the amount of activated sludge was mixed with the sewage; in one-third the time if the amount of sludge returned was trebled. There is a limit to the amount of sludge that can be returned to the system practically, but this later work suggests that the increased rate of purification was due to the introduction of greater numbers of protozoa. By operating culture tanks for protozoa to be fed to the raw sewage, it may be found possible to effect enormous savings in the building and operation of activated-sludge plants.

Gas Production Restricted in Turner Valley, Canada

Gas production in Turner Valley has been restricted to 40 per cent of its flow by the Government of Alberta, as a result of a recent conference of oil and gas operators with government representatives, according to the Department of Commerce. Gas waste has been steadily increasing during the past five years, and on March 11 was reported as at least 517,000,000 cubic feet a day. In January, 1930, the Dominion Government, following research by a special commission, stated that for each barrel of naphtha recovered there was a waste of 50,000 cubic feet of gas and 7 gallons of volatile products. No action was taken by the Dominion, but the problem of waste gas becomes a provincial one with the return of natural resources to the province last October.

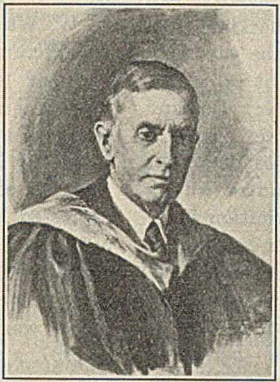
The restriction of production will take place under a provincial law passed in 1926 under the impression that the natural resources would be transferred to the province at that time. The final transfer occurred four years later, but the act is operative. It empowers the government to compel restriction by dividing the field into different areas, and causing each to stop operations for a day or more each week. The Alberta Government, in coöperation with the operators, expects to test the wells to determine to what extent conservation can be effected.

Turner Valley field produced on the average 350,000,000 cubic feet of gas daily during 1930. Of the yearly production 6,966,778,000 feet were sold to the Canadian Western Natural Gas, Light, Heat and Power Company, and distributed by it to 23,083 consumers in Calgary, Lethbridge, and intervening towns. Domestic consumers took 4,365,906,000 cubic feet of the total; the average price received by the company was $0.299 a thousand cubic feet.

An additional 1,250,000,000 cubic feet was transported to the Imperial Oil Refinery for use as fuel. Medicine Hat, Redcliff, Edmonton, Wainwright, and a number of smaller towns continued to be supplied with natural gas; they bought approximately 5,000,000,000 feet during 1930. Production and gasoline consumption reached new high points in Alberta in 1930, and the province was forced to ship surplus gasoline to Saskatchewan.

AMERICAN CONTEMPORARIES

Arthur Amos Noyes



From a painting by S. Seymour Thomas

Arthur Amos Noyes

> TILL a voice, as bad as Conscience, rang interminable changes
> On one everlasting Whisper day and night repeated—So:
> "Something hidden. Go and find it. Go and look behind the Ranges—
> "Something lost behind the Ranges. Lost and waiting for you. Go!"

A voice, low and vibrant, rhythmically intoned Kipling's well-known lines. The class in chemical principles, welcoming this change from the customary problems, listened with rapt attention.

> And the faith that moveth mountains didn't seem to help my labours
> As I faced the sheer main-ranges, whipping up and leading down.

This inspiriting poem, "The Explorer," was read to the class that day to symbolize the urge, the struggle, the reward of Research. Upon the listening students it created a deep impression. To others of us who knew, rather more intimately, the ideals, character, and life of the reader, these stanzas were profoundly moving. To us Kipling's unforgettable lines were the epitome of the career of Arthur A. Noyes himself.

> Have I named one single river? Have I claimed one single acre?
> Have I kept one single nugget—(barring samples)? No, not I.
> Because my price was paid me ten times over by my Maker.
> But you wouldn't understand it. You go up and occupy.

* * * * * *

Among the venturesome pioneers who settled, in the year 1635, the little town of Newbury on the Massachusetts shore were two brothers of the Noyes family name. The harbor site at the mouth of the Merrimac River was later known as Newburyport. It was here some two hundred and thirty years later that Amos Noyes married Anna Page Andrews of Salem. From these two sturdy ancestral lines Arthur Noyes has inherited his New England common sense, ingenuity, tenacity of purpose, fairness, and courage.

The father was an able lawyer with a local reputation as an absent-minded scholar and philosopher. Not too absent-minded, however, to have evinced an interest in the education of his son, whom he himself instructed in Latin, chess, swimming, rowing, and sailing, accomplishments in which Arthur Noyes today takes a just pride. The mother was by nature sociable and hospitable, and keenly interested in beauty and the arts. Being very much younger than her husband, she became the close companion of Arthur, her eldest son. After the age of eight, the boy went to public schools, carried morning papers, built office fires to earn money, took a healthy interest in railroads, conductors, cabooses, engineers, and birds' eggs. But even in these early activities his efforts were not haphazard. "A voice as bad as Conscience" whispered that behind railroads there was a System, behind birds' eggs, a Science. He sought and obtained an official license from the Boston Museum of Natural History. He formed a debating society, which he says was of the greatest value to him, questions of a political and social nature being the subjects of discussion.

His first interest in science was developed by the study of physical geography and physics, but it remained for Oliver Merrill, of the Newburyport High School, to inspire the youth with a great interest in chemistry.

Samuel Mulliken, a boyhood friend, gives me certain reliable information on this phase. The dining room of the Noyes homestead, he says, was large, lined with books, and used by Amos Noyes as a study. It seemed to the youthful chemists, Sam and Arthur, an ideal place to carry out certain important experiments. Using Steele's Fourteen Weeks of Chemistry as a guide, they set up their apparatus on the table, for the purpose of preparing phosphoretted hydrogen. They brought alcoholic potash to boiling and added yellow phosphorus, when—it happens to the best of chemists—the flask broke with dire results to rug, table, and law books. These, in the gathering twilight, developed an entrancing phosphorescence, viewed by the chagrined investigators with profound alarm. That night, I am told, fearing spontaneous combustion, the youthful Arthur slipped downstairs for a weary, sleepless vigil.

The immediate result of the accident, however, was not a conflagration, but an edict—parental—which banished all future activities to the attic and woodshed of the Noyes and Mulliken homes, respectively. In these newly founded laboratories the boys worked through all the experiments in Eliot and Storer's texts on chemistry and on qualitative analysis.

Upon graduating from the high school, Noyes, desirous of entering M. I. T., but finding himself with insufficient funds, decided to attempt the freshman work at home. This he accomplished, conscientiously and successfully, mastering alone all the subjects of the first year except drawing. Not only did he enter the sophomore class, with the aid of the Wheelwright scholarship established for Newburyport students, but, characteristically, he entered it with high standing.

According to his own modest account, Noyes was not a brilliant student at Technology, and never became skilful in analytical manipulation, though he "wasted" much time over it. During his senior year, a great interest in organic chemistry having been aroused by the lectures of L. N. Norton, he started research on the action of heat on ethylene. After graduating in 1886 with the S.B. degree, he continued this organic chemical research to receive in the following year the M.S. degree in chemistry. At this time he was appointed assistant in analytical chemistry, and was given full charge of a class of about forty in qualitative analysis. The close friendship which he formed with two promising students, George E. Hale and Harry M. Goodwin, is perhaps to him the most important event of this strenuous first year of teaching.

The next year Noyes went to Leipzig and started organic chemical research with Wislicenus. Later, inspired by Ostwald, he made the far-reaching decision to concentrate his activities in the field of physical chemistry. During the progress of this new research he became intimately associated with Ostwald, Nernst, LeBlanc, and Beckmann.

On receiving the Ph.D. degree in 1890, he returned to M. I. T., and for a decade was actively engaged in teaching analytical, organic, and physical chemistry. During this period he prepared and published the first edition of his well-known work on qualitative analysis, and carried out with his students many researches relating to the ionic theory of electrolytes. He also initiated an extensive investigation which, after many years, led to the publication (with W. C. Bray) of the scheme of qualitative analysis for the rare elements. Noyes thereby established an enviable reputation for himself, not only in this country, but also abroad.

My first personal introduction to Noyes was in the year 1898. He and W. R. Whitney, both my teachers at Technology, had been on a bicycle trip, and by chance, after checking their "wheels" (permissible in those unhurried days of the gay nineties), boarded my train for Boston. Being brought up in the South, I was intimidated by the smoke screen of New England reserve which Noyes threw out, but on closer contact I learned to realize what genuine friendliness this traditional demeanor cloaked. His favorite method of becoming acquainted with a student, I soon discovered, was to proffer an invitation for a tramp or a bicycle trip to the open country, a minor exploration which usually developed into a sort of traveling research conference. Such sociable jaunts with his most promising students often synchronized with periods when Noyes' own mind was occupied with some particular problem or new idea. He would then think aloud, so to speak, and then solicit advice or criticism. Frequently these "thoughts" would later appear more definitely formulated in print, or would lead to some new and important line of investigation.

Recently C. G. Abbot, in an address to Technology students, paid a graceful tribute to Noyes and to his practice of encouraging the honors student. He told of a time in his own career when both engineering and science had lured him with the odds in favor of engineering. Noyes, who discerned the possibilities of young Abbot as a scientist (although modesty prevented the speaker from making this point), invited him to dine at an unrecalled Boston restaurant, and was quoted as follows: "Mr. Abbot, if you are interested in molecules you ought to study physics, not engineering."

The minutes of similar meetings between Noyes and Whitney are not recorded, but it is a matter of common knowledge that these two scientists developed (1896–98) and put in operation at Jamestown, N. Y., a profitable process for the recovery of alcohol and ether vapors lost hitherto in the manufacture of photographic films. Likewise, that soon thereafter Noyes established the first pure-science research laboratory at M. I. T., and Whitney was called, by the General Electric Company, to lay the foundations of the great industrial research laboratory at Schenectady. Noyes not only established in 1903 this Research Laboratory of Physical Chemistry, but for seventeen years he personally contributed half the expense of its current maintenance.

During the first years of his directorship, Noyes maintained the same intimacy with the laboratory group which he had previously maintained with his individual research students. This intercourse was considerably furthered by the purchase of a sizable, seaworthy yawl, immediately rechristened "The Explorer." During the summer selected groups from the laboratory were invited to explore the myriad bays and inlets of the Maine coast from Portland to Eastport. That we once sailed into Bar Harbor flying the signal of distress (unwittingly hoisted by E. W. Washburn) was one of many similar incidents which furnished abundant material for good-natured chaff at our winter reunions.

It was on these cruises that we became acquainted with Noyes' real personality, which he so effectively hides from the outside world. We learned of his almost passionate fondness for poetry which he would recite from memory by the hour with intonation and diction never to be forgotten. We learned also that the day's work with him habitually started at four in the morning and ended at eight in the evening; and we commenced to comprehend that infinite capacity for taking pains, which is, perhaps, the keynote of his success. But more than all we began to catch the spirit of this gentle, retiring man, albeit a born leader, and, in our own various ways, to profit by it.

That this intangible spirit of Noyes permeated the whole laboratory is evidenced by the extraordinarily large number of men—latterly leaders of science in America—who came in contact with him at an early period of their own development. By way of illustration I might name W. R. Whitney, W. D. Coolidge, H. M. Goodwin, G. N. Lewis, W. C. Bray, C. S. Hudson, Yogoro Kato, C. A. Kraus, K. G. Falk, R. C. Tolman, W. D. Harkins, E. W. Washburn, R. B. Sosman, John Johnston, F. G. Keyes, and there are many others of this and later periods of his life.

About 1904–5 Technology circles were stirred by the proposal of a merger with Harvard. Many viewed such a step with alarm as a definite trend away from the conception of the institute by its founder, that great educator Wm. B. Rogers. At meetings of the faculty Noyes actively opposed the merger, and expressed his own views on education more fully in an article published in the *Technology Review* (1905), entitled "The Ideals of the Institute."

It was consequently no great surprise to his friends when Noyes was invited to become acting president of Technology in 1907, a very critical time in its history. The acceptance of this responsibility and honor entailed to one of his temperament and mode of life serious sacrifice and real hardship. Such a position necessitated constant contact with an outside world which he had hitherto purposely shunned. But he gladly accepted this important duty until two years later Richard C. MacLaurin, a man of like ideals, was chosen as his successor.

When Noyes again took up the directorship of the research laboratory, pressure of administrative work prevented in some degree the former close intimacy with his staff. Vacation periods, however, were frequently spent in travel with some honors student or associate, but always with some definite purpose. In this way he found time to write up with me for publication the course in chemical principles which had been evolved over a long period of years at Technology.

When the "voice as bad as Conscience" again called, it came, not as a whisper, but as a summons, and literally from a "land behind the Ranges"—California. In building up the staff of the great Mt. Wilson Observatory, George E. Hale had foreseen the need of a great educational institution in this new and rapidly developing section of the country. He had with characteristic acumen and enthusiasm set about the transformation of the already flourishing Throop College in Pasadena. Hale's policy has always been first to select the best man available for a position, and then to refuse to take no as an answer. Moreover, he has many subtle ways of accomplishing his ends, and doubtless would have succeeded (even without the coöperation of CLIMATE) in securing first Noyes, then Millikan, and those who have followed to help build up the now well-known California Institute of Technology.

For a while Noyes divided his activities between M. I. T. and C. I. T., but at the end of the war, after his obligations to the Nitrate Division of the National Research Council were fulfilled, he made what must have been a painful decision to sever connection permanently with his alma mater and to accept the directorship of the Gates Chemical Laboratory in Pasadena. He saw in this new institute a great opportunity to put into effect some of his cherished ideals of education.

Here he has not only succeeded in building up a strong graduate department, but has exerted considerable influence in determining the general educational policies. He has made in this congenial environment the opportunity to continue on a large scale his earlier personal practice of giving the honors student preferential treatment. At C. I. T. students of the junior year who have qualified in the honors group compete among themselves for travel prize scholarships, at least two awards being made each year. The winners, selected on a basis of leadership as well as scholastic standing, are granted leave of absence at the beginning of the spring term and provided with funds for travel in Europe. On their return in the fall they publicly give an account of their experiences.

If Noyes feels any pangs of homesickness on this alien soil, he represses them successfully. In Pasadena he will, beaming proudly, exhibit his tropical substitutes for apple trees and zinnias. Furthermore, he will extol their excellencies with all the gusto of a native son. It is, however, significant that he never seems so happy as when at Corona del Mar—summer home and winter retreat for creative thinking. Here, overlooking the lovely, sunny harbor of Balboa filled with pleasure craft (and rum-runners?), he has purchased a veritable granite castle. Immediately adjoining it is the newly established Kerckhoff Marine Laboratory of C. I. T., in which, by special permission of the Department of Biology, he has fitted up an analytical laboratory for honors students in chemistry to carry out special research problems.

Old Newburyport to new Balboa. Atlantic to Pacific Ocean. Attic to Marine Laboratory. Only Sam Mulliken is needed to complete the cycle.

MILES S. SHERRILL

NOTES AND CORRESPONDENCE

Our Engineer President

The editor of our esteemed contemporary, *Science*, saw fit to admit to the pages of the issue for January 16, 1931, an anonymous criticism of the President of the United States and his relation to science under the heading, "An Engineer in Authority."

We consider it unfortunate that, if an anonymous communication from some disgruntled soul who apparently failed to obtain some coveted appointment should have been published at all, the same issue might not have carried a few statements to enable those who may read to form their own conclusions.

Unfortunately, criticism always travels farther and faster than commendatory statements, and whatever we or any others, even *Science* itself, may now publish, it is quite unlikely that it will receive the same attention as the sharp criticism to which we refer. This has already been reprinted in other widely read periodicals. What was said, if it deserved the light of day, could easily have waited until some one could have presented a few facts.

The man who accomplishes most for science is not necessarily he who works with microscope, spectroscope, test tube, geologist's hammer, or statistician's curve. Many executives are, in effect, scene shifters and stage managers, who contribute most to the advance of science through their ability to maintain conditions under which others shall be fitted for their tasks, can do their best work, and accomplish most. Presidential appointments, often criticized by individuals, are made with peculiar requirements of a particular task in mind, and those not in possession of all the facts are not in a position to criticize the choice.

It seems unnecessary to set forth in detail here the early work of Herbert Hoover. The anonymous writer does not question his record as an engineer prior to his entrance into the Department of Commerce, but of his attitude since that time he says:

> It is, however, said that Mr. Hoover, as a member of the cabinets of Mr. Harding and Mr. Coolidge, did not support the scientific work under his charge, and there seems to be no evidence since he has climbed to the Presidency that he realizes the dependence of our civilization on scientific research and its applications.

As Secretary of Commerce Mr. Hoover was administrative head of one of the two departments which maintain those relations with industry affording the greatest opportunity for constructive research; the other is the Department of Agriculture. One need only take time to familiarize himself with what has been accomplished in the department for which Mr. Hoover was responsible, to learn of his sympathetic encouragement to the scientific man, of his activities in obtaining funds for expansion, of his support of special programs of research and investigation, to say nothing of what was accomplished in convincing American industry that in the Department of Commerce, if in no other, the business man had an understanding friend at the Nation's Capital.

Lest there be any misunderstanding, let it be said that it is the part of the executive to administer. He must delegate responsibility and authority to bureau chiefs, but work under these chiefs cannot progress without his sanction, and those who have worked with Herbert Hoover know that his approval of a project follows only after understanding and acquaintance with that project. We hold it fair to argue, therefore, that certain researches already under way when he came to the Department of Commerce could continue with new support only with his approval and help.

Shortly after becoming Secretary of Commerce, in March, 1921, Herbert Hoover took a leading part in movements which resulted in the creation of the Federal Specifications Board, the Division of Simplified Practice, the Division of Building and Housing, the Division of Specifications, the Federal Specifications Board, the Industrial Standardization Board, and the National Conference on City and Highway Safety. He was also very active as the first president of American Engineering Council, one report of which, on "Waste in Industry," was directly due to his inspiration. This report has had a wide circulation in book form, and has been translated into many languages. Under the auspices of the Division of Simplified Practice there have been carried to successful completion programs initiated by the interested industries involving, after research, the elimination of a great number of unnecessary varieties in sizes, dimensions, models, and types of over one hundred commodities. This work continues, and industry attributes to these waste-elimination programs savings running into hundreds of millions of dollars.

The Division of Building and Housing coöperated closely with *Better Homes in America*, and has continued to work with business, technical, and commercial groups to encourage improvement in standards for building construction, to modernize building codes, to facilitate city planning and zoning, and to help distribute building activity throughout the year.

The Division of Specifications has worked with public purchasing agents and others to provide an encyclopedia covering the entire field of standards, specifications, simplifications, and tests, which may be determined as the best adapted for public purchases. Two of the ten volumes of this encyclopedia have been issued, and comprise lists of testing laboratories and college research laboratories, as well as details concerning some five thousand manufacturers willing to supply commodities guaranteed by them to comply with the requirements of more than three hundred nationally recognized specifications and standards. This division has also issued an Annual Directory of Commodity Specifications.

The Federal Specifications Board has formulated about seven hundred specifications for the mandatory use of the several departments of the Government, resulting in great savings in price and improvement in the quality of goods purchased for the federal service. All of this requires extensive research.

The National Conference on City and Highway Safety was attended by hundreds of delegates, at first in December, 1924, and again in March, 1926. The importance of this work is indicated by the fact that 600 attended the first, and 1000 delegates the second meeting. A third conference, held in May, 1930, adopted a summary of recommendations, including the findings of all conference committees. Twenty-five states have enacted laws based on the Uniform Vehicle Code. Many municipalities have put into effect the model municipal traffic ordinance, and great gains have been made throughout the country in traffic signs, signals, and markings, based on a manual prepared by the conference. This organization continues in active work.

Mr. Hoover, while Secretary of Commerce, appeared before and supported the National Conference on Weights and Measures. He encouraged the closest relations between industry and the Bureau of Standards, with the result that the research associates at the bureau increased from twenty-one in 1923 to nearly one hundred, representing forty industrial groups, in 1929. He also encouraged participation in technical and scientific societies, and at all times furthered close coöperation with national groups which could be helped by participation of the bureau's staff in such activities. Under his leadership also the Bureau of Standards became more truly a national physical laboratory, coöperating with other federal departments in scientific, technical, and engineering matters. Under this plan other branches of the Government transferred to the bureau funds for specific research projects in increasing annual amounts, beginning in 1923 with a little less than $200,000, reaching more than $300,000 in 1929, and totaling in that interval $1,620,639. The new National Hydraulic Laboratory, just authorized to be established at the Bureau of Standards, was actively supported by the President. The initial appropriation is $350,000.

We cannot go into the detailed research program of the Bureau of Standards as it increased and unfolded under Mr. Hoover as Secretary of Commerce. Reports of the bureau must speak for themselves, but some indication can be gleaned from the funds available for scientific and technical investigations from 1923 to 1929, inclusive:

1923	$1,557,360	1927	1,722,030
1924	1,589,500	1928	1,964,580
1925	1,654,160	1929	2,139,589
1926	1,655,910		

The results of much research throughout the country are reported first in patent applications. Therefore, the betterment of patent-office procedures and facilities is of interest to the industrial scientist and also to those who work in pure science. An examination of the appropriations from 1926 to 1929 shows increases designed to aid in improving the Patent Office. Mr. Hoover was instrumental in having the salaries in the Patent Office materially increased after the Patent Office was transferred from the Department of the Interior to the Department of Commerce. He was instrumental in obtaining better equipment, in having proper quarters assigned in the new Commerce Building, and supplemented the personnel of the Committee on Patent Office Procedure by the appointment of three engineers. Results of great value have been obtained. He took a very active interest in the international convention which met at The Hague in 1925, and materially aided the delegates in the performance of their duties.

The Lighthouse Service is a part of the Department of Commerce. Thanks to the interest and leadership of Mr. Hoover as Secretary of Commerce, the United States now possesses nearly half the radio beacons of the world, the first of which was established near New York in May, 1921. Radio was extended to benefit lighthouse keepers. The lighting of airways has been in accordance with the original suggestions of Secretary Hoover for the development of civil aeronautics through the use of existing agencies of the department, and there have been both extension and improvement in aids to navigation for marine use. These improvements have all rested upon investigation and research involving, for example, the extension of automatic acetylene or electrical installations of improved reliability and distinctive characteristics, with better service and lower costs. These devices have permitted aids to navigation to be established in locations where attended lighthouses would have been prohibitive in cost.

The regular work of the Coast and Geodetic Survey consists of projects extending over a number of years, but there are outstanding milestones in the progress of this important survey. While Herbert Hoover was Secretary of Commerce this progress was evidenced by increased appropriations to expedite the work and an enlargement of the scope of its activities. The bureau undertook a control survey of the Mississippi River area. It has been able, with increased appropriations, to obtain more detailed knowledge of the currents in important waters, and by enlarging the personnel of the Division of Tides and Currents, it has issued annual editions of "Predicted Currents in Important Harbors and Waterways." It has undertaken the preparation of airway maps, and has conducted an intensive study of the relative merits of the present ground method and aerial photography for topographic surveys.

During Mr. Hoover's incumbency as Secretary of Commerce the growth of the Bureau of Fisheries was the most phenomenal in its history, and scientific research of great importance to the fishing industry has been conducted.

It is difficult to realize that the Aeronautics Division of the Department of Commerce was only organized in 1926. In keeping with his idea that "research, both in pure science and its application to the arts, is one of the most potent impulses to progress," Mr. Hoover took immediate steps to establish a constructive research program which was very comprehensive and far-reaching. It involved engineering research and research on aids to air navigation. Engineering research became centered on wind-tunnel investigations, of which two reports have been published and two additional are in preparation, and upon the investigation of welded joints and tubular members of aircraft structures, on which both a general and a detailed technical report have already been published. A third point was soundproof airplane cabins, two reports on which have been published. Under aids to air navigation should be listed aeronautic radio research and aeronautic lighting equipment, many phases of which have been discussed in numerous technical papers and reports. A number of important questions have been assigned to special coöperating committees, and the appropriations for the work of the Aeronautics Division have steadily increased as the need for investigations and research has become apparent.

Radio broadcasting was begun while Mr. Hoover was Secretary of Commerce. The Radio Division of the Department of Commerce was set up in 1923, with an appropriation of $130,000; in 1929 it was $526,160. In the appropriation for 1928, $80,000 were included for the purchase of scientific apparatus, which has recently been installed at Grand Island, Nebr., at nine other offices, and on six test cars. The building of the test cars and the field-strength apparatus used on them may be said to be the result of Mr. Hoover's suggestion when he informed the Radio Division that efforts should be made to determine the service range and interference range of broadcasting stations. He presided over four national radio conferences held for the purpose of obtaining coöperation between station owners, resulting in a high degree of self-regulation. He appeared before congressional committees at hearings in connection with proposed radio legislation, and his advice was of great value.

During Mr. Hoover's administration as Secretary of Commerce, the research appropriations for the Bureau of Mines were increased, and special funds were obtained for coöperative work with the Geological Survey in the investigation of potash deposits, for developing new and cheaper processes for extracting potash from ores, for research into methods of treating oil shale, and for investigating the applicability of various geophysical methods as an aid in discovery of hidden bodies of minerals and oils. The other activities of a continuing nature under the auspices of the Bureau of Mines must be well known to our readers.

The White House Conference on Child Health and Protection is a scientific approach to a question of public importance and the project is one in which the President is greatly interested.

In addition to these official activities, of which we have mentioned but a few, Mr. Hoover has taken an active interest in a number of scientific and educational projects. He served as the chairman of the national committee on the Prize Essay Contest of the AMERICAN CHEMICAL SOCIETY. He attended and addressed many scientific gatherings of national and international nature; he was accessible for conference on any worthwhile project designed to advance scientific research in this country; and he placed behind the effort of the National Academy of Sciences to obtain large funds for basic research his advice, his active support, and his leadership. "The Vital Need for Greater Financial Support to Pure Science Research" was the subject of his address before the American Society of Mechanical Engineers, where he delivered the first Henry Robinson Towne lecture in December, 1925. The work initiated is being carried forward by a committee of distinguished scientists and industrialists, who seek to complete a fund of $20,000,000 for the support of research in pure science. His interest in the better training of men and women which comes from higher education is reflected in the address, entitled "Higher Education and the State Government," delivered at the commencement exercises of the University of Georgia in June, 1926. Before the American Association for the Advancement of Science in Philadelphia in December, 1926, he spoke on "The Nation and Science," discussing certain relationships of research in pure and applied science to public policies and, above all, the national necessity for enlarged activities in support of pure science research.

But why continue? It is an axiom in military circles that one should never use more force than is necessary to overcome the adversary. Perhaps we have already disregarded that axiom in the presentation of a few of the things which may be attributed to the continuing substantial interest and sympathetic support which Herbert Hoover, whether as a private citizen, Secretary of Commerce, or President of the United States, has for science and research. It is one thing to be an outstanding engineer or scientist, and quite another to exemplify the best in executives. A combination of these ideal qualifications is seldom, if ever, found. In Herbert Hoover we have the nearest approach to that ideal in any individual whom we have ever had in high office.

HARRISON E. HOWE

New Books

Addition-Subtraction Logarithms to Five Decimal Places. BY L. M. BERKELEY. 135 pages. White Book and Supply Co., New York, 1930. Price, $3.25.

Proceedings of the Thirty-third Annual Meeting, Vol. 30, 1930. Part I—Committee Reports, Tentative Standards. 1336 pages. **Part II—Technical Papers.** 1085 pages. AMERICAN SOCIETY FOR TESTING MATERIALS, Philadelphia, Pa., 1930. Parts I and II, each, paper, $6.00; cloth, $6.50; half-leather, $8.00.

Studies in the Painting of Wood

I—Influence of Wood Structure on Paint Behavior

Editor of Industrial and Engineering Chemistry:

Since the publication of our paper under this title, IND. ENG. CHEM., **23**, 226 (1931), the attention of the authors has been called to the following statements, in the paper, that might be misinterpreted and should be clarified:

(1) "Primary tissue" refers to "important tissue" and is not used in the botanical sense.

(2) "Dovetailed fibers" should read "overlapping fibers."

(3) In speaking of the formation of spring and summer wood, the word "period" should have been "periods" to indicate that alternating seasonal growths are involved.

(4) All medullary rays are not continuous from the center of the tree, but from the standpoint of their importance in paint penetrability they are practically continuous through the thickness of average flat-grained boards. Also the surface area occupied by these ray cells is considered by some authorities to be approximately 10 per cent, instead of approximately 20 per cent as stated.

(5) Resin ducts are intercellular spaces and not cells. Figure 16 was intended to show a resin canal, but owing to the low magnification the actual canal does not show although the resin that has exuded from the canal is plainly visible.

There are no published data proving that summer wood in yellow pine contains more resin than spring wood.

(6) There seem to be conflicting and unsettled opinions among the ranks of wood technologists on points concerning penetration of liquids into wood. The opinions of Scarth [*Paper Trade J.*, **86**, 53–8 (April 26, 1928)], used in this paper, are apparently at variance with the opinions of other wood technologists.

The function and operation of the bordered pits is another subject that is open to controversy and the number of these pits on a given fiber is less than might be supposed by the statement that the fiber walls are "covered with bordered pits."

(7) The work and data presented relating to the shrinkage and swelling of wood were not complete and may apply only to the particular wood studied. This fact was mentioned in the paper but perhaps was not emphasized sufficiently. The choice of yellow pine for this study was obviously made because it is recognized as a wood which is subject to painting troubles.

(8) A mistake due to a typographical error in Figure 17 shows flat and edge grain surfaces reversed.

(9) Figure 5 was intended to show microscopical differences in wood that might have an influence on paint behavior.

It is hoped that the above mentioned corrections will serve to clarify the text of the paper.

J. H. HASLAM
S. WERTHAN

NEW JERSEY ZINC COMPANY
PALMERTON, PA.
March 13, 1931

Sizing by Elutriation of Fine Ore Dressing Products

Editor of Industrial and Engineering Chemistry:

It is commendable that so many of the students in flotation are giving thought to elutriation. The article by Gaudin, Groh, and Henderson [IND. ENG. CHEM., **22**, 1363 (1930)] is a timely one. However, some of the trouble they encountered with sulfides may be alleviated easily. They say:

> With material composed mainly of metallic sulfides or other non-polar substances or non-polarly filmed substances, such as flotation concentrates, it is often impossible to effect reliable sizing if water is the liquid medium. This derives from the great tendency towards flocculation and flotation exhibited by non-polar substances. To obtain reliable sized fractions from flotation concentrates or other non-polar substances it is necessary to use another liquid medium than water.

Of all the stubborn and refractory products under the conditions as outlined above, a galena flotation concentrate probably stands at the head of the list. Fortunately, however, it may be subjugated so that elutriation can continue in water in normal fashion. The treatment required is a simple one. Dichromate has long been known to deaden the surface of galena. By the use of it, lead concentrates have been made completely docile. In the first step of preparation the sample is treated with a very dilute solution of sodium dichromate, acidified with sulfuric acid. When the dichromate solution has spent its oxidizing strength (only a few minutes are required), gum arabic is added and the sample is vigorously shaken to complete the deflocculation. Then the wet screening and all the subsequent steps in elutriation will follow with all the precision desired.

WILL H. COGHILL

MISSISSIPPI VALLEY EXPERIMENT STATION
U. S. BUREAU OF MINES, ROLLA, MO.
December 31, 1930

……

Editor of Industrial and Engineering Chemistry:

We are in accord with Mr. Coghill's statement concerning the use of a slightly acid solution of dichromate to deaden the surface of galena so that it may be elutriated in water. We have used the method.

Figure 1 shows a galena particle whose surface was treated in an acid dichromate solution after protecting it in part with paraffin. The paraffin was removed before photographing. The dull portion is that which was etched by the dichromate. Its appearance is due to the formation of lead chromate or a mixture of lead chromate and lead sulfate.

Our objection to treating galena in the manner suggested by Mr. Coghill is twofold. Firstly, it makes analysis for lead in the elutriated products somewhat more difficult, owing to the chromate radical. Secondly, some of the coating from the coarse particles may slough off, increasing the lead content of the finest grade. Also, some lead appears to go into solution and to be precipitated in the solution, and not at the surface of the galena particles.

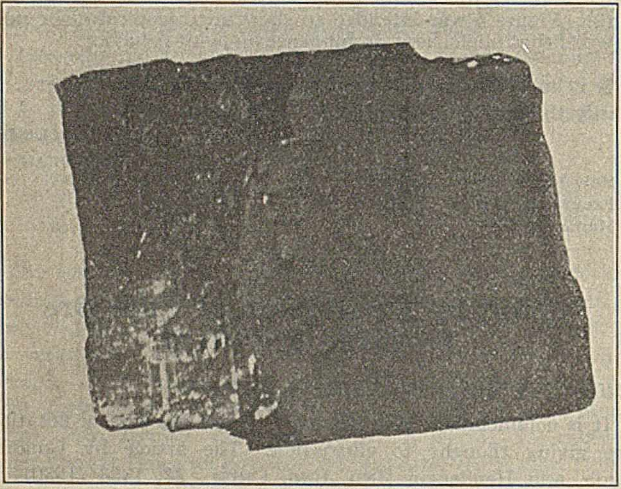


Figure 1

We favor acetone instead of water for the elutriation of concentrates, even though the sulfides may be deadened sufficiently for water elutriation so that there is no danger of inaccuracies from flotation of coarse particles. In addition to the fact that elutriation is more rapid in acetone than in water, owing to the low viscosity of acetone, that method gives cleaner products since it removes effectively any slime coatings from the surface of mineral particles.

Since our paper was submitted for publication, another type of elutriator (Figure 2) has been put in use for sizing with acetone. The design was evolved after conference with G. G. Griswold, Jr., research engineer for the Anaconda Copper Mining Company, who has used this type of elutriator for the study of mill products. The apparatus is similar to the type described in our paper except that a piezometer is used to control the overflow. The elutriator was made from a 250-cc. dispensing buret. Once calibrated, the piezometer permits rapid setting of the apparatus to secure the desired acetone velocities. An elutriator of the above size may be used throughout the range from 150 to 1600 mesh (100 to 9μ for quartz).

It has been found convenient first to deslime in water the material to be elutriated in acetone. This allows the acetone to be used several times before it is necessary to purify it by distillation. Considerable economy of acetone is effected, since the distillation losses are rather high with ordinary laboratory equipment.

E. J. Hall, of Columbia University, has suggested the use of tap water freed of dissolved gases by a vacuum pump in place of distilled water. Such water is suitable if it does not contain sufficient dissolved substances to cause flocculation or to introduce adsorbed foreign salts in the finest fraction of an elutriated sample.

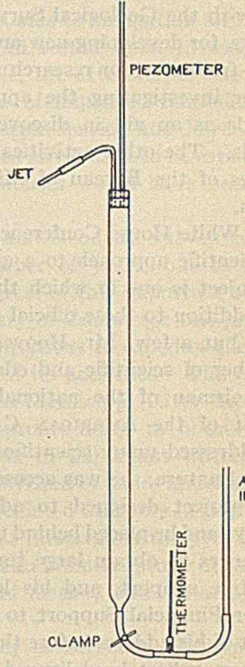


Figure 2

A. M. GAUDIN
J. O. GROH
H. B. HENDERSON

MONTANA SCHOOL OF MINES
BUTTE, MONT.
January 30, 1931

Corrections

In my paper entitled "Purified Wood Fiber. A Study of the Physical and Chemical Properties," IND. ENG. CHEM., 23, 131 (1931), the following corrections should be made:

The first sentence in the Method for Determining Copper Number should read: "A 3-gram sample of bone-dry shredded pulp is placed in a 1.5-liter round-bottomed flask. a water-jacketed reflux condenser is attached to the flask, *250 cc. of water are added*, and the pulp suspension is quickly brought to the boiling point."

In the last part of this same method, the liberated iodine is titrated with *0.20 N* sodium thiosulfate, instead of *20 N* sodium thiosulfate.

In my paper entitled "Purified Wood Fiber. The Paper-Making Characteristics of Wood Fiber High in Alpha-Cellulose," IND. ENG. CHEM., 23, 266 (1931), the following corrections should be made:

The last sentence of the synopsis should read: "The presence of *sulfite* wood pulp imparts physical weakness, particularly in respect to tearing resistance and fold endurance."

On page 266, under "Beating in Ball Mills," the reference to Figures 1 and 2 should be deleted from the second sentence.

On page 267 the caption under Figures 1 and 2 applies only to Figure 1. Figure 2 should be described as "Experimental Paper Machine of the Brown Company."

On page 271, the reference to Figure 8 should be deleted from the third line above the table in the first column.

Figure 4, turn right side to bottom.

GEO. A. RICHTER

BOOK REVIEWS

Report of the Water Pollution Research Board for the Year Ended 30th June, 1930. R. ROBERTSON, Chairman. With the Report of the Director of Water Pollution Research, H. T. CALVERT. 33 pages. Department of Scientific and Industrial Research. H. M. Stationery Office, London. Price, 9 d., net. The British Library of Information, 5 East 45th St., New York, N. Y.

This third report of the board by the chairman (14 pages) notes the beginning of the printing of the monthly summaries of current literature dealing with water supplies, sewage, trade waste waters, river pollution, and relevant subjects that had been distributed in neostyled form since October, 1927. It also describes the various activities of the board's research work and of coördinated activities of other research committees.

The report of the director of research gives the general results of the survey of the River Tees and of a semi-commercial test of gravel, slag, and clinker filters which, in the 88-day campaign at the beet-sugar factory near Colwick, treated about 2 million gallons of diluted pulp press liquor to give a purification of 80 to 90 per cent. Experiments were continued on base-exchange water softening and on activated-sludge sewage treatment. In coöperation with the Institution of Gas Engineers improvements in cooling and scrubbing were developed, and it was also found at Cheltenham that spent gas liquor, up to 0.5 per cent of the dry weather flow admitted continuously to sewers, could be handled at the sewage works to give a satisfactory effluent.—W. D. COLLINS

The Protection and Decoration of Concrete. BY MAXIMILIAN TOCH. 54 pages. 12 × 18.5 cm. D. Van Nostrand Company, Inc., New York, 1931. Price, $2.00.

This chatty little volume is more of an excellent example of the printer's art than a contribution to technical knowledge. It reads as though Doctor Toch were extemporaneously regaling his "concrete" friends with some of his recollections of his work in protecting and decorating concrete.

Consequently, it does not appear to have been thoughtfully developed or carefully written and corrected. Chapter titles seem to introduce a topic, after which the author may digress to topics previously discussed or about to be discussed in other chapters. To avoid appearing too technical, the author presents no data or formulas. However, he allows himself to be rather loose in describing certain chemical reactions; for example, in the one between concrete structures and the double fluosilicate of zinc and magnesia, he states that the "zinc precipitates zinc hydroxide." A little careful rereading would have removed such faults as well as the reference in the text to certain illustrations by numbers, whereas none of the illustrations are numbered.

On the whole, it is an interesting but not instructive brochure. —P. H. BATES

Oil, Its Conservation and Waste. BY JAMES H. WESTCOTT. 273 pages. Beacon Publishing Company, New York, 1930. Price, $3.00.

Westcott's book is likely to give the reader who is not thoroughly acquainted with the oil industry an erroneous impression of that industry. For instance, he makes much of the "waste" attending the production of oil. This is most improper unless the circumstances surrounding oil production at the time the waste is charged are explained. It is true that for many years in remote fields natural gas was blown into the air or burned in perpetual flambeaux, but this was because there was no market for the gas. As fast as economic conditions permitted, the gas has been put to use. For many years much of it has been used for the manufacture of carbon black, but this was a limited field. Lately, as the technology and engineering of pipe-line construction have been developed so that gas can be transported at high pressures, natural gas has been brought to the furnaces and stoves of thousands of homes as far as a thousand miles from the gas fields.

From a sternly individualistic business the petroleum industry has become one of coöperation and collective planning, as conditions have dictated, reducing the amount of crude oil brought out of the ground and increasing the yield of gasoline from the crude produced.

One has only to look at the reduction during the past year in the daily crude production from 2,680,000 barrels to 2,089,000 barrels to prove that coöperation is at work.

Westcott's erroneous viewpoint is particularly illustrated in the chapter devoted to cracking. For instance, there is not now, and never has been, a process known to the oil industry as the Adams process; and yet Westcott gives the "Adams gasoline cracking inventions" nearly ten pages, the Burton cracking process nearly eight pages, the Holmes-Manley process nearly six pages, the "tube and tank" nearly four pages, the Cross installations four and a half pages, and the Dubbs cracking process a single line.

All in all, this work is by no means recommended to anyone wishing to obtain a correct picture of the petroleum industry as it operated in 1930.—GUSTAV EGLOFF

Bioassays. A Handbook of Quantitative Pharmacology. BY JAMES C. MUNCH. 958 pages. The Williams & Wilkins Company, Baltimore, 1931. Price, $10.00.

This book represents an elaborate and exhaustive examination of the literature covering pharmacological tests and includes some associated chemical and toxicological information. In general, quantitative and qualitative bioassays are given and the reaction of certain species of animals noted, beginning with the unicellular organism and continuing through the scale of zoölogical importance to man. The animal of preference to be employed in the tests is given and the most acceptable method outlined in sufficient detail to permit the carrying out of the test and the interpretation of the results by technical workers of some training and experiment in pharmacology.

It should be of value to those engaged in the testing or standardization of drugs, as it gives clearly their principal physiological action and the effects most readily measurable. The comparative value of chemical assays and their relation to the physiological activities or expressions are included where available. The author stresses the fact that chemical assays fail to give a true expression of drug activity; side reactions are not detected chemically and physiological tests are necessary to ascertain secondary effects manifested by the living organism. A discussion of the several tests of standard employment is followed by the author's conclusion as to the most practical. The percentage of accuracy of tests is also often included. The variety of the plant (or glandular extract or what not) which is most suitable for test is given and whether or not the crude article or one of its more active components is best.

The bibliography at the end of each chapter should prove helpful. Some 17,000 references are listed and in Chapter V, Drugs Affecting the Circulation, over 1200 leading articles upon this phase of the work are noted.

The chapter upon Experimental Technique is very brief and, if the work is to be used by one rather untrained in the field of bioassays or lacking basic anatomical and physiological training, had best be augmented by reference to a text on experimental pharmacology.

This volume will be of particular value to those investigators not primarily trained in physiological experimentations or interpretations but who find confirmatory tests necessary to their chemical and toxicological exploitations.—EDGAR S. LINTHICUM

Industrial Research Laboratories of the United States, Including Consulting Research Laboratories. National Research Council, *Bulletin* 81. 4th edition. Compiled by CLARENCE J. WEST and CALLIE HULL. 267 pages. National Research Council, Washington, D. C., 1931. Price, $2.00.

The fourth edition of that exceedingly informative and useful compilation of Industrial Research Laboratories of the United States has recently been issued. The present edition includes information concerning consulting research laboratories, but federal, state, municipal, and educational laboratories which may engage in some phase of industrial research have not been included. Details are given concerning more than 1620 separate laboratories. There is a list of directors alphabetically arranged, geographical distribution of the organizations, and a separate index classified by laboratory activities.

In so far as the companies have been willing to supply the information, the reader finds in this volume the name and location of the laboratory, its principal line of activity, the name of its director, the size of the staff classified along major lines, and a concise outline with indication of the principal research undertaking.

The compilers state that names of new laboratories were obtained by a thorough search of periodicals and membership lists and from notices appearing in technical publications. This effort yielded fifty new laboratories. The increase over the one thousand listed in the third edition is thus not due entirely to the organization of new laboratories, although it is true that a larger number of companies returned the data requested. The laboratories starred are those which did not reply to the last request; hence the repetition of the former information, there being good ground for belief that the laboratory is still in operation.

There is no similar list. It is of great value to those working in the research field of chemistry, and it is one of the most useful bulletins issued by the Research Information Service of the National Research Council.

Drying and Processing of Materials by Means of Conditioned Air. Edited by D. C. Lindsay. 210 pages. Illustrated. Published by Carrier Engineering Corporation, Newark, N. J., 1929. Price, $3.00.

This book consists of two parts. The first explains in very simple language the phenomena of vapor pressure, evaporation, and evaporative cooling. It also explains the meaning of absolute and relative humidity and other terms commonly used in drying and air-conditioning practice. A section is devoted to the explanation of the use of the standard humidity chart and numerous illustrative problems are used. The useful Carrier form of the humidity chart is included. These parts of the book should be found particularly helpful to one without a technical education desiring to become familiar with the fundamentals of evaporation processes and with the use of the humidity chart.

The second section of the book includes informative descriptions of the applications of the Carrier ejector drier in the drying of a number of different materials. This section, comprising over two-thirds of the text, is in reality a well-written manufacturer's catalog.—Thomas K. Sherwood

Toxikologie und Hygiene des Kraftfahrwesens (Auspuffgase und Benzine). Schriften aus dem Gesamtgebiet der Gewerbehygiene herausgegeben von der deutschen Gesellschaft für Gewerbehygiene in Frankfurt/A. M. Neue Folge. Heft 29. By E. Keeser, V. Froboese, R. Turnau, E. Gross, G. Ritter, E. Kuss, and W. Wilke. 106 pages. 23 figures. Julius Springer, Berlin. Price, 10.30 marks.

The publication is primarily a report of a laboratory investigation of the composition and toxicology of automobile exhaust gas and a field study of atmospheric contamination by these gases which was conducted coöperatively by the Reichsgesundheitsamt and the I. G. Farbenindustrie. The important phases of the study are: (*a*) comparison of the composition of the exhaust gases when using various kinds of fuel, including gasoline containing iron carbonyl antiknock, and when operating under various conditions of load; (*b*) examination of the exhaust gases for toxic constituents, particularly the presence of important constituents other than carbon monoxide; (*c*) distribution or dilution of exhaust gas behind a standing or moving motor vehicle; and (*d*) a determination of the contamination of the air of the streets in Berlin and of the Hamburg-Elbtunnel. The problem is attacked from the combined viewpoint of a chemist, an engineer, and a physician, and the data are presented and discussed from the viewpoint of hygiene in motor transportation.

The most important contribution to previous information on the subject is the comprehensive investigation of the exhaust gases for toxic constituents of importance other than carbon monoxide. Toxicological tests made with the various fractions and condensates gave neither evidence of a compound of unusual toxicity nor information which changes the present viewpoint that carbon monoxide is the significant acute toxic constituent. Also no information was obtained which explains the question of chronic injury.

The results of the analysis of air in the streets of Berlin for exhaust gas are similar to those found in investigations made in other parts of Europe and in America, and indicate no widespread public health hazard.

No attempt was made to have the scope of the study include all the toxicological and hygienic problems involved in motor transportation or to have the report present complete information and engineering data for the solution of all problems which might arise. Some of the information given is a confirmation of that previously known. In certain instances the data are not so complete nor so well substantiated by experimental work as those given by previous investigators. On the other hand, the publication contains much information of value for supplementing previous knowledge of the composition, toxicology, and behavior of exhaust gases in their relation to hygiene. For the most part the work appears reliable and acceptable, but certain observations and data are open to critical comment. A particular case is a statement that guinea pigs and white mice endure a concentration of 0.6 per cent carbon monoxide for 3 hours. Judging from the experience of the reviewers with the response of these animals to carbon monoxide, the statement is rather incredible. It is also thought that the ataxia and apparent narcotic action attributed to substances other than carbon monoxide might have been due to the 0.3 per cent of the latter that was present at the time the observations were made.

The results are clearly presented and can be readily understood by the technical reader and in the main by the non-technical reader. Test procedures and analytical methods are described in detail, and constitute an important part of the publication.

A bibliography of 240 references on toxicology and hygienic problems of exhaust gases, and particularly the determination of small amounts of carbon monoxide in air, is given.—William P. Yant and P. H. Mautz

Die neueren Fortschritte der technischen Elektrolyse. By Jean Billiter. 328 pages. Wilhelm Knapp, Halle (Saale), 1930. Price, bound, 22 marks.

This book is a supplement to the "Technischen Elektrochemie" by the same author. The book gives a rather good idea about the modern technology of the main electrolytic processes. The first part deals with the electrometallurgy of aqueous solutions, the second part with electrolysis in aqueous solutions without separation of metals using insoluble anodes, the third with electrolysis in the molten phase, and the fourth part contains tables and flow sheets of copper, zinc, and cadmium electrolysis. Emphasis is laid on the refining of copper and zinc, and especially on the electrolysis of water. Different cells pertaining to the last process are described in detail. Electrolysis under pressure is also treated and discussed.

The book contains very good photographs and sketches which give an interesting variation to the rather dry and precise text. The abundant patent and literature references are also of considerable value.—Kurt Dorph

Handbuch der technischen Elektrochemie. I Band—Die technische Elektrolyse wässeriger Lösungen. A—Die technische Elektrometallurgie wässeriger Lösungen. Edited by Victor Engelhardt. 613 pages. Akademische Verlagsgesellschaft, m. b. H., Leipzig, 1931. Price, 58 marks.

This is the first volume of what is intended to be a very comprehensive handbook of applied electrochemistry. The rapid growth of the electrochemical industry throughout the world has created a growing demand for a book of reference which would not only discuss the underlying principles of the various electrochemical reactions, but would cite in as much detail as possible actual operating conditions for the manufacture of an ever increasing host of electrochemical products and by-products.

This first volume, Part I, is devoted to the hydrometallurgy of iron, manganese and chromium, nickel, cobalt, zinc, cadmium, bismuth, antimony, tin, lead, and mercury. Other volumes in the course of preparation, probably ten or a dozen all told, will deal with the electrometallurgy of copper, gold, etc., the electrolytic production of hydrogen, chlorine, etc., electric furnaces and products, electrochemical gas reactions, electroösmosis, and cataphoresis.

The editor, Doctor Engelhardt, is one of the foremost German electrochemists. He has assigned the various chapters to experts in the particular field. Thus we find in the volume before us that Victor Hybinette, of Wilmington, has contributed the chapter on nickel; W. Pfanhauser, of Leipzig, the one on iron; Chas. L. Mantell, of Brooklyn, the one on tin; W. Schopper, of Hamburg, the one on lead, etc.

The introductory chapters on theory and accessories, and the detailed literature references throughout add a great deal to the value of the book. In general, the record throughout the pages is that of present practice, and not too much space is devoted to obsolete processes.

Although the book is intended primarily for European readers, Americans will find it to be a worthy and important addition to their reference library.—Colin G. Fink

MARKET REPORT—MARCH, 1931

THESE PRICES UNLESS OTHERWISE SPECIFIED ARE THOSE PREVAILING IN THE NEW YORK MARKET, MARCH 15, FOR COMMERCIAL GRADES IN CARLOAD QUANTITIES

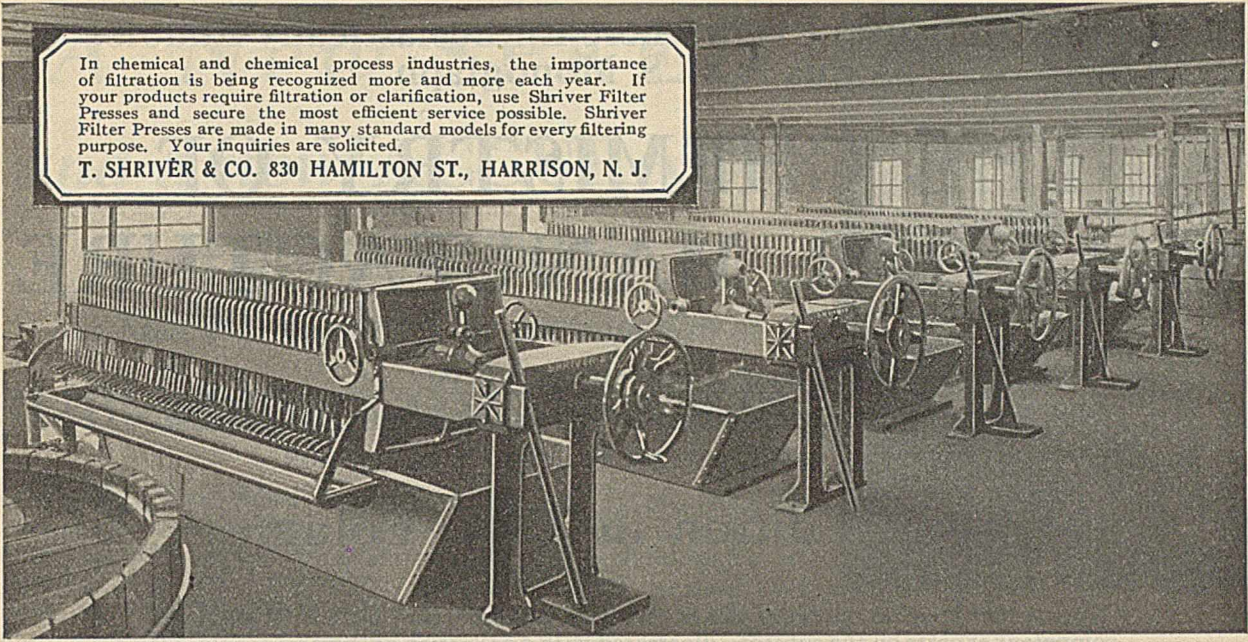
Newer Chemicals

Acetaldehyde, drums, lc-l., wks.	lb.	.18½
Acetaldol, 50-gal. drums	lb.	.27
Acetylene tetrachloride, *see* Tetrachloroethane		
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.	.50
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
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.	5.00
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 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.	.10
Acetphenetidin, bbls.	lb.	1.25
Acid, acetic, 28%, c/l., bbls.	100 lbs.	2.60
56%, c/l., bbls.	100 lbs.	4.85
Glacial, c/l., bbls.	100 lbs.	9.23
Glacial, U. S. P., c/l., carboys	100 lbs.	9.73
Acetylsalicylic, bbls.	lb.	.85
Anthranilic, 99–100%, drums	lb.	.85
Benzoic, tech., bbls.	lb.	.40
Boric, bbls.	lb.	.06⅛
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.	.15
Cinnamic, bottles	lb.	3.25
Citric, U. S. P., kegs, bbls.	lb.	.40
Cresylic, pale, drums	gal.	.58
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
Hydrofluosilicic, 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.	.13½
Sulfanilic, 250-lb. bbls.	lb.	.15
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.	.31½
Tungstic, kegs	lb.	1.40
Valeric, C. P., 10-lb. bot.	lb.	2.50
Alcohol, U. S. P., 190 proof, bbls.	gal.	2.62
Amyl, from pentane, tanks	lb.	.236
Amyl, Imp. drums	gal.	1.75
Butyl, drums, c/l., wks.	lb.	.15½
Cologne spirit, bbls.	gal.	2.69
Denatured, No. 5, comp. denat., c/l., drums	gal.	.39
No. 1, comp. denat., drums	gal.	.41
Isoamyl, drums	gal.	4.00
Isobutyl, ref., drums	lb.	1.00
Isopropyl, ref., drums	gal.	.60
Propyl, ref., drums	lb.	1.00
Wood, *see* Methanol		
Alpha-naphthol, bbls.	lb.	.73
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.	ton	22.90
Aluminum chloride, anhyd., commercial, wks., drums extra, c/l.,	lb.	.05
Aluminum stearate, 100-lb. bbl.	lb.	.18
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.	.38
Carbonate, tech., casks	lb.	.10½
Chloride, gray, bbls.	100 lbs.	5.40
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.	.11½
Sulfate, bulk, wks.	100 lbs.	1.80
Thiocyanate, tech., kegs	lb.	.36
Amyl acetate, tech., from pentane, drums	lb.	.22
Aniline oil, drums	lb.	.15
Anthracene, 80–85%, casks, wks.	lb.	.60
Anthraquinone, subl., bbls.	lb.	.50
Antimony, metal	lb.	.07⅛
Antimony chloride, drums	lb.	.13
Oxide, bbls.	lb.	.10
Salt, dom., bbls.	lb.	.22
Sulfide, crimson, bbls.	lb.	.25
Golden, bbls.	lb.	.16
Vermilion, bbls.	lb.	.38
Tartrolactate, bbls.	lb.	.45
Argols, red powder, bbls.	lb.	.07½
Arsenic, metal, kegs	lb.	.30
Red, kegs, cases	lb.	.09⅜
White, c/l., kegs	lb.	.04
Asbestine, bulk, c/l.	ton	15.00
Barium carbonate, bbls., bags, wks.	ton	58.00
Chloride, bbls., wks.	ton	63.00
Dioxide, drs., wks.	lb.	.12
Hydroxide, bbls.	lb.	.05¼
Nitrate, casks	lb.	.07½
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.	.19
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.	1.25
Bismuth, nitrate, 25-lb. jars	lb.	1.25
Oxychloride, boxes	lb.	2.95
Subnitrate, U. S. P., 25-lb. jars	lb.	1.50
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
British gum, com., c/l.	100 lbs.	4.37
Bromine, bot.	lb.	.36
Bromobenzene, drums	lb.	.50
Bromoform, jars	lb.	1.80
Butylacetate, drums, c/l.	lb.	.17
Cadmium bromide, 50-lb. jars	lb.	1.40
Cadmium, metal, cases	lb.	.70
Cadmium sulfide, boxes	lb.	.90
Caffeine, U. S. P., 5-lb. cans	lb.	2.40
Calcium acetate, bags	100 lbs.	2.00
Arsenate, bbls.	lb.	.07
Carbide, drums	lb.	.05½
Chloride, drums, wks.	ton	20.00
Cyanide, 100-lb. drums	lb.	.30
Lactate, U. S. P., bbls.	lb.	.37

Nitrate, bbls.	ton	40.00
Phosphate, monobas., bbls.	lb.	.08
Tribas., bbls.	lb.	.11
Calcium carbonate, tech., bgs.,	100 lbs.	1.00
U. S. P., precip., 175-lb. bbl.	lb.	.06½
Camphor, Jap., cases	lb.	.55
Camphor, monobrom., cs.	lb.	1.85
Caramel, bbls.	gal.	.63
Carbazole, bbls.	lb.	.75
Carbon, activated, drums	lb.	.08
Carbon bisulfide, drums	lb.	.05½
Carbon black, cases	lb.	.06
Carbon dioxide, liq., cyl.	lb.	.06
Carbon tetrachloride, drums	lb.	.06¼
Casein, stand. gr., bbls.	lb.	.09
Cellulose acetate, bbls.	lb.	.80
Cerium oxalate, kegs	lb.	.32
Charcoal, willow, powd., bbls.	lb.	.06
China clay, bulk	ton	8.00
Chloral hydrate, drums	lb.	.70
Chloramine, U. S. P., 5-lb. bot.	lb.	1.50
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.	2.10
Cod-liver oil, bbls.	bbl.	30.00
Collodion, drums	lb.	.15
Copperas, c/l., bulk	ton	13.00
Copper, metal, elec.	100 lbs.	10.00
Copper carbonate, bbls.	lb.	.08½
Chloride, bbls.	lb.	.22
Cyanide, drums	lb.	.41
Oxide, red, bbls.	lb.	.15½
Sulfate, c/l., bbls.	100 lbs.	4.25
Cotton, soluble, bbls.	lb.	.40
Cream tartar, bbls.	lb.	.23¾
Cyanamide, bulk, N. Y.	Nitrogen unit	1.39
Diaminophenol, kegs	lb.	3.80
Dianisidine, bbls.	lb.	2.35
Dibutylphthalate, drums, wks.	lb.	.24½
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.	.29
Diphenylamine, bbls.	lb.	.37
Diphenylguanidine, bbls.	lb.	.30
Epsom salt, tech., bbls., c/l., N. Y.	100 lbs.	1.70
Ether, nitrous, bot.	lb.	.80
Ether, U. S. P., drums	lb.	.13
Ethy acetate, drums, c/l.	lb.	.08
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	15.00
Ferric chloride, tech., bbls.	lb.	.05
Ferrous chloride, cryst., bbls.	lb.	.06
Ferrous sulfide, bbls.	100 lbs.	2.50
Fluorspar, 98%, bags	ton	41.00
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.	.12½
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	60.00
Lead, metal, N. Y.	100 lbs.	4.50
Lead acetate, bbls., white	lb.	.11½
Arsenate, bbls.	lb.	.13
Oxide, litharge, bbls.	lb.	.08¾
Peroxide, drums	lb.	.20
Red, bbls.	lb.	.103
Sulfate, bbls.	lb.	.06¾
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
Lithium carbonate, 100-lb. kgs.	lb.	1.35
Lithopone, bbls.	lb.	.04½
Magnesite, crude	ton	36.00
Calcined, 500-lb. bbls., wks.	ton	50.00
Magnesium, metal sticks, wks.	lb.	.85
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., 25 lbs.	lb.	1.63
Mercury, flasks, 76 lbs.	flask	103.00
Meta-nitroaniline, bbls.	lb.	.67
Meta-phenylenediamine, bbls.	lb.	.80
Meta-toluylenediamine, bbls.	lb.	.67
Methanol, pure, synthetic, drums, wks.	gal.	.42
Tanks, wks.	gal.	.40
Methyl acetone, drums	gal.	.57
Salicylate, cases	lb.	.42
Methyl chloride, cylinders	lb.	.45
Michler's ketone, bbls.	lb.	3.00
Naphtha, solvent, tanks	gal.	.35
Naphthalene, flake, bbls.	lb.	.04½
Nickel, metal	lb.	.35
Nickel salt, single, bbls.	lb.	.10½
Double, bbls.	lb.	.10½
Niter cake, bulk	ton	12.00
Nitrobenzene, drums	lb.	.09
Oil, castor, No. 1	lb.	.11½
China wood, bbls.	lb.	.07
Coconut, Ceylon, tanks	lb.	.05½
Cod, N. F., tanks	gal.	.44
Corn, crude, tanks, mills	lb.	.07⅜
Cottonseed, crude, tanks	lb.	.06⅛
Lard, edible, bbls.	lb.	.13¼
Linseed, bbls.	lb.	.094
Menhaden, crude, tanks	gal.	.21
Neat's-foot, pure, bbls.	lb.	.11
Oleo, No. 1, bbls.	lb.	.07½
Olive oil, denat., bbls.	gal.	.82
Foots, bbls.	lb.	.06½
Palm, Lagos, casks	lb.	.05⅛
Peanut, crude, bbls.	lb.	nom.
Perilla, bbls.	lb.	.10
Rapeseed, bbls., English	gal.	.71
Red, bbls.	lb.	.08⅜
Soy bean, crude, bbls.	lb.	.07
Sperm, 38°, bbls.	gal.	.84
Whale, bbls., natural, winter	gal.	.72
Ortho-aminophenol, kegs	lb.	2.15
Ortho-anisidine, drums	lb.	2.50
Ortho-dichlorobenzene, drums	lb.	.08
Ortho-nitrochlorobenzene, drums	lb.	.28
Ortho-nitrophenol, bbls.	lb.	.85
Ortho-nitrotoluene, drums	lb.	.16
Ortho-toluidine, bbls.	lb.	.27
Palladium, metal	oz.	22.00
Para-aminophenol, kegs	lb.	.84
Para-dichlorobenzene	lb.	.17
Para-formaldehyde, cases	lb.	.38
Paraldehyde, tech., drums	lb.	.20½
Para-nitroaniline, 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.	.44
Paris Green, 250-lb. kegs	lb.	.25
Phenol, drums	lb.	.14¼
Phenolphthalein, drums	lb.	1.10
Phenylethyl alcohol, 1-lb. bot.	lb.	7.00
Phosphorus, red, cases	lb.	.42
Phosphorus trichloride, cyl.	lb.	.35
Phthalic anhydride, bbls.	lb.	.15
Platinum, metal	oz.	29.00
Potash, caustic, drums	lb.	.06⅛
Potassium acetate, kegs	lb.	.28
Bicarbonate, casks	lb.	.09½
Bichromate, casks	lb.	.09
Binoxalate, bbls.	lb.	.14
Bromate, cs.	lb.	.35
Carbonate, 80–85%, calc., casks	lb.	.05¼
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.	.38
Yellow, casks	lb.	.18½
Titanium oxalate, bbls.	lb.	.21
Pyridine, drums	gal.	1.50
Quinine bisulfate, 100 oz.	oz.	.40
Sulfate, 100-oz. cans	oz.	.40
Resorcinol, tech., kegs	lb.	.90
Rochelle salt, bbls., U. S. P.	lb.	.19
R salt, bbls.	lb.	.42
Saccharin, cans	lb.	1.70
Salt cake, bulk	ton	16.00
Saltpeter, gran., bbls.	lb.	.06⅛
Silica, ref., bags	ton	22.00
Silver nitrate, 16-oz. bot.	oz.	.23⅜
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.	2.00
Bichromate, casks	lb.	.07
Bisulfite, bbls.	lb.	.04
Bromide, bbls., U. S. P.	lb.	.34
Chlorate, kegs	lb.	.05¾
Chloride, bags	ton	12.00
Cyanide, cases	lb.	.15½
Fluoride, bbls.	lb.	.08
Metallic, drums, 12¼-lb. bricks	lb.	.19½
Naphthionate, bbls.	lb.	.52
Nitrate, crude, bags, N. Y.	100 lbs.	2.05
Nitrite, bbls.	lb.	.07¼
Perborate, bbls.	lb.	.18
Peroxide, cases	lb.	.21
Phosphate, trisodium	100 lbs.	3.15
Picramate, kegs	lb.	.69
Prussiate, bbls.	lb.	.11½
Silicate, drums, tanks, 40°	100 lbs.	.75
Silicofluoride, bbls.	lb.	.04
Stannate, drums	lb.	.23½
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.	.81
Strontium carbonate, tech., bbls.	lb.	.07¼
Nitrate, bbls.	lb.	.09
Strychnine alkaloid, 100 oz., powder	oz.	.56
Sulfate, powder	oz.	.46
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.	.26½
Tin tetrachloride, anhydrous, drums, bbls.	lb.	.19¼
Oxide, bbls.	lb.	.26
Titanium dioxide, bbls., wks.	lb.	.21
Toluene, tanks	gal.	.29
Tribromophenol, cases	lb.	1.10
Triphenylguanidine, drums	lb.	.58
Triphenyl phosphate, bbls.	lb.	.60
Tungsten	Wos unit	15.50
Urea, pure, cases	lb.	.15
Whiting, bags	100 lbs.	1.00
Xylene, 10°, tanks, wks.	gal.	.28
Xylidine, drums	lb.	.36
Zinc, metal, N. Y.	100 lbs.	4.35
Zinc ammonium chloride, bbls.	lb.	.05½
Chloride, granulated, drums	lb.	.05¾
Oxide, Amer., bbls.	lb.	.06½
Stearate, bbls.	lb.	.19
Zinc dust, bbls., c/l.	lb.	.06



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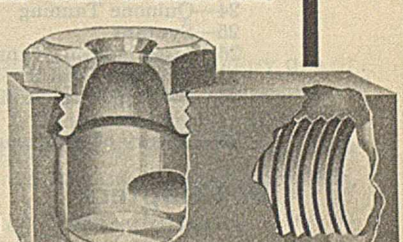

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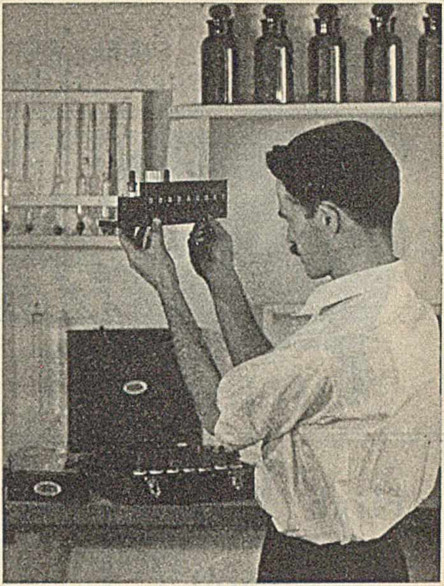

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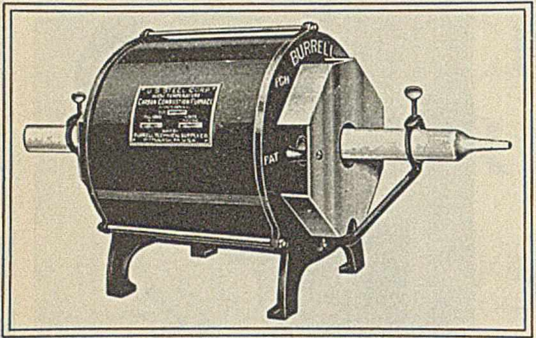
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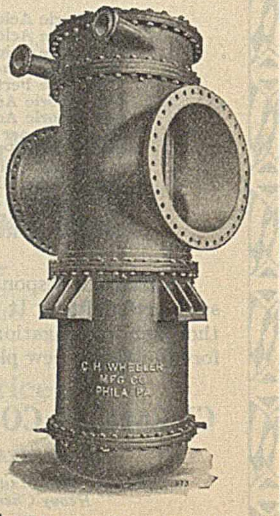
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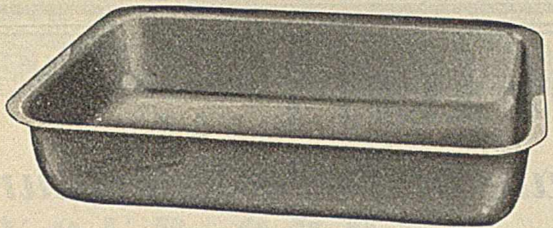

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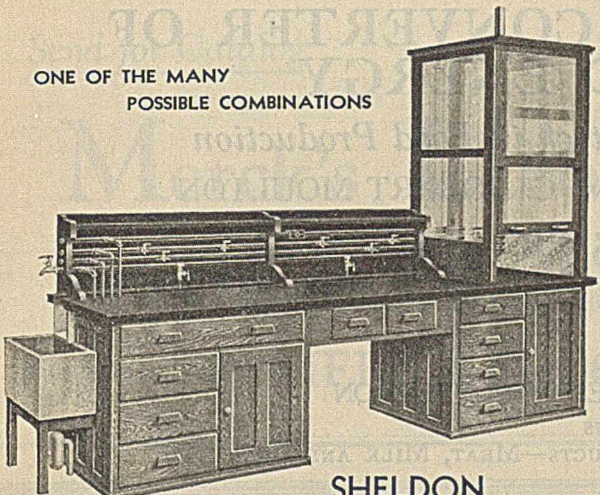

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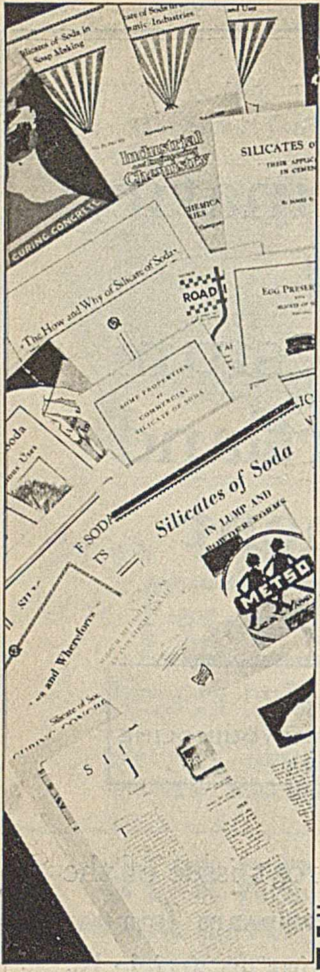
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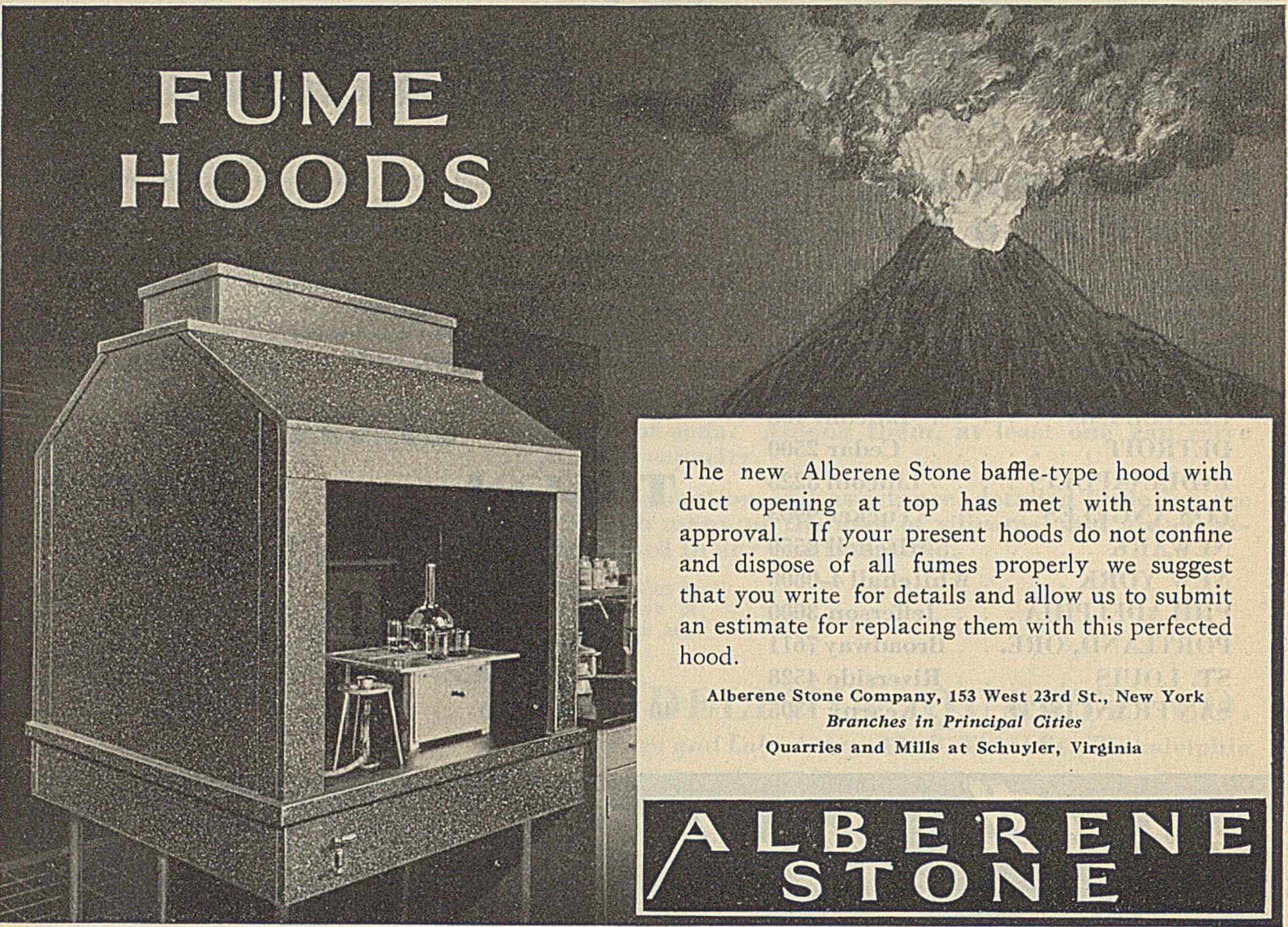

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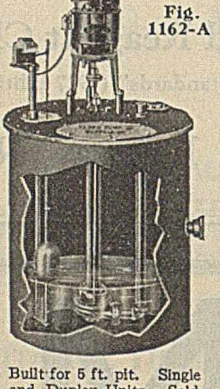

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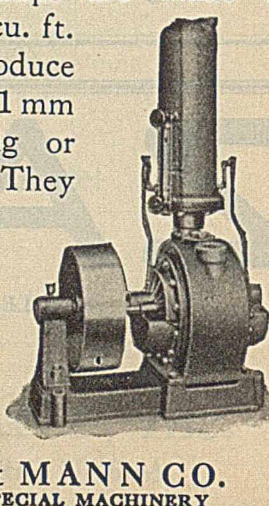

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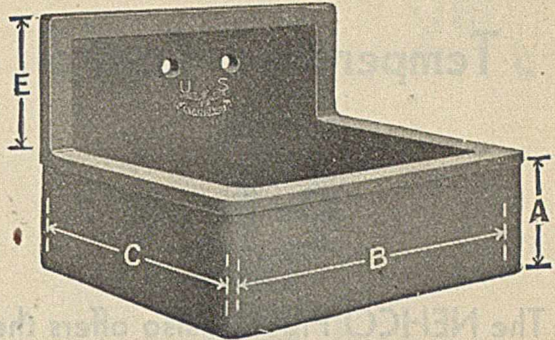

Fig. 112-A Laboratory Sink with Integral Back

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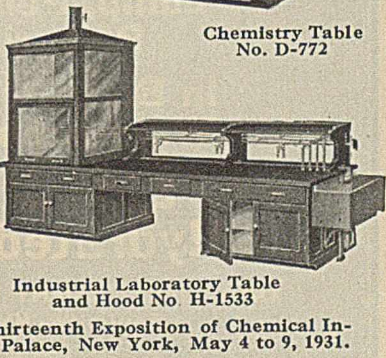

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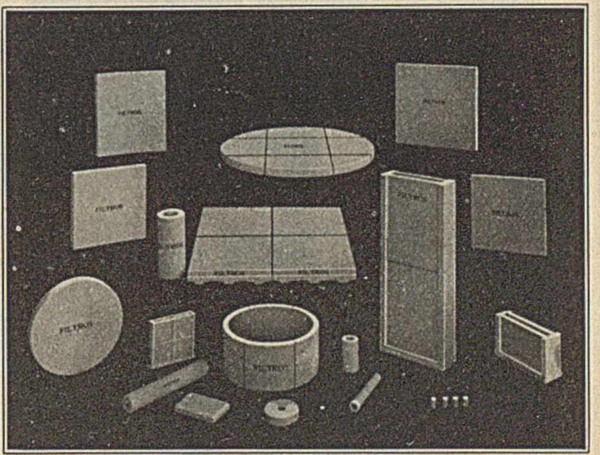

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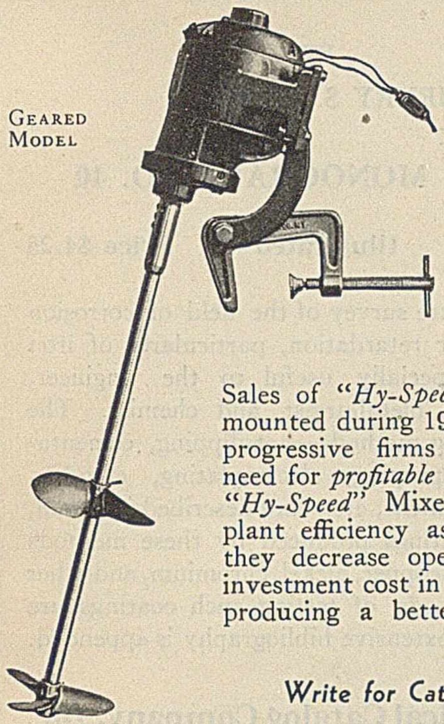

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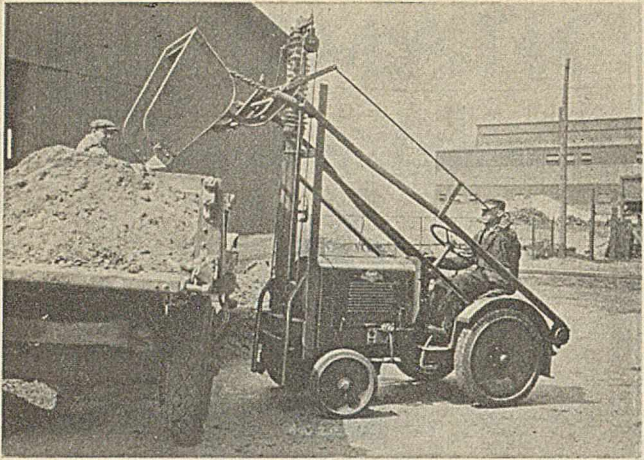

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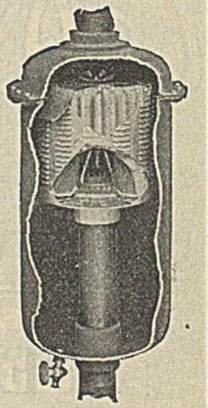

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