Industrial
AND ENGINEERING
Chemistry

VOLUME 24
NUMBER 3

MARCH
1932

HARRISON E. HOWE, EDITOR

The Editor's Point of View

SATISFACTION. The difference in men is often marked by that which affords them a thrill of satisfaction. With some it is the creation of new things. In others there is a certain pride in destruction. Some enjoy building. Others get more satisfaction from demolition.

It was our privilege not long since to be standing in a group watching tests on a new material. The object of the experiments was to show whether or not the new substance was as satisfactory, when compared to the old, as its discoverers had thought and to ascertain the reasonable limitations in its use. A man in our group remarked, "For my part, I get far more satisfaction from learning how to use a new material in the right way than I do from trying to stop its introduction." To the constructive mind there is certainly a stimulating thrill in making a thing go, notwithstanding the difficulties. In the office of one of our successful and most often quoted engineers there hangs a motto which goes something like this: "If Columbus could have landed in mid-ocean, America would never have been discovered." It is a sentiment worthy of a place in every institution where new things are being done and great dreams dreamed.

⁂

KNOWLEDGE, EXPERIENCE, AND TRADE SECRETS. The modern consolidation process gives rise to a series of events that sooner or later lead to new competition for the commercial giants. The very formation of the merger may displace a number of men who are generally those thought by the company to be either holding posts which others in the organization can fill or are not so valuable as men retained for the same work. The operation of the large company may become such that the younger men with ideas become restless, and decide that it is not worth while to wait longer for their opportunity. They feel the best procedure is to undertake a business venture on their own responsibility. We must expect in any case that some of the men displaced or who leave on their own account for various reasons will turn to an industrial activity similar to that with which they have been identified. Their knowledge, strengthened by experience, has best fitted them for just that sort of thing. Manufacturing chemistry has become too highly specialized logically to expect anything else to happen. The man undertakes an activity in the field which he knows best.

If such an adventurer promises to be at all successful his progress becomes a matter of concern to the large company that prefers to dominate the field. If he is unsuccessful it does not matter. If he shows any signs of making his way, his achievements may be sources of irritation and means must be found to stop him. There is an old adage that there are several ways of killing a cat besides choking it with butter. But of late the favored method of disposing of this particular feline has been by way of the courts.

Few people appreciate how many ways there are of hindering, embarrassing, and harassing another through court procedures. A defendant can be put to the most unreasonable trouble by outlandish charges. Although on the face of them they may be foolish, the plaintiff, if he is so disposed, can cause no end of trouble and expense. To receive a legal notice issued on behalf of some strong concern is calculated to terrorize the defendant, while the very existence of the suit is expected to hamper his business, frighten his customers, and thus weaken him financially to the point where he may surrender without a court struggle. A favorite charge seems to be the unlawful use of knowledge and experience gained while in the service of the plaintiff and the divulgence of secret information.

There is certainly a distinction between knowledge and experience and secret trade information. The latter should not be disclosed or used under any acceptable standard of ethics. But an employer should in all fairness recognize that knowledge and experience are the stock in trade of the professional and technical man and steps which would prevent its use would be equivalent to depriving him of his right to make a living and take advantage of his opportunities. We hold no brief for those who capitalize the secret processes and other information of a former employer. A man must be careful to distinguish between this property and his own intellectual property. It would be disastrous to the whole profession if the courts should fail likewise to make such careful distinction. If a man is not to be allowed to capitalize his knowledge and experience, then upon entering the employ of a company he would become essentially bound for life or required at some future time, when the connection might be severed, completely to alter his course and with great disadvantage to himself begin a new career at some time in life when this would be most difficult.

It would be easy for injustice to be done alike to the employer and the former employee, but it is most important that these questions be settled with extreme fairness to all. There are cases now in the courts which because of this point should be watched with care by the chemical profession. A single decision can be momentous in its effects.

⁂

INDEX TO INTERNATIONAL CRITICAL TABLES. We have been concerned with International Critical Tables for very nearly the entire life of the project. We recognize the shortcomings of the seven volumes; we know that, now its pioneering work has been completed, a second effort would yield a far more acceptable research tool; and we also know what a stupendous piece of work it has been. Individuals whose only acquaintance with the tables has come from their use can have no adequate conception of the thousands of man-hours that have been put into the compilation, into the critical selection of material after original sources have been combed, and into the process of preparing the copy and seeing it through the press. Literally hundreds of thousands of dollars have been involved. The net result has been a notable addition to the implements with which scientists can attack their work.

Experience has shown that the index supplied, while comparable with that which has accompanied other less pretentious works, is inadequate and without sufficient detail. The trustees, having a few thousand dollars from unexpended royalties in hand, now propose to use that money, together with receipts from its sale, to prepare and distribute a very thorough index. At one time it was hoped that such an index might be published and distributed without obligation to the subscribers, but a close analysis clearly showed that more money would be required. It was finally decided to ask the present owners of the volumes if they would be willing to pay four dollars as a maximum for an adequate index of the dictionary type.

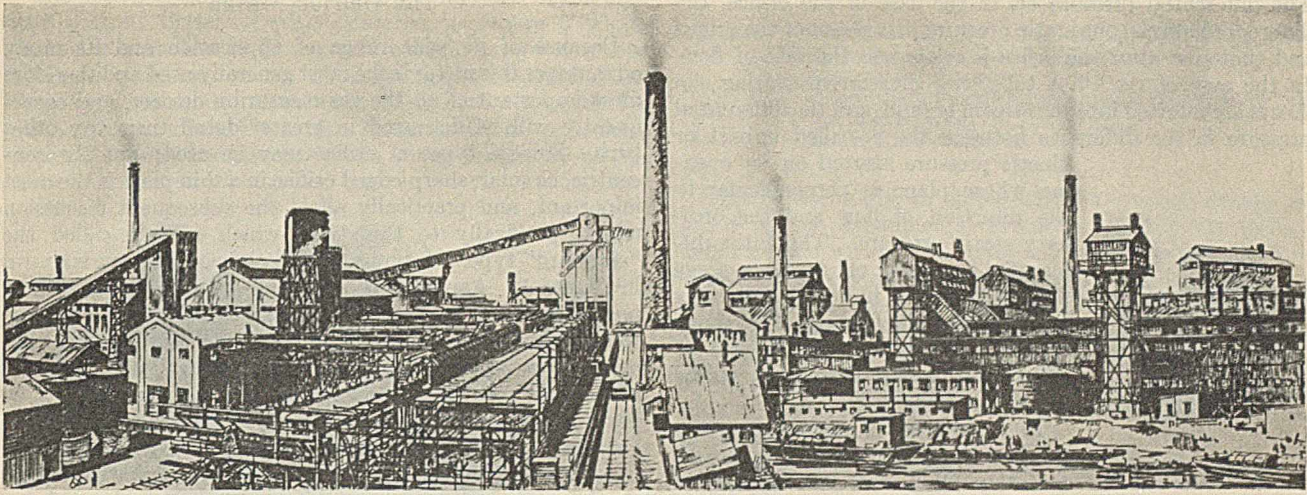
We are very gratified to report that considerably more than the minimum number specified have placed their orders for the index and that the work of preparation will proceed without delay. Because of changes of address and other circumstances, nearly one hundred of these letters have been returned as undeliverable. If you were a subscriber to these volumes and have not received a communication about the index, perhaps you are one of those whose letters went astray. In that case you should, if interested, communicate with the National Research Council, 2101 Constitution Avenue, Washington, D. C. Self-interest would indicate the wisdom of placing an order without delay. The larger the number of indexes ordered, the smaller promises to be the ultimate cost, and in any case it will not exceed four dollars. This is a very small sum to add to the investment already made, and its very addition will increase the value of the total investment quite out of proportion to this further sum. Sets without the index will suffer by comparison.

Users generally, whether owners or not, will be delighted with this news, and we have every reason to believe that the addition of the index will serve to make the volumes enormously useful and to break down practically every barrier which thus far has been found to interfere with their use as a handy reference and veritable storehouse of information.

⁂

ATTENDANCE. We occasionally find chemists who have difficulty in arranging their schedules so as to attend meetings of local sections of the SOCIETY. Once home from the laboratory and plant, it is difficult for them to journey down town, little realizing how much they miss in the contact with their fellows and in the discussion of scientific problems. The man who lives nearest his work is the one most often tardy. Consider by way of contrast the January meeting of the Florida Section held at Panama City. There were twenty-one chemists and members of the section in attendance who did not live at Panama City. These twenty-one people traveled an average of 559 miles per person, or a total of 11,736 miles to make this meeting. Two members held the records, one making a round trip of 1766 miles, and the other 1406 miles to meet with their fellow chemists.

While these figures convey some idea of the size of the state, they are more important as indicative of interest in local section meetings. Comparable distances are traveled by members elsewhere. Such enthusiasm should shame some of our friends who live in populous centers within a few minutes of a meeting, but who never seem to have time to make an appearance.



Measurement of the Flow of Gases and Vapors

Barnett F. Dodge, Chemical Engineering Department, Yale University, New Haven, Conn.

The steadily growing demand by industry for more precise control of processes has greatly stimulated the study of methods of measurement and control and has resulted in many improvements in apparatus and technic. It is the purpose of this paper to review some of the modern methods for continuously measuring and recording gas flow which are in extensive use in industry. The term "gas" will be understood to include condensable vapors, such as steam, but the discussion will refer more specifically to gases that are not condensed at ordinary atmospheric conditions.

IT IS well to bear in mind from the very start that the result of a gas measurement is desired in terms of a volume at some standard condition or in terms of weight if a vapor is being measured. There is no one standard condition that has been agreed upon. Perhaps the most widely used standard to which gas volume is referred is 60° F., 30 inches of mercury (at 32° F.) absolute pressure, and complete saturation with water vapor.

The conditions encountered in the measurement of gas flow are many and varied. The volume of flow may vary from a few thousand cubic feet per hour or even less, to several million cubic feet. The velocity of flow and the pressure, temperature, and composition of the gases to be metered may show great differences. Some gases may be readily condensable or contain condensable components, they may contain solid or liquid particles in suspension, or they may contain corrosive constituents or sulfur compounds, etc. The flow may be quite steady or it may fluctuate over wide limits, and the period of the fluctuations may be quite different from one case to another. The temperature, pressure or composition of the gas being measured by a given meter will usually not be constant. There are difficulties introduced by pulsations or by flow disturbances owing to proximity of the meter to fittings in the line. In some cases a high degree of accuracy is essential, and in others a very moderate degree of accuracy is all that is needed. It may be important that the metering device does not offer appreciable obstruction to the flow, or a considerable loss in pressure may be readily permissible. These are just a few of the problems encountered by the flow-meter manufacturer. It is to be expected that no one type of meter will be entirely satisfactory to meet this wide variety of conditions. Hence, one finds several different types of meters in commercial use and many variations of a given general type.

There are two fundamental elements in all gas meters: (1) the primary element which is inserted into the gas stream and is acted upon by, or exerts an influence on, the flow; and (2) a secondary element or device for registering either the rate of flow or the total flow. The classification given below is based entirely on the first element.

1. Differential pressure meters (also called head meters or kinetic meters)
    - *a.* Orifice
    - *b.* Venturi
    - *c.* Pitot tube
    - *d.* Shunt meter
2. Volumetric or volume-displacement meters
    - *a.* Wet drum-type rotary meters
    - *b.* Diaphragm or bellows type
    - *c.* Rotary type
    - *d.* Gas holders or meter provers
3. Calorimetric or thermal meters
    - *a.* Thomas meter
4. Current or windmill type meters
    - *a.* Turbine meters
    - *b.* Anemometers
5. Miscellaneous Methods
    - *a.* Dilution
    - *b.* Pressure receiver
    - *c.* Area meters

The common feature of all the meters in class 1 (excluding *d* for the moment) is the measurement of two pressures whose difference is related to the velocity of flow. Thus, they directly measure rate of flow rather than total quantity. In the case of 1*a* and 1*b*, a constriction is inserted in the flow line which produces a momentary increase in the average velocity of flow with a consequent decrease in static pressure.

The differential pressure or, in the case of the orifice, the difference between the static pressure just ahead of the orifice and that just after the orfice is related to the rate of flow. In the case of the Pitot tube, two pressure-measuring elements are inserted into the stream of fluid, and the differential pressure is the difference between the so-called impact or kinetic pressure exerted on an opening whose plane is perpendicular to the direction of flow and the ordinary static pressure. The Pitot differential is related, not to the average flow in the pipe, but to the velocity at a particular point. The shunt meter is a rather special type of differential-pressure meter and will be treated separately.

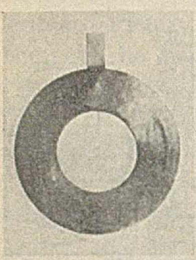

Courtesy of Brown Instrument Co.

FIGURE 1. THIN PLATE ORIFICE

In the volumetric meters, compartments of definite volume are alternately filled with and emptied of batches or isolated volumes of gas. Therefore quantity rather than rate of flow is directly measured. Type 2*a*, though once of considerable importance, is now practically obsolete for large-scale measurement of gases and will not be discussed. Type 2*d* is used only for testing or calibrating other types of meters and will receive very brief consideration.

The principle of the thermal meters is very simple, consisting merely in adding heat to the gas stream; the resulting increase in temperature is a measure of the flow if the rate of adding heat is constant. Conversely, the temperature rise may be maintained at a constant value, in which case the amount of energy dissipated to the gas stream is a measure of the flow. The latter scheme is used in the Thomas meter, the only representative of this class of meters that is used commercially.

In the current meters, a fan wheel or turbine is inserted into the gas stream, and its speed or rotation is related to the velocity of gas flow. Small meters of this class, known as anemometers, are useful for test purposes; but the principle has not been successfully applied to the continuous measurement of large volumes of gas.

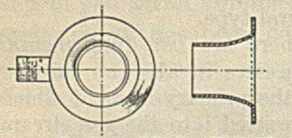

Courtesy of Bailey Meter Co.

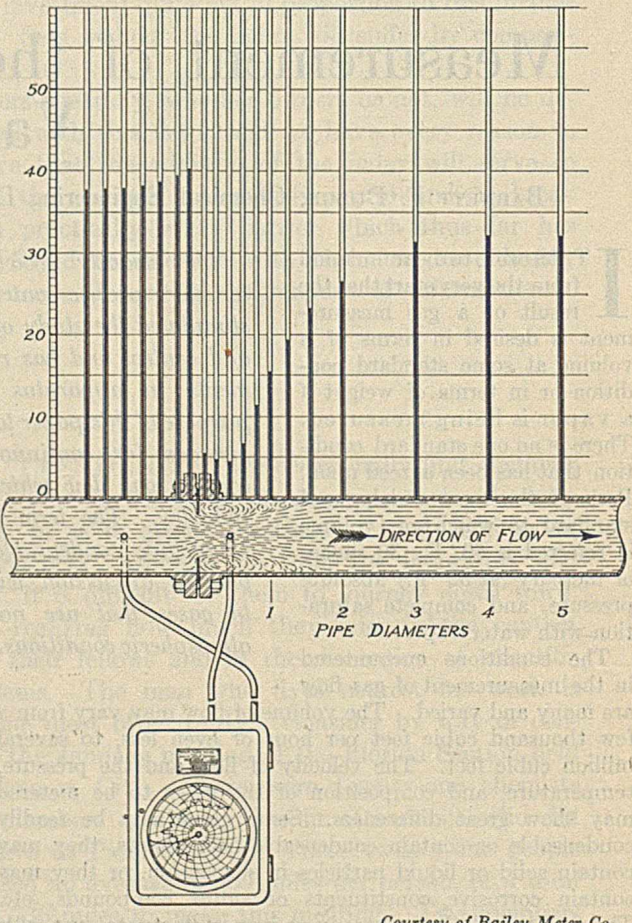
FIGURE 2. FLOW NOZZLE

The methods in class 5 are not regularly used in metering large volumes, but are mentioned for the sake of completeness and because they are sometimes very useful for special cases. In 5*a*, a foreign gas is added to the gas stream to be metered and, after complete mixing has occurred, a sample is taken for analysis. From the content of foreign gas and its known rate of addition, the rate of flow of the main gas stream is readily calculated. As far as the author is aware, this method has not been applied to the commercial metering of gases. It has proved quite useful for test and experimental purposes. To cite one example, it has been applied on a large scale to determine the volumetric efficiency of blast-furnace blowing engines. It has also been used for the calibration of other flow meters, notably steam meters.

Type 5*b* consists simply in determining the pressure increase of a constant-volume receiver as gas is pumped into it. It is useful in testing compressors. Type 5*c* consists of a movable element suspended in the gas stream, the motion of which causes the area through which the gas must flow to vary. The element will take up an equilibrium position such that its weight is balanced by the differential pressure across the constricted area. Meters of this type have been used to measure the compressed-air consumption of drills and other pneumatic tools.

THE ORIFICE METER

Because of its wide range of application and its many advantages this meter is the most generally used and therefore most important of all the gas-measuring devices, and consequently will be discussed in greater detail than any other type. Several types of orifice may be used; but the concentric, circular, sharp-edged orifice in a thin plate is the most important, and practically all of the subsequent discussion refers specifically to this type, which will be called the "standard" type. A typical orifice plate of this type is shown in Figure 1. Another type of orifice, usually called a flow nozzle, is shown in Figure 2. Such a nozzle costs more than the standard orifice, especially in the larger sizes, and is used only in exceptional circumstances. Practically its only advantage over the standard type is the approximately 40 per cent greater flow capacity for a given pressure differential. Orifices shaped like the segment of a circle (segmental orifice), or circular orifices installed eccentrically in the pipe have some special applications to be mentioned later.

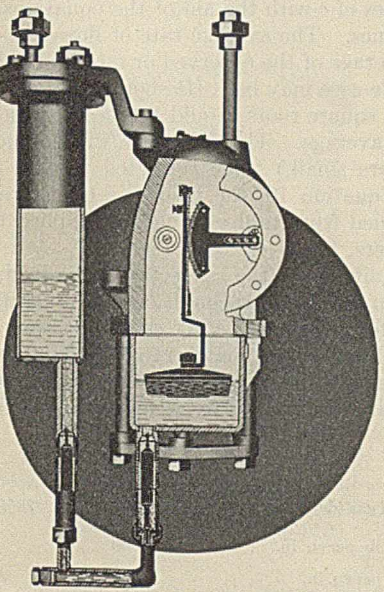


Courtesy of Bailey Meter Co.

FIGURE 3. DIAGRAM OF ACTION OF AN ORIFICE

The orifice plate may be of various metals, usually monel, bronze, nickel, or stainless steel, and is generally from $^1/_{32}$ to $^1/_{16}$ inch thick. In the large sizes where the plate must be thicker to secure the necessary rigidity or because of a large differential pressure, it is chamfered on the downstream side to leave a thin edge. It goes without saying that the orifice must be very accurately machined to a definite size. It is usually installed in the line between flanges, care being used to secure a reasonably accurate centering. The differential pressure is obtained by pressure taps suitably located, one on either side of the orifice plate.

The action of an orifice on the flow conditions in the pipe may best be discussed with reference to Figure 3 which shows the variation in fluid pressure along a pipe line containing a standard orifice. (This particular diagram is for water flow, but conditions are entirely similar for the case of a gas.) At approximately 1 pipe diameter (it is convenient to use this unit because it enables many results to be expressed in a form that is nearly independent of pipe size) above the orifice, the pressure is substantially constant for a small change in tap location. It rises sharply to a maximum as the orifice is approached and then drops abruptly as the orifice is passed. The pressure continues to drop for a short distance below the orifice and then gradually rises to a new constant value at about 4 diameters downstream, which is distinctly less than the constant value above the orifice. The point of minimum pressure has been shown to coincide with the point at which the stream of fluid issuing from the orifice contracts to a minimum diameter (the so-called Vena Contracta). The exact shape of the static-pressure curve depends on many factors, but the general outline is the same for all fluids and practically all conditions of flow. The extent to which the pressure returns to the value above the orifice is mainly a function of the ratio of the diameter of the orifice to that of the pipe. When this ratio is 0.40, the percentage loss in pressure is about 80 per cent, and, when it is 0.70 (about the upper limit for a standard orifice in good practice), it is 50 per cent.



Courtesy of Foxboro Co.

FIGURE 4. MERCURY-FILLED DIFFERENTIAL GAGE

QUANTITATIVE RELATIONSHIPS. The starting point for the development of all fluid-flow equations is the Bernoulli theorem which is a special case of the first law of energy. The general formula for gaseous flow through an orifice is based on the assumption of reversible (frictionless) adiabatic flow. The details of this development may be secured by consulting some of the sources given in the bibliography at the end of this article. For practically all the cases that occur in practice in the measurement of large volumes of gas, the pressure differential across the orifice is a relatively small percentage of the absolute static pressure. For this special case, where the fluid may be considered to be incompressible, the general formula is very much simplified in that it reduces to the simple hydraulic formula:

$$\sqrt{u_2^2 - u_1^2} = c\sqrt{2g\,\Delta h} \qquad (1)$$

where u_1 = av. linear velocity of fluid in pipe just above orifice
u_2 = av. linear velocity of jet issuing from orifice
g = acceleration of gravity
Δh = differential pressure around orifice expressed in head of fluid flowing
c = an empirical coefficient

This is essentially an empirical equation, and its use depends on the experimental evaluation of the constant, c, under a wide variety of conditions. When a consistent set of units is used, c is remarkably constant at a value around 0.60 for a wide variety of conditions. Thus it has practically the same value whether the fluid be a gas, steam, water, or oil. The value of c does depend, however, on the location of the pressure taps, and may be quite a little different from the value given above for certain locations that are used in practice.

By eliminating u_1 in terms of r and u_2, where r = ratio of orifice diameter to pipe diameter or $\frac{d}{D}$, and u_2 in terms of V_0, the volume flowing per unit of time under the orifice conditions, and substituting $\frac{\Delta p}{\rho_0}$ for Δh, where Δp = differential pressure and ρ_0 = density of the gas at the orifice conditions, Equation 1 is transformed into:

$$V_0 = c\,\frac{\pi\, d^2\sqrt{2g\,\Delta p}}{4\sqrt{1 - r^4}}\sqrt{\frac{1}{\rho_0}} \qquad (2)$$

Since the pressure of the gas and hence its density are different on the two sides of the orifice, the value of c will depend to some extent on whether upstream, downstream, or average conditions are chosen for V_0 and ρ_0. The choice is a purely arbitrary one and not of very great practical importance when the differential is small, but for the sake of definiteness upstream conditions will be taken as standard. In much of the flow-meter literature, another coefficient, c', which = $\frac{c}{\sqrt{1 - r^4}}$, is used. The difference is significant when r is greater than 0.35, which includes most of the actual cases.

It is probable that c depends somewhat on r and on the properties of the fluid, but the effects are small and not yet very definitely known. Recent careful measurements by various experimenters, using air, water, and steam, indicate that c approaches a value of 0.597 as r decreases and $\frac{\Delta p}{p}$ (the fractional drop in pressure) decreases. At large values of r (0.8 for example) c is of the order of 0.62. Increase in $\frac{\Delta p}{p}$ results in a decrease in c when the rate of flow is expressed as a standard volume; but, if the mean density instead of the upstream density is used, c is practically constant for a wide variation in $\frac{\Delta p}{p}$. Thus when c is based on upstream conditions, its value is appreciably affected if the pressure drop is as much as 5 per cent of the static pressure, whereas the c based on mean conditions is affected to about the same extent by a 50 per cent pressure drop.

To put Equation 2 in a directly useful form, V_0 must be transformed to the volume at the desired standard condition and ρ_0 must be expressed in terms of the pressure, temperature, and composition of the gas. No general relationship applying to all cases is available, since it depends on the properties of the particular fluid concerned under the given conditions. Fortunately, the ideal gas laws can be assumed without serious error for the great majority of cases. This furnishes a relatively simple solution of the problem that is applicable to all gases and vapors which may be considered ideal.

Applying the gas laws, one obtains

$$V_s = V_0 \frac{1 - x_0}{1 - x_s} \left(\frac{P_0}{P_s}\right) \left(\frac{T_s}{T_0}\right) \tag{3}$$

where V_s = volume flowing at standard conditions
x_0 = volume fraction or mole fraction of water vapor at orifice condition
x_s = mole fraction water vapor for saturation at standard condition
P_0 = abs. pressure at upstream tap = $P_G + B$ where
P_G = gage pressure and B = barometric pressure
P_s = abs. standard pressure
T_0 = abs. temp. at orifice = $t_0 + 459.6°$ F.
T_s = abs. standard temp. = $t_s + 459.6°$ F.

Also, from the gas law,

$$\rho_0 = \frac{P_0 M_0}{R\ T_0} \tag{4}$$

where R = gas constant
M_0 = mol. weight of gas at orifice conditions which = $M_D(1 - x_0) + 18\, x_0$, where M_D = mol. weight of dry gas

Making these substitutions in Equation 2, there results:

$$V_s = C_1 \sqrt{\Delta p} \left(\frac{1 - x_0}{1 - x_s}\right) \left(\frac{T_s}{P_s}\right) \sqrt{\frac{P_G + B}{M_0(t_0 + 459.6)}} \tag{5}$$

where C_1 stands for $\dfrac{\pi c d^2 \sqrt{R} \sqrt{2g}}{4 \sqrt{1 - r^4}}$

Having chosen the units and the standard conditions, and having determined what the average upstream orifice conditions will be, all the terms on the right-hand side of the equation are fixed except $\sqrt{\Delta p}$. Therefore,

$$V_s = C_2 \sqrt{\Delta p} \tag{6}$$

C_2 is an orifice coefficient which would be furnished by the meter manufacturer. Knowing the average value of the square root of the differential pressure, the standard volume is readily obtained by a single multiplication.

The meter will be used under average conditions which are not necessarily the same as those for which the coefficient was figured. Thus if x_0', P_G', B', M_0', and P_0' are the actual average conditions of the gas just above the orifice, and V_s' is the corrected volume for these conditions, then, by writing Equation 5 for the two cases and dividing, one obtains

$$V_s' = V_s \left(\frac{1 - x_0'}{1 - x_0}\right) \sqrt{\frac{P_G' + B'}{P_G + B}} \sqrt{\frac{M_0}{M_0'}} \sqrt{\frac{t_0 + 459.6}{t_0' + 459.6}} \tag{7}$$

or

$$V_s' = V_s f_1 \times f_2 \times f_3 \times f_4 \tag{8}$$

The V_s computed from the value of the coefficient and the average of the $\sqrt{\Delta p}$ by Equation 6 can be corrected by multipliers for variations from the conditions on the basis of which the coefficient was computed. The factor f_1, to correct for moisture, is frequently omitted because it may generally be neglected and is difficult to determine. The factor f_3 also involves the moisture content in any rigorous treatment. Here also the moisture is usually neglected and $\sqrt{\frac{M_0}{M_0'}}$ is frequently used in the form $\sqrt{\frac{S_0}{S_0'}}$ where S = specific gravity of the dry gas at some standard condition of pressure and temperature referred to dry air at the same condition.

In those cases where the value of P_0 (the absolute pressure of the gas at the orifice) varies widely, it is generally more satisfactory to retain P_0 as a variable and transform Equation 5 to

$$V_s = C_3 \sqrt{P_0 \Delta p} \tag{9}$$

and Equation 8 then becomes

$$V_s' = V_s \times f_1 \times f_3 \times f_4 \tag{10}$$

It is practically impossible to test gas meters under the conditions of use, and hence the standard procedure for calibration is to compute the coefficients (C_2 or C_3) from the known values of c with the aid of the equations given above or similar ones. The average rate of flow is then computed from the average of the observed or recorded values of Δp or $P_0\, \Delta p$ as the case may be. (It should be noted that strictly the average square roots should be used and not the square root of the average. The difference will not be great if the variations are small.) The corrected volume is then computed by Equation 10, the values of the correction factors being obtained from tables or charts supplied by the meter manufacturers.

The magnitude of the corrections involved, due to departure from the assumed conditions for which the coefficient was computed, may be readily estimated from Equation 7. A numerical illustration may serve to make this clear. Suppose that the assumed conditions for calculation of an orifice coefficient and the actual average flow conditions were as follows:

	ASSUMED CONDITIONS	ACTUAL CONDITIONS
Composition of gas (dry basis)	75% H_2 and 25% N_2	78% H_2 and 22% N_2
Dew point, ° F.	70	50
Gage pressure, lb. per sq. in.	1.00	1.50
Temperature, ° F.	80	70
Barometer, lb. per sq. in.	14.50	14.70

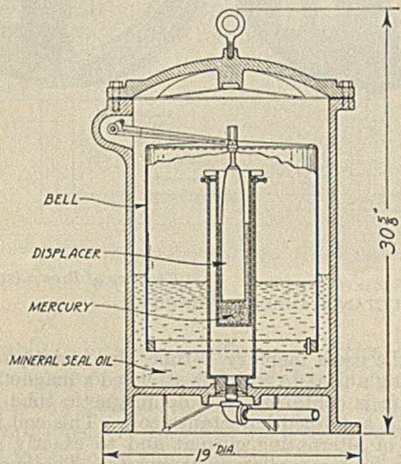
At 50° F. the vapor pressure of water = 0.178 pound per square inch, and at 70° F. it equals 0.363. Therefore, $x_0' = \frac{0.178}{16.20} = 0.01098$; $x_0 = 0.0234$; $M_0 = 0.9766\ (0.75 \times 2.016 + 0.25 \times 28.00) + 0.0234 \times 18 = 8.732$; $M_0' = 7.844$; $f_1 = 1.011$; $f_2 = 1.0222$; $f_3 = 1.054$; and $f_4 = 1.009$.

Substituting in Equation 8, $V_s' = 1.10\ V_s$.

Therefore, a neglect to correct for these rather slight changes in condition would result in a 10 per cent error. Generally, the correction factors will not all be greater or less than unity, as the case may be, but will compensate somewhat. On the other hand, there are other cases where the variation from the assumed average conditions will result in much greater error than in the illustration given.

Steam meters may sometimes be checked in place by collecting and weighing or determining the volume of the condensate, but this is only in exceptional cases. In the case of meters operating on saturated steam, there is the additional correction necessary for priming which amounts to about 1 per cent for each 1 per cent of priming.

LOCATION OF PRESSURE TAPS. There are three different locations of taps that are in common use. Location of the upstream tap 2.5 pipe diameters from the orifice, and the downstream one 8.0 diameters away is commonly used in the natural-gas industry, but is otherwise rarely employed. In this case the differential pressure is the over-all loss in pressure due to the orifice acting as an obstruction in the line. The differential produced by a given flow is naturally less than for the closer tap locations. This location requires a greater run of straight pipe but has the advantage that the taps do not need to be very accurately located, since the pressure changes very slowly on either side of these points. The most widely used location is at approximately 1 diameter upstream, and at the Vena Contracta on the downstream side. This gives very nearly the maximum differential; and, since the Vena Contracta is a minimum point, the change in pressure with a slight change in location will be the least as compared with any of the adjacent locations. Considerable experimental work has been carried out to locate the minimum point for a wide variety of conditions. The published data indicate that its location is nearly constant at 0.5 diameter. The meter manufacturers publish tables giving their recommended location of the taps for each size of pipe and value of r (ratio of diameters). Another location commonly used is to drill into the flanges themselves so that the centers of the holes are approximately 1 inch from the nearer face of the orifice plate. Some firms supply special flanges with the taps already in them for use with their orifices. Recent work of the Bureau of Standards on orifice coefficients shows that there is no appreciable difference between the two last-mentioned locations when the pressure differential is small and the diameter ratio does not exceed 0.7.



Courtesy of Bailey Meter Co.

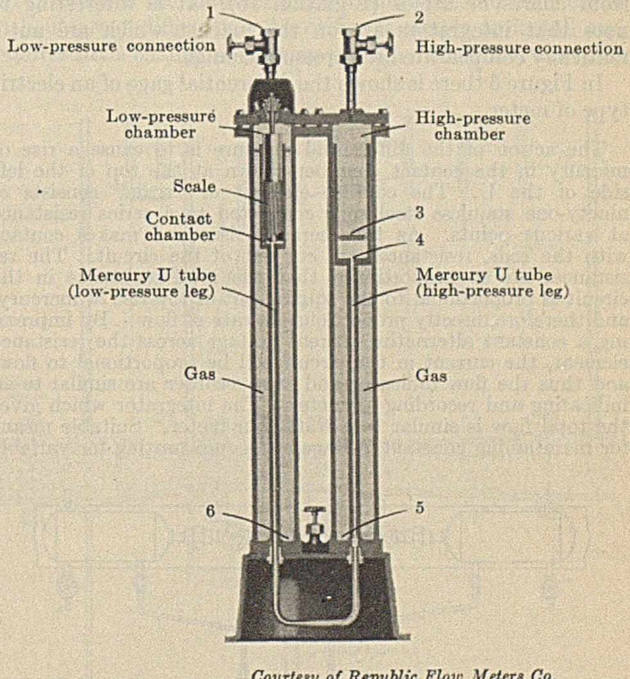
FIGURE 5. OIL-SEALED GAGE FOR SMALL DIFFERENTIAL PRESSURES

INDICATING, RECORDING, AND INTEGRATING THE FLOW. The differential pressure around an orifice is measured in terms of a fluid head by a differential gage, which may be an ordinary U-tube manometer, and the observed head is an indication of the instantaneous rate of flow. For commercial purposes it is generally necessary to know the total flow over a given period and is very desirable to have a time record of the rate of flow. By a suitable mechanism the differential pressure can be made to move a pen over a chart driven by clockwork so that a curve of the change of Δp with time is traced. It is also possible to integrate continuously the instantaneous rates to obtain the total flow. Various ingenious methods for accomplishing these ends have been developed, but it will be possible to describe only some of them here in barest outline. In all cases there is a differential gage which is essentially a U-tube filled with a fluid, usually mercury or a mineral oil. The mechanism which is acted upon by the differential may be purely mechanical or it may involve electrical circuits.

Figure 4 shows one form of the mechanical type of differential gage. The motion of the mercury in the U-tube is transmitted to the pen arm by the float and segment lever mechanism, and the pen traces a differential pressure line on the circular chart. Since the static pressure may vary considerably and since it has been shown that a knowledge of the average static pressure is necessary to compute the flow, a static pressure-recording mechanism is usually combined with the differential gage so that both pressures are recorded on the same chart.

Another differential gage of the mechanical type is shown in Figure 5.

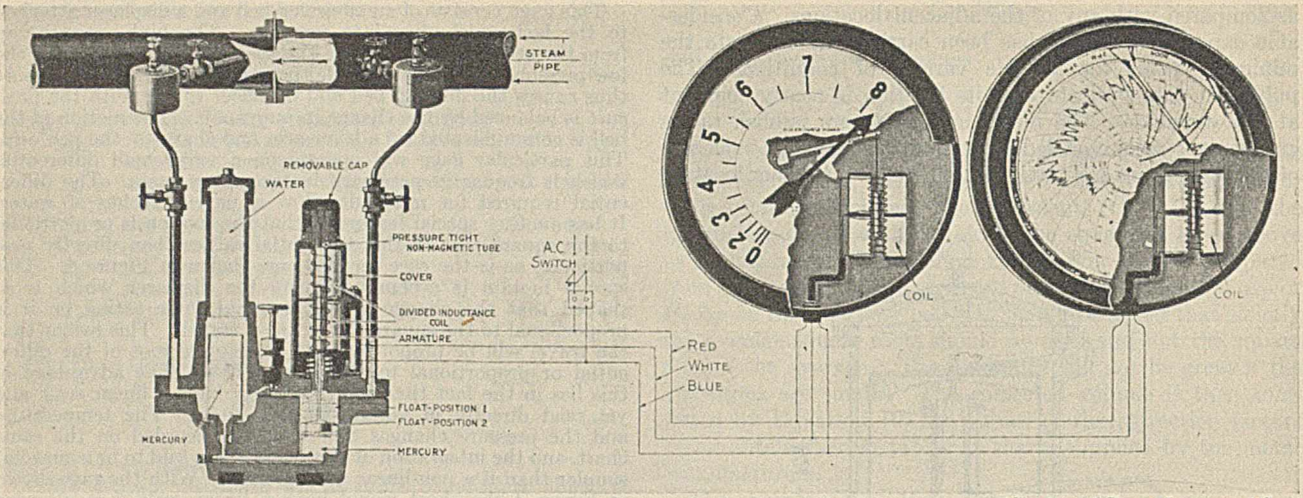
This gage consists of an oil-sealed bell and a displacer attached to the bell which dips into mercury. The high-pressure tap from the orifice is connected to the space inside the bell, and the low-pressure tap to that outside the bell. A differential pressure thus causes the floating bell and displacer to rise until the pressure is balanced by the change in buoyancy. The motion of the bell is communicated by a lever arm and shaft to the pen arm. This particular gage will operate on a very small differential which is frequently necessary in measuring gases. The differential required for maximum flow is only 2 inches of water. It has another special feature in that the motion is proportional to the square root of the differential rather than directly proportional, as is the case for the gage shown in Figure 4. This special motion is accomplished by the displacer which is so shaped that the change of the buoyant force acting on it is proportional to the square of the linear travel. This means that the travel will be proportional to the square root of the differential or proportional to the rate of flow. The advantage of this lies in the fact that the chart may have a linear scale and yet read directly in volume of flow units. The temperature and the pressure changes can easily be recorded on the same chart, and the integration of the rate curve is said to be somewhat simpler than if a non-linear scale is used. With the gage shown in Figure 4 the chart would have a linear scale if it recorded differential pressure, but, if it recorded rate of flow, it would have a square-root scale.



Courtesy of Republic Flow Meters Co.

FIGURE 6. DIFFERENTIAL GAGE OF AN ELECTRIC TYPE OF ORIFICE METER

The total flow may be readily obtained from the charts with the aid of planimeters. If it is assumed that the chart is a time record of the differential pressure and the static pressure, then by means of an ordinary radial planimeter the average values of p and Δp are obtained; and the products of their square roots multiplied by the time and by a factor (Equation 9) give the total flow for that period of time. If p and Δp vary widely, a special planimeter which averages square roots should be used because the flow is proportional to average square roots and not to the square root of the average. If the static pressure does not vary much, the meter may be equipped with an automatic planimeter or integrator which follows the variations in differential pressure or rate of flow and records the total flow by a counter. Whatever method is used to obtain the total flow, it is still subject to the corrections already discussed, owing to variations of pressure, temperature, humidity, and specific gravity. This can be taken care of by multiplying factors obtained



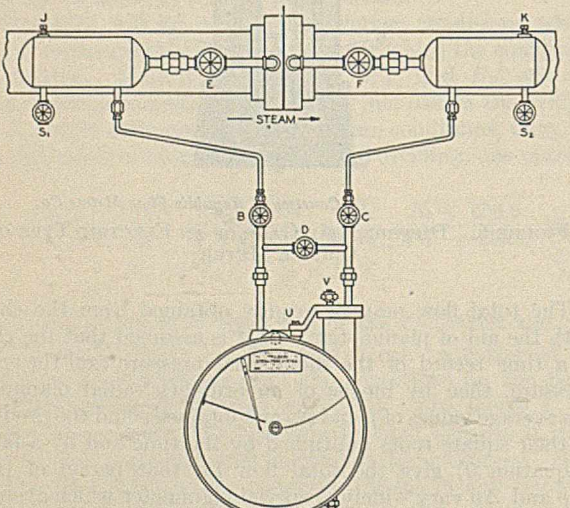
Courtesy of Brown Instrument Co.

FIGURE 7. DIFFERENTIAL PRESSURE GAGE USING INDUCTANCE BRIDGE PRINCIPLE

from charts or tables (Equation 10). It is interesting to note that integrators are on the market which are automatically compensated for pressure change.

In Figure 6 there is shown the differential gage of an electric type of meter.

The action of the differential pressure is to cause a rise of mercury in the contact chamber shown at the top of the left side of the U. The contact element or "scale" consists of ninety-one stainless steel rods connected to a series resistance at various points. As the mercury rises and makes contact with the rods, resistances are cut out of the circuit. The resistances are so proportioned that the total resistance in the circuit is proportional to the square root of the rise of mercury, and therefore directly proportional to rate of flow. By impressing a constant alternating-current voltage across the resistance element, the current in the circuit will be proportional to flow, and thus the flow indicator and flow recorder are similar to an indicating and recording ammeter. The integrator which gives the total flow is similar to a watt-hour meter. Suitable means for maintaining constant voltage and compensating for variable external resistance are incorporated in the meter. For very small differentials, the motion of the mercury in the contact chamber may be magnified by the use of a floating bell and a displacer.



Courtesy of Foxboro Co.

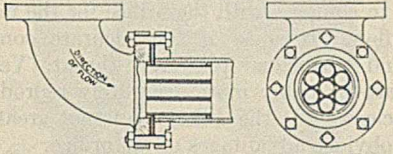
FIGURE 8. TYPICAL PIPING ARRANGEMENT FOR STEAM METER

Another electrical type involving an interesting principle is shown in a schematic way in Figure 7.

There is the usual mercury U-tube, the variation in mercury level operating a float to which is attached a magnetic armature. The armature is contained in a nonmagnetic tube surrounding which there is a divided inductance coil. This coil is connected to a source of alternating current and to exactly similar coils in indicating and recording instruments. The motion of the armature attached to the float causes a change in the ratio of the voltage drops across the two coils, which causes changes in the magnetic flux in coils located in the instruments, resulting in unbalanced magnetic forces which are balanced by a motion of armatures suspended in the instrument coils. The armatures move to such a position that the voltage ratios across the two sections of the divided coils will be equalized in all three sets of coils. The motion of the armature is transmitted to a pointer or a pen to indicate or record the flow. The motions of the armatures in the instruments are proportional to that of the armature attached to the float and therefore to the differential pressure. For direct reading instruments, a square root scale is therefore necessary. The total flow is obtained in the same way as in the case of the mechanically operated meters. The particular gage shown in Figure 7 is for steam where the allowable differential pressure is generally much greater than for gases. For small differentials of the order of a few inches of water, the armature is moved by a floating bell.

The chief advantage of the electrical type of flow meter is that it permits the locating of the instruments at practically any distance desired from the point of measurement. A large number of instruments can be conveniently located in a central control room. With the mechanically operated meters the remote location of the recorder is a more difficult matter because the connection to the primary element is by pipe lines which must be absolutely tight and free from any pockets where liquids could collect which would cause a false registering of the differential. On the other hand, the mechanical types are entirely self-contained. Both types can be obtained for a wide range of differential and of static pressures. It should be noted that the differential gages of any meter installation can be readily checked against known differential pressures and readjusted or corrected for any errors that may be found. In fact, a regular servicing of the meters after they are installed is highly desirable and practically necessary if they are to continue functioning with good accuracy.

NOTES ON ORIFICE INSTALLATION. The size of orifice to use is readily calculated by Equation 2 when the average flow conditions are known and the maximum differential pressure has been decided upon. The maximum differential pressure may be limited to a few inches of water for gases that are flowing at pressures only slightly above that of the atmosphere. For steam or gases at pressures well above atmospheric, the allowable differential pressure is determined more by the requirements of the differential gage to be used than by anything connected with the flow. In the measurement of very large flows, the cost of power necessary to force the gas through the orifice may be a factor in determining the size. It is inadvisable to have the orifice diameter greater than 0.7 of the pipe diameter for a concentric orifice because at high values of this ratio, extreme accuracy in centering is required, because the pipe diameter must be known more accurately, and because roughness of the pipe surface has more effect on the results.



Courtesy of Republic Flow Meters Co.

Figure 9. Use of Straightening Vanes

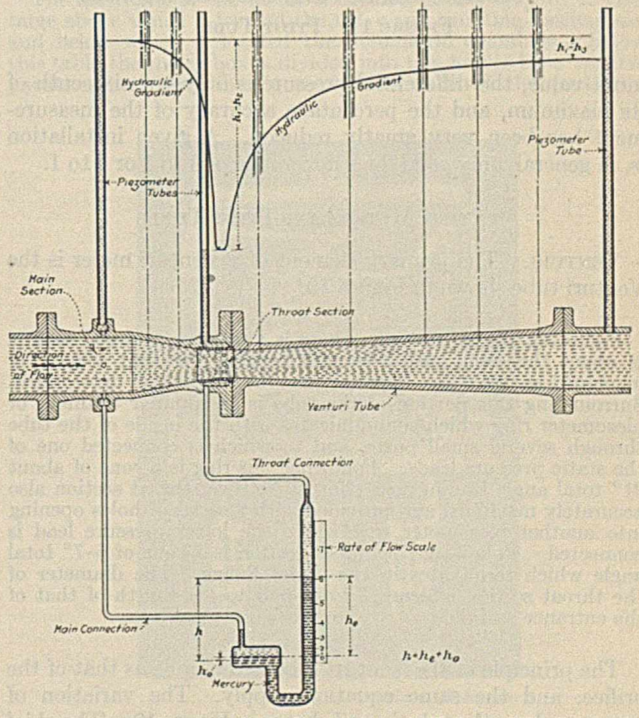
It is desirable to locate the orifice in a vertical line because there is less chance of solids or liquids settling from the gas and accumulating behind the orifice plate and disturbing the flow conditions. If installed in a horizontal gas line, the pressure taps should run from the top of the pipe and be provided with drain cocks at low points. One large meter company advocates the use of segmental orifices or circular orifices installed eccentrically so that the bottom of the orifice is flush with the bottom of the pipe for all horizontal lines, to minimize the trouble from accumulations of foreign material. As far as the author is aware, there are few published data on the flow characteristics of such orifices. They are said to be preferable to the concentric orifice where a large ratio of orifice diameter to pipe diameter is necessary, and they also throw the position of the Vena Contracta further downstream from the orifice plate, which is sometimes desirable.

When condensable vapors are to be measured, the two pressure leads must be filled with the liquid condensate to the same level so that the heads of liquid over the mercury in the gage will be exactly equal in the two leads when no flow is taking place, and will differ only by the amount equal to the differential head of mercury when a flow is being measured. Figure 8 shows a typical piping arrangement for a steam meter. The two chambers beside the pipe are condensers to aid in maintaining the water levels in the same horizontal plane when the flow is varying. The orifice plate for a steam meter is also generally provided with a small drain hole that is located at the bottom of the pipe and allows liquid to pass through the plate instead of accumulating behind it.

In order that the standard values of the orifice coefficients can be relied upon with an accuracy of a few per cent, it is necessary that the orifice be at certain minimum distances from any fittings which are apt to cause disturbances of the flow. This is especially true on the upstream side. It is not possible to give any hard and fast rule to cover this point, but in general the orifice should be not less than 10 to 15 pipe diameters from any fittings or obstructions on the approach side, and at least 2 diameters on the downstream side. Where the proper runs of straight pipe ahead of the orifice cannot be obtained, straightening vanes (Figure 9) are commonly installed. These are made in various forms, but consist in general of a "honeycomb" of some sort which eliminates the larger eddies or swirls.

Corrosive gases introduce special problems. The majority of the differential gages are constructed of steel and contain mercury, and hence they would not be suitable for gases that attack these materials. The gages can be sealed with liquids to prevent the gas from coming in direct contact with the gage, but all gases are soluble in all ordinary liquids and this does not completely prevent attack. The use of absorbent chambers in the pressure lines can be used in some cases. Thus, for gases containing hydrogen sulfide, a purifier filled with an active iron oxide should be suitable. If a flow indication without record is all that is needed, the orifice installation is very much simplified, and various special materials can be used to combat corrosion.

Advantages and Limitations of Orifice Meters. The orifice method has a very wide range of application. It can be used for almost any rate of flow and for a wide variety of pressures and temperatures. Orifices as large as 70 inches in diameter have been made, and differential gages for pressures as high as 5000 pounds per square inch are available. The first cost is relatively low; and, as the size of the pipe increases, the only part of the meter that increases is the orifice, which is relatively inexpensive. There are no moving parts in the line of flow, and chances of clogging from impurities in the gas are at a minimum. The only part to get out of order is the differential gage, and that can be checked without great difficulty. An orifice is simple to install and requires little change in existing piping. The space occupied is small. A given installation can easily be changed to meter different rates of flow merely by changing orifice plates. It is portable and therefore available for test purposes, and several orifices can be connected to one differential gage which is sometimes useful for plant tests.

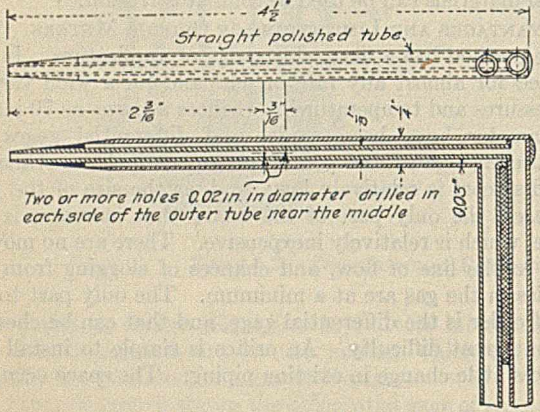


Courtesy of American Society of Mechanical Engineers

Figure 10. Cross Section of Venturi Meter

From the previous discussion of the factors affecting the orifice meter, it should be evident that any figure cited as to the accuracy of an orifice meter would have but little meaning. Besides all the factors affecting the primary element, there are sources of inaccuracy in the secondary element also that must be included in any over-all estimate of the accuracy of an orifice meter. When installed and operated under ideal conditions and when all known precautions are taken and all corrections applied, the flow might be determined with an accuracy of 1 per cent or better. Probably in the majority of cases the accuracy is between 2 and 5 per cent, and in many instances the error is probably greater than 5 per cent.

An orifice meter is not satisfactory where the rate of flow varies over wide limits. Thus, from the orifice equation it can be seen that if the flow drops to one-fourth of its maximum value, the differential pressure is only one-sixteenth of its maximum, and the percentage accuracy of the measurement has been very greatly reduced. A given installation is, in general, only good for a flow range of 3 to 1 or 4 to 1.



Courtesy of American Society of Mechanical Engineers

FIGURE 11. PITOT TUBE

VENTURI METERS AND PITOT TUBES

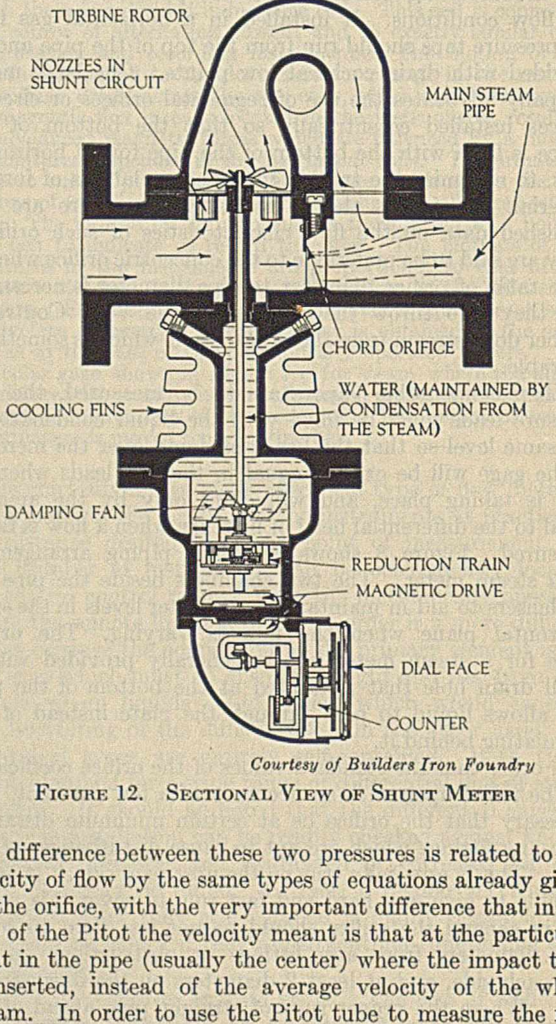
VENTURI. The primary element of a Venturi meter is the Venturi tube shown in Figure 10.

> Following the inlet flange, there is a short cylindrical section of about the same inside diameter as the pipe, but accurately machined so that the diameter may be accurately determined. Surrounding this portion of the tube is an annular chamber or piezometer ring which communicates with the inside of the tube through several small ports, and to which is connected one of the static pressure leads. Following this ring is a cone of about 21° total angle leading to a short cylindrical throat section also accurately machined and provided with a series of holes opening into another piezometer ring where the lower pressure lead is connected. Following the throat section is a cone of 5–7° total angle which terminates in the outlet flange. The diameter of the throat section is generally one-half to one-fourth of that of the entrance section.

The principle of the Venturi tube is the same as that of the orifice, and the same equations apply. The variation of pressure along the tube is well shown in Figure 10. The chief difference from the orifice lies in the fact that the flow through the Venturi is nearly frictionless and that there is no contraction of the jet of fluid to a smaller diameter than the throat diameter, as occurs in the orifice. As a result, the coefficient (Equation 2) varies between 0.95 and 0.99 instead of the 0.60 value for a sharp-edged orifice. The shape of the exit tube from the throat section is such that the static pressure lost owing to the increase in velocity is nearly all regained so that the over-all drop in pressure for a Venturi is quite small. This is one advantage of the Venturi over the orifice, which may be an important factor in some cases. Thus, if the conditions of the installation were such that a permanent pressure drop of 2 inches of water was all that could be allowed, this would limit the maximum differential in the case of an orifice to something between 2 and 3 inches of water; and, if the flow varied much, the lower rates would not be measured very accurately. On the other hand, a much higher differential for the same permanent loss in pressure could be used with the Venturi, and it would be accurate over a wider range. The secondary elements of a Venturi meter installation (that is, the differential gage and the methods for indicating, recording, and integrating the flow) are the same as for the orifice.

The Venturi has a greater initial cost than the orifice meter (especially in the larger sizes), is more difficult to install, is less easily changed to meter different flows, and is more likely to become clogged. For these reasons it is seldom able to compete with the orifice for the measurement of gaseous flow. Because of the accurate control of the approach and recession from the throat, Venturi-meter coefficients are probably more accurately reproducible than orifice coefficients, but the difference is not great enough to balance the obvious advantages of the orifice.

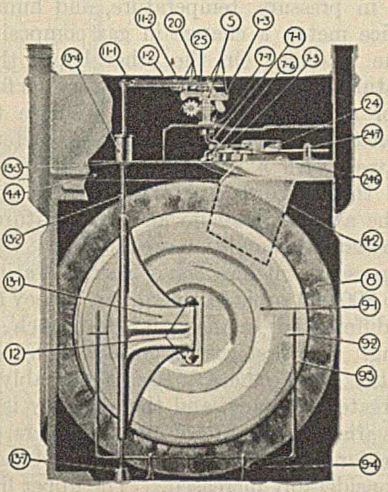
PITOT TUBE. Instead of placing a constriction in the line which produces a differential static pressure, the Pitot tube consists merely of two pressure-measuring tubes, one of which (the impact tube) measures the kinetic head of the fluid and the other (the static tube) measures the static pressure. The difference between these two pressures is related to the velocity of flow by the same types of equations already given for the orifice, with the very important difference that in the case of the Pitot the velocity meant is that at the particular point in the pipe (usually the center) where the impact tube is inserted, instead of the average velocity of the whole stream. In order to use the Pitot tube to measure the rate of volume flow, it is necessary either to explore the cross section of the pipe to obtain an average velocity, or to place the impact tube at the center of the pipe and rely on previously determined data to give the ratio between the average velocity and the maximum velocity at the center. The first method is obviously out of the question for commercial metering, and the second suffers from the disadvantage that



Courtesy of Builders Iron Foundry

FIGURE 12. SECTIONAL VIEW OF SHUNT METER

the ratio $\frac{u_{av.}}{u_{max.}}$ is not accurately known for a wide range of conditions. The Pitot tube is also more sensitive to disturbances of the flow than either of the other differential-pressure methods. Furthermore, since the Pitot tube does not produce any acceleration of the flow, the differential pressure produced is small except at high velocities of flow, and is difficult to measure accurately. Thus, air at atmospheric pressure and 70° F., flowing at a velocity at 20 feet per second, would produce a Pitot differential of only 0.14 inch of water. This could not be measured accurately by the commercial types of differential gage now available. With an orifice, the differential pressure can be brought to any desired value merely by proper choice of orifice diameter. For these reasons the Pitot tube has practically no application to the commercial metering of gases. It is very useful, however, as a portable instrument for test purposes where high accuracy is not required. A convenient form of tube for this service is one in which the two tubes are combined, as shown in Figure 11. The coefficient for such a tube is very close to unity. The insertion in the pipe line is very easily accomplished, provided the pressure is not far from atmospheric. For higher pressures it would be better to use separate tubes securely fastened through the pipe wall. For low differential pressures some form of inclined or other multiplying gage would be necessary.



Courtesy of American Meter Co.

FIGURE 13. BELLOWS TYPE OF DISPLACEMENT METER

SHUNT METER

In Figure 12 is shown a recently developed type of meter for small installations, known as a shunt meter, which is a true differential-pressure meter, but which differs radically from the differential-pressure types previously discussed.

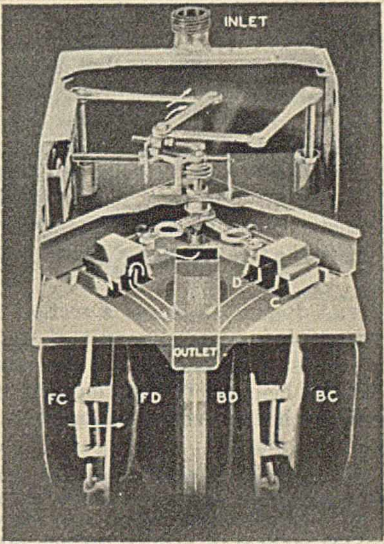
The primary and secondary devices are combined in a single unit. A chord type of orifice in the main line of flow produces a differential pressure which causes a flow through the nozzles into the shunt circuit. The stream through the nozzles impinges on a small turbine wheel whose speed of rotation is proportional to the square root of the differential head produced. Since the flow rate is also proportional to the one-half power of the differential head, the rotations of the turbine wheel are proportional to the total flow. It is thus a true differential-pressure meter, the shunt circuit and turbine being merely a special device for translating differential pressure into total flow. The rotating shaft is magnetically coupled to another shaft operating a counter in an entirely separate compartment. At the lower end of the turbine shaft is a fan wheel rotating in a water-filled chamber. This serves to damp the motion of the turbine so that the speed of rotation is relatively low, reducing wear on the bearings and also minimizing the relative importance of bearing friction.

This meter is built in three sizes only, for 2-, 3-, and 4-inch lines. There are two ranges of differential pressure used, one with 80 inches of water as the maximum, and the other with a maximum of 20 inches of water. Its advantages are that it is cheap and simple, easy to install, and entirely self-contained. It can be used on larger than 4-inch lines by installing it in a by-pass around a standard orifice. It is applicable over a considerable range of pressures and temperatures. It is claimed by the makers to have an accuracy of ±2 per cent over a 10 to 1 range of flow. This refers to the accuracy obtained in calibration. Under actual operating conditions it is subject to error due to variation in pressure, temperature, specific gravity, etc., from the conditions assumed in calibration, just as the other differential-pressure meters are. As far as the author is aware, there are no published scientific data on its performance.

DISPLACEMENT METERS

DIAPHRAGM TYPE. The construction of this type of meter may be seen from Figures 13 and 14.

The steel case of the meter is divided horizontally by a steel table above which is located the valve and counting mechanism, and below which is located the volumetric chambers. Below this table the meter box is divided into two halves by a vertical partition best seen in Figure 14. In each of the partitions there is a leather bellows or diaphragm (8 in Figure 13) to which is fastened the disk, 9–1. Thus there are formed four gas chambers (*FC*, *FD*, *BD*, and *BC* in Figure 14), and the volume of each can be increased or decreased by the motion of the diaphragm and disk. The inflow and outflow of gas from the compartments are controlled by slide valves best seen in Figure 14. The differential pressure across the meter causes the diaphragms to move, alternately emptying and filling the chambers. The motion of the diaphragm on one side of the partition operates the series of cranks and levers which control the valves to the parts which connect to the chambers on the other side. No gas can leave any chamber while gas is flowing into it, and thus a definite volume is taken in and discharged on each stroke.



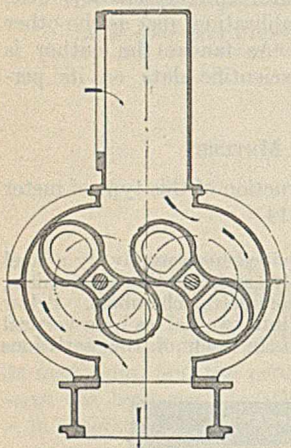
Courtesy of American Meter Co.

FIGURE 14. DIAGRAM OF OPERATION OF BELLOWS TYPE OF METER

In Figure 14 the diaphragm on the left side is moving to the right so that compartment *FC* is filling and *FD* is empting. The other diaphragm is at the end of its stroke, *DB* being empty and *BC* filled. As soon as the left-hand diaphragm reaches a certain point in its travel, the slide valve will move so as to permit *BC* to discharge and *BD* to fill. Thus a cycle of changes occurs quite similar to what occurs in a duplex direct-driven steam pump.

The meter illustrated here is suitable only for low pressures and is built in sizes up to a maximum capacity of 17,500 cubic feet per hour. By placing the same metering mechanism in a cast-iron case, pressures up to 250 pounds can be measured at a maximum rating of about 90,000 cubic feet (standard conditions) per hour.

These meters are used mainly for measuring the gas supplied to consumers in a large gas-distribution system. They are relatively cheap and simple, and require a minimum amount of attention. They will measure accurately any rate of flow from zero up to their maximum rated capacity. The gas measured must be clean, noncorrosive, and without effect on the leather diaphragms. It must not deposit any liquid which would stay in the diaphragm compartments and rot the leather bellows. The range of pressure and temperature over which these meters can be used is obviously quite limited. The accuracy will be affected by pressure, temperature, and humidity changes, but not by changes in specific gravity due to changes in composition. They do not record the rate of flow, but only the total volume of gas that has passed through them. The pressure is the chief variable affecting the accuracy, and an instrument known as a base pressure index is available which, when attached to the meter, automatically compensates for pressure variation and gives the total volume corrected to the standard pressure.



Courtesy of Roots-Connersville-Wilbraham Division of International-Stacey Corp.

FIGURE 15. SECTION THROUGH ROTARY DISPLACEMENT METER

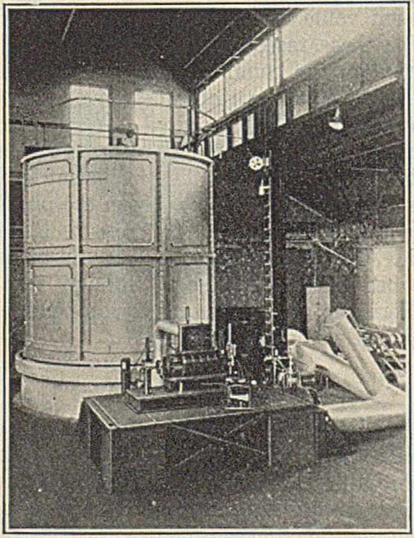
ROTARY TYPE. Figure 15 shows a section through this type of meter which is a development of the well-known blowers and exhausters operating on the same principle, the chief difference being in the bearings which have been improved to reduce the friction to a minimum.

The two shafts carrying the rotating pistons turn in opposite directions, and the cylinder and rotors are so proportioned and accurately machined that all clearances are reduced to a very small figure. Gas pockets of definite volume are formed between the rotors and the cylinder walls; and, as the rotation occurs, owing to the action of a pressure differential between inlet and outlet, these pockets are alternately filled and emptied of gas. Four of these compartments of definite volume are filled and discharged on each complete revolution. Thus, the number of revolutions is proportional to the total volume of gas passed through, and the totalizing instrument is merely a revolution counter. The displacement can be accurately calculated from the dimensions of the meter. The volume metered will be slightly less than the displacement, owing to a leakage or "slip" of gas from inlet to outlet through the small clearances between the impellers and the cylinder. The amount of slip must be determined by calibration of the meter against an absolute standard, preferably at the normal rate of operation, since the slip varies with the speed of rotation. Some published tests on this type of meter show the slip to be of the order of 0.2–0.3 per cent at rated capacity or practically negligible, but at small flows the error due to slip becomes much greater. The larger sizes are provided with a handwheel (Figure 16) to make a check on the amount of slip. With the valve on the outlet line closed, the handwheel is turned to operate the meter at such a speed as to give the operating differential. The ratio of the r. p. m. under these conditions to the r. p. m. in normal operation at the same differential is a measure of the slip. The slip is not determined under the actual conditions of operation, but this simple test furnishes a useful check on the functioning of the meter. It is essential, if such a test is to be reliable, that the valve on the outlet line be checked as to leakage.

As with any displacement meter, the standard volume is obtained from the indicated volume by applying corrections for changes in pressure, temperature, and humidity. Unlike the orifice meter, a change in gas composition has no effect on the reading. On the other hand, the pressure- and temperature-correction factors occur as the first power of the ratios of absolute pressure and absolute temperature instead of as the one-half power. These meters are commonly equipped with a pressure–temperature–rate of flow recorder, all three records appearing on one chart. From this chart the average pressure and temperature for use in correcting to standard condition are obtained.

The low-pressure meters have normal ratings ranging from 6500 to 800,000 cubic feet per hour. They operate on a very small differential—namely, 0.5 to 1 inch of water at normal rating. The first cost is greater than for the orifice meter, but the displacement meter is probably capable of somewhat greater accuracy, and the accuracy is maintained over wider variations in rate of flow. Meters of this type are available for higher pressures (up to 350 pounds), but the cost is considerably increased. The upper limit of temperature at which they can be used is about 250° F. They cannot, of course, be used with corrosive gases, and the gas should also be reasonably free from suspended matter. They are self-contained and require no outside source of power.

Referring to displacement meters in general, one of their chief advantages is simplicity. There are no complicated mechanisms or complex electrical circuits to get out of order. There is almost nothing that can happen to this type of meter that would not be at once evident, whereas a complex mechanism might get out of adjustment and give inaccurate results without any warning. It is more rugged and more positive in its action than the differential-pressure or thermal meters. A given meter is accurate over a wide range of flows. They are not sensitive to flow disturbances due to

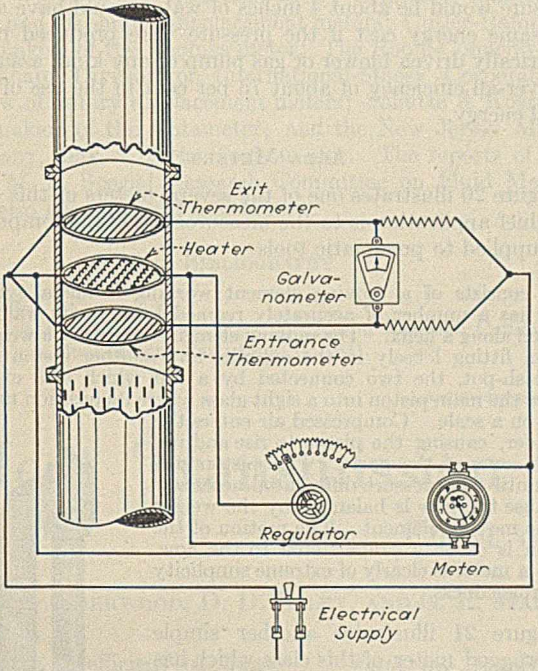


Courtesy of Roots-Connersville-Wilbraham Division of International-Stacey Corp.

FIGURE 16. TEST OF ROTARY DISPLACEMENT METER BY GAS HOLDER

fittings, and the flow may be intermittent, fluctuating, or pulsating without seriously affecting the accuracy.

Gas Holders or Meter Provers. This type of displacement meter finds important application as a primary standard for the calibration of other types of meters. Thus, most of the values of orifice coefficients for gases are based on the gas holder as the absolute standard. There are two general types similar to the two types of large holders used for gas storage: (1) the liquid-sealed floating bell and (2) the dry or piston type. In Figure 16 a 2800 cubic foot piston type is shown set up for testing an 800,000 cubic feet per hour rotary displacement meter. The average diameter of the cylinder or the floating bell and the distance of travel can be accurately measured, and the limiting factor in the accuracy of such a prover is frequently the difficulty of measuring accurately the average temperature of the gas in it. In recent tests of large gas meters by the Bureau of Standards, a water-sealed holder, 168 feet in diameter, was used as the primary standard, and the results were considered accurate to about 0.5 per cent.



Courtesy of American Society of Mechanical Engineers

Figure 17. Diagram of Thomas Meter

Thermal Meters

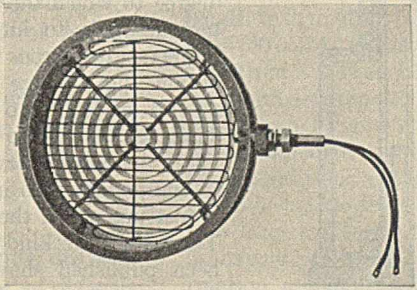
The simplest meter of this class is the hot-wire anemometer which has been used for experimental work, but has never been adapted for commercial metering. In principle it consists of an electrially heated wire placed in the fluid stream, the rate of heat transfer from which is dependent upon the flow rate. If the voltage across the terminals is maintained constant, the average temperature of the wire will change as the flow rate changes; thus the resistance and hence the current will likewise change. Either the current or the resistance is related to the rate of flow and may be used as a measure of it. There is, however, no simple relationship between the rate of flow and the electrical quantities measured which could be used to calibrate such an instrument, and presumably it would have to be calibrated against another flow method under the conditions of use. This has probably been a very important factor in preventing its development for commercial use.

The only commercial representative of this class is the Thomas meter, which is quite different in principle from the hot-wire anemometer. It is essentially a calorimeter and thus independent of rate of heat transfer. Three elements are placed in the stream of fluid, two thermometers with a heating element between them (Figure 17). Electrical energy is supplied to the heating element (in theory various means of supplying heat could be used, but electrical heating is the only one actually utilized), and the heat dissipated to the fluid results in an increase in temperature. The very simple quantitative relationship is given by the following equation:

$$V_s = \frac{Q}{(t_1 - t_2)C_p}$$

where V_s = volume at standard condition
Q = quantity of energy added
$(t_1 - t_2)$ = temp. rise of gas stream
C_p = heat capacity at constant pressure of 1 standard cu. ft.

If a constant input of energy to the heating element were maintained, the difference between the readings of the two thermometers would be inversely proportional to the rate of flow, assuming C_p is constant. On the other hand, if the temperature difference were maintained constant, then the energy input to the heating element would be directly proportional to the flow. The second of these methods is the one actually used, as it has very definite practical advantages over the first one. In the first place, the integration to obtain total flow is much simpler with the second method, because of the straight proportionality between flow and energy input; whereas with the first method an inverse relation exists. Further disadvantages of the first method are that the heat losses are more variable, and time lag is a more important factor owing to the wide variations in temperature.



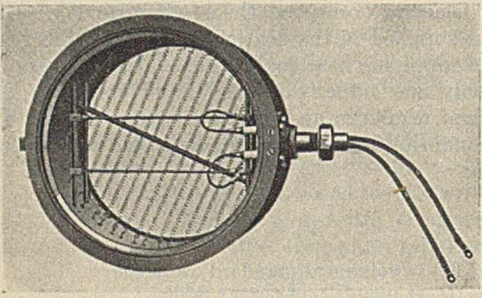
Courtesy of Cutler-Hammer, Inc.

Figure 18. Thermometer Unit of Thomas Meter

The thermometers, one of which is shown in Figure 18, consist of a nickel resistance wire encased in a flexible lead-covered tube which is wound back and forth in the circular frame. The two resistance thermometers are connected in a Wheatstone bridge circuit, and the variable resistance in the circuit is set so that the galvanometer is at zero when the temperature difference is 2° F. Any change in the rate of flow will tend to change this 2° difference, resulting in an unbalance of the bridge with a consequent deflection of the galvanometer. By an ingenious mechanism, a deflection of the galvanometer needle is caused to operate a motor-driven rheostat which increases or decreases the current to the heater (Figure 19) so as to restore the 2° difference. The variation in watts supplied to the heater is a measure of the rate of flow so that the rate-of-flow recorder is a recording wattmeter. The total flow is obtained from a watt-hour meter.

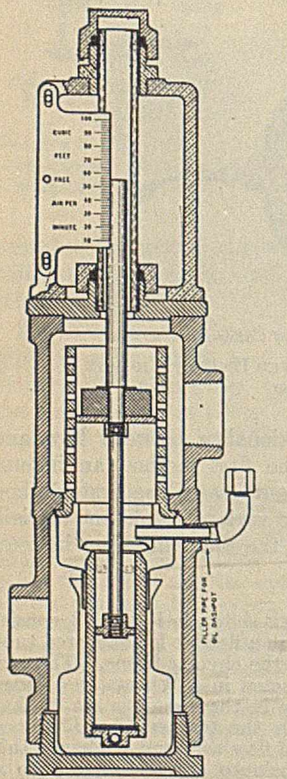
The Thomas meter is used mainly as a station meter in large gas plants. It is built in thirteen sizes ranging from

25,000 to 2,000,000 cubic feet per hour. It is the only meter which is not affected by pressure and temperature changes, since it depends only on the heat capacity of the gas which is practically independent of pressure and temperature over the range of variations that would occur in practice. It will be affected somewhat by composition change, but not greatly since the molal heat capacities of the common gases are not greatly different. If the moisture content of the gas is far from the value for saturation at the standard condition, then a moisture correction may be necessary.



Courtesy of Cutler-Hammer, Inc.

Figure 19. Heater Unit of Thomas Meter



Courtesy of New Jersey Meter Co.

Figure 20. Cross Section of Tool-om-eter

The calibration of the meter depends on an accurate knowledge of the specific heat of the gas and of the change in resistance of the thermometers with temperature. The recording and totalizing instruments can be separately calibrated by standard methods. Its accuracy also depends on the degree to which the thermometers are able to integrate the temperatures across the pipe to obtain the average and to respond quickly to changes. There is no way to check the meter in actual service except to compare it with other types of instruments in the same line. The tests of this kind which have been published show that the Thomas meter is as accurate as the other meters used for the same service.

The initial cost is high as compared with an orifice meter, and it involves rather delicate mechanisms which might conceivably get out of adjustment. It introduces practically no obstruction to the flow, which is an advantage in the special case of slow rates of flow where the total pressure differential is very small. It can be used where the rate of flow varies over wide limits. If the gas being measured contains any liquid in suspension, there will obviously be a serious error due to vaporization. For this reason the meter could not be used for saturated vapors. An advantage, as compared with the rotary displacement meter, is that the recording instruments can be located at considerable distances from the point where the primary instrument is located. The cost of electrical energy to operate the meter is relatively small. Thus, it may readily be calculated that with a flow of 1,000,000 cubic feet per hour of a diatomic gas, the energy required per hour would be 10.7 kw-hours. At a unit cost of 2 cents per kw-hour. the daily cost would equal $5.10. A differential-pressure meter operating on such a differential that the permanent loss in pressure would be about 4 inches of water would have about the same energy cost if the pressure were produced by an electrically driven blower or gas pump of any kind, assuming an over-all efficiency of about 75 per cent in the use of electrical energy.

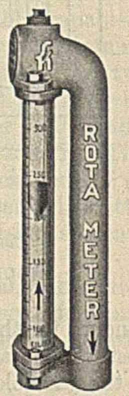
Area Meters

Figure 20 illustrates one of the several meters of this class. Its chief application is to the measurement of the compressed air supplied to pneumatic tools.

It consists of a moving element working inside a cylinder that has a number of accurately reamed holes in its walls, arranged along a helix. The moving element consists of a weighted piston fitting loosely in the cylinder and another piston in an oil dash-pot, the two connected by a rod which also extends above the main piston into a sight glass where its position may be read on a scale. Compressed air enters the cylinder, causing the piston to rise and uncover some of the ports. The piston will rise until the pressure differential necessary to cause the flow is balanced by the weight of the moving element. The motion of the piston is directly proportional to the flow. Such a meter is clearly of extreme simplicity and ruggedness.

Figure 21 illustrates another simple and rugged meter of this class which has recently been put on the market.

It consists of a vertical transparent tube with tapered bore containing a float. As gas flows up through the tube, it causes the float to rise and assume an equilibrium position such that the pressure differential necessary to cause the gas to flow through the annular space exactly balances the weight of the float. The tube is so proportioned that the position of the float is made proportional to the flow. The float is the only moving part and is so shaped that it assumes a central position in the tube and does not touch the wall. Owing to the simplicity of the meter, it can be made of a wide variety of materials and thus might be particularly useful for corrosive gases. It is clear that any changes which affect the density of the gas will affect its accuracy. Any deposits on the glass wall of the tapered tube will also affect the accuracy, but such deposits are visible and the tube can readily be removed for cleaning. For 4-inch or larger pipes, the meter is used as a shunt around an orifice in the main line.



Courtesy of Schutte & Koerting Co.

Figure 21. Thru-flow Type of Rotameter

Before concluding this discussion of gas meters, the question of pulsation deserves some mention, as it often has an important effect on flow measurement, particularly with the differential-pressure meters. Theories of pulsation, more or less quantitative, have been worked out, but the limitations of space do not permit a discussion of this subject. Pulsations in a line, due to proximity to a reciprocating compressor or a positive pressure blower, will cause an orifice meter to read high. The orifice should be placed as far away as possible from the source of the pulsation; but, if that does not remedy the trouble, then it is necessary to interpose between them an expansion chamber or a damping resistance in the form of another orifice or a combination of both.

Acknowledgment

The information on which this paper is based has been gleaned from a wide variety of sources, and it has not been feasible to make proper acknowledgment. The writer is particularly indebted to the following companies who have supplied much of the information and permitted the re-

production of cuts from their bulletins: the Builders Iron Foundry, makers of Venturi meters and the shunt meter; the Brown Instrument Company; the Foxboro Company, the Bailey Meter Company, and the Republic Flow Meters Company, makers of orifice and related meters; the Metric Metal Works of the American Meter Company, makers of orifice and diaphragm displacement meters; Cutler-Hammer, Inc., makers of the Thomas meter; The Roots-Connersville-Wilbraham Division of International-Stacey Corporation, makers of rotary displacement meters; Schutte & Koerting Co., makers of the Rotameter; and the New Jersey Meter Company, makers of the Tool-om-eter. The reports of the A. S. M. E. Special Research Committee on Fluid Meters have also been of great assistance.

BIBLIOGRAPHY

GENERAL

(1) Am. Soc. Mech. Eng., Rept. of Special Research Committee on Fluid Meters, Parts I and II, 1931.

(2) Bean, Benesh, and Buckingham, *Bur. Standards J. Research*, 7, 93–144 (1931).

(3) Brenner, E. C., *Gas Age-Record*, 51, 503–4 (1923).

(4) Bur. Standards, *Circ.* 309 (1926).

(5) Turner and Winship, *Chem. Met. Eng.*, 30, 633 (1924).

DIFFERENTIAL-PRESSURE METERS

(1) Am. Meter Co., Bull. E-2, 1931.

(2) Bean, Buckingham, and Murphy, Bur. Standards, *Research Paper* 49 (1929).

(3) Beitler and Bucher, *Trans. Am. Soc. Mech. Eng., Hydraulics*, 52 (7a), 77–87 (1930).

(4) Foxboro Co., "Principles and Practice of Flow Meter Engineering—The Orifice Meter for Gas and Liquid Measurement," 1930.

(5) Smith, *Trans. Am. Soc. Mech. Eng., Hydraulics*, 52(7b), 89–109 (1930).

(6) Spitzglass, J. M., *Mech. Eng.*, 45, 342–8 (1923).

(7) Spitzglass, J. M., *Iron Steel Eng.*, 7, 217–26 (1930).

(8) Witte, R., *Z. Ver. deut. Ing.*, 72, 1493–1502 (1928).

DISPLACEMENT METERS

(1) Am. Meter Co., Handbook E-4, 1930.

RECEIVED November 30, 1931.

Heat Transmission to Oil Flowing in Pipes

Effect of Tube Length

T. K. SHERWOOD, D. D. KILEY, AND G. E. MANGSEN, Worcester Polytechnic Institute, Worcester, Mass.

Data are reported on heating a light hydrocarbon oil flowing in both viscous and turbulent flow through each of several horizontal lengths of 0.593-inch i. d. copper tube. Heat was supplied by steam condensing outside the tube; oil rate, steam temperature, and inlet and outlet oil temperatures are recorded. A mechanical stirrer was used to mix the oil thoroughly before measuring its outlet temperature.

In the turbulent-flow region, the data are well correlated by the method of plotting of Morris and Whitman, although this method is unsatisfactory in the viscous region. In the viscous-flow region the data are well correlated by the method of plotting of Drew, Hogan, and McAdams, whose empirical curve is substantiated for tube lengths greater than about 100 diameters. As the oil velocity is increased, the observed sudden rise of the outlet temperature of the oil indicates a critical value of the Reynolds number which compares well with the accepted values for isothermal flow.

THE coefficient of heat transfer between a tube and a fluid flowing through it has been assumed to be influenced in two quite different ways by the length of the tube. Various German writers have discussed a heat-penetration effect, or increased difficulty of heat inflow to the fluid core as the fluid moves along the tube. The fluid near the tube wall becomes heated (or cooled) nearly to the tube temperature, and the rate of heat flow per degree difference, between the temperature of the tube and the mean temperature of the fluid, would be expected to be decreased. Graetz (*3*) has derived a theoretical relation for viscous flow which indicates a considerable effect of tube length on the fluid-temperature rise per unit length of pipe. For turbulent flow, the rate of heat transfer might be expected to be influenced by the turbulence normally present at the tube inlet, following a contraction or elbow in the line. Since the effect of this turbulence in improving heat transmission is probably concentrated over the first few diameters of the tube, the average rate of heat flow for the pipe as a whole should be a function of the tube length. This effect has been discussed by McAdams and Frost (*5*), who proposed a factor $\left(1 + \frac{50}{r}\right)$ by which the coefficient should be multiplied. *r* represents the ratio of tube length to diameter.

A previous article (*4*) describes the results of a study of the effect of tube length on heat transfer to water flowing in turbulent motion. Four lengths of pipe were used, the ratio of length to diameter *r* being varied from 59 to 224. A sharp contraction from a 1.44-inch hard-rubber approach pipe to the 0.593-inch internal diameter test pipe was designed to simulate turbulence conditions at the entrance to a tube held in the tube sheets of a large condenser or tubular exchanger. In spite of this contraction and consequent probable turbulence at the inlet, the data were found to fall, within the accuracy of the work, on a single line when plotted in the usual ways. It was concluded that, for water in turbulent flow, the effect of tube length on the rate of heat flow is negligible.

In the well-known work of Morris and Whitman (*6*) on heating and cooling oils, only one pipe was used, and consequently no information was gained as to the possible effect of tube length or end effects. Recently Drew, Hogan, and McAdams (*2*) have suggested a method of correlation of viscous-flow data, based on the Graetz theoretical equation mentioned above. These authors plot $(t_2 - t_1)/(Tw - t_1)$ vs. Wc/kL, using the data of two investigators on heating a light Velocite B oil. The first group is the ratio of the temperature rise to the initial temperature difference; and in the second group *W* represents the weight rate of flow, *c* the specific heat, *k* the thermal conductivity, and *L* the heated length of the tube. The slope of the line representing the Graetz theoretical relation is negative and numerically much less than unity; an appreciable effect of tube length on the temperature rise per unit length is consequently indicated. The data plotted indicated a similar line, although falling considerably above the theoretical curve. The data reported, however, were obtained using tube lengths of 55 and 59 inches, respectively, and consequently throw little light on the validity of the effect of tube length indicated by the Graetz relation.

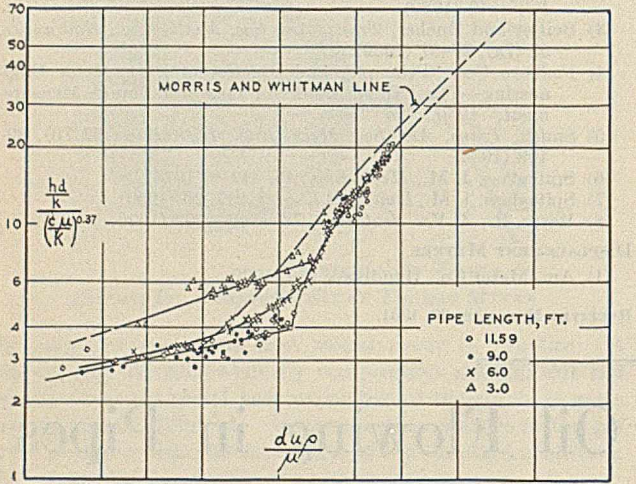


Figure 1. Data Plotted, Using Coördinates of Morris and Whitman

The present article describes the results of experiments on heating oil in both the viscous and turbulent regions, using four lengths of 0.593-inch i. d. copper tube. The oil used was a light heat-transfer oil, and the apparatus was slightly modified from that used by Lawrence and Sherwood (*4*).

Apparatus

The apparatus consisted of the double-pipe heater under test, an outlet mixing chamber with stirrer, a double-pipe cooler, receiving tanks, circulating pump, and the usual accessories. The test section was supported in small tube sheets held in a standard 4-inch steel jacket, forming the steam space. The oil approached the tube sheet at the inlet end through a 1.44-inch i. d. hard-rubber pipe, the section contracting at the ferrule to the 0.593-inch i. d., 0.75-inch o. d., copper test section. At the outlet end the section expanded from that of the copper tube to a short section of standard 4-inch steel pipe in which was placed the thermometer indicating the temperature of the oil at the outlet. Between the outlet of the test tube and this thermometer was inserted a stirrer driven by a small electric motor, ensuring thorough mixing of the oil before measuring its average temperature. The zinc blade of the stirrer was $3^1/_2 \times 2$ inches, attached to a shaft passing through a packing gland in the wall of the 4-inch pipe. No attempt was made to measure the surface temperature of the copper tube, for the reason that, in heating oil with steam, the steam-side resistance is but a small fraction of the over-all resistance to heat flow, and may be estimated with sufficient precision. The weight rate-of-flow of oil was obtained by direct measurement in every run, using a stop-watch to measure the time required to collect from 1 to 2 gallons, which quantity was then weighed. Except for the omission of the thermocouples and the addition of the motor-driven stirrer at the tube outlet, the apparatus was essentially unchanged from that used and described by Lawrence and Sherwood (*4*).

When starting with the apparatus cold, 1 to 2 hours were required to attain constant conditions. The steam and oil temperatures, oil rate, and condensate rate were then measured. The latter was obtained by direct weighing of condensate collected over a measured time interval. Centigrade thermometers, reading to 0.1° and carefully calibrated against each other, were used at the oil inlet and outlet. With each tube length, blanks were run with no oil flowing to determine the rate of heat loss from the apparatus. The inside of the test tube was cleaned frequently with a stiff brush to prevent the formation of dirt or scum.

Physical Properties of the Oil

The hydrocarbon oil used was described by the manufacturer as a light asphaltic-base heat-transfer oil. Its specific gravity, as determined by a Mohr-Westphal balance, was 0.923 at 15° C. A standard Saybolt viscometer was used to determine its viscosity-temperature curve, the coördinates of which are given in Table I. Its thermal conductivity expressed as B. t. u. per hour per square foot per ° F. per foot was (*8*) 0.0765 at 30° C. (86° F.), 0.0755 at 75° C. (167° F.), and 0.0748 at 100° C. (212° F.). A constant value of 0.076 was used in the calculations.

Table I. Viscosity of Oil

Temperature		Viscosity	
		Kinematic	Absolute
° C.	*° F.*	$\frac{\textit{Centipoises}}{\textit{Grams/cc.}}$	*Pounds/(hours) /(feet)*
18.3	65.0	72.0	161
26.5	79.8	44.0	98
33.3	92.0	31.5	70.2
39.4	103.0	24.0	53.5
44.1	111.5	18.8	41.9
47.7	118.0	16.4	36.5
52.7	127.0	13.4	29.8
60.0	140.0	10.6	23.6
67.9	154.0	8.0	17.8
83.2	181.9	5.4	12.0

The specific heat used was an average value determined by direct measurement. A small covered Dewar flask was fitted with an electric heating coil, stirrer, and thermometer, with ammeter and voltmeter in the heating circuit. The electrical input to the heater was measured for a blank test with water, and the heat loss to the surroundings calculated. An equal volume of oil was then tested, first adjusting the current by trial to have the oil heated over the same temperature range in the same length of time. Under these conditions the heat loss as determined by the blank with water was assumed to apply, and the average specific heat between 20° C. (68° F.) and 86° C. (186.8° F.) calculated to be 0.442.

Results

The experimental results are tabulated in Tables II–V, with the runs placed in order of the oil rates. The tube length for each series is indicated at the head of the corresponding table. The inlet and outlet temperatures reported have been corrected for thermometer errors by comparisons with calibration curves for each thermometer. In addition, the outlet temperature has been corrected for the small effect of the heat supplied by the motor-driven stirrer. To determine this correction, the apparatus was run several hours with no steam supply, until the outlet oil temperature corresponded exactly with the inlet temperature. The stirrer was then started, and a rise of 0.20° C. noted in the outlet temperature. It was found that this effect could be reproduced within 0.02–0.03° C. for a constant oil velocity of 3.3 feet per second through the tube. In correcting the observed outlet temperature, the temperature rise due to the stirrer at other velocities was assumed to be inversely proportional to the oil velocity. The correction involved was in general only 5–6 per cent and never over 11 per cent of the temperature rise observed, and was, in every case, a negligible fraction of the temperature difference between oil and steam.[1]

---

[1] When part of these data appeared in connection with a paper presented at the Swampscott, Mass., meeting of the American Institute of Chemical Engineers [*Trans. Am. Inst. Chem. Eng.*, **26**, 81 (1931)], k was taken as 0.078, and no allowance was made for the relatively small temperature rise due to the action of the stirrer.

TABLE II. PIPE LENGTH 11.59 FEET

Run[a]	Inlet Temp. ° C.	Cor. Outlet Temp. ° C.	Av. Steam Temp. ° C.	Oil Lbs./hour	h	$\frac{du\rho}{\mu}$	$\frac{Wc}{kL}$	$\frac{t_2 - t_1}{T - t_1}$
50	47.51	64.69	100.0	284	27.7	280	143	0.327
20	46.06	62.16	100.0	317	28.3	293	159	0.299
49	48.41	64.72	100.0	349	32.8	348	175	0.316
44	50.12	61.52	100.0	467	30.0	452	235	0.229
48	49.52	60.88	100.0	468	29.6	445	235	0.225
47	49.94	59.50	100.0	601	31.5	556	302	0.191
45	49.82	59.20	100.0	615	31.7	590	308	0.187
46	50.22	57.99	100.0	768	32.5	700	385	0.156
43	51.27	57.95	100.0	936	34.6	866	469	0.138
8	48.51	54.84	99.0	942	31.3	783	472	0.125
42	51.42	57.96	100.0	968	34.9	898	486	0.135
41	51.72	57.79	100.0	1080	36.1	1000	542	0.126
40	52.12	57.71	100.0	1180	36.6	1090	594	0.117
9	50.87	55.29	99.5	1390	33.2	1200	700	0.091
32	53.63	57.86	99.2	1470	35.6	1420	740	0.093
52	56.54	60.38	100.0	1570	36.4	1660	789	0.088
31	54.83	58.56	99.2	1680	34.4	1670	842	0.084
38	53.23	57.18	100.0	1720	37.9	1620	863	0.084
39	52.52	56.78	100.0	1730	40.9	1606	870	0.090
19	56.95	60.85	99.5	1750	42.1	1860	880	0.092
37	53.33	57.09	100.0	1790	37.8	1690	901	0.080
36	53.28	57.00	100.0	1870	38.9	1760	940	0.080
35	53.33	56.92	99.8	1910	38.4	1800	960	0.077
51	56.64	60.02	100.5	2050	41.1	2140	1030	0.077
53	56.14	59.31	100.5	2130	39.5	2200	1070	0.072
34	53.45	56.92	100.0	2130	41.4	2000	1070	0.074
58	65.92	70.94	100.0	2140	68.0	3130	1075	0.147
33	53.03	56.48	100.0	2470	47.4	2290	1240	0.073
60	65.30	70.47	99.5	2500	105	3540	1250	0.151
30	65.85	71.02	99.2	2550	111	3710	1280	0.155
59	65.50	70.72	100.0	2550	111	3640	1280	0.151
28	65.00	70.16	99.2	2550	107	3630	1280	0.151
29	65.90	70.55	99.2	2580	99.0	3710	1295	0.140
27	65.30	70.43	99.0	2630	111	3830	1320	0.152
57	66.65	71.82	100.5	2630	112	3930	1320	0.153
56	67.20	72.24	100.5	2700	114	4110	1360	0.151
18	63.02	68.13	100.0	2820	108	3750	1415	0.138
55	67.70	72.96	100.0	3180	148	4890	1595	0.163
54	68.60	73.84	99.0	3260	162	5180	1630	0.172
17	63.50	68.40	99.5	3280	125	4410	1645	0.136
25	65.60	70.67	100.0	3330	138	4900	1670	0.148
11	59.95	64.16	99.0	3340	98.0	3950	1675	0.108
16	63.31	68.10	99.5	3360	123	4460	1685	0.132
14	61.94	66.36	99.0	3360	110	4200	1685	0.120
26	65.60	70.67	99.0	3370	145	4950	1690	0.152
15	62.58	67.28	99.0	3370	120	4370	1690	0.129
12	60.95	65.26	99.0	3390	104	4150	1700	0.113
24	65.45	70.45	99.0	3420	144	4920	1720	0.149
10	59.34	63.86	100.0	3430	103	3960	1720	0.111
13	62.24	66.66	99.0	3450	114	4420	1730	0.120
22	67.35	72.91	99.2	3480	176	5360	1750	0.174
21	66.70	72.35	100.0	3510	172	5340	1760	0.170
23	67.80	73.20	99.0	3560	179	5570	1785	0.173

[a] Runs 1–7 were discarded because the steam separator was not in operation, and the steam contained a large amount of water.

TABLE III. PIPE LENGTH 9.0 FEET

Run	Inlet Temp. ° C.	Cor. Outlet Temp. ° C.	Av. Steam Temp. ° C.	Oil Lbs./hour	h	$\frac{du\rho}{\mu}$	$\frac{Wc}{kL}$	$\frac{t_2 - t_1}{T - t_1}$
40	49.24	60.19	100.0	354	27.5	332	229	0.216
36	50.42	58.86	100.0	470	28.1	436	304	0.170
39	49.92	57.74	100.0	541	29.4	489	350	0.156
37	49.57	57.67	100.0	638	35.8	561	412	0.161
38	50.10	55.82	100.0	848	35.5	741	548	0.115
35	51.10	56.43	100.3	873	32.1	781	565	0.108
34	51.47	56.26	99.8	966	31.4	873	625	0.099
30	51.80	55.88	100.0	1021	29.0	923	660	0.085
33	51.72	56.19	100.2	1068	33.2	986	680	0.092
41	50.32	54.98	99.9	1090	34.6	936	705	0.094
31	51.57	55.90	100.0	1100	33.1	987	710	0.090
29	52.22	56.41	100.0	1150	34.2	1060	740	0.088
43	51.30	55.41	99.5	1150	32.5	1020	740	0.084
32	51.82	55.77	100.2	1230	33.6	1100	795	0.082
42	51.02	55.12	99.9	1260	35.5	1110	815	0.084
44	51.62	55.38	99.6	1355	33.6	1200	880	0.078
28	52.83	56.05	99.9	1370	31.1	1260	890	0.068
26	52.63	56.20	100.0	1450	36.6	1330	940	0.076
25	52.93	56.31	100.0	1520	36.6	1410	980	0.072
20	51.97	55.65	100.2	1530	39.2	1370	990	0.076
45	52.63	55.56	100.1	1620	33.6	1480	1050	0.062
24	53.38	56.58	100.0	1690	38.8	1570	1090	0.068
27	52.88	56.13	99.9	1690	38.9	1570	1090	0.069
21	52.12	55.49	100.0	1690	39.7	1520	1090	0.070
46	53.23	56.15	100.0	1900	38.6	1760	1230	0.062
23	53.48	56.31	99.8	2050	46.4	1910	1320	0.061
22	52.98	55.66	99.8	2190	44.6	2010	1410	0.057
19	52.02	54.91	99.7	2300	42.1	2050	1490	0.060
48	64.80	68.91	100.7	2300	92.0	3100	1490	0.114
49	65.05	69.17	100.5	2380	90.4	3380	1540	0.116
18	65.20	69.27	100.2	2410	98.3	3430	1560	0.116
50	65.08	69.22	100.4	2450	101	3480	1580	0.117
51	65.15	69.27	100.1	2450	102	3480	1580	0.118
17	65.25	69.27	100.3	2520	101	3580	1630	0.115
47	64.30	68.43	99.7	2630	115	3550	1700	0.124
52	64.90	69.08	99.9	2700	114	3680	1740	0.119
16	65.45	69.65	100.2	3150	135	4470	2040	0.121
15	65.45	69.75	100.2	3400	151	4830	2200	0.124
14	65.58	69.65	100.2	3430	143	4860	2220	0.118
11	65.80	70.05	100.2	3440	152	4880	2220	0.124
13	65.50	69.65	99.8	3490	151	4950	2250	0.121
10	65.10	69.45	100.3	3530	157	5020	2280	0.124
9	65.60	69.85	100.5	3550	155	5030	2290	0.122
2	65.20	69.50	99.7	3570	160	5070	2310	0.125
12	65.65	69.85	100.0	3580	158	5090	2310	0.122
7	65.25	69.46	100.0	3590	156	5010	2320	0.121
4	64.90	69.16	99.7	3600	158	5050	2330	0.122
8	65.43	69.71	99.2	3610	166	5120	2330	0.127
3	65.10	69.36	99.5	3620	162	5140	2340	0.124
5	65.15	69.41	100.1	3620	159	5130	2340	0.122
1	65.10	69.36	99.5	3660	163	5200	2370	0.124
6	65.20	69.46	100.0	3700	163	5260	2390	0.122

At low oil velocities the rate of heat transfer to the oil was frequently less than the heat lost to the room. Under such conditions good heat balances were difficult to obtain, and the condensate rates are not reported. In spite of this difficulty the heat balances checked within 10 per cent in considerably over half the runs. At high oil rates consistent checks were obtained, in spite of the fact that for these runs the temperature rise was small. This seemed to indicate that the calculated heat picked up by the oil was reliable, and that heat-balance discrepancies should be attributed either to the difficulty of measuring small condensate rates, or to the uncertainty involved in applying a radiation correction larger than the rate of heat flow to the oil. Consequently, for all runs the oil-side coefficients, h, were calculated from the heat picked up by the oil.

The values of h were obtained from the calculated over-all thermal resistance by subtracting the tube-wall resistance and a steam-side resistance corresponding to a steam-side coefficient of 2000 B. t. u. per hour per square foot per ° F. As pointed out above, this procedure is justified by the fact that the steam-side resistance was probably never more than about 7 per cent of the over-all resistance.

As may be seen from the tables, the steam temperature was practically constant at 99–101° C., with the inlet oil temperature varying from 43° to 68° C. The oil rate was varied from 284 to 4090 pounds per hour, corresponding to linear velocities of 0.71 to 10.3 feet per second. The oil-side coefficients varied from 27 to 179 B. t. u. per hour per square foot per ° F.

The data are first plotted as shown in Figure 1, using the coördinates suggested by Morris and Whitman. The curve obtained by them (*6*) for heating oils is shown dotted, with the coördinates changed to the self-consistent units employed in Figure 1. In the turbulent region, for values of $du\rho/\mu$ greater than about 2000, the points are seen to fall on a reasonably smooth curve (shown by the solid line) roughly paralleling that of Morris and Whitman, but somewhat lower.[2] For values of $du\rho/\mu$ below 2000, the points are widely scattered, although a rough correlation is obtained for each individual tube length. The break in the lower curve indicates the location of the critical point, the points to the right representing runs in the turbulent region, and those to the left runs in the straight-line or viscous-flow region. Although a reasonably smooth curve is obtained above the critical point, the Morris and Whitman coördinates are clearly inadequate for the correlation of the data in the viscous-flow region.

Figure 2 shows the data for runs of $du\rho/\mu$ less than 2000, using the coördinates suggested by the theoretical relations of Graetz, and employed by Drew, Hogan, and McAdams (*2*). For these tests the resistance on the oil side was so large compared with that on the steam side that the steam temperature is used in place of the tube-wall temperature without introducing appreciable error. The present data are seen to be well correlated by this method of plotting, in spite of the fourfold variation in tube length. Although data of runs in

---

[2] The solid line, from $du\rho/\mu$ of 2300 to 6000, checks almost exactly a considerable amount of unpublished data obtained under the direction of W. H. McAdams at the Massachusetts Institute of Technology.

Table IV. Pipe Length 6.0 Feet

Run	Inlet Temp. ° C.	Cor. Outlet Temp. ° C.	Av. Steam Temp. ° C.	Oil Lbs./hour	h	$\frac{du\rho}{\mu}$	$\frac{Wc}{kL}$	$\frac{t_2 - t_1}{T - t_1}$
50	46.91	52.23	101.0	696	35.5	530	675	0.0985
46	48.51	52.45	100.0	955	36.6	750	926	0.0765
47	47.79	51.74	100.0	971	36.8	740	941	0.0755
48	47.56	51.36	100.0	1050	38.0	800	1020	0.0725
49	47.61	51.32	101.0	1100	38.0	830	1060	0.070
39	50.67	53.40	100.5	1510	41.1	1270	1460	0.055
40	50.17	52.95	99.5	1530	42.9	1250	1480	0.056
45	49.62	52.56	99.5	1530	44.9	1240	1480	0.059
44	49.92	52.76	100.2	1590	44.7	1300	1540	0.0565
23	51.22	53.88	100.5	1730	46.5	1470	1680	0.054
37	51.72	54.18	101.0	1820	45.0	1560	1770	0.050
21	52.52	54.88	100.5	1820	43.4	1610	1770	0.049
38	51.22	53.68	100.5	1820	45.0	1560	1770	0.050
43	50.32	52.74	99.5	1870	45.5	1530	1810	0.049
42	50.37	52.70	99.5	1990	46.8	1630	1930	0.047
36	53.46	55.60	101.0	2050	45.4	1900	1990	0.045
41	50.27	52.50	99.5	2060	46.1	1690	2000	0.045
20	54.13	56.41	100.5	2090	51.0	1930	2030	0.049
24	51.42	53.75	99.5	2130	51.2	1820	2070	0.048
22	51.77	54.16	100.3	2150	50.6	1870	2090	0.049
19	57.64	59.98	101.0	2220	59.9	2360	2150	0.054
26	52.42	54.61	100.5	2230	50.2	1980	2160	0.0455
27	52.93	55.11	100.0	2240	51.5	2040	2170	0.046
25	52.02	54.31	100.0	2240	53.1	1950	2170	0.048
35	53.93	56.12	100.5	2260	52.9	2090	2190	0.046
34	54.44	56.57	100.5	2280	52.3	2190	2210	0.046
33	55.08	57.33	100.5	2360	58.0	2280	2290	0.0495
32	53.33	57.53	100.5	2410	58.4	2360	2340	0.049
15	58.64	60.94	100.0	2450	68.1	2700	2380	0.056
31	56.04	58.13	100.5	2480	58.1	2520	2410	0.047
7	58.64	60.89	100.5	2490	67.1	2700	2420	0.054
16	56.84	59.28	100.5	2520	71.1	2640	2440	0.056
13	59.59	62.04	100.5	2600	78.6	2950	2520	0.060
30	57.04	59.44	100.5	2730	75.6	2880	2650	0.055
18	58.24	60.95	100.5	2810	91.2	3050	2730	0.064
14	59.44	62.04	99.5	2810	93.0	3180	2730	0.065
28	53.78	55.84	100.0	2820	62.5	2610	2730	0.0445
29	55.33	57.65	100.5	2860	73.6	2790	2770	0.051
17	57.54	60.26	100.0	2880	94.1	3070	2790	0.064
12	59.59	62.54	101.0	3140	116	3600	3050	0.071
11	59.39	62.35	100.7	3270	121	3700	3170	0.071
8	59.04	62.06	101.0	3300	123	3700	3200	0.072
10	59.34	62.30	100.5	3400	127	3860	3300	0.072
9	59.34	62.35	100.7	3440	130	3890	3340	0.073
4	59.32	62.31	100.0	3700	142	4930	3590	0.073
6	58.74	61.68	101.0	3720	134	4130	3610	0.070
2	59.54	62.58	100.0	3770	149	4310	3660	0.075
5	58.82	61.58	101.5	3800	127	4210	3680	0.065
3	59.54	62.56	100.0	3810	149	4360	3690	0.075
1	59.54	62.56	100.0	3850	141	4400	3730	0.075

Table V. Pipe Length 3.0 Feet

Steam temperature 100.5° C.

Run	Inlet Temp. ° C.	Cor. Outlet Temp. ° C.	Oil, W Lbs./hour	h	$\frac{du\rho}{\mu}$	$\frac{Wc}{kL}$	$\frac{t_2 - t_1}{T - t_1}$
40	43.75	46.98	863	48.6	550	1670	0.056
39	44.0	47.00	925	48.7	594	1790	0.053
38	44.85	47.64	1340	67.1	876	2600	0.050
37	44.95	47.82	1380	71.2	910	2680	0.052
36	45.20	47.73	1460	66.6	975	2830	0.046
34	45.40	47.64	1560	62.9	1042	3030	0.041
33	45.56	47.74	1580	62.1	1064	3070	0.040
31	45.68	47.80	1640	62.5	1112	3180	0.039
35	45.30	47.50	1660	65.6	1092	3220	0.040
30	45.71	47.68	1750	67.3	1185	3390	0.039
29	45.71	47.76	1790	66.5	1210	3470	0.037
32	45.66	47.67	1810	65.0	1220	3510	0.036
28	45.81	47.92	1880	72.0	1280	3640	0.038
27	46.01	48.12	1880	72.5	1284	3640	0.039
17	46.41	48.31	1980	69.0	1386	3840	0.035
16	46.51	48.28	2000	64.9	1395	3880	0.033
25	46.21	48.08	2010	68.9	1387	3900	0.034
24	46.21	48.03	2040	68.1	1407	3960	0.034
23	46.26	48.08	2100	69.9	1446	4060	0.034
22	46.41	48.19	2130	69.5	1480	4140	0.033
21	46.41	48.19	2160	70.1	1503	4190	0.033
26	46.21	47.99	2210	71.9	1522	4290	0.033
20	46.41	48.21	2230	72.8	1543	4320	0.033
12	48.06	49.70	2270	70.1	1670	4410	0.031
19	46.41	48.19	2280	74.5	1570	4420	0.033
13	47.56	49.10	2280	65.5	1630	4420	0.029
14	47.11	48.69	2290	67.1	1630	4440	0.030
18	46.41	48.00	2390	69.4	1650	4640	0.029
15	46.86	48.35	2480	68.1	1740	4810	0.028
3	51.82	53.33	2630	81.1	2240	5100	0.031
2	52.12	53.63	2680	83.2	2340	5200	0.031
11	48.51	49.83	2890	74.2	2140	5610	0.025
10	48.86	50.14	3230	79.6	2440	6260	0.025
9	49.12	50.34	3460	81.5	2640	6710	0.024
4	51.47	53.15	3520	122.2	2970	6830	0.034
8	51.62	53.15	3520	111.2	3000	6830	0.031
5	51.32	52.76	3630	107	3050	7050	0.029
6	51.62	53.16	3870	123.3	3300	7510	0.032
7	51.52	52.96	3900	117	3310	7560	0.029
1	51.72	53.26	4090	130.6	3480	7950	0.031

turbulent flow scatter widely when plotted in this way (plot not shown), it is evident that, when restricted to the viscous-flow region, these coördinates offer an excellent method of correlation. The dotted line shown is the empirical curve determined by Drew, Hogan, and McAdams from the data on Velocite B in 0.494-inch i. d. tubes, 55 and 59 inches long.

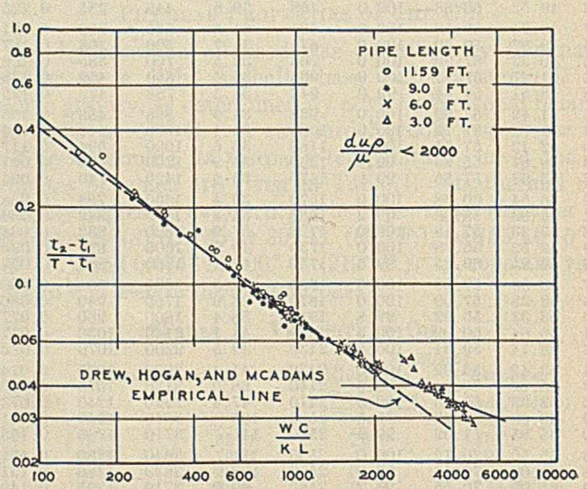


Figure 2. Data for Runs of $du\rho/\mu$ Less than 2000

Except for the shortest of the four pipes, the data are seen to agree excellently with the line determined by these authors. For the 3-foot pipe the points fall roughly 10–30 per cent above this line. Influences of free convection on the steadiness of the laminar flow would not be expected to vary appreciably with tube length. It seems reasonable, therefore, to attribute the difference to the effect of the contraction at the tube inlet. Such a contraction would certainly be expected to cause a mixing of the otherwise smooth laminar flow, and a consequent improvement in the rate of heat flow near the tube inlet. It may be concluded that the empirical curve of Drew, Hogan, and McAdams is well substantiated by the present data for tube lengths greater than about 100 diameters.

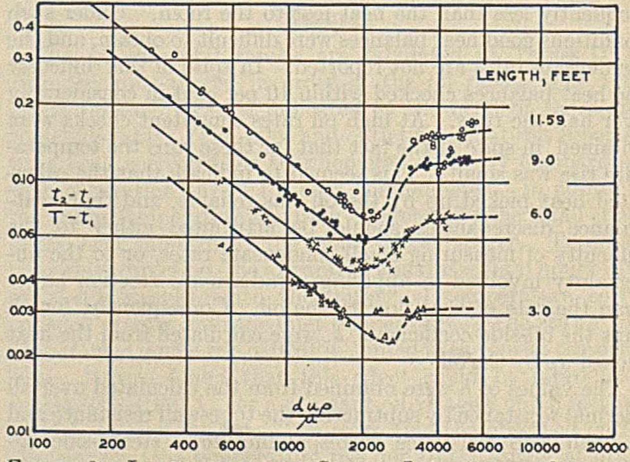


Figure 3. Illustrating the Sudden Increase in Outlet Oil Temperature at the Critical Velocity

The data have been replotted in Figure 3, using the ordinate, $(t_2 - t_1)/(T - t_1)$, of Figure 2, and the abscissa, $du\rho/\mu$, of Figure 1. At any one value of the Reynolds number $du\rho/\mu$, the temperature rise is, of course, greater for the longest tube, and the data fall in order of the tube lengths. In the viscous region the temperature rise decreases as the Reynolds number increases, but rises suddenly at the critical point and tends to flatten out in the turbulent region. At still higher values of $du\rho/\mu$ the ratio, $(t_2 - t_1)/(T - t_1)$, would doubtless decrease again. The minimum is particularly interesting because of its physical significance: with an increase in velocity at the critical point, the oil actually leaves the apparatus hotter. This sudden jump in the outlet temperature has been used by Barnes and Coker (*1*) as a means of locating the critical point. The location of the minimum points of Figure 3 compare well with the lower critical obtained by Schiller (*7*) at a value of $du\rho/\mu$ of 2320, using water at constant temperature.

The sudden increase in the ratio $(t_2 - t_1)/(T - t_1)$ at the critical point is entirely analogous to the rise of the fluid friction coefficient as the Reynolds number is increased at the critical point, and the two phenomena are doubtless closely related. Figure 3 may be seen to bear a striking resemblance to the curves of the friction coefficient plotted against the Reynolds group.

ACKNOWLEDGMENT

The authors are indebted to the American Brass Company for the copper tubes, and to the White and Bagley Company, who supplied the oil used. Special thanks are due J. F. D. Smith of Harvard University, who obtained the values given for the thermal conductivity of the oil. W. H. McAdams and T. B. Drew kindly reviewed the manuscript.

TABLE OF NOMENCLATURE

Any set of consistent units may be used in the coördinates of the three figures, all of which involve dimensionless groups; the units given below are merely illustrative.

c = specific heat, B. t. u./pound/° F.
d = tube diameter, feet
G = mass velocity, i. e., weight rate of flow per unit of cross-sectional area, pounds/hour/square foot = $4W/\pi d^2 = u\rho$
h = average surface coefficient of heat flow between tube and fluid, averaged over length of tube, B. t. u./hour/square foot/° F.
k = thermal conductivity, B. t. u./hour/square foot/° F./foot
L = length of heating surface, feet
r = ratio of tube length to diameter
t_1 = inlet temperature of fluid
t_2 = outlet temperature of fluid, when mixed
T = average steam temperature
u = mean fluid velocity, feet/hour
W = weight rate of flow, pounds/hour
μ = absolute viscosity of fluid at mean or main-body fluid temperature, pounds/hour/foot, taken at $(t_1 + t_2)/2$
ρ = fluid density, pounds/cubic foot

LITERATURE CITED

(1) Barnes and Coker, *Proc. Roy. Soc.* (*London*), 74, 341 (1905).
(2) Drew, Hogan, and McAdams, IND. ENG. CHEM., **23**, 936 (1931).
(3) Graetz, *Ann. Physik*, 18, 79 (1883); 25, 337 (1885); Drew, *Trans. Am. Inst. Chem. Eng.*, preprint (June, 1931).
(4) Lawrence and Sherwood, IND. ENG. CHEM., **23**, 301 (1931).
(5) McAdams and Frost, *Refrigerating Eng.*, **10**, No. 9 (1924).
(6) Morris and Whitman, IND. ENG. CHEM., **20**, 234 (1928).
(7) Schiller, *Forsch. Arb.*, 248 (1922).
(8) Smith, IND. ENG. CHEM., **22**, 1246 (1930).

RECEIVED November 27, 1931. Presented before the meeting of the American Institute of Chemical Engineers, Atlantic City, N. J., December 9 to 11, 1931. This paper is based on a thesis submitted by D. D. Kiley and G. E. Mangsen in partial fulfilment of the requirements for the degree of bachelor of science. T. K. Sherwood's present address is Massachusetts Institute of Technology, Cambridge, Mass.

Solid Matter in Boiler-Water Foaming

I. Experiments at Atmospheric Pressure

C. W. FOULK AND V. L. HANSLEY, Department of Chemistry, Ohio State University, Columbus, Ohio

THIS paper is one of a series (*4*) on the general subject of the foaming and priming of boiler waters. It contains the results of certain laboratory technics not previously used in studying the question, and some information gained by simple boiling experiments.

Readers may raise the question, what is the use of experimenting in glass vessels in studying the foaming and priming of boiler water, since the conditions of such experiments are so different from those in an actual boiler? The answer is: Such experiments give fundamental information concerning the theories of surfaces, the formation and stability of foams, and the behavior of finely divided solids on liquid surfaces; and they suggest experiments and working hypotheses regarding the behavior of water in steam boilers. This latter point is more important than would seem at first sight. Every investigator's scientific imagination is limited, but it can be stimulated by outside suggestions, and in a complex subject like boiler-water foaming there is no better source of such suggestions than laboratory experiments in glass vessels, however far removed from actual boiler conditions they may be.

The experimental work of the paper was planned specifically to see what value might lie in measuring surface viscosities, and surface tensions of water and water solutions of sodium salts with finely divided solid matter as a constituent of the system; and to find, if possible, the reason for the high foam-stabilizing effect of boiler scale. The second one of these questions will be considered first.

NEW FORM OF GLASS BOILING APPARATUS

For laboratory foaming experiments with water solutions boiling at atmospheric pressure, the apparatus illustrated in Figure 1 has proved so satisfactory that it is described in detail. Its advantage lies in the fact that boiling can continue without change in concentration, and that additions of either solids or liquids can be made through the open tube under the condenser. The condensate quickly washes such additions into the flask.

Since the rate of boiling has a pronounced influence on the amount of foam produced, effort was made to keep this rate constant. A four-unit burner with the flames playing upon the unprotected bottom of the Pyrex flask was used, with the flask resting on an iron ring 11 cm. in diameter. Under these conditions the rate of evaporation was approximately 3 cc. per second per square foot (929 sq. cm.) of water surface. This is not a high rate of evaporation, and consequently the most favorable conditions for foaming were not present. A slow rate of foam-formation is, however, more favorable for indicating the effect of changes in conditions, such, for example, as the presence of more or less solid matter.

No quantitative results can be obtained with such a boiling apparatus, except an estimate of the thickness of the layer of foam on the surface; therefore it is necessary to define the qualitative terms used in describing the observed phenomena.

Reference to Figure 2 will help in understanding these terms. Foam, as used in this paper, means a continuous layer of froth over the surface. If the layer of bubbles is not over the whole surface, it is not called a foam. Special attention is called to the portion marked "particle membrane" in the drawing. It contains floating solid particles and could aptly be described as a scum on the surface. Its outstanding property is its resistance to penetration. This means that bubbles rising from below cannot readily get through this membrane, and therefore the rate at which bubbles burst on the surface is greatly retarded. In other words, this particle membrane exhibits one of the ways in which solid matter stabilizes a foam, and the experiment suggests at least the possibility of a similar situation in a steam boiler. The same effect was observed with the plastic solid layer which forms on the surface of a saponin solution. Bubbles rising from below, instead of pushing up a hemispherical mound on the surface, simply flattened against the underside of the surface layer in which the saponin was concentrated. Attention is also called to the attempt in Figure 2 to show both a cross section and round section of the flask with a foaming mixture in it.

The experimental work of this paper falls into two classes: boiling of various salt solutions containing finely divided solids; and determinations of surface viscosities and of surface tensions of water and water solutions with their surfaces covered with floating particles. The boiling experiments showed that different kinds of solid matter exhibited greatly differing degrees of foam-stabilizing power, and that this stabilizing power was lost in some cases on prolonged boiling. It was also shown that absorbed oil was the determining factor in the stabilizing effect of the boiler scale used. The determinations of surface viscosity and surface tension were made largely to satisfy scientific curiosity. The results were in harmony with existing theories.

EFFECT OF ADSORBED OIL ON STABILIZING POWER OF SOLIDS

A hint from the art of ore flotation prompted the examination of some boiler scale for oil. A considerable amount was found, which fact in turn suggested the experiments outlined in Table I. In these experiments the boiling apparatus was employed, the flask being charged with 500 cc. of the salt solution used. This was brought to boiling, and then half-gram portions of the solids (corresponding to 1000 p. p. m.) were successively introduced through the opening under the condenser until 4000 p. p. m. had been added. Since 1000 p. p. m. of solids produced no foam, the behavior of the solutions with this amount is not recorded.

An inspection of the results in Table I shows that the untreated boiler scales were the best foam-stabilizers and, in the case of scale No. I, that extraction or destruction of the oil greatly reduced its foaming tendencies. The rest of the materials were selected because they had little or no tendency to float. The one exception was galena which was chosen because it is a natural floater[1] but contains no oil.

The following experiments performed after the completion of those in Table I constitute an important addition because they show that the foam-stabilizing properties of certain solids are lost by prolonged boiling in a salt solution. These experiments were carried out in the boiler described in Figure 1.

Experiment I. A solution of 8000 p. p. m. of sodium sulfate, to which 5000 p. p. m. of finely ground dolomite were added, foamed vigorously on boiling, but, after boiling for $2^{1}/_{2}$ hours, the foaming almost ceased.

Experiment II. A solution of 8000 p. p. m. of sodium sulfate was boiled with 5000 p. p. m. of finely ground limestone. The foaming was vigorous at first but ceased after boiling for 10 hours.

Experiment III. The solution from II, after the limestone had been filtered off, was returned to the boiler, and 5000 p. p. m. of fresh limestone added. This mixture foamed vigorously on boiling and continued to do so for 3 hours, when the experiment was stopped.

Experiment IV. The limestone from II, which had lost its foam-stabilizing property by boiling for 10 hours in a salt solution, was filtered and washed several times with distilled water, and then added to a fresh solution of 8000 p. p. m. of sodium sulfate. This mixture did not foam when boiled.

Experiment V. Experiments II, III, and IV were repeated, but instead of limestone a finely ground boiler scale was used. The foaming was even greater than that with the limestone but, after boiling for 13 hours, it ceased. When this boiler scale was then added to a fresh sodium sulfate solution, no foaming occurred on boiling; but, when a fresh portion of boiler scale was added to the old salt solution, the foaming was as vigorous as at first.

The experiments in Table I, in the preceding paragraphs, are in harmony with the following generalizations which are also suggested by theoretical considerations and by the experience of ore flotation.

(1) Some kinds of solid matter are more effective than others in stabilizing the foams of boiling salt solutions. These differences may be due to the specific nature of the substances or to adsorbed material, especially adsorbed oil. So far as these experiments go, it appears that the solids which stabilize foam are those that are not readily wet by the solutions in question and therefore float when in a finely divided state.

(2) Prolonged boiling in a salt solution causes some kinds of solid matter to lose the power of stabilizing foam. This is probably due to a modification of the surface of the solid. The boiling possibly removes the film of oil or otherwise increases the wettability.

SURFACE-VISCOSITY EXPERIMENTS

Wilson and Ries (*10*) have advanced the theory that the stability of a film may be explained on the assumption that it possesses the properties of a plastic solid. To understand this statement, the following definition of Bingham must be used: "If a body is continuously deformed by a very small shearing stress, it is a liquid; whereas, if the deformation stops increasing after a time, the substance is a solid."

Wilson and Ries tested this theory quantitatively by measuring the surface viscosities of various solutions by means of a torsion pendulum rotating in the surface of the solution.

No curves or tables of surface viscosities will be given, though many measurements were made, largely because it seemed undesirable to let any method go untried. In general it can be said that finely divided boiler scale on the surface of distilled water or on a salt solution gives a strong plastic solid effect. No effect, however, is produced unless the layer of scale is continuous; that is, if the scale is in floating patches, the plastic effect is not apparent. Also, if the water contains a little castor oil, even a continuous layer of scale gives no plastic solid effect.

SURFACE-TENSION MEASUREMENTS

Again the urge to leave nothing untried prompted a series of surface-tension experiments. Specifically it was hoped to learn whether the oil in the foam-producing solids was imparted to the water during a foaming experiment, or whether it remained with the solid matter. The measure-

---

[1] A brief account of the floating of substances heavier than water is found in a paper by Edser, *Brit. Assocn. Advancement Sci. 4th Rept.*, **1922**, 263.

ments were all made by the ring method with a du Nöuy apparatus, and the surfaces under examination were manipulated in a narrow copper trough 74 cm. long, the use of which was suggested by the experiments of Aiken (*1*) and Pockels (*8*).

This trough was leveled and filled just to the top, so that the surface of the liquid could be wiped with a straight edge. In this way the surface could be cleaned and, if desired, the impurities could be concentrated at one end. It was particularly easy, for example, to produce and maintain a continuous layer of floating particles.

There should also be mentioned a special technic involved in the ring method of surface-tension measurements of liquids, the surface of which is covered with floating solid particles. There are obviously three situations in which the ring of the du Nöuy apparatus may be pictured:

A continuous layer of solid particles is on the surface, inside but not outside of the ring. It was found impossible to maintain this situation.

A continuous layer of particles is on the outside but not on the inside of the ring. Under these conditions a lowering of the surface tension of about 3 dynes was obtained.

A continuous layer of particles is both inside and outside the ring. In this situation the maximum lowering of surface tension was obtained.

WATER WITH POWDERED MATERIAL DUSTED ON THE SURFACE. The following substances were employed: boiler scale No. I, untreated; boiler scale No. I after heating several hours at 490° C.; calcium carbonate prepared by boiling a solution of the bicarbonate (every effort being used to keep it free from grease) and ground flint that had been heated to redness.

None of these substances when dusted on the surface of water affected the surface tension of the water unless a continuous layer was formed, which could easily be done by pushing the straight edge along the trough. When the particles were in a continuous layer, the untreated boiler scale and the calcium carbonate had the greatest effect, the surface tension being 64 and 67 dynes per centimeter, respectively. (The surface tension of the water used was 74.5 dynes per centimeter.) These numerical values, however, should not be taken too seriously. The main point is that the surface tension is lowered. The ground flint, being a non-floating material, had no effect.

In all cases in which the powdered solids were wiped off the surface with the straight edge, the original surface tension of the water was restored.

WATER SATURATED WITH OIL. Paraffin oil that had been boiled with water, and engine oil of unknown history were used. Water was saturated with these oils by boiling with an excess of the oil and finally filtering several times through paper wet with water. No visible evidence of oil droplets was left.

The paraffin oil and the engine oil had no effect on the surface tension of water until the straight edge had pushed the surface constituents well into the end of the trough. In the case of the paraffin oil, the surface tension was not affected until the straight edge was within 5 cm. of the end of the trough; that is, until the surface constituents had been greatly concentrated. The reading was then 68 dynes. The engine oil did not require so much concentration. By the time the straight edge was moved half the length of the trough, the surface tension began to fall off, and with the maximum concentration the surface tension was 58 dynes.

WATER WITH OIL-TREATED SOLIDS ON SURFACE. Since many of the experiments listed above show that absorbed (or adsorbed) oil is the indirect cause of the foam-stabilizing properties of solids, the idea of causing non-foaming solids to take up oil and thus become foam-forming naturally suggested itself. The practice of ore-flotation also suggested such experiments. Various methods were tried, the most effective being the heating of the pulverized material in an excess of oil at about 110° C. The powder was then filtered and washed several times with ether and finally dried at 110° C.

Ground flint, since it was non-foaming and non-floating, was treated with highly purified petroleum (Nujol) in the manner described above. The resulting dry powder floated on water, and, when in a continuous layer, lowered the surface tension about the same as the boiler scale. If this flint was wiped off with the straight edge, the original surface tension of the water was restored. When tried in the boiling apparatus (Figure 1), however, no foam was produced; the apparent reason for this was that the boiling salt solution rapidly extracted the adsorbed oil so that the flint no longer floated. It might also be guessed that Nujol would be an antifoam like castor oil, but direct experiment showed that Nujol did not have that effect. A heavy layer of the floating flint particles also sank after boiling a few minutes in a beaker of water and then, if filtered off and dried, was found to have lost most of its floating power.

The specimen of clay (experiment 8, Table I) was also treated with paraffin oil. It floated, but its behavior otherwise was erratic. When the floating particles were pushed together in the trough to form a continuous layer, they began to sink on touching each other, and traces of oil were left on the surface. Time did not permit the investigation of this remarkable phenomenon.

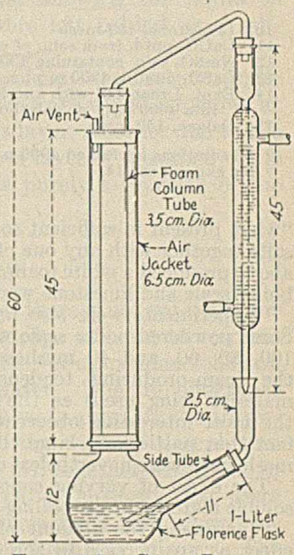


FIGURE 1. GLASS BOILING APPARATUS

Finally, a number of experiments were made with castor oil. These will be described in another paper. It is sufficient to say here that they all pointed towards the belief that the oil is retained by the solid particles in those cases in which the effects are apparent in boiling solutions.

One experiment which is made possible by the way solids in a surface can be manipulated in the trough is worth special mention, though at first sight it seems to be mere laboratory play. A continuous layer of floating powder was first produced on the surface of the liquid in the trough (pure water or a solution can be used) by pushing the particles together with the straight edge; then, by blowing through a bent glass tube, bubbles as much as 1 cm. in diameter were formed, so stable that they could be lifted out on filter paper and dried, leaving the solid particles in place like a fairy-built vaulted ceiling. It would be hard to find a more convincing example of stabilization.

PREVIOUS WORK ON FOAM STABILIZATION BY SOLIDS

The only extensive paper on the stabilization of foams by solid matter in solutions boiling at atmospheric pressure is the first one by Foulk (*4*), the relevant data of which can be summarized as follows:

> At least one hundred trials were made with various kinds of insoluble powders—pumice, sulfur, pyrolusite, bone black, galena, boiler scale, precipitated calcium carbonate, and limestone. It is interesting to note in the light of the present paper that all of these substances are floaters to a greater or less degree.
>
> When the above substances were boiled in distilled water, no appreciable foaming was observed. If solutions of sodium salts were used instead of distilled water, it was found that

Table I. Foam-Producing Tendencies of Various Kinds of Finely Divided Solids in Sodium Chloride Solution[a]

Expt.	Substance Used and Method of Treatment	Height of Foam: 2000 p. p. m. solids	Height of Foam: 3000 p. p. m. solids	Height of Foam: 4000 p. p. m. solids
		Cm.	*Cm.*	*Cm.*
1	Boiler scale No. I from untreated water, pulverized to pass 150 mesh[b]	3.1	6.3	6.3. A few bubbles as high as neck of flask
2	Boiler scale No. I, extd. with ether and then benzene; small amt. of oily matter that looked and smelled like lubricating oil was obtained	No foam	0.6	2.5
3	Boiler scale No. I heated white hot for 2 hours	No foam	Faint signs of foam	Foam slowly rose to 1.3
4	Boiler scale No. I heated 2 hours at 490° C.	No foam	Very slight foam	Very slight foam
5	Boiler scale No. II from a boiler in which an antiscale was used; untreated	1.9	2.5	2.5
6	Boiler scale No. III, scraped from interior of a tea kettle; untreated	1.9	2.5	2.5
7	Finely ground flint; untreated	No foam	No foam	No foam
8	Clay; untreated	No foam	No foam	No foam
9	$CaCO_3$; grade used in J. L. Smith method for determining Na and K	No foam	No foam, bubbles lasted a little longer	No foam
10	Limestone, 150-mesh	No foam	0.6	0.6
11	$CaCO_3$ pptd. from soln. of calcium bicarbonate by boiling	No foam	1.3	1.3
12	Na_2SO_4 soln. containing 4000 p. p. m.; no solids added	No foam	No foam	No foam
13	$CaSO_4$ used in 4000 p. p. m. Na_2SO_4 soln. of 12	No foam	No foam	No foam
14	Expt. I repeated with another portion of untreated boiler scale No. I in a 4000 p. p. m. solution of NaCl	3.8	5	6.3. Some bubbles in neck of flask
15	Galena, 150-mesh	Not tried	Not tried	1

[a] All solutions contained 4000 p. p. m. NaCl, unless otherwise stated.

[b] See experiment 14.

"when present in sufficient concentration, any one of the sodium salts together with any one of the insoluble materials mentioned above produced a white foam. Among the solids tried, powdered boiler scale and limestone were most effective as foam producers.

"Experiments were also made on the effect of particle size. Some powdered boiler scale was sifted into portions that passed 100, 80, 60, and 40 meshes to the inch. It was found that the foam-producing tendencies increased (equal weights of material being used) as the size of particle decreased. Quite the most interesting observation made here, however, was the fact that particles so large that all failed to pass through a 40-mesh sieve were nevertheless effective in producing foam."

The effect of varying concentrations of both soluble and insoluble material in the boiling flasks was also tried.

"Increasing the amount of insoluble material had the same effect as an increase in the concentration of the soluble salts. One of them therefore could take the place of the other, so that foams could be produced with a small amount of soluble material, provided a large amount of insoluble solid was present, and vice versa. There was, however, a lower limit at about 500 p. p. m. for both soluble and insoluble material; that is, if the soluble salts were much less than this, no reasonable amount of insoluble matter would produce foam, and, if less than this amount of insoluble matter was present, no concentration of soluble salts was sufficient to make the liquid foam."

In the paper published in the *Journal of the American Water Works Association*, Foulk (*4*) also records experiments made in a glass flask under a pressure but little above that of the atmosphere. This flask was so equipped that, while a solution was boiling in it, a rather large outlet could be opened suddenly. This left the liquid in the flask at atmospheric pressure but of course at a degree or two higher in temperature than its boiling point. The result was a few seconds of very violent ebullition. When this experiment was made with both salt solution and finely divided solid matter in the flask, the ejection of water with the steam on opening the large outlet was far greater than with any other combination. Quantities of liquid would literally hit the ceiling, thus showing that, under the conditions employed, the effect of the solid matter was very great.

Effect of Solids on Foaming of Salt Solutions Boiling at High Pressures. It is not the intention to discuss here the effect of solids on the foaming of solutions boiling at pressures comparable with those in steam boilers. That is reserved for future papers. Attention should, however, be called to the scarcity of published experimental evidence on this point and also to the lack of agreement among these publications. For example, in 1927 Joseph and Hancock (*6*) and in 1930 Hancock (*5*) recorded experiments with a small laboratory boiler operated at pressures of over 100 pounds and also experiments with commercial boilers; in all cases their evidence showed that the presence of finely divided solid matter had no effect on the foaming and priming of the boilers. On the other hand, the Water Service Committee of the American Railway Engineers Association for 1929 (*2*) gives data on the operation of certain commercial boilers which show that the presence of solids in the boilers increases the water in the steam (foaming and priming). There is also an important paper by Koyl (*7*) on the behavior of a locomotive boiler in service; but some uncertainty exists in the interpretation of his crucial experiment, because, under the conditions, the concentration of dissolved matter was also increasing along with the increase of suspended solids. It should be noted, however, that Koyl, who recorded the conditions of his experiment, ascribed the increasing amount of water in the steam which he observed to the coincident increasing amount of solids in the boiler.

Discussion

Although the general subject of this investigation is a study of all the causes of wet steam, the present paper deals only with the effect of finely divided solid matter on the foams or froths of certain salt solutions boiling at atmospheric pressure. In fact it does not cover even this small field. For example, the effects of varying the ratio of salt concentration to concentration of solids has not been touched. Reference to this point is made in a former paper (*4*); since that time much new information is at hand (particularly personal communications from men in the field) with the result that the question now has sufficient importance to warrant a separate and thorough study, to be undertaken in the future.

The work of this paper falls naturally into two parts: the experiments with boiling solutions; and experiments with the surfaces of cold solutions. These latter were made perhaps more to satisfy scientific curiosity than with an expectation of practical results.

Boiling Experiments. The results, as presented in Table I and in the reports of later experiments, show that, under the conditions employed, different kinds of solid matter stabilize the foams of salt solutions in greatly different degree, and some kinds of solid matter lose their foam-stabilizing properties on prolonged boiling in a salt solution. Furthermore, it was shown that the oil in the boiler scale employed was a determining factor in its high stabilizing power. This latter point powerfully suggests a possible explanation for some of the varying effects of solids in actual boiler practice. According to the operation of the boiler, there will be much, or little, or even no oil in the water, and consequently varying amounts of oil in the scale. It could well be then that two boilers of the same design and using the same water, would exhibit contrary effects owing to precipitated solids. One boiler might be operating a reciprocating engine with returned condensed steam carrying a great deal of oil, and the other one might have no return or, for some other reason, no oil. The boiler containing solids with adsorbed oil would foam badly, and the other one with an equal concentration of solids would not, or there might at least be a great difference in the behavior of the two boilers.

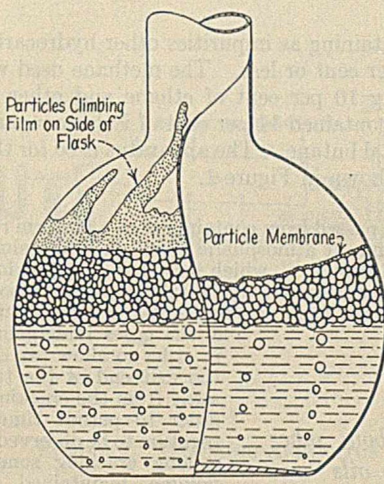


FIGURE 2. APPEARANCE OF BOILING MIXTURE IN BOILING APPARATUS

The prolonged boiling experiments (I–V), which resulted in the solids losing their stabilizing properties, also suggest a possible explanation of certain varying effects of solids. If solid matter is appearing slowly in a boiler, it will necessarily be relatively longer in contact with the boiling water, and it might be that the stabilizing property would be lost at about the same rate or faster than the solid is formed. The result of such a situation would be that a high concentration of such solids would have little or no effect on the foaming. It should also be pointed out that this loss of stabilizing power would probably go faster in a steam boiler than in an open flask, because of the much higher temperature of the water. It is proposed to study this point later.

Finally, it must be pointed out that it is hazardous to make comparisons among different foaming experiments and particularly to draw general conclusions from such experiments because the results are influenced by so many conditions that are either unknown or rarely thought of. For example, the design of the vessel in which the experiment is made affects the result in many cases, which is another way of saying that a steam boiler is a very poor type of instrument for measuring foaminess.

SURFACE EXPERIMENTS. The interesting point in the surface-viscosity experiments is the fact that there must be a continuous layer of floating particles on the surface before the plastic solid effect results. This is in line with the theory of Wilson and Ries (*10*). It is also important to note that the presence of a little castor oil destroys the plastic solid effect and also destroys the foam of a boiling salt solution. However, the foaming of a salt solution containing no solids is also destroyed by castor oil.[2]

The surface-tension experiments are also interesting in that they are in direct line with the surface-viscosity results; that is, surface tension is not affected unless there is a continuous layer of floating particles on the surface. The effect with the few solids tried was always a pronounced lowering of the surface tension, which is in harmony with the theory applying to soluble matter—namely, concentration in the surface layer lowers the surface tension, and, it might also be added, the foamiest mixtures are those in which the surface concentration is higher than that of the mass.

The question of the mechanism of stabilization by solid matter naturally arises. The effect is apparently purely mechanical. Bancroft (*3*) says that the solids make the film more viscous. At any rate a greater structural strength is imparted to the bubble film by the coating of solid particles. This is clearly shown above by the experiment of lifting out such coated bubbles on paper and allowing the liquid to evaporate. The solid particles were left behind as a self-supporting structure.

The fact that the surface tension of the liquid returns to its original value when the solid particles are wiped off shows at least that the effect of a continuous layer, whether due to the solids as such or to the solids with a layer of adsorbed oil, is not imparted to the liquid. It is purely a function of the floating solids.

CONCLUSION

The authors of this paper feel that there is not yet sufficient experimental and theoretical knowledge at hand to warrant a sweeping statement about the effect of suspended solids on the foaming and priming of boiler water. The preponderance of opinion seems to be that solids always promote the throwing of water into the steam, but the work of Joseph and Hancock (*6*) and later of Hancock (*5*), together with some of the evidence brought out in this paper, suggests that there may be exceptions. This, however, need not alarm the zealous proponents of the suspended-solids theory. The study of any problem as complex as that of the entrainment of water by steam always brings out conflicting evidence that is harmonized later by more data and particularly by a better understanding of the underlying physical and chemical laws. Suspended solid matter is still on trial for causing thousands of cases of wet steam, even if it can be proved in a few instances that the accused, although present, was not guilty.

Work on the subject will be continued at the Ohio laboratory under a grant from the Boiler Feedwater Studies Committee. This will enable the construction of several types of experimental boilers in which various kinds of solid matter can be tried, with the boiler operating at high pressure.

ACKNOWLEDGMENT

Grateful acknowledgment is made to A. S. Richardson, of the Procter and Gamble Company in Cincinnati, for the loan of the surface viscometer which he had built for his studies on the foaming of soaps. This instrument is described by Preston and Richardson (*9*).

LITERATURE CITED

(1) Aiken, *Proc. Edinburgh Soc.*, **12**, 56 (1882–3).
(2) American Ry. Eng. Assocn., Water Service Committee, *Proc. Am. Ry. Eng. Assocn.*, **29**, Appendix D-1, 143 (1929).
(3) Bancroft, "Applied Colloid Chemistry," 2nd ed., p. 364, McGraw-Hill, 1926.
(4) Foulk, IND. ENG. CHEM., **16**, 1121 (1924); *Mech. Eng.*, **48**, 1364 (1926); *J. Am. Water Works Assocn.*, **17**, 160 (1927); IND. ENG. CHEM., **21**, 815 (1929).
(5) Hancock, *J. Soc. Chem. Ind.*, **49**, 369T (1930).
(6) Joseph and Hancock, *Ibid.*, **46**, 315T (1927).
(7) Koyl, *Railroad Gaz.*, **34**, 423 (1902).
(8) Pockels, Frl., *Nature*, **43**, 437 (1891).
(9) Preston and Richardson, *J. Phys. Chem.*, **33**, 1142 (1929).
(10) Wilson and Ries, *Colloid Symposium Monograph*, **1923**, 146.

RECEIVED October 10, 1931.

---

[2] These facts about castor oil as an antifoam are from a series of experiments not yet offered for publication.

Pyrolysis of Simple Paraffins to Produce Aromatic Oils

F. E. Frey and H. J. Hepp, Research Laboratory, Phillips Petroleum Co., Bartlesville, Okla.

The pyrolysis of gaseous hydrocarbons other than methane to produce aromatic oils was studied with emphasis on the part played by the time factor. Maximum yields were obtained over a wide temperature range by using the time of contact appropriate to each temperature. The formation of aromatics took place with evolution of heat. Simple diolefins, chiefly cyclopentadiene, accompanied the benzene in greatest amount during the early stages of its formation.

During recent years there has developed an increased interest in the conversion of hydrocarbon gases into motor fuels. This is mostly due to the growth of a large production of natural gas and refinery vapors without a satisfactory market. Of the possible outlets for products derived from such gases, only the motor-fuel market is large enough to put to use more than a small fraction of the available gas. Of the proposed methods for converting hydrocarbon gases into motor fuel, cracking to produce benzene is perhaps the simplest and has received the most attention. Cracking temperatures above 700° C. are required, and this introduces practical difficulties not encountered in oil cracking. Methane, in spite of its abundance, offers less promise perhaps at the present time as a source of benzene than the other gaseous hydrocarbons because of the high temperatures needed to decompose it and the low yields of benzene obtained. Fractionator vapors from refineries and gasoline plants, composed chiefly of gaseous hydrocarbons other than methane, are more suitable for conversion into benzene and are available in large quantities.

The pyrolysis of gaseous hydrocarbons other than methane under conditions which produce aromatic hydrocarbons was first investigated by Berthelot (*1*) and has since interested a number of investigators. The literature has been recently reviewed by Hurd (*13*), Hague and Wheeler (*11*), and Egloff, Schaad, and Lowry (*6*). Since cracking attained commercial significance, laboratory researches have been conducted by Zanetti (*26*), Zanetti and Leslie (*27*), Davidson (*4*), Williams-Gardner (*24*), Dunstan (*5*), Hurd (*14*), Hague and Wheeler (*10, 12*), and Wheeler and Wood (*23*). The utilization of natural gas as a commercial source of benzene has been discussed by Burrell (*2*). Williamson (*25*) mentions the operation of a plant for producing benzene from natural gas by pyrolysis. Podbielniak (*20*) describes semi-large-scale experiments.

The present laboratory investigation was conducted primarily for the purpose of obtaining information bearing on possible commercial operation. The results have also a bearing on coal carbonization and the enrichment of fuel gas by cracking oil, both of which are conducted at temperatures sufficiently high to form benzene.

In the present work more emphasis has been placed on the role of the time factor than in earlier investigations in this field, and a more intimate knowledge of some of the chemical changes involved has been gained by the use of more thorough analytical methods.

EXPERIMENTAL PROCEDURE

Of the gaseous hydrocarbons used in these experiments, ethane, ethylene, propane, and butane were commercial products, containing as impurities other hydrocarbons to the extent of 4 per cent or less. The methane used was natural gas containing 10 per cent of ethane and other impurities. The butane contained 11 per cent of isobutane, and 86 to 88 per cent normal butane. The apparatus used for the cracking operation is shown in Figure 1.

The gas was passed from container *A* at a uniform rate through flowmeter *B* and, at atmospheric pressure, into a single straight length of silica tubing, *C*, which served as the cracking chamber. The silica tube was mounted in a tube furnace, *D*, so as to slope slightly downward from the horizontal in the direction of flow of the gases undergoing cracking, in order to allow tar deposited in the exit end of the tube to flow away from the cracking zone. In order to permit time and temperature to be observed separately, a long cracking zone of known volume, maintained at an even temperature, was provided. The tube furnace was 90 cm. in length, wound in three sections controlled by separate rheostats. In this way a 50-cm. cracking zone with a temperature uniform to within 5° C. was obtained. The cracked gases issuing from the tube passed through electric precipitator *E*, in which the suspended tar was collected; through condenser *F* immersed in a solid carbon dioxide-acetone bath to condense the volatile liquid hydrocarbons; and finally into receiver *G*, or, when large amounts of material were handled, through a wet test meter. When a run was completed, the volatile liquid hydrocarbons dissolved in the tar in *E* were distilled into condenser *F*. This was accomplished by connecting the tar precipitator to the condenser, still immersed in the cooling bath, reducing the pressure to 2 mm. of mercury by a vacuum pump connected to the exit of the condenser, and boiling the tar in the precipitator gently for 10 minutes. The tar volatilized was allowed to condense on the walls of the precipitator while the vapors uncondensed at room temperature were driven over into condenser *F*. A fractional distillation of the oils had shown that the components boiling between xylene and naphthalene were present in such small amounts under high-yield conditions that the separation of xylene and lower hydrocarbons from the tar was fairly sharp and reproducible.

The tar collected in the tar precipitator was estimated by weighing, and to the weight was added that of the tar deposited in the exit end of the cracking tube. Carbon formed in the cracking zone was determined by burning to carbon dioxide at 550° C. in a stream of oxygen, absorbing in soda lime, and weighing. In most cases the gaseous products were analyzed by means of the Bureau of Mines Precision Orsat apparatus (*22*). The paraffins, determined by slow combustion, were calculated as methane and ethane. The values for ethane, obtained in this way, may be in error to the extent of 1 per cent or even more.

When a more complete analysis was desired, the gas was separated by fractional distillation into fractions containing methane and gases of lower boiling point—ethane plus ethylene, propane plus propylene, butane plus butene, and liquid hydrocarbons. The gaseous fractions were then analyzed by the Orsat method, olefins being determined by absorption in sulfuric acid, and paraffins by slow combustion. The analytical fractionating column used has been described by Oberfell and Alden (*15*) Podbielniak (*19*), and Fitch (*7*). No attempt was made to determine acetylene, which is known to be formed in small amounts at temperatures high enough to produce aromatic hydrocarbons.

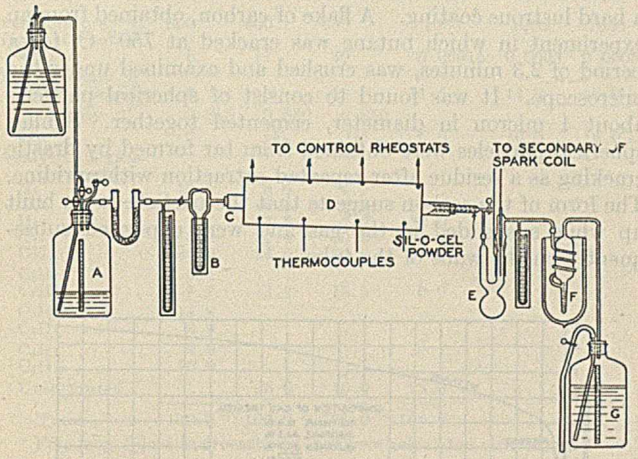


Figure 1. Cracking Apparatus

The time of contact was calculated from the volume of the section of the silica tube at cracking temperature and the flow rate of the gas at the temperature of the reaction. A volume increase took place during the reaction, but, since the increase occurred in the brief initial decomposition, the average flow rate was assumed to be that of the products leaving the cracking zone.

During most of the experiments, temperatures were taken only by four thermocouples spaced at equal intervals along the outside of the silica tube. Effects due to heat of reaction caused an appreciable temperature drift during experiments at the higher temperatures, and this, as well as the increased rate of heat transfer, no doubt affected the accuracy of the time and temperature values, especially at the higher temperatures. Such errors are not serious, since the reaction is not responsive to small differences in time and temperature under the conditions which produce aromatic hydrocarbons.

Effect of Time and Temperature

Since other investigators had placed the most emphasis on the temperature factor, it appeared desirable to conduct experiments of an exploratory character to study the effect of independent variation in time as well as temperature. A gas mixture similar to gasoline-plant fractionator vapors of the composition methane 18.6 per cent, propane 44.7 per cent, *n*-butane 32.7 per cent, and isobutane 4.0 per cent, was cracked at several temperatures—namely, 700°, 750°, 850°, and 950° C.—and propane at 1050° C. Several flow rates were used at each temperature. The results obtained with propane are entirely comparable, as will be shown, with those obtained using the gas mixture, since the average molecular weight and carbon-hydrogen ratio are the same. Because of the wide range of cracking times covered, it was necessary to select silica cracking tubes ranging from 25 mm. diameter for the lower temperatures to 2 mm. for the highest. A simplified type of experiment was deemed adequate in which only the volume change of the gas due to cracking and the concentration of volatile liquid hydrocarbons were determined, for the purpose of calculating the yield of volatile oils (essentially benzene as later experiments show).

The concentration of volatile oils was determined by the method of Burrell (*3*). The gas discharged from the tar precipitator was drawn into an evacuated bulb to a final pressure of atmospheric, the inlet stopcock closed, and the bulb was then cooled to −190° C., after which it was brought to −79° C. in an acetone–solid carbon dioxide bath. The uncondensed gases were then withdrawn to a final pressure for 1 mm. The hydrocarbons boiling above room temperature were retained, and the quantity was estimated by warming to room temperature and by reading on an attached manometer the partial pressure of the evaporated residue. The base of the tar precipitator was kept at 60° C. during the cracking operation to avoid condensation of toluene or lower-boiling components, which were not formed in concentrations too high to be retained by the gas. From the volume change due to cracking and the concentration of volatile oils, the yield in weight per cent was calculated.

The yield data are shown graphically in Figure 2. Within this rather wide temperature range the maximum yield was approximately constant for that range of contact time appropriate to each temperature. No doubt the composition of the oils was affected somewhat by temperature. From these data there were selected minimum values of time required to develop a roughly maximum yield of volatile oils within this temperature range. These values are related to the temperature by the following empirical formula:

$$T = 691 - 100 \log t$$

where T = temperature in ° C.
and t = time in minutes

More accurate subsequent experiments confirmed the values selected. The temperature coefficient of reaction rate is distinctly lower than that of the primary decomposition of propane and butane for which Pease (*16*) found a temperature coefficient of about 2.75 per 25° C. A lower coefficient for the polymerization of olefins has been observed by Pease (*17*) and Geniesse and Reuter (*9*). The polymerization reactions play an important role in the complex reactions leading to the formation of aromatics, and perhaps determine chiefly the reaction rate.

Effect of Time Factor

Since variation in time or in temperature gave equivalent results in respect to yield of volatile oils over a rather wide temperature range, an intermediate temperature, 850° C., was selected for a series of experiments in which the time factor alone was varied, and more complete data taken. The gas subjected to cracking was the same as that used for the preceding experiments. Sufficiently large quantities of gas were cracked to give several grams of liquid products in each experiment. Tar and volatile oils were collected and measured separately and the gases were analyzed. The data are shown in Table I.

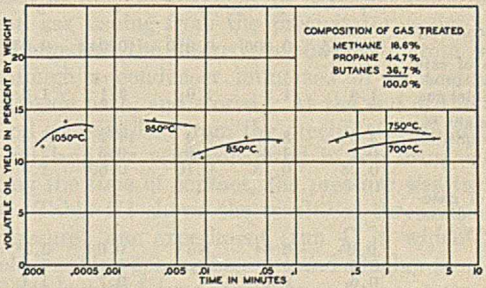


Figure 2. Effect of Time and Temperature on Yields of Volatile Oils

Composition of Gaseous Products. The sequence of changes taking place during the reaction is best shown by the change in the composition of the gases (Figure 3). The primary decomposition of the propane and butanes into simpler paraffins and olefins was nearly complete in 0.0025 minute during which time oil formation was negligible. The time consumed by the succeeding oil-forming stage of the reaction was many times greater. During this stage methane formation increased to a high final value, hydrogen increased somewhat, and with the exception of ethylene and ethane the other gaseous hydrocarbons were quickly destroyed. Because of the relatively long time required by the oil-forming stage of the pyrolysis, certain reactions which have been observed in association with the more rapid primary decomposition of paraffins have an opportunity to play an important part. The reversible hydrogenation of ethylene to ethane maintains ethane in nearly equilibrium concentration when the gas composition is changing slowly, as experiments to be discussed will show. Work in progress indicates that the hydrogenation of olefins higher than ethylene, such as propylene and the butenes, results in the formation of products of primary decomposition of the corresponding paraffins; and, since breaking of the carbon chain takes place and methane is an important product, much of the methane is probably formed in this way without the intermediate formation of polymers. Ethylene and ethane survive because the two-carbon chain is not subject to breaking of the carbon-carbon bond.

LIQUID PRODUCTS. The effect of time of contact on the yield of liquid products is shown in Figure 4. During the early part of the oil-forming stage of the reaction, the yield of volatile liquid products increased rapidly, accompanied by a rather rapid decrease in gaseous olefins, then became constant during the period 0.03 to 0.08 minute while the olefins decreased more slowly. The volatile oil was associated with very little tar during the early stages of its formation, but tar continued to increase after a maximum yield of volatile oils had formed, owing, no doubt, to the formation of tar from the latter. Carbon formation became marked at a still later stage and accelerated only when much tar had formed, due to its formation in turn by the degradation of tar. The volatile oils first formed contained unsaturated hydrocarbons, but the oil surviving the longest exposure time of 0.40 minute crystallized partly at 0° C. and consisted almost entirely of benzene. The effect of change in time on the composition of the volatile liquid products is shown in more detail in a later section.

TABLE I. CRACKING OF GAS MIXTURE[a] AT 850° C. WITH VARYING TIME OF CONTACT

Run	1	2	3	4	5	6
Time of contact, minutes	0.0025	0.006	0.010	0.042	0.08	0.40
Vol. ratio of exit gaseous products to inlet gas	1.8	1.8	1.9	2.1	1.8	2.2
Yields, weight %:						
Volatile oils	3.0	8.1	9.4	14.2	13.5	8.7
Tar	0.2	1.4	1.9	9.5	12.5	14.7
Carbon	0.03	0.13	0.10	0.60	1.3	11.5
Analysis of gaseous products, % by vol.:						
CO_2	0.0[b]	0.0[b]	No analysis	0.0[c]	0.3[c]	0.0[c]
N_2	3.4	5.7		3.1	7.6	0.5
O_2	0.6	0.0		0.7	1.4	0.6
H_2	12.3	13.2		18.5	18.4	25.9
CO	0.0	0.3		0.7	0.3	0.0
CH_4	32.8	41.3		48.5	58.0	63.5
C_2H_4	22.6	26.6		..	..	..
C_2H_6	5.2	3.3		5.8	0	0
C_3H_6	10.7	3.8		..	..	..
C_3H_8	7.2	4.7		..	..	..
C_4H_8	1.5	0.9		..	..	..
C_4H_{10}	1.8	0.2		..	..	..
Higher hydrocarbons	1.9[d]	..		..	..	..
Unsaturates	..	..		22.7	14.0	9.5
Total	100.0	100.0		100.0	100.0	100.0

[a] Composition of gas mixture: methane 18.6%, propane 44.7%, n-butane 32.7%, isobutane 4.0%.

[b] Fractionation analysis.

[c] After removal of benzene (Orsat analysis).

[d] Volatile oils present.

Portions of tar from runs 3, 5, and 6 were dissolved in five volumes of pyridine, and to the solution was added an equal volume of pentane. The tar from a 0.01-minute exposure gave no precipitate, but tar from the 0.08- and 0.40-minute exposures gave increasingly heavy brown precipitates, presumably of aromatic hydrocarbons of high molecular weight formed by protracted cracking.

CARBON. Some carbon was always obtained in the form of a hard lustrous coating. A flake of carbon, obtained from an experiment in which butane was cracked at 750° C. for a period of 2.3 minutes, was crushed and examined under the microscope. It was found to consist of spherical particles about 1 micron in diameter, cemented together. Similar spherical particles were obtained from tar formed by drastic cracking as a residue after repeated extraction with pyridine. The form of the carbon suggests that the particles were built up while suspended in the gas and were deposited subsequently on the walls of the tube.

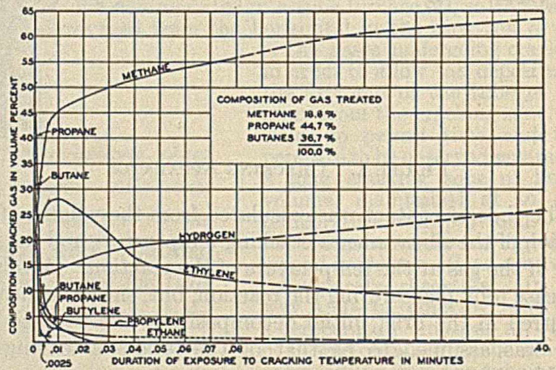


FIGURE 3. EFFECT OF TIME OF CONTACT AT 850° C. ON COMPOSITION OF GAS

HEAT OF CRACKING REACTION. From the heat of formation of the reactants and products, the variation in heat content through the cracking period was calculated, assuming a constant temperature of 850° C. For the heats of formation of volatile oils and tar there were taken for convenience the values per unit weight for benzene and naphthalene, respectively (*8*). Figure 5 shows the calculated heat-content curve. About 650 calories per gram were required to heat the uncracked gas to reaction temperature, after which the rapid primary decomposition took place with absorption of heat followed by the slower oil-forming reactions with evolution of heat. The point of maximum heat content corresponds to the formation of a maximum concentration of gaseous olefins at an exposure time of about 0.0025 minute. The exothermic heat developed between 0.0025 and 0.08 minute was about 190 calories per gram, enough to raise the temperature about 200° C. In large-scale experiments to be described, a marked exothermic effect from this cause has been observed.

A large-scale experimental unit for cracking gas was constructed in which the endothermic and exothermic reaction stages were conducted separately under conditions suitable for each. The endothermic cracking took place in a tube coil of chromium-alloy steel. The charging stock was butane, which was cracked at 750° to 770° C. at 2 atmospheres pressure to a maximum content of unsaturates of 43 per cent by volume. The gas at 770° C. then passed into an insulated chamber in which the formation of aromatic hydrocarbons took place without any further introduction of heat and over a much longer period of time. The temperature rose 50° C. during the passage through the chamber. Under these conditions a maximum yield of benzene was obtained with a minimum time of contact. By reducing the flow rate of the gas and thus increasing the time of contact, the formation of a larger amount of tar took place with a corresponding increase in exothermic heat. Under such conditions a temperature rise in the chamber proper exceeding 100° C. was observed.

TABLE II. EXPERIMENTS AT EXTREME TEMPERATURES

Run	1	2	3	4	5	6
Material treated	Butane	Butane	Butane	Propane	Propane	Propane
Temperature, ° C.	600	600	600	1050	1050	1050
Time of contact, minutes	5	11	30	0.00015	0.0003	0.0005
Yields, weight %:						
Volatile liquids	3	13	13	11.5	14.0	13.0
Density d_4^{25}	0.815	0.830	0.850	...	..	..
Tar	0	(4)	(5)	6.0	10.0	16.0
Analysis of gaseous products:[a]						
N_2	10.5	0.0	4.2	...	..	..
CO_2	0.0	0.4	0.0	0.6	..	..
H_2	...	4.8	7.2	33.9	..	..
CO	0.0	2.4	0.3	0.8	..	..
CH_4	30.0	24.0	55.9	35.8	..	..
C_2H_4	9.1	...	...	...	..	..
C_2H_6	7.7	43.4	15.5	0.0	..	..
C_3H_6	14.8	...	...	...	..	..
C_3H_8	3.9	...	...	...	..	..
C_4H_8	4.0	...	...	...	..	..
C_4H_{10}	20.0	...	...	...	..	..
Unsaturated	...	25.0	16.9	28.9	..	..
Total	100.0	100.0	100.0	100.0	..	..

[a] Free from liquid hydrocarbons; analyses calculated air-free.

EXPERIMENTS AT EXTREME TEMPERATURES. While the yield of oils and the general course of the cracking reactions are substantially the same within a wide temperature range, certain differences are to be expected at different temperatures. Table II shows the results of experiments in which butane (11 per cent isobutane) was cracked at 600° C., and propane was cracked at 1050° C., using several times of contact for each. The hydrogen concentration, in both the early and later stages of oil formation, was much higher at the high temperature than at the low one. This may be attributed to the increase in the dissociation of the paraffins (especially ethane) into olefin and hydrogen with increase in temperature. The volatile oils formed at 600° C. increased in density as the time was prolonged, reaching 0.850 in 30 minutes, which is only a little lower than the density of benzene. This indicates that chiefly aromatics were formed even at this rather low temperature. The liquid hydrocarbons formed at 1050° C. (presumably aromatic) were not examined.

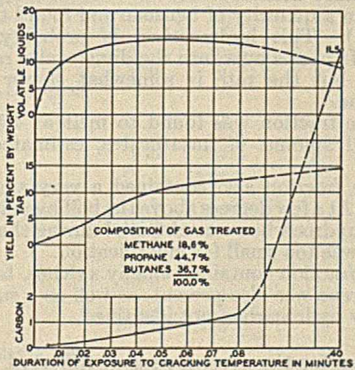


FIGURE 4. EFFECT OF TIME OF CONTACT AT 850° C. ON YIELDS OF VOLATILE LIQUIDS, TAR, AND CARBON

At 850° C. the primary decomposition was nearly complete before the formation of liquid hydrocarbons from the olefins so produced became appreciable (Table I). But since the temperature coefficient of rate is higher for the former reaction than the latter, it would be expected that at low temperatures the formation of oils would get under way before the primary decomposition was complete. In the experiments at 600° C. this effect is apparent. Table II, run 2, shows the formation of a nearly maximum yield of volatile oils, while much ethane and higher paraffins still survive. This is shown by the analysis of the gases produced. The paraffins were determined by combustion and calculated as methane and ethane. The low apparent value of methane is due to the presence of paraffins higher than ethane.

EFFECT OF PRESSURE

The cracking of an ethane-propane fraction of natural-gas condensate under pressure to obtain aromatic hydrocarbons has been studied by Davidson (*4*). Two reaction stages were observed, but the interpretation was complicated by the fact that the pressure and time factors were not separated. It appeared desirable to conduct experiments in which the time factor was varied independently. For this purpose, propane of 99 per cent purity was cracked at one pressure (9.5 atmospheres) and 750° C., using several times of contact. The method was the same as that used in the preceding experiments except for modifications made in the apparatus to permit the use of pressure. The cracking was conducted in a silica tube of 6 mm. inside diameter. The tube was fitted snugly into a chrome-steel tube, and the end was cemented to the steel tube to prevent the passage of gas over the steel surface. The propane was introduced under the cylinder pressure into the tube, and the products were withdrawn at the pressure of the system through a condenser and electrical precipitator kept at a temperature of 0° C. The clean gas issuing from the precipitator under pressure was discharged at the desired constant rate from a needle valve through a condenser immersed in an acetone–solid carbon dioxide bath, and stored. At the end of the run the volatile oil was distilled from the precipitator; and the gas, volatile oil, and tar were separated in the usual way. In calculating the time of contact, the pressure was taken into account. Table III shows the results of three experiments under pressure; one experiment (run 4) in which propane was cracked at atmospheric pressure and a higher temperature (850° C.) is included for comparison. In run 1 the time of contact was not quite long enough to complete the primary decomposition. The formation of liquid hydrocarbons did not become marked until the primary decomposition was nearly completed. Carbon appeared in significant amounts when a considerable amount of tar had formed. In these respects the results are analogous to those obtained at atmospheric pressure (Table I). Since the rate of polymerization is increased by pressure, it would be expected that the rate of oil formation would be increased in this case. Such an effect is not sufficiently marked to be shown by these few data. The yield of volatile oils was about the same as that obtained at atmospheric pressure. In the later stages of cracking, much ethylene was tied up in the form of ethane. This

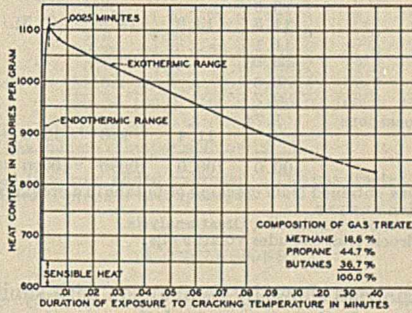


FIGURE 5. EFFECT OF TIME OF CONTACT AT 850° C. ON HEAT CONTENT

should decrease its rate of conversion into oils and allow any further yield increase to be offset by the conversion of volatile oils into tar.

Table III. Cracking of Propane under Pressure

Run	1	2	3	4	5[a]
Temperature, ° C.	750	750	750	850	750
Pressure, atmospheres	9.5	9.5	9.5	1.0	1.0
Time of contact, minutes	0.09	0.22	0.30	0.04	0.70
Vol. ratio exit gaseous products to inlet gas	1.45	1.9	1.8	2.0	0.95
Yields, weight %:					
Volatile oils	3.5	13.5	16.0	15.5	15
Tar	0	..	11.0	8.0	
Carbon	..	..	1.4	..	..
Analysis of gaseous products, % by vol., air-free:					
CO_2	0.0[b]	0.2[c]	0.0[c]	0.8[c]	..[b]
H_2	6.7	6.9	7.9	22.8	12.9
CO	0.6	1.7	0.0	1.3	1.7
CH_4	25.8	66.2	68.8	55.8	56.7
C_2H_4	13.5	..	..	..	12.1
C_2H_6	11.3	13.6	14.3	(0.3)	3.7
C_3H_6	11.1	..	..	..	0.9
C_3H_8	28.0	..	..	..	0.0
C_4H_8	0.6	..	..	..	0.0
C_4H_{10}	0.7	..	..	..	0.0
Higher hydrocarbons	1.7[d]	..	..	..	0.0
Unsaturates	..	11.4	9.0	19.0	(N_2) 12.0
Total	100.0	100.0	100.0	100.0	100.0

[a] Gas used was obtained from cracking of butane in a previous experiment.
[b] Fractionation analysis.
[c] After removal of volatile oils; Orsat analysis.
[d] Higher hydrocarbons includes volatile oils.

The gas analyses show, by comparison with similar experiments at atmospheric pressure and the same temperature, a much higher ratio of ethane to ethylene. The reaction

$$C_2H_6 \rightleftharpoons C_2H_4 + H_2$$

is driven to the left by increase in pressure; and, because of the comparative rapidity of the reaction, equilibrium is approached. Calculating from the data of Pease and Durgan (*18*) at 750° C.,

$$K \frac{(C_2H_4)(H_2)}{(C_2H_6)} = 0.45$$

concentrations being expressed in atmospheres. Assuming the unsaturates in the gas from run 3 to be only ethylene, $K = 0.50$. Ethane, ethylene, and hydrogen were present in nearly equilibrium proportions. For comparison an experiment (run 5) is included in Table III in which another gas, produced by the cracking of butane, was cracked again at the same temperature but at atmospheric pressure. The calculated value of K is 0.40, also in good agreement with the equilibrium value. Where satisfactory ethane determinations are available, the concentrations found are not far from equilibrium values, provided that the cracking has proceeded so far that the gas composition is changing slowly.

Composition of Volatile Oils

While the sequence of changes taking place during the cracking of simple paraffins to produce aromatic oils is affected little by temperature except in respect to velocity over a wide temperature range, temperature no doubt has an effect on the composition of oils formed at equivalent time-temperatures, especially at the lower temperatures and in the initial stages of their formation.

In order to obtain more detailed information about the composition of the volatile oil, several experiments with different flow rates were conducted at an intermediate temperature, 850° C. (Table IV), under the conditions of those reported in Table I, except that sufficient quantities of gas were treated to furnish liquid products for a complete analysis. For these experiments, butane containing 11 per cent isobutane was pyrolyzed.

Analysis of Liquid Hydrocarbons. The liquid hydrocarbons were condensed from the gas at −78° C. to insure the condensation of the low-boiling hydrocarbons above propane. The lower-boiling part of the tar was separated by distillation and added to the volatile oil which was then promptly subjected to a careful fractional distillation below 15° C. in a modified form of the column used for gas analysis. The distillate was collected in the following fractions: propylene, butenes, pentenes, hexenes, benzene, benzene-toluene intermediate fraction, toluene, toluene-xylene intermediate fraction, xylene-styrene fraction, and tar. The condensate obtained from run 2, for which the time of contact was short, contained a high proportion of unsaturates and for this reason was selected for an examination of the fractions as follows:

To the butene fraction cooled in an acetone–solid carbon dioxide bath was added dropwise a small excess of bromine. After standing overnight at room temperature, the excess bromine was removed and the bromides distilled at a pressure of 1 mm. of mercury to a final temperature of 90° C. The residue was identified as the tetrabromide of 1,3-butadiene by separating 50 per cent of it as the higher-melting isomer, melting at 118° C. A separate portion of the butene fraction in the gaseous condition was passed into 65 per cent sulfuric acid in the Orsat apparatus, and found to consist chiefly of isobutene, which is absorbed more readily than butadiene or the normal butenes in acid of this concentration.

During the separation of the pentene fraction, a small proportion, assumed to be pentenes, was observed to boil around 36° C. and most of the remainder at a constant temperature of 42° C. Both cyclopentadiene and piperylene boil at 42° C. The fraction was shown to contain little but the former substance by keeping it at room temperature for several days to permit polymerization of any cyclopentadiene, which proceeds much more rapidly than in the case of the other pentadienes. The fraction was then distilled. The distilling temperature rose immediately to 170° C., the boiling point of the cyclopentadiene dimer. Little distillate was obtained at a lower temperature, which indicated that only small amounts of hydrocarbons other than cyclopentadiene were present. The identity of this component with cyclopentadiene was confirmed by condensing it with acetone in the presence of sodium ethoxide according to Thiele (*21*).

The hexene fraction was found by bromination to contain chiefly diolefins. A hydrocarbon was present which gave a condensation product with acetone. It was later separated in the pure state from a quantity of benzene and found to boil at 72.7° C. (760 mm.). This hydrocarbon is probably methylcyclopentadiene. It passes over into the dimer quite rapidly at room temperatures, but the rate is somewhat slower than that of cyclopentadiene.

The benzene fraction was found to melt at 4.5° C. It contained a small amount of unsaturates, estimated by bromine titration.

The toluene fraction also contained a very small amount of unsaturates. At a few degrees above the boiling point of toluene, a bright yellow hydrocarbon was obtained during the fractionation. The quantity was too small for identification.

The xylene fraction contained chiefly xylenes, but a large proportion of styrene was also present, as well as a small amount of another yellow hydrocarbon not identified.

The analyses for the several runs at different flow rates are shown in Table IV. In the early stages of benzene formation, butadiene, and cyclopentadiene, as well as less abundant higher unsaturates, are present in fairly large amount. With prolonging of the reaction time, the proportion of these diolefins decreases. They should be regarded as transient in character, the rate at which they are destroyed exceeding the rate of formation from gaseous olefins as the concentration of the latter decreases. The concentration of toluene also decreases somewhat with increased reaction time. Benzene, however, continues to increase up to the longest reaction time used. A comparison with the data of Table I indicates that a further increase in time would have decreased the yield of volatile oils. While significant amounts of unsaturates of 4 and 5 carbon atoms per molecule were formed, very little of the unsaturates were found in the boiling range of benzene and toluene. The tendency for larger hydrocarbon molecules other than aromatics to survive is evidently small. Nearly all the unsaturates occurring in benzene formed at this temperature were diolefins, and of these the cyclopentadienes were present in largest amount.

Effect of Raw Material Cracked on Benzene Yield

Since all the lower normal paraffins except methane decompose into smaller paraffins and olefins in a time much shorter than that required for subsequent benzene formation, it is evident, as has been pointed out by Hague and Wheeler (*10*), that the optimum time-temperature conditions for benzene formation should be nearly the same for all. The lower olefins and other lower paraffins should also require the same conditions. A high yield of methane is invariably formed along with the aromatic hydrocarbons by reactions involving the consumption of hydrogen, and no other paraffins usually survive in significant amounts. Since the carbon required to form methane is unavailable for the formation of aromatic hydrocarbons, the yield of oils depends upon the carbon not consumed in this way, and the carbon-hydrogen ratio of hydrocarbon material to be converted into aromatic oils may be used as an index of the yield to be expected. Table V shows the results of experiments in which several different hydrocarbons were cracked under conditions giving a maximum weight per cent yield of volatile oils containing little but benzene and toluene. Ethane (runs 1 and 2) gave a distinctly lower yield than propane (run 3). Ethylene (run 4) gave a greater yield. The addition of hydrogen to propane caused a marked decrease (run 5). Kerosene (run 7) gave a slightly lower yield than would be expected from its hydrogen-carbon ratio, but this should perhaps be expected in the case of high molecular-weight hydrocarbons which are not wholly converted into small molecules by the primary decomposition.

Table IV. Composition of Volatile Oils from Butane at 850° C.

Run	1	2	3	4	5
Time of contact, minutes	0.0015	0.015	0.04	0.065	0.12
Vol. ratio exit gaseous products to inlet gas	2.0	1.9	2.1	2.3	2.4
Yields, weight %:					
Volatile oils	3	10.5	15.5	16.0	17.0
Tar	0.0	5.0	9.5	11.0	17.0
Analysis of gaseous products, % by vol.:					
CO_2	0.0	0.0	No analysis	0.7	0.1
H_2	10.0	16.7		16.6	28.1
CO	0.0	0.5		2.1	0.5
CH_4	23.1	48.4		57.4	60.0
C_2H_6	4.2				
C_2H_4	25.5	..		..	..
C_3H_6	16.9	..		..	..
C_3H_8	0.0	..		..	..
C_4H_8	4.4	..		..	..
C_4H_{10}	15.9	..		..	..
Unsaturates	..	34.4		23.2	11.3
Total	100.0	100.0		100.0	100.0
Analysis of volatile oils, weight %:					
Propylene		3	0.9	0.7	1.9
Butenes		5	5	3	
Butadiene		4			
Pentenes		1	4	2.5	
Cyclopentadiene		6			
Hexadienes		1	0.3	0.5	
Benzene		61.1	74.8	82.8	92.0
Intermediate		0.9	1.0	1.0	0.3
Toluene		9.85	12.0	9.5	5.8
Intermediate		0.15	0.0	0.0	0.0
Xylenes plus styrene		8	(2)	..	..
Total		100.00	100.0	100.0	100.0

The properties of the tar varied with the material cracked. The tars produced by the cracking of ethane, and of propane plus hydrogen, were transparent, yellow-brown, and quite fluid. The tar from ethylene was almost black and quite viscous. This difference is probably due to a difference in concentration of hydrogen, a high hydrogen content favoring the formation of a light tar, perhaps by destroying certain components.

Table V. Yield of Volatile Oils from Several Hydrocarbons

Run	1	2	3	4	5	6	7
Material cracked	C_2H_6	C_2H_6	C_3H_8	C_2H_4	C_3H_8 + H_2	Kerosene[a]	Kerosene[a]
Temperature, ° C.	850	850	850	725	850	850	850
Time of contact, minutes	0.05	0.10	0.04	1.0	0.05	0.02	0.05
Vol. ratio exit gaseous products to inlet material	1.5	1.5	2.0	0.92	1.5	4.8[b]	6.3[b]
Yields, weight %:							
Volatile oils	10.5	10.5	15.5	23.5	9.5	16.5	19.0
Tar	3.0	..	8.0	18.5	6.0	22.0	32.0
Analysis of gaseous products,[c] % by vol.:							
CO_2	(N_2) 1.2	0.1	0.8	0.3	1.0[d]	0.0	0.2
H_2	37.1	41.8	22.8	14.8	7.8	22.1	25.0
CO	1.0	0.6	1.3	0.9	1.0	0.0	0.2
CH_4	22.8	34.9	55.8	33.8	57.6	48.0	55.3
C_2H_6	6.9	4.8	(0.3)	20.7	3.6	2.2	0
Unsaturates	31.0	17.8	19.0	29.5	29.0	27.7	19.3
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0

[a] From Midcontinent crude.
[b] Ratio of gas volume to vapor volume.
[c] Free from volatile oils.
[d] Calculated free from added hydrogen. The gas treated was a mixture of equal volumes of propane and hydrogen.

Conclusions

1. The cracking of the lower paraffins, with the exception of methane, to produce benzene and toluene may be conducted within the rather wide temperature range of 700° to 1050° C., provided that the correct time-temperature values are used.

2. The pyrolysis proceeds through a rapid endothermic decomposition in which simple olefins are formed, which is followed by a much slower exothermic reaction during which the olefins are converted into aromatic hydrocarbons.

3. In the neighborhood of 850° C., butadiene and cyclopentadiene are the chief low-boiling hydrocarbons formed, other than the benzene and toluene which predominate in the volatile oils.

4. The yield of benzene and toluene from the lower paraffins and olefins increases with the carbon-hydrogen ratio.

Acknowledgments

The authors are indebted to G. G. Oberfell and R. C. Alden for their generous support, and to J. A. Guyer for information obtained from large-scale experimentation.

Literature Cited

(1) Berthelot, *Compt. rend.*, 62, 905, 947 (1866); 63, 788, 834 (1866); *Bull. soc. chim.*, [2] 7, 217 (1867).
(2) Burrell, *Natl. Petroleum News*, 21, 79 (Jan. 9, 1929).
(3) Burrell, Seibert, and Robertson, U. S. Bur. Mines, *Tech. Paper* 104, 26 (1915).
(4) Davidson, J. Ind. Eng. Chem., 10, 901 (1918).
(5) Dunstan, *Fuel*, 8, 334 (1929).
(6) Egloff, Schaad, and Lowry, *J. Phys. Chem.*, 34, 1617 (1930).
(7) Fitch, *Natl. Petroleum News*, 23, 66 (June 24, 1931).
(8) Francis, Ind. Eng. Chem., 20, 277 (1928).
(9) Geniesse and Reuter, *Ibid.*, 22, 1274 (1930).
(10) Hague and Wheeler, *J. Chem. Soc.*, 1929, 378.
(11) Hague and Wheeler, *Fuel*, 8, 512 (1929).
(12) Hague and Wheeler, *Ibid.*, 8, 560 (1929).
(13) Hurd, "The Pyrolysis of Carbon Compounds," Chemical Catalog, 1929.
(14) Hurd and Spence, *J. Am. Chem. Soc.*, 51, 3353, 3561 (1929); Meinert and Hurd, *Ibid.*, 52, 4540 (1930); Hurd and Meinert, *Ibid.*, 52, 4978 (1930); Hurd and Meinert, *Ibid.*, 53, 289 (1931).
(15) Oberfell and Alden, *Oil and Gas J.*, 27, 142 (Oct. 18, 1928).
(16) Pease, *J. Am. Chem. Soc.*, 52, 1262 (1930).
(17) Pease, *Ibid.*, 53, 613 (1931).
(18) Pease and Durgan, *Ibid.*, 50, 2715 (1928).

(19) Podbielniak, *Oil Gas J.*, 28, 38 (Jan. 17, 1929); *Ibid.*, 29, 235 (Oct. 2, 1930).
(20) Podbielniak, *Ibid.*, 29, 22 (May 14, 1931).
(21) Thiele, *Ber.*, 33, 666 (1900).
(22) U. S. Bur. Mines, *Bull.* 197 (1926).
(23) Wheeler and Wood, *J. Chem. Soc.*, 1819 (1930).
(24) Williams-Gardner, *Fuel*, 4, 430 (1925).
(25) Williamson, "In a Persian Oil Field," p. 70, Benn, 1927.
(26) Zanetti, J. Ind. Eng. Chem., 8, 674 (1916).
(27) Zanetti and Leslie, *Ibid.*, 8, 777 (1916).

Received October 31, 1931. Presented as part of the Symposium on "The Utilization of Gaseous Hydrocarbons" before the Division of Petroleum Chemistry at the 82nd Meeting of the American Chemical Society, Buffalo, N. Y., August 31 to September 4, 1931.

Thermal Decomposition of Alunite

S. C. Ogburn, Jr., and H. B. Stere, Department of Chemical Engineering, Bucknell University, Lewisburg, Pa.

The progressive stages of decomposition of Utah alunite, effected by heating the material at constant temperatures and over a temperature range from 100° to 850° C., have been observed through the medium of chemical analysis. Combined water is liberated at 460° C., and complete decomposition of the aluminum sulfate to form alumina results at 800° C. Potassium sulfate is not decomposed by heating at this temperature and has been leached from the calcined material and recovered as 99.26 per cent pure potassium sulfate. The residue after leaching consists mainly of aluminum oxide containing small amounts of silica, iron oxide, and magnesia.

ALUNITE as a possible commercial raw material for chemical industry was brought into the field of active investigation in 1912 when Butler and Gale (*2*) published results of their investigation of the chemical and geological nature of the alunite deposits found near Marysvale, Utah. A report by Waggaman (*12*) in the same year discussed "Alunite as a Source of Potash" and showed that potassium sulfate could be leached from alunite which had been calcined at about 700° C. Following these reports, several patents were issued on methods of recovering potash and other compounds from alunite.

A process by Tilley (*11*) recovers the potash as potash alum by digesting the crushed ore with sulfuric acid at 90° C. for 24 to 48 hours. The undissolved ore residue is converted to aluminum sulfate by roasting, and is recovered as such. Moldenke (*10*) has proposed a similar treatment, except that calcination is carried out in steps in a circulating atmosphere of sulfur dioxide and oxygen.

Chappell (*7*) treats the alunite with sulfuric acid and, after precipitating the aluminum as hydrate with ammonium hydroxide, produces mixed sulfates of ammonium and potassium to be used for fertilizer. In other patents (*5, 6*) he recommends slow calcination at 750° to 1000° C. in a strong current of air, and calcination in two steps, first at 600° C. and finally at 900° to 1000° C., after which the hot material is dumped into water to leach out potassium sulfate.

Cameron (*3*) calcines the ore at 500° C., causing a restricted evolution of sulfur oxides. The soluble aluminum compounds are leached and alum separated. The latter is then calcined at 750° C., forming potassium sulfate and alumina, which is digested with hot water to yield a solution of the potash salt.

Cameron and Cullen (*4*) obtain potassium alum by digestion of the ore with sulfuric acid at 110° C., and recover the product in a way similar to the process of Tilley.

Detwiller (*9*) prepares a nitric acid solution of the alumina and potassium while the silica remains insoluble. Soluble nitrates and sulfates are recovered.

Blough and McIntosh (*1*) sinter a mixture of finely ground alunite and sodium chloride at 800° C. and leach out soluble salts, after which the sodium sulfate and insoluble alumina are heated together at temperatures less than 1500° C. to form soluble sodium aluminate.

Although the greater number of patents include decomposition of the ore by heating, no literature has been found to show either the rate or completeness of decomposition at given temperatures.

The work presented herewith was done to determine by means of chemical analyses the course of the thermal decomposition of Marysvale alunite.

Chemical Nature of Alunite

Alunite is a naturally occurring, hydrated double sulfate of aluminum and potassium of the approximate composition represented by $K_2O{\cdot}3Al_2O_3{\cdot}4SO_3{\cdot}6H_2O$. Impurities, such as silica and salts of iron, magnesium, and sodium, are usually present in small and varying amounts.

Table I. Analyses of Alunite from Various Sources

Source	SiO_2 %	Al_2O_3 %	SO_3 %	K_2O %	Na_2O %	Fe_2O_3 %	MgO %	H_2O^a %	H_2O^b %
Theoretical (*8*)	..	37.0	38.6	11.4	..	...	...	..	13.0
Marysvale, Utah^c	0.95	38.38	35.52	10.21	0.56	0.13	0.84	0.14	13.02
Marysvale, Utah (*2*)	0.22	37.18	38.34	10.46	0.33	Trace	...	0.09	12.90
Marysvale, Utah (*2*)	5.28	34.30	36.54	9.71	0.56	Trace	...	0.11	13.08
Rico Mts., Colo. (*2*)	2.54	42.35	35.24	3.27	4.02	...	...	0.13	11.99
Rico Mts., Colo. (*2*)	1.79	37.66	37.92	6.77	2.12	...	0.38	0.06	13.03
Silverton, Colo. (*2*)	0.50	39.03	38.93	4.26	4.14	...	...	...	13.35^{a,b}
Tres Cerritos, Calif. (*2*)	2.64	38.05	38.50	4.48	2.78	0.23	Trace	Nil	11.92

[a] Water removed at 105° C.
[b] Water of combination removed at 460° C.
[c] Alunite used in this investigation.

Table I shows the composition of representative samples of raw alunite from different localities and from different mines in the same locality.

The natural product is practically insoluble in water, but, after calcination at temperatures which produce partial decomposition of the original structure, potassium sulfate and aluminum sulfate may be leached from the material. From a consideration of the analysis of alunite used in this work, it is to be noted that there is an insufficient amount of SO_3 present to combine with all of the alumina, potassium oxide, and sodium oxide to form sulfates. Hence it would not be possible to recover all of these oxides as sulfates without addition of sulfuric acid or its equivalent in SO_3. Since the interest in this investigation was centered on the thermal changes, such possible intermediate products were not investigated.

Effect of Temperature on Extent of Decomposition

A study of the thermal decomposition of alunite must necessarily include both the effect of temperature of calcination and the time of heating at selected temperatures. Uniformity of sampling and careful temperature control are recognized prerequisites.

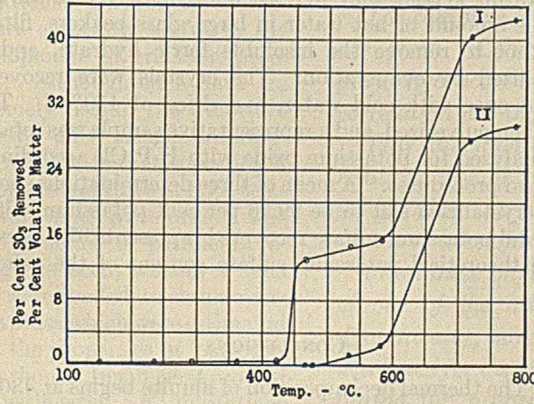


Figure 1. Effect of Temperature on Decomposition

Curve I. Percentage volatile matter at given temperatures
Curve II. Percentage SO_3 removed at given temperatures

The material used in this work was crushed to pass a 40-mesh sieve. The calcination was effected in an electric muffle furnace with variable temperature control actuated by a platinum-platinum rhodium thermocouple as the thermo-unit. The accuracy of control was ±8° C. at 1000° C.

To determine the effect of the temperature of calcination, duplicate samples of 1.0000 gram of alunite were weighed into platinum crucibles and placed in the furnace in which the temperature was maintained constant. The samples were removed periodically, cooled in desiccators, and weighed quickly. Heating was continued until no further loss in weight of the samples was noted. In this manner the total volatile matter removed from alunite at definite temperatures between 110° and 780° C. was determined. New samples were used for each temperature of calcination studied.

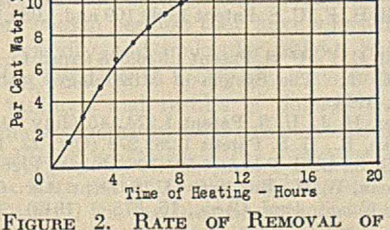


Figure 2. Rate of Removal of Water at 460° C.

These calcined samples were analyzed for SO_3 content, since, in the temperature ranges used, SO_3 and water are the major volatile constituents. The percentage of SO_3 removed from the material and the percentage of volatile matter at given temperatures are shown in Figure 1.

The decomposition of alunite is accomplished in two stages, the first being approximately completed at 460° C. with complete removal of water of combination; the second stage is approximately completed by heating to 800° C., at which temperature oxides of sulfur are removed. Analyses of the evolved gases in this latter stage of decomposition have shown approximately 90 per cent SO_3 and 10 per cent SO_2.

Rate of Decomposition at Constant Temperatures

To study the rate of removal of combined water near the end of the first stage of decomposition, duplicate samples were heated at a constant temperature of 460° C. The samples were weighed at regular intervals, and the percentage of water removed was calculated. The time rate of removal of water under these conditions is shown diagrammatically in Figure 2.

Water was liberated continuously as the time of heating was increased, until ultimately the entire six molecules of combined water were removed. Since removal of water is so regular, it is evident that no intermediate hydrates form during calcination of the alunite. Curve I (Figure 1) and Figure 2 both show this regularity in decomposition.

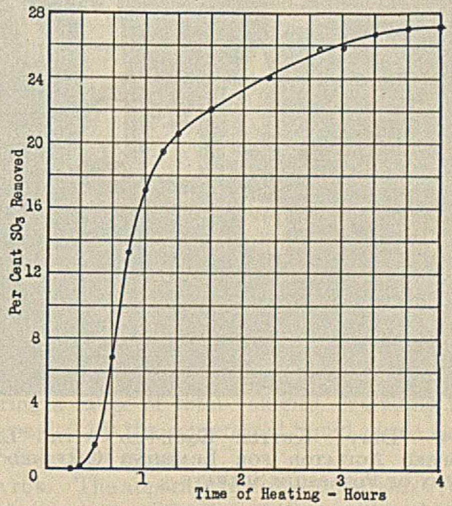


Figure 3. Rate of Removal of SO_3 at 805° C.

The rate of decomposition of a 1-inch bed of alunite has been determined by heating the material at a constant temperature of 805° C. and removing samples at definite time intervals. These samples were analyzed and the percentage of SO_3 removed over a period of 4 hours was computed. The rate of removal of SO_3 under these conditions is shown in Figure 3.

After 4 hours of heating, the SO_3 remaining (16.78 per cent) was slightly in excess of that required for combination with the potassium oxide and sodium oxide present to form sulfates. Later experiments conducted on a larger scale have confirmed these data and show that prolonged heating is essential to complete decomposition of the aluminum sulfate when the material is heated in a stationary bed.

It is seen from Figure 3 that decomposition of a 1-inch bed of alunite is practically completed in 4 hours of heating at 805° C. To determine the nature of the compounds remaining after such treatment and the possibility of recovering potassium sulfate from the calcined material, it was necessary to prepare a larger quantity than previously used in these studies.

About 12 pounds of calcined material were prepared by heating several lots of −40-mesh alunite at a temperature of about 850° C. The alunite was heated for 8 hours in fire-clay muffles supported in a coal-fired furnace. The increased period of heating was necessitated because of the thicker bed of material which was being calcined. In a later experiment, by the use of an electrically heated rotary calcining furnace, the time required to reduce the percentage of SO_3 in the raw ore to the value of 16.78 per cent, as mentioned above, was found to be less than 1 hour.

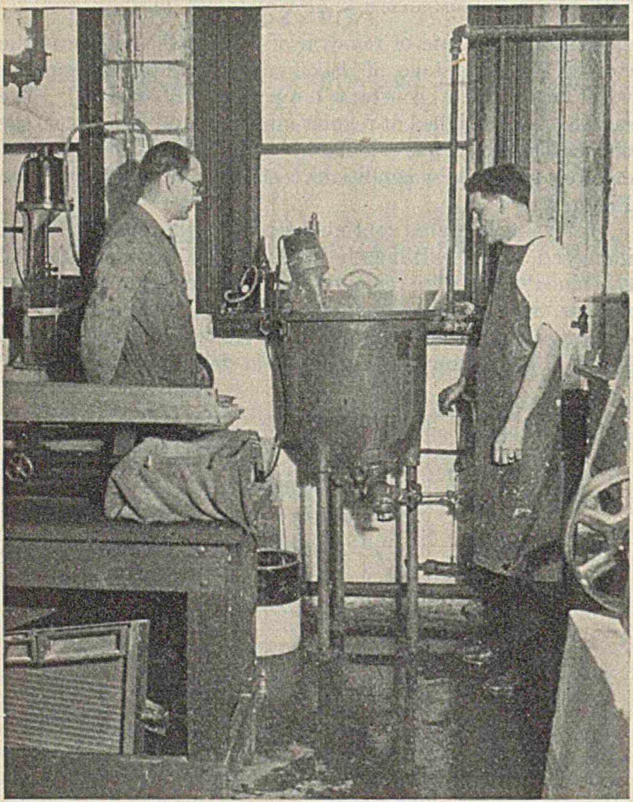


Figure 4. "Dopp" Kettle Equipped with "Lightnin" High-Speed Agitator for Leaching Calcined Ore in Recovery of Potassium Sulfate

The several lots were thoroughly mixed, and a representative sample of the whole was reserved for analysis. Ten pounds of the remainder were mixed with sufficient water to make a sludge of approximately 5 per cent solids. This slurry was heated to approximately 90° C. and agitated for 2 hours in a steam-jacketed kettle. The mixture was then filtered through a pressure filter of the leaf type, the cake was washed thoroughly with hot water, and filtrate and washings were returned to the steam-jacketed kettle to be evaporated to crystallize the potassium and sodium sulfates. The filter cake was removed from the press, dried at 110° C., and broken up; a representative sample was retained for analysis.

The analysis of the calcined alunite both before and after leaching with water are shown in Table II together with the analysis of the raw ore.

Table II. Analyses of Products

Constituents	Raw Alunite	Calcined Alunite	
		Unleached	Leached
	%	%	%
SiO_2	0.95	1.29	2.30
Al_2O_3	38.38	63.28	92.40
Fe_2O_3	0.13	2.11	2.73
SO_3	35.52	16.31	0.43
K_2O	10.21	14.89	0.50
Na_2O	0.56	0.89	Nil
MgO	0.84	1.08	2.03
H_2O-	0.14	..	..
H_2O+	13.02	..	..

In the case of the calcined alunite before leaching, it is seen that the SO_3 present is about 2.5 per cent in excess of the amount necessary to combine with the potassium oxide and sodium oxide present. This indicates the presence of a small amount of undecomposed aluminum sulfate. This excess is not apparent after leaching; it is believed therefore that a small amount of potassium sulfate has remained in the residue, but that any undecomposed aluminum sulfate has been dissolved out.

Recovery of Potassium Sulfate

After the filtrate and washings had been evaporated to a volume of about 1 gallon, the crystals were separated from the mother liquor by filtering through paper supported by large glass funnels. The crystals obtained in this manner were contaminated with a small amount of iron from the evaporating kettle; they were therefore dissolved in the least possible amount of hot water in large glass beakers, filtered while hot to remove the insoluble ferric hydrate, and recrystallized by evaporation. The crystals were recovered, washed once with cold water, and dried at 110° C. They were then pulverized, and a representative sample was retained and analyzed for potassium oxide with H_2PtCl_6 according to standard procedures. A mean of three determinations showed the recrystallized salt to be 99.26 per cent potassium sulfate. The total potassium sulfate recovered represents 97.0 per cent of the theoretical potassium sulfate content of the calcined ore.

Conclusions

1. The thermal decomposition of alunite begins at 430° C. with the liberation of water of combination.

2. No intermediate hydrates are formed during dehydration.

3. At temperatures of 575° to 800° C. the aluminum sulfate is decomposed, while potassium and sodium sulfates remain as such. At the higher temperature, decomposition of the aluminum salt is practically complete.

4. A good grade (99.3 per cent) of potassium sulfate can be obtained by leaching the residue after calcining at about 800° C.

5. The purity of the alumina residue after leaching out soluble salts was found to be 92.40 per cent with 2.30 per cent silica, 2.73 per cent iron oxide, 2.03 per cent magnesia, and small amounts of potassium oxide and SO_3.

Literature Cited

(1) Blough, E., and McIntosh, T., U. S. Patent 1,214,991 (Feb. 6, 1917).
(2) Butler, B. S., and Gale, H. S., U. S. Geol. Survey, *Bull.* **511** (1912).
(3) Cameron, F. K., U. S. Patent 1,233,977 (July 17, 1917).
(4) Cameron, F. K., and Cullen, J. A., U. S. Patent 1,329,768 (Sept. 11, 1917).
(5) Chappell, H. F., U. S. Patent 1,070,324 (Aug. 12, 1913).
(6) Chappell, H. F., U. S. Patent 1,089,109 and 1,089,110 (March 3, 1914).
(7) Chappell, H. F., U. S. Patent 1,336,508 (April 13, 1920).
(8) Dana, E. S., "The System of Mineralogy," 6th ed., p. 974, Wiley, 1914.
(9) Detwiller, H. J., U. S. Patent 1,274,145 (July 30, 1918).
(10) Moldenke, R., U. S. Patent 1,282,273 (Oct. 22, 1918).
(11) Tilley, G. S., U. S. Patent 1,591,798 (July 6, 1926).
(12) Waggaman, W. H., Bur. Soils, U. S. Dept. Agr., *Orig. Com. 8th Intern. Congr. Appl. Chem.*, 15, 375–9 (1912).

Received October 12, 1931. Extract from thesis of H. B. Stere presented to the faculty of Bucknell University in partial fulfilment of the requirements for the degree of master of science, May, 1930. Mr. Stere's present address is Aluminum Research Laboratories, Aluminum Co. of America, New Kensington, Pa.

Physical and Thermal Properties of Petroleum Distillates

W. H. Bahlke and W. B. Kay, Research Laboratory, Standard Oil Company (Indiana), Whiting, Ind.

The P-V-T relationships of two light-petroleum fractions—one a commercial gasoline and the other a rather narrow boiling-range naphtha—have been determined experimentally over a wide range of conditions, extending from near atmospheric pressure to well beyond the critical region.

The complete P-V-T data on these two mixtures are given. Comparison with the properties of pure hydrocarbons is made, and methods of correlation are indicated.

This investigation has shown that the P-V-T relationships of petroleum hydrocarbon mixtures are similar in all respects to those of binary mixtures heretofore investigated.

From these physical data the thermal properties of one of the mixtures was calculated thermodynamically, making use of an equation of state developed for the superheated vapor region. Combining the properties calculated and previously published data on the specific heat of the liquid and vapor at atmospheric pressure, a total heat temperature chart is presented.

ACCURATE data on the physical and thermal properties of petroleum hydrocarbon mixtures, extending over a wide range of temperatures and pressures, are desirable as an aid in the development of petroleum-refining operations. Data of this character are especially useful in the development of cracking processes. Although such data are extremely useful, the literature contains only meager information relative to the properties of petroleum mixtures at high temperature and pressure. The usual practice in petroleum refining has been, whenever such data were needed, to assume certain values which were estimated from the properties of pure hydrocarbons. Insufficient proof of the justification and limitations of these assumptions exists.

In view of the paucity of data in this field, the present authors initiated a program of research in this laboratory which, it was believed, would establish the general behavior of complex hydrocarbon mixtures and ultimately lead to the possibility of readily estimating the properties of petroleum fractions. This program contemplated the measurement of physical properties of a number of fractions and the general correlation of these properties with one another as well as with other more easily determined properties of the fractions, such as A. S. T. M. boiling range, specific gravity, and molecular weight. Further, it was proposed to calculate thermal properties from physical properties and obtain a similar correlation. The development of means of ready measurement of some of these properties, for cases where very precise data in the high pressure–high temperature region are required, was also included in the program.

This paper presents some of the data obtained in this program. It gives data on the physical properties of two petroleum fractions—one a commercial gasoline and the other a rather narrow boiling-range naphtha. These two distillates were chosen because they have approximately the same A. P. I. gravity and molecular weight, but markedly different boiling ranges with nearly the same average boiling point. The methods and results of determination of the pressure-volume-temperature-state relationships over a wide range of conditions are given. The behavior around the critical region were rather closely studied, and the results are given. Further, the methods and results of calculations of the following thermal properties of the naphtha are given:

1. Difference in specific heats at constant pressure and constant volume as a function of pressure and temperature.
2. Joule-Thomson coefficients as a function of pressure and temperature.
3. Latent heats of vaporization.
4. Total heats as a function of pressure and temperature.

Method of Determination of Physical Properties

For determining the pressure-volume-temperature-state relationships, a small sample of the air-free liquid was confined over mercury in a thick-walled capillary tube which was heated to a constant temperature by the vapors of a series of pure organic compounds. The capillary tube communicated with a mercury-filled compressor for regulating the pressure on the sample and with a gas manometer for measuring the pressure. The tube had been carefully calibrated so that it was possible to measure the total volume occupied by the sample as well as the volume of the separate phases present. Equilibrium between the liquid and vapor phases was assured by stirring with an electromagnet stirrer. Observations of the pressure and volume of liquid and vapor phases at a constant temperature were made for a number of temperatures and covering a range of total volumes, extending from the volume occupied by the compressed-liquid phase to that by the expanded-vapor phase.

Apparatus. The apparatus for determination of the P-V-T relationships was a modification of that employed by Sydney Young and is shown in Figure 1.

It consisted of the long steel compressor block, *A*, securely fastened in a horizontal position with three vertical branches at right angles to it. The block, *A*, was fitted with a section, *B*, through which the plunger, *D*, passed, a pressure-tight joint being insured by the stuffing box, *C*. One end of the plunger was threaded and held in a correspondingly threaded section of *B*. It could be turned by means of the hand wheel, *F*, and thus permitted the volume of the space, *E*, which was filled with mercury, to be changed at will.

Each of the vertical branches was fitted with a stuffing box through which passed a thick-walled capillary tube. The tube was held in position by an enlargement, *G*, which rested on rubber washers against the loose-fitting steel ring, *H*. The packing of the stuffing box consisted of a perforated cylindrical rubber stopper *I* which was forced around the tube by the gland, *J*, by screwing down the cap, *K*. The compressor was immersed in a water bath whose temperature near that of the room was held constant to within 0.02° F. (0.01° C.).

The liquid under investigation was confined over mercury in the experimental tube, *L*, which was constructed of Pyrex capillary tubing of about 1.5 mm. bore with an intermediate section of 4 mm. bore. The tube was carefully calibrated, and the volume from the sealed end was expressed in terms of the distance from a reference line etched around the tube near the sealed end. This distance was measured to 0.05 mm. by means of a cathetometer.

To bring about equilibrium quickly between the liquid and

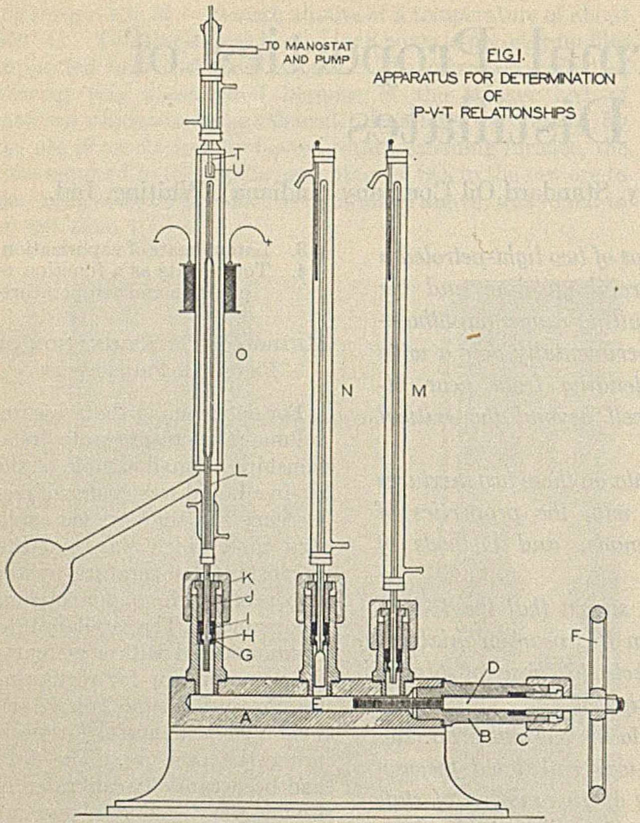


FIG.1. APPARATUS FOR DETERMINATION OF P-V-T RELATIONSHIPS

vapor phases of the sample, the experimental tube was provided with a stirrer, consisting of a small rod of soft iron about 0.75 inch (1.9 cm.) long and of dumb-bell shape. The stirrer was moved by means of an electromagnet outside the apparatus.

In calculating the volume of the liquid and vapor phases of the sample from the experimental data, the following factors were taken into account: the volume of the mercury and liquid menisci; the thermal expansion of the tube; and the volume of the iron stirrer.

The experimental tube, surrounded by the jacket, *O*, was heated to a constant temperature by the vapors of a series of pure organic liquids whose boiling points lay within the temperature range desired. By boiling the liquid under reduced pressure, a 70° F. (38.9° C.) range of temperatures, constant to within 0.02° F. (0.01° C.), was obtained with a single liquid. The liquids recommended by Young (*7*) were used. The temperature of the vapor bath (that is, the temperature to which the experimental tube was heated) was measured by a copper-constantan thermocouple, *T*, inside a thin-walled glass tube, projecting into the vapor bath (as shown) to a point just above the experimental tube. To prevent the cold liquid condensate from running back on the couple, which would thereby give too low temperature readings, and also to shield the couple from radiation from the electric heater (not shown) surrounding the jacket, a bell-shaped metal guard, *U*, with several holes drilled through the side near the top, was placed over the end of the couple. The couple was calibrated using the standard temperatures of the boiling points of water, aniline, naphthalene, benzophenone, and sulfur. Melting ice served to maintain a constant cold junction temperature, and a Leeds and Northrup type K potentiometer measuring to 0.001 mv. was used for the e. m. f. measurements.

The pressure was measured by means of the two gas manometers, *M* and *N*. The internal diameter of *M* (1 mm. bore), which served for the measurement of moderate pressures, was the same throughout. *N*, which served to measure high pressures, was provided with a reservoir of relatively large capacity at the open end. Both tubes were carefully calibrated and filled with pure nitrogen. The gas constant for the low-pressure manometer was determined by comparing it with a direct column of mercury in a tube of about 1.5 meters in height, which temporarily replaced the experimental tube. This tube was later replaced by a glass rod, and the constant for the high-pressure manometer determined by taking readings simultaneously on both manometers. The pressure as determined by the manometer was corrected: for the difference in level of the mercury (corrected to standard temperature) in the experimental tube and manometer; for the pressure of the column of unvaporized liquid; for capillarity and the vapor pressure of mercury when necessary; and for the deviation of nitrogen (in the manometer) from Boyle's law.

PREPARATION OF SAMPLE

REMOVAL OF MATERIAL REACTIVE WITH MERCURY. Petroleum distillates, even though rather highly refined, contain compounds which react with mercury and cause a finely divided precipitate to settle out. These compounds were removed by first shaking the sample with mercury at room temperature and finally by vaporizing in contact with mercury vapor at 675° F. (357.2° C.).

REMOVAL OF WATER. The sample was dried by standing over metallic sodium for several days or in contact with P_2O_5 for about half an hour.

REMOVAL OF AIR. The general plan of deaërating the sample without changing its composition appreciably was to reflux it for some time under high vacuum with the temperature of the condenser such as to condense the more volatile hydrocarbon vapors but permit the exit of the air and other noncondensable gases. The apparatus for removing the air and filling the experimental tube with an air-free sample is shown in Figure 2.

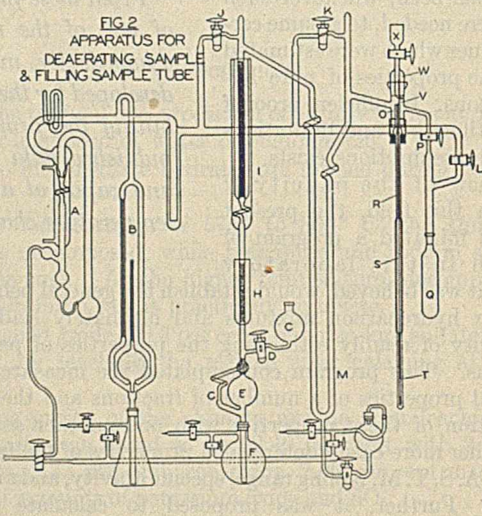


FIG.2 APPARATUS FOR DEAERATING SAMPLE & FILLING SAMPLE TUBE

A high-vacuum mercury diffusion pump, *A*, was backed by a Cenco-Hy-Vac oil pump. The pressure in the apparatus was measured by the MacLeod gage, *B*, capable of measuring less than 10^{-5} mm. mercury pressure. The sample (about 175 to 200 cc.) in *C* was introduced through the mercury-sealed stopcock, *D*, and stood over the mercury in the boiler, *E*. This stopcock contained no lubricant and was prevented from sticking by filling the lower compartment of the sheath with mercury. The height of the mercury in the boiler, *E*, was regulated by the pressure over the mercury in the vessel, *F*. The by-pass tube, *G*, a small section of which was wrapped with electrical heating wire, served as a thermocirculator for the liquid sample as well as to cause gentle boiling. The hydrocarbon vapors, together with the air, passed to the condensers, *H* and *I*, where the vapors were condensed and returned to boiler *E* while the air and noncondensable gas were removed from the system through the vacuum pump. Condenser *H* was cooled with a mixture of carbon dioxide snow and acetone; *I* was cooled with the same mixture or with liquid air, as the volatility of the sample demanded. The sample was refluxed at a pressure of 0.001 to 0.0001 mm. for about 6 hours which, experience showed, was sufficient to remove all dissolved air.

FILLING TUBE WITH AIR-FREE SAMPLE. When the sample had been sufficiently degassed, stopcocks *J*, *K*, and *L* were closed; and, as soon as the condensers warmed up to near room temperature, the sample was forced up through the condensers several times by controlling the pressure in vessel *F*,

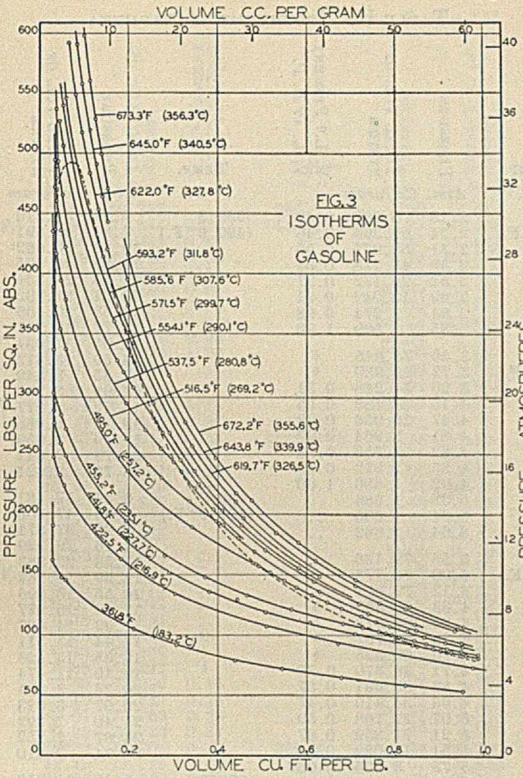


FIG. 3 ISOTHERMS OF GASOLINE

in order to flush out the more volatile constituents which had adhered to the walls. Likewise, the line from the condenser through the U-tube, *M*, to the compartment, *O*, surrounding the experimental tube, was flushed out several times by small quantities of the degassed liquid which was discarded to the vessel, *Q*, through the stopcock, *P*. Stopcock *P* was then closed and the liquid allowed to cover the end of the experimental tube, *R*, which was held in an inverted position in compartment *O* by a tight-fitting rubber stopper. The stopper was covered with a layer of mercury and made vacuum-tight by a mercury seal.

In order to introduce the desired quantity of liquid into the experimental tube, a very narrow hair-like capillary, *S*, was drawn and inserted in the tube to the point *T*, about 3.5 cm. from the end. This capillary tube was held in a fixed position by an offset, *V*, near the top. The top projected into the compartment, *W*, which was connected to *O* through a mercury-sealed ground joint. When the liquid sample covered the end of the experimental tube, the liquid flowed in and completely filled the tube. Mercury was then introduced from *X* until the end of the tube was covered, when, by gently tapping the tube, the mercury entered and displaced all of the liquid sample except that below the end of the small capillary. The apparatus was then brought to atmospheric pressure, section *W* removed, and the capillary withdrawn while the end of the tube was still covered with mercury. The experimental tube was then removed from the apparatus, the end firmly closed with the finger, and the tube turned up in the compressor at an angle of about 45° with the open end under mercury. Any air that might have been trapped in the open end was forced out by carefully warming the sample until it suddenly expanded. The tube was then fixed in place in the compressor.

The weight of liquid in the tube was determined from the volume as measured with the cathetometer and the density as determined on a portion of the air-free sample in a pycnometer.

RESULTS OF PHYSICAL MEASUREMENTS

The A. P. I. gravity, A. S. T. M. distillation, and average molecular weight (determined by freezing-point lowering of benzene) of the two distillates as determined on the deaërated samples are given in Table I.

A number of isotherms were determined experimentally, covering a range from near atmospheric conditions to above the critical region. These data are given in Tables II and III. In the determinations, particular attention was paid to the phenomena occurring in the critical region. Thus the properties in this region were determined to be as given in Table IV.

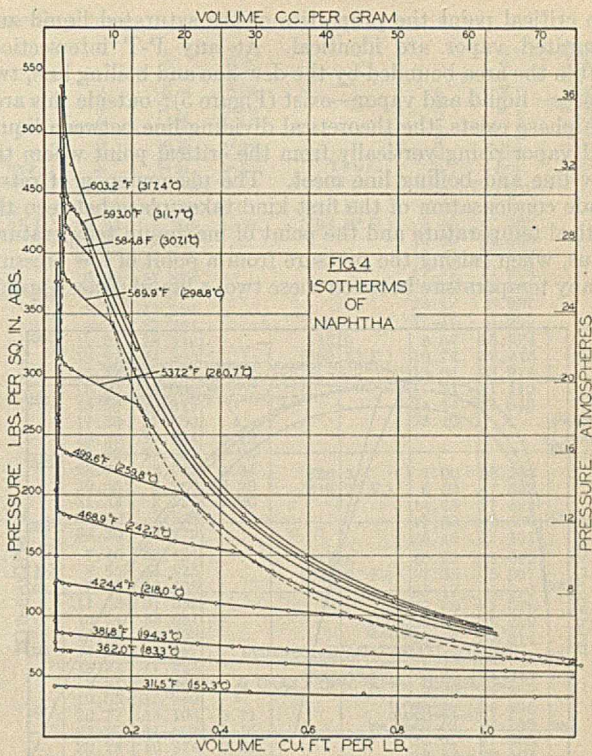


FIG. 4 ISOTHERMS OF NAPHTHA

TABLE I. PHYSICAL MEASUREMENTS OF DISTILLATES

	Mol. Wt.	A. P. I. Grav.	A. S. T. M. Distillation										
			Initial	10	20	30	40	50	60	70	80	90	Max.
			° *F.*	° *F.*	° *F.*	° *F.*	° *F.*	° *F.*	° *F.*	° *F.*	° *F.*	° *F.*	° *F.*
Gasoline	109	57.3	98	149	191	230	260	282	302	325	348	371	414
Naphtha	110	57.1	211	230	238	245	252	258	264	272	282	295	326

The isotherms are shown in Figures 3 and 4, and the data are presented in somewhat different form in Figure 5. Referring to Figure 5, it is notable that the boiling line increases regularly with pressure and temperature, whereas the dew line passes through both a maximum of temperature (termed "point of maximum temperature") and a maximum of pressure in the region of the critical point. This is particularly evident from an examination of the data for the gasoline. The dew line and boiling line meet at the critical point. At

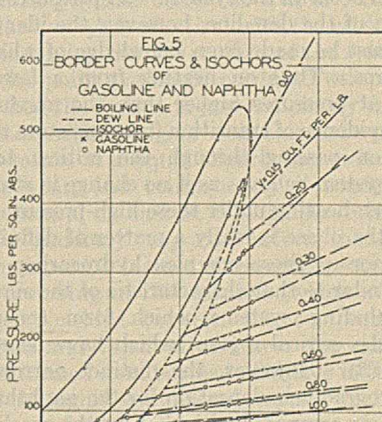


FIG. 5 BORDER CURVES & ISOCHORS OF GASOLINE AND NAPHTHA

the critical point the properties of the saturated liquid and saturated vapor are identical. At any P-T intersection, within the area bounded by the dew line and boiling line, two phases—liquid and vapor—exist (Figure 5); outside this area one phase exists, the theoretical dividing line between liquid and vapor rising vertically from the critical point where the dew line and boiling line meet. The phenomenon of retrograde condensation of the first kind takes place between the critical temperature and the point of maximum temperature. Thus, when raising the pressure from a point of low pressure at any temperature between these two, a liquid phase appears at the lower intersection of the dew line; and, on further compression, the volume of this phase first increases, then decreases, and finally disappears at the upper intersection of the dew line. At the critical temperature, condensation proceeds in a normal fashion as the pressure is increased until, when the system is just completely condensed, it suddenly vaporizes. At the critical point and in the region of retrograde condensation, opalescence occurs on change of state.

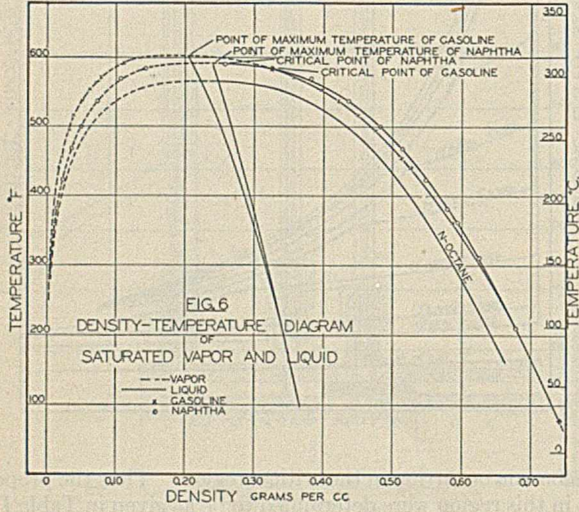


FIG. 6
DENSITY-TEMPERATURE DIAGRAM OF SATURATED VAPOR AND LIQUID

On changing conditions of the system at pressures below the maximum pressure of the dew line, the phases are readily identified according to the known starting point and the changes which occur in the system. At pressures higher than the maximum of the dew line, however, the identification of the phases must be made from knowledge of what occurs at lower pressures. Thus on heating from a low to a high temperature at pressures higher than the maximum of the dew line, no evidence of transition from one state to another is observed when passing through the critical temperature. Visually the system behaves as if no change in state occurs at any point when heating under these high-pressure conditions, and naming the phase is really a matter of definition.

The behavior of these complex hydrocarbon systems is, in general, similar to that characteristic of the simpler binary systems (excluding systems which form constant-boiling mixtures in the critical region) which have heretofore been investigated (*3*). However, the distinct narrowing of the region of retrograde condensation for the naphtha of narrow boiling range, as compared with that for the gasoline of wider boiling range, is noteworthy.

The causes of retrograde condensation, such as is characteristic of these two hydrocarbon systems, may at first appear obscure. For this reason the authors present the following explanation based on a study of the data of Caubet (*3*) on binary mixtures: Caubet has shown that for mixtures of normal liquids the critical temperature lies between that of the higher-boiling and that of the lower-boiling component.

TABLE II. ISOTHERMS OF NAPHTHA

TEMP. ° *C.*	PRESSURE *Atm.*	TOTAL VOL. OF SYSTEM *Cc./gram*	V. L.[a] PRESENT / V. L. AT B. P.
155.3 (311.5° F.)	2.18	78.680	0.42
	2.24	69.266	0.46
	2.31	58.077	0.55
	2.40	45.218	0.64
	2.52	29.132	0.77
	2.69	12.042	0.91
	2.81	3.274	0.98
	2.85	1.599	1.00
183.3 (362.0° F.)	3.56	75.645	[b]
	3.72	65.030	[b]
	3.90	51.248	0.31
	4.16	34.182	0.55
	4.47	16.956	0.78
	4.81	3.964	0.97
	4.82	3.553	0.98
	4.85	2.812	0.99
	4.92	1.686	1.00
	5.28	1.686	..
	6.51	1.686	..
	8.64	1.662	..
194.3 (381.8° F.)	3.85	79.196	..
	4.00	75.778	..
	4.12	72.911	..
	4.32	68.655	[b]
	4.34	67.572	[b]
	4.39	64.757	[b]
	4.46	60.825	[b]
	4.71	46.370	0.28
	4.83	39.491	0.37
	4.93	34.419	0.47
	5.07	27.768	0.59
	5.21	21.859	0.67
	5.51	11.089	0.84
	5.78	3.905	0.96
	5.84	2.6458	0.99
	5.92	1.726	1.00
	6.44	1.724	..
	8.66	1.721	..
	13.86	1.717	..
	25.58	1.703	..
218.0 (424.4° F.)	4.09	79.128	..
	4.39	73.257	..
	4.58	69.874	..
	4.89	64.908	..
	5.14	61.256	..
	5.41	57.713	..
	5.77	53.320	..
	6.18	49.297	..
	6.73	44.089	..
	6.78	43.447	[b]
	6.85	41.802	[b]
	6.94	39.300	[b]
	7.11	34.538	0.20
	7.28	29.738	0.29
	7.49	24.353	0.40
	7.70	19.189	0.54
	7.45.	14.038	0.69
	8.56	3.715	0.95
	8.65	2.734	0.98
	8.72	2.117	..
	8.76	1.826	1.00
	10.16	1.821	..
	13.90	1.816	..
	17.96	1.809	..
	21.27	1.802	..
	26.64	1.795	..
242.7 (468.9° F.)	6.69	48.588	..
	7.58	41.828	..
	8.22	37.831	..
	8.79	34.749	..
	9.29	32.249	..
	9.86	29.738	..
	10.43	26.653	[b]
	10.57	24.600	[b]
	10.82	20.981	0.25
	10.99	18.618	0.33
	11.23	15.905	0.42
	11.32	14.380	0.49
	12.37	3.825	0.92
	12.48	3.043	0.95
	12.66	1.949	1.00
	14.30	1.944	..
	17.59	1.935	..
	20.59	1.926	..
	26.61	1.907	..
259.8 (499.6° F.)	5.86	59.219	..
	7.81	42.891	..
	10.23	30.662	..
	11.82	25.105	..
	12.45	23.334	..
	13.01	21.792	..
	13.63	20.166	[b]
	13.72	19.757	..
	14.05	17.034	0.15
	14.50	13.412	0.35
	15.85	3.849	0.89
	15.99	3.210	0.92
	16.27	2.077	1.00
	18.12	2.068	..
	19.79	2.056	..
	22.79	2.042	..
	26.72	2.021	..
280.7 (537.2° F.)	6.34	57.181	..
	7.58	47.106	..
	9.23	37.574	..
	11.16	29.729	..
	13.58	22.883	..
	14.99	19.767	..
	16.55	16.896	..
	17.52	15.277	..
	17.92	14.607	..
	18.44	13.811	[b]
	18.65	13.428	[b]
	19.10	11.474	0.16
	20.73	3.906	0.83
	20.97	3.023	0.93
	21.40	2.292	1.00
	24.07	2.252	..
	28.24	2.210	..
298.8 (569.9° F.)	6.10	61.258	..
	7.20	51.543	..
	8.83	41.412	..
	11.99	28.832	..
	14.24	23.043	..
	17.77	16.778	..
	20.73	12.792	..
	25.42	3.925	0.75
	25.67	3.318	0.87
	26.12	2.620	1.00
	26.19	2.613	..
	28.11	2.521	..
	30.53	2.450	..
	33.06	2.394	..
307.1 (584.8° F.)	6.45	59.348	..
	7.72	49.358	..
	9.98	37.079	..
	12.48	28.341	..
	17.65	17.898	..
	22.41	11.997	..
	28.36	3.799	0.72
	28.63	3.420	0.87
	28.81	3.063	1.00
	30.02	2.831	..
	32.75	2.630	..
	36.64	2.503	..
310.5 (590.9° F.)	18.71	16.763	..
	22.83	11.948	..
	25.51	9.336	..
	29.37	4.080	..
	29.55	3.857	[c] Critical point
	29.65	3.601	..
	29.94	3.301	..
	30.51	3.049	..
	32.04	2.819	..
	37.1	2.561	..
311.7 (593.0° F.)	24.1	9.566	..
	29.69	4.153	[d] Point of max. temp.
	29.85	3.8876	..
	30.09	3.544	..
	30.43	3.251	..
	31.35	2.975	..
	33.82	2.734	..
317.4 (603.2° F.)	6.31	61.253	..
	7.86	49.590	..
	10.21	37.135	..
	12.17	30.203	..
	15.82	21.703	..
	23.68	11.778	..
	32.26	3.930	..
	36.02	2.905	..
	41.76	2.618	..

[a] V. L. = volume of liquid.
[b] Liquid phase too small in amount to be measured.
[c] Liquid present but not measurable.
[d] Minute trace of liquid on mercury meniscus.

TABLE III. ISOTHERMS OF GASOLINE

TEMP.	PRESSURE	TOTAL VOL. OF SYSTEM	V. L.[a] PRESENT/V. L. AT B. P.
° C.	Atm.	Cc./gram	
183.2	3.63	59.257	..
(361.8° F.)	3.97	51.344	0.35
	4.40	42.332	0.47
	4.89	33.933	0.54
	5.39	27.280	0.59
	6.23	19.158	0.66
	7.15	13.157	0.78
	9.89	3.578	0.94
	10.19	3.009	0.96
	11.00	1.702	1.00
	12.95	1.702	..
216.9	4.99	60.890	[b]
(422.5° F.)	6.343	41.909	0.19
	7.28	31.805	0.32
	9.13	19.037	0.51
	11.08	11.391	0.68
	15.22	3.397	0.92
	15.82	2.749	0.96
	16.83	1.840	1.00
	19.49	1.836	..
	29.59	1.825	..
227.7°	5.52	61.674	..
(441.8° F.)	5.68	59.831	..
	5.85	57.775	..
	6.03	55.240	..
	6.18	52.991	..
	6.25	52.344	0
	6.43	49.884	[b]
	6.86	44.292	[b]
	7.53	37.936	0.16
	8.10	31.649	0.24
	8.61	27.763	0.29
	9.25	23.740	0.37
	10.33	18.202	0.48
	12.29	12.025	0.62
	16.95	3.559	0.91
	17.60	2.818	0.95
	18.78	1.899	1.00
	20.26	1.895	..
	22.06	1.890	..
235.1	5.64	61.604	..
(455.2° F.)	5.85	59.190	..
	6.04	57.079	..
	6.32	54.227	..
	6.50	52.566	..
	6.73	50.447	..
	6.93	48.521	..
235.1	7.00	47.674	0
(445.2° F.)	7.21	45.408	[b]
	7.45	42.641	[b]
	8.23	35.307	[b]
	9.06	29.020	0.22
	10.04	23.195	0.31
	11.32	17.540	0.42
	13.22	12.046	0.58
	18.46	3.556	0.89
	19.20	2.891	0.94
	20.46	1.949	1.00
	22.94	1.938	..
	26.45	1.929	..
257.2	6.13	59.375	..
(495.0° F.)	6.38	56.961	..
	6.71	53.899	..
	7.01	51.564	..
	7.31	49.112	..
	7.58	47.055	..
	7.85	45.162	..
	8.29	42.483	..
	9.06	38.104	..
	9.86	34.324	..
	10.34	32.340	..
	10.80	30.289	0
	10.84	29.986	[b]
	12.90	21.400	0.16
	16.08	12.370	0.43
	22.95	3.579	0.88
	24.02	2.867	0.93
	25.38	2.103	1.00
	28.47	2.078	..
	32.13	2.058	..
269.2	6.34	59.280	..
(516.5° F.)	7.07	52.850	..
	8.00	46.161	..
	9.23	39.202	..
	10.55	34.109	..
	11.52	30.049	..
	12.25	27.820	..
	13.01	25.659	..
	13.11	25.115	0
	13.23	24.731	[b]
	14.36	20.966	[b]
	15.70	17.056	0.17
	17.92	12.205	..
	16.41	15.323	0.24
	25.74	3.548	0.83
269.2	26.79	2.944	0.91
(516.5° F.)	28.31	2.205	1.00
	29.71	2.186	..
	33.65	2.149	..
280.8	6.59	57.874	..
(537.5° F.)	7.16	53.126	..
	8.19	45.854	..
	9.79	37.351	..
	12.27	28.416	..
	13.91	24.390	..
	15.14	21.683	..
	16.05	19.930	..
	16.59	18.812	0
	17.36	17.000	[b]
	18.39	14.834	0.15
	19.92	12.069	0.25
	28.70	3.549	0.81
	29.66	2.969	0.90
	31.33	2.355	1.00
	32.60	2.328	..
	33.30	2.279	..
290.1	7.40	52.621	..
(554.1° F.)	8.55	44.825	..
	9.82	38.358	..
	11.58	31.539	..
	13.84	25.531	..
	15.34	22.203	..
	16.69	19.697	..
	18.21	17.224	..
	18.81	16.362	0
	19.05	15.989	[b]
	20.77	13.103	0.11
	21.67	11.698	0.16
	22.28	10.874	0.20
	31.68	3.251	0.83
	33.49	2.518	1.00
	36.52	2.424	..
299.7	7.58	52.188	..
(571.5° F.)	8.90	44.003	..
	10.59	36.200	..
	13.04	28.329	..
	16.06	21.754	..
	18.20	18.203	..
	19.89	15.908	..
	22.17	13.220	..
	22.57	12.837	0
	24.54	10.423	0.10
	34.43	3.344	0.80
	35.85	2.811	1.00
307.6	8.98	43.787	..
(585.6° F.)	12.13	31.456	..
	16.50	21.667	..
	23.89	12.279	..
	36.90	3.312	Critical point
311.8	6.95	58.558	..
(593.2° F.)	8.50	47.567	..
	10.13	39.156	..
	13.44	28.529	..
	17.72	19.905	..
	23.32	13.081	..
	28.17	8.987	[d]
	37.13	3.685	..
316.9	8.67	46.984	..
(602.5° F.)	10.74	37.415	..
	13.61	28.674	..
	17.31	21.119	..
	24.44	12.648	..
	33.46	[c]	Point of max. temp.
326.5	7.00	58.238	..
(619.7° F.)	8.59	47.563	..
	14.35	27.492	..
	17.50	21.369	..
	25.40	12.401	..
327.8	40.23	4.092	..
(622.0° F.)	37.35	5.067	..
	35.17	5.999	..
	32.88	7.028	..
	30.85	8.259	..
	28.59	9.514	..
339.9	7.15	58.708	..
(643.8° F.)	8.26	51.314	..
	9.59	44.366	..
	10.97	38.595	..
	12.57	33.155	..
	14.82	27.558	..
	18.83	20.401	..
	26.87	12.293	..
340.5	40.17	5.310	..
(645.0° F.)	37.94	6.082	..
	35.33	7.120	..
	33.39	7.989	..
	31.48	8.871	..
	30.14	9.525	..
355.6	7.24	59.486	..
(672.2° F.)	8.40	51.913	..
	9.93	44.336	..
	12.00	36.366	..
	14.43	29.716	..
	16.81	24.707	..
	21.46	18.158	..
	28.30	12.450	..
356.3	40.62	6.279	..
(673.3° F.)	38.08	7.119	..
	35.95	7.919	..
	33.95	8.762	..
	32.00	9.529	..

[a] V. L. = volume of liquid.

[b] Liquid too small in amount to measure.

[c] Mercury meniscus was in an irregular section of the tube, and total volume of tube had not been calibrated at this point.

[d] Trace of liquid present. With increase in pressure, quantity of liquid at first increased, reached a maximum, and then decreased until at succeeding reading no liquid was present. Temperature was too unsteady to measure volume of liquids.

Moreover, the critical temperature of any mixture is fixed by its composition; that is, in any normal mixture the greater the concentration of the constituent of higher critical temperature the higher the critical temperature of the mixture, and vice versa.

Now in any condensation of a normal mixture below the critical temperature the liquid formed is less rich in the more volatile component than is the vapor from which it is condensed; but, as condensation proceeds, the liquid becomes richer in the more volatile component until, when the system is totally condensed, the composition of the liquid is equal to that of the original vapor from which it was produced.

TABLE IV. PROPERTIES OF GASOLINE AND NAPHTHA IN CRITICAL REGION

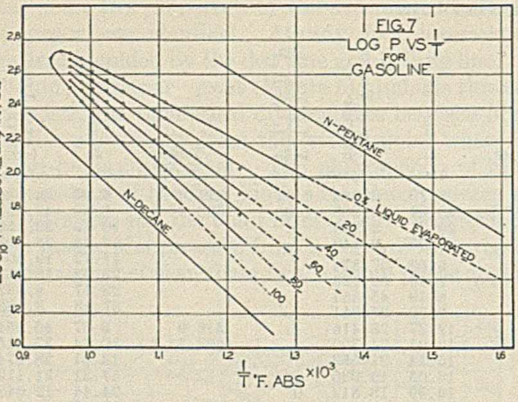
	PROPERTIES AT CRITICAL POINT			PROPERTIES AT POINT OF MAX. TEMP.		
	Pressure	Temp.	Density	Pressure	Temp.	Density (vapor)
	Lb./in.² abs.	° F.	Gram/cc.	Lb./in.² abs.	° F.	Gram/cc.
Gasoline	542	586	0.325	492	603	0.204
Naphtha	434	591	0.258	436	593	0.239

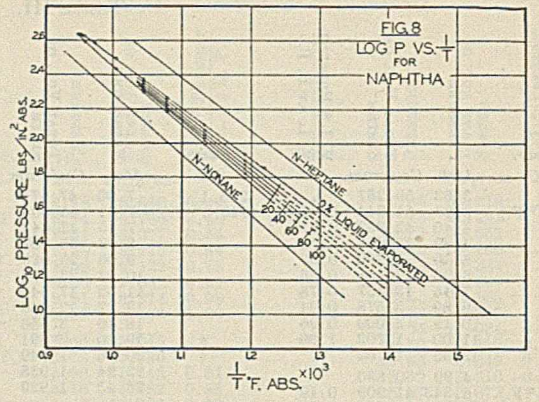
It follows from what has just been said that, as condensation progresses, at constant temperature below the critical from a lower to a higher pressure, the liquid produced has a progressively lower critical temperature. Now if condensation is carried out at progressively higher temperatures (starting at a temperature below the critical), a temperature is finally reached which is identical with the critical temperature of a liquid having the composition of the system in question, and at this point the liquid produced will pass into the vapor state when the system is just completely condensed.

A temperature slightly higher than this corresponds to the critical temperature of a liquid slightly less rich in the more volatile component, and consequently if condensation occurred in the normal manner at this temperature, the liquid formed would suddenly vaporize before the system was completely condensed. Instead of the condensation-vaporization process occurring in this manner (which would lead to anomalous relationships between the composition of the saturated liquid and vapor at and near the critical point), the liquid first formed soon begins to dissolve in the relatively large amount of highly compressed vapor remaining and is eventually revaporized by this means.

While the hydrocarbon systems studied here are much more complex than any studied by Caubet, the explanation of retrograde condensation as given above is still tenable.

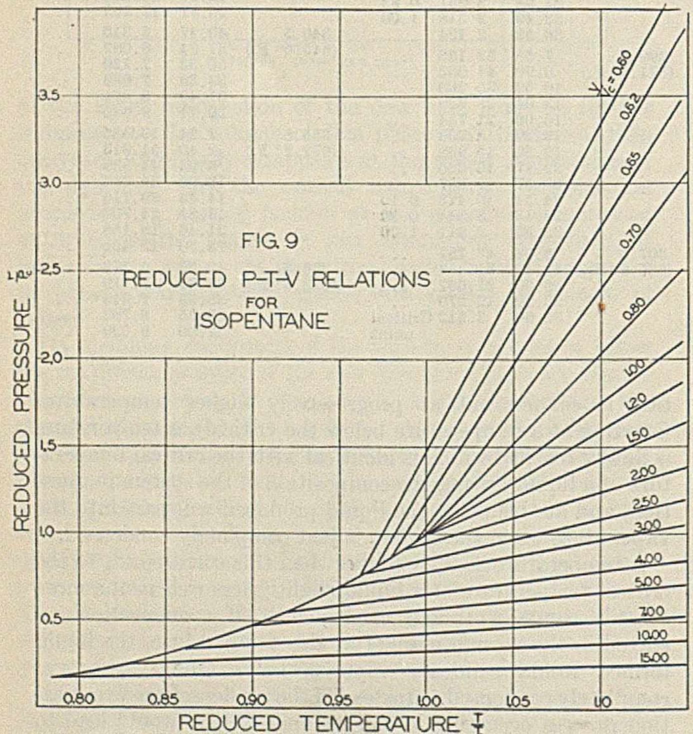
The relationships between density and temperature for the saturated liquid and vapor are shown in Figure 6, which includes also the data of Young on normal octane. It will be noted that the density-temperature relationships for these hydrocarbon mixtures are, in general, similar to the behavior





of pure compounds except that in the case of mixtures the mean density line passes through the point of maximum temperature rather than the critical point. However, in this respect also these complex systems are similar in behavior to the simpler binary systems.

The relationships between pressure, temperature, and percentage of liquid evaporated are shown in Figures 7 and 8 where log pressure is plotted against the reciprocal of the absolute temperature for various percentages evaporated. As might be expected, a straight line relationship between P and $\frac{1}{T}$ holds at constant percentage evaporated, except in the region of retrograde condensation.



Correlation of Physical Properties

Data such as are given in the preceding paragraphs are extremely useful in the development of high-pressure high-temperature processes in the petroleum industry. However, the determinations of the isotherms over a useful range of pressures is a laborious and time-consuming operation, and it is therefore desirable to have some method of correlation if possible, so that a number of determinations required can be reduced to a minimum.

For the purpose of correlation the theorem of corresponding states offers perhaps the best possibility. This theorem has been rather generally tested by Young (*8*) who found that it holds with quite good accuracy for certain closely related substances whose critical pressures are very nearly equal, and with fair accuracy for closely related substances having quite different critical pressures.

If the theorem of corresponding states were strictly true, all pressure-temperature-volume relationships for pure compounds could be represented by a single relationship such as is shown in Figure 9 where the reduced isochors, $\frac{V}{V_c}$ = constant, for isopentane (*9*) are shown as related to reduced temperature $\frac{T}{T_c}$ and reduced pressure $\frac{P}{P_c}$. As shown by Figure 10, however, where similar relationships for five hydrocarbons are given, the theorem of corresponding states is only approximately correct. There appears, however, a systematic shift with molecular weight which could no doubt be evaluated if necessary.

The theorem of corresponding states was applied to the two hydrocarbon systems studied here, and the reduced isochors are shown in Figure 11 in comparison with the data of isopentane. The agreement between the two hydrocarbon systems in the superheated vapor region is as good as might be expected. Moreover, the data are in fair agreement with those of isopentane except in the critical region. It appears, therefore, that the data for some other hydrocarbon system in the superheated region could be estimated over a fair range of pressures and temperatures from Figure 11, together with a determination of the critical temperature, pressure, and volume.[1]

The relationships, as in Figure 11, along the saturation lines are a function of the boiling range of the fraction under consideration, and further data are necessary before general correlation can be made.

Calculation of Thermal Properites

The P-T-V data are not only valuable in themselves but serve for the calculation of various thermal properties which are difficult to measure with accuracy. From the data in the foregoing sections it is possible to calculate, using the exact

---

[1] Since this paper was compiled, Cope, Lewis, and Weber [Ind. Eng. Chem., **23**, 887 (1931)] have presented a method of calculating the P-V-T data of a hydrocarbon in the superheated region, based on a modification of the theorem of corresponding states. Values of the specific volume of the vapor of gasoline and naphtha calculated by this method agree with the experimental to within about 4 per cent. However, within the range of the experimental data, for pressures and temperatures near the critical region, the deviations are somewhat greater and are of the order of 5 to 10 per cent.

laws of thermodynamics, the following thermal properties: change of specific heat with pressure; difference in specific heat at constant pressure and constant volume; Joule-Thomson coefficients; latent heats of vaporization; and ratios of specific heats.

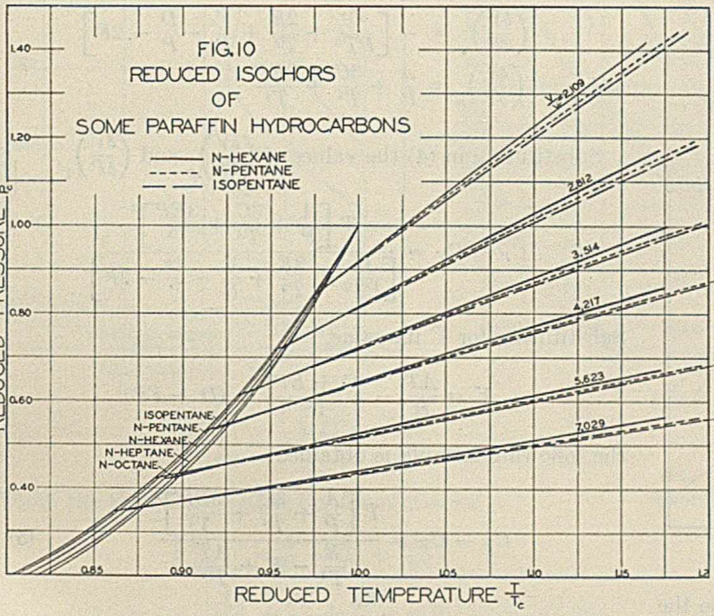


FIG. 10
REDUCED ISOCHORS OF SOME PARAFFIN HYDROCARBONS

From the values of the above thermal properties and a temperature–total heat relationship under one condition, a complete temperature–pressure–total heat diagram can be constructed. This has been done for the naphtha studied here, and the method and results of the calculations are given in the following paragraphs.

The first and second laws of thermodynamics provide the basis of the equations necessary for the calculation of thermal properties. The derivation of the equations are in all cases perfectly general; hence they apply to mixtures as well as to pure substances. The derivation of the equations used below for calculation of thermal properties are given in most textbooks of thermodynamics and have therefore been omitted here.

For calculation of the various thermal properties the following equations were used:

1. Change of specific heat with pressure,

$$\left(\frac{\delta C_p}{\delta P}\right)_T = -T\left(\frac{\delta^2 V}{\delta T^2}\right)_P$$

2. Difference in specific heats,

$$C_P - C_V = -T\,\frac{\left(\frac{\delta V}{\delta T}\right)_P^2}{\left(\frac{\delta V}{\delta P}\right)_T}$$

3. Joule-Thomson coefficient,

$$\mu = \left(\frac{\delta T}{\delta P}\right)_H = T\,\frac{\left(\frac{\delta V}{\delta T}\right)_P - V}{C_P}$$

4. Latent heat of vaporization,

$$dH = TdS + VdP$$

The evaluation of the above equations can be accomplished either graphically or through use of an equation of state by differentiation. Since, for most refinery operations, the evaluation of the thermal properties in the vapor state are most useful, an equation of state applying to the vapor state serves to the most probable range of utility. The heat of vaporization, however, is best evaluated graphically as will be shown.

In selecting an equation of state, one may be guided by the forms which have been shown to express the relationships for similar substances (*2*). However, simplicity of mathematical form must be considered if the equation is to be of greatest use in the calculation of the various properties. For the present purpose various equations were examined by the authors, and the one finally chosen was that proposed by Linde (*6*) for superheated steam. In its expanded form it is as follows:

$$PV = AT - \frac{P(C + EP)}{T^3} + P(D + FP)$$

where A, C, D, E, and F = constants

As applied to naphtha, the constants in the above equation were evaluated as follows:

$A = 157$
$C = 7234 \times 10^7$
$D = 20$
$E = 102 \times 10^7$
$F = 0.52$
When P = lb. per sq. in. abs.
T = ° Rankine
V = cu. in. per lb.

The degree to which the equation fits the experimental data is shown in Figure 12. The solid lines represent the experimental data while the broken lines were calculated using the equation of state. The agreement is excellent except near the saturation line. At 200 pounds per square inch the deviation is insignificant, but at higher pressures it becomes appreciable. For this reason all thermal properties calculated, using the equation, are certain to be in error to some extent in this region. The regions where this occurs have been indicated by broken lines in the various plots of these properties.

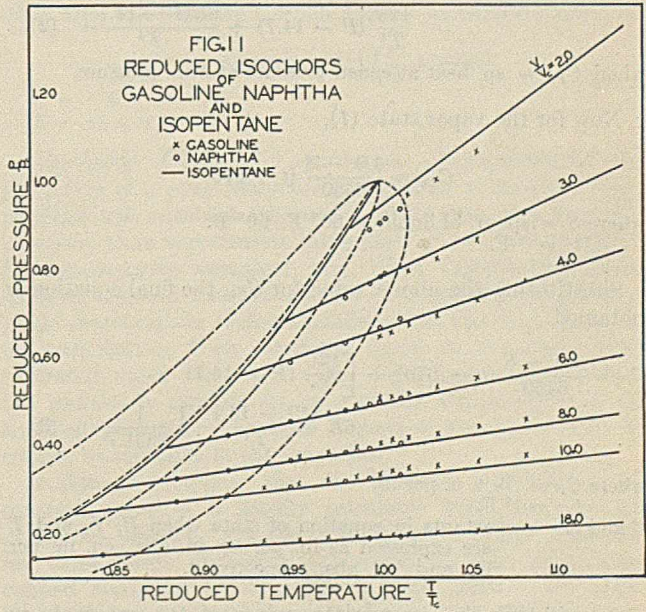


FIG. 11
REDUCED ISOCHORS OF GASOLINE NAPHTHA AND ISOPENTANE

1. CALCULATION OF SPECIFIC HEAT C_p AT HIGH PRESSURE. The thermodynamic formula is:

$$\left(\frac{\delta C_p}{\delta P}\right)_T = -T\left(\frac{\delta^2 V}{\delta T^2}\right)_P \qquad (1)$$

From the equation of state by differentiation,

$$P\left(\frac{\delta V}{\delta T}\right)_P = A + \frac{3CP}{T^4} + \frac{3EP^2}{T^4}$$

and

$$P\left(\frac{\delta^2 V}{\delta T^2}\right)_P = \frac{-12CP}{T^5} - \frac{12EP^2}{T^5}$$

or
$$\left(\frac{\delta^2 V}{\delta T^2}\right)_P = \frac{-12C}{T^5} - \frac{12EP}{T^5}$$

Substituting in Equation 1,

$$\left(\frac{\delta C_p}{\delta P}\right)_T = \frac{12C}{T^4} + \frac{12EP}{T^4}$$

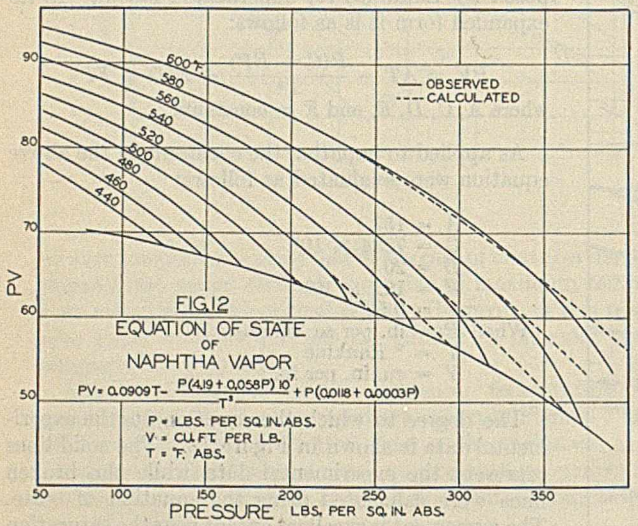


FIG. 12
EQUATION OF STATE OF NAPHTHA VAPOR

Integrating the above equation (T = constant) between the limits of a pressure, P, and atmospheric pressure,

$$C_P - C_{P_0} = \left[\frac{12CP}{T^4} + \frac{6EP^2}{T^4}\right]_{14.7}^{P} = \frac{12C}{T^4}(P - 14.7) + \frac{6E(P^2 - 14.7^2)}{T^4} \qquad (2)$$

where C_{P_0} = sp. heat at const. pressure at atm. pressure.

Now for the vapor state (*1*),

$$C_{P_0} = \frac{4.0 - S}{6450}(t + 670)$$

where S = sp. gr. of liquid at 60° F./60° F.
t = ° F.

Substituting the above value for C_{P_0}, the final equation is obtained:

$$C_P = \frac{4.0 - S}{6450}(t + 670) + \left[\frac{12C}{T^4}(P - 14.7) + 6E\frac{(P^2 - 14.7^2)}{T^4}\right]\frac{1}{9331.7} \qquad (3)$$

where C_P = B. t. u. per lb.
t = ° F.
C and E = constants in equation of state when P, V, and T are expressed as lb. per sq. in. abs., cu. in. per lb., and ° F. abs., respectively.

Substituting the appropriate values of the constants in Equation 3, the following equation for the specific heat at constant pressure of naphtha as a function of temperature and pressure is obtained:

$$C_P = \frac{4.0 - 0.7500}{6450}(t + 670) + \frac{(9.316P + 0.065P^2 - 151)10^7}{(t + 459.6)^4}$$

This equation has been used to calculate the specific heat at constant pressure from atmospheric pressure to 350 pounds per square inch abs. The results of the calculation have been plotted and are shown in Figure 13.

2. Calculation of $C_P - C_V$. The thermodynamic formula is:

$$C_P - C_V = \frac{-T\left(\frac{\delta V}{\delta T}\right)_P^2}{\left(\frac{\delta V}{\delta P}\right)_T} \qquad (4)$$

From the equation of state by differentiation,

$$\left(\frac{\delta V}{\delta P}\right)_T = -\left[\frac{C}{PT^3} + \frac{2E}{T^3} + \frac{V}{P} - \frac{D}{P} - 2F\right]$$

and
$$\left(\frac{\delta V}{\delta T}\right)_P = \frac{A}{P} + \frac{3C}{T^4} + \frac{3EP}{T^4}$$

Substituting in (4) the values of $\left(\frac{\delta V}{\delta T}\right)_P$ and $\left(\frac{\delta V}{\delta P}\right)_T$,

$$C_P - C_V = \frac{T\left[\frac{A}{P} + \frac{3C}{T^4} + \frac{3EP}{T^4}\right]^2}{\left[\frac{C}{PT^3} + \frac{2E}{T^3} + \frac{V}{P} - \frac{D}{P} - 2F\right]}$$

Substituting for V its value,

$$V = \frac{AT}{P} - \frac{(C + EP)}{T^3} + (D + FP)$$

the following formula is obtained:

$$C_P - C_V = \frac{T\left[\frac{A}{P} + \frac{3C}{T^4} + \frac{3EP}{T^4}\right]^2}{\frac{E}{T^3} - F + \frac{AT}{P^2}} \qquad (5)$$

Equation 5 may be simplified by rearrangement to give

$$C_P - C_V = \frac{[AT^4 + P(3C + 3EP)]^2}{T^4\,[P^2(E - FT^3) + AT^4]\,9331.7} \qquad (6)$$

where $C_P - C_V$ = B. t. u. per lb.
A, C, E, and F = constants in equation of state when P, V and T are expressed as lb. per sq. in. abs., cu. in. per lb. and ° F. abs., respectively.

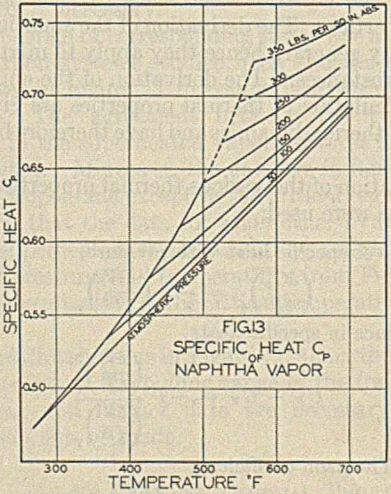


FIG. 13
SPECIFIC HEAT C_P OF NAPHTHA VAPOR

Substituting the appropriate values of the constants in Equation 6, the following formula for the difference in the specific heats of the naphtha is obtained:

$$C_P - C_V = \frac{[157T^4 + P(21730 + 305P)10^7]^2}{T^4[P^2(948{,}970 \times 10^7 - 4805T^5) + 1{,}465{,}000T^4]}$$

The results calculated from the above formula for pressures from atmospheric to 350 pounds per square inch absolute are given in Figure 14.

3. Calculation of Joule-Thomson Effect. The thermodynamic equation is:

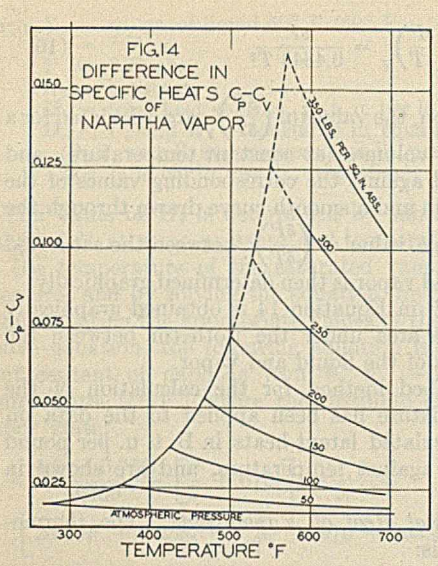


FIG. 14 DIFFERENCE IN SPECIFIC HEATS $C_P - C_V$ OF NAPHTHA VAPOR

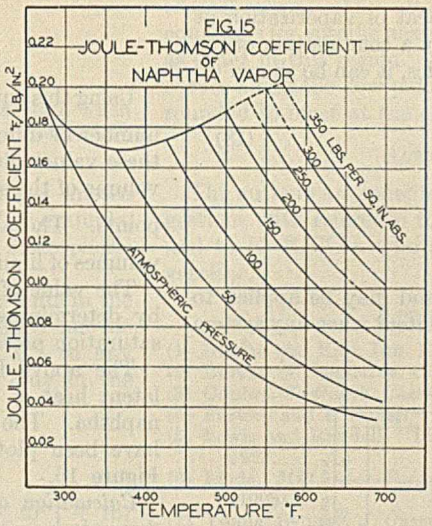


FIG. 15 JOULE-THOMSON COEFFICIENT OF NAPHTHA VAPOR

$$\mu = \left(\frac{\delta T}{\delta P}\right)_H = \frac{T\left(\frac{\delta V}{\delta T}\right)_P - V}{C_P} \tag{7}$$

From the equation of state by differentiation

$$\left(\frac{\delta V}{\delta T}\right)_P = \frac{A}{P} + \frac{3C}{T^4} + \frac{3EP}{T^4}$$

Then

$$\mu = \frac{\frac{AT}{P} + \frac{3C}{T^3} + \frac{3EP}{R^3} - V}{C_P} \tag{8}$$

Now

$$V = \frac{AT}{P} - \frac{(C + EP)}{T^3} + (D + FP)$$

and from Equation 3

$$C_P = \frac{4.0 - S}{6450}(t + 670) + \left[\frac{12C}{T^4}(P - 14.7) + 6E\frac{(P^2 - 14.7^2)}{T^4}\right]\frac{1}{9331.7}$$

Substituting these values in Equation 8 and simplifying

$$\mu = \frac{[T(4C + 4EP) - T^4(D + FP)]\,9331.7}{T^4\left[\frac{4.0 - S}{6450}(t + 670)\right] + 12C\,(P - 14.7) + 6E\,(P^2 - 14.7^2)} \tag{9}$$

where μ = ° F. per lb. per sq. in.
$T = t$° F. + 459.6
P = lb. per sq. in. abs.
S = sp. gr. at 60° F./60° F. of liquid
C, D, E, and F = constants in equation of state

When the appropriate constants are substituted into Equation 9, the following equation for the Joule-Thomson coefficient for naphtha results:

$$\mu = \frac{T(3.10 + 0.044P)10^7 - T^4(0.0022 + 0.00006P)}{T^4\left[\frac{4.0 - 0.750}{6450}(t + 670)\right] + P(9.31 + 0.065P)10^7}$$

The coefficient for various pressures from atmospheric to 350 pounds per square inch have been calculated and are shown in Figure 15.

4. CALCULATION OF TOTAL HEAT CONTENT FROM 0° F. The heat required to change a liquid distillate at 0° F. (−17.8° C.) to a superheated vapor may conveniently be divided into three parts: (1) the heat required to heat the liquid from 0° F. to the boiling point; (2) the heat required to vaporize the liquid; and (3) the heat required to heat the vapor.

Heat Content from 0° F. (−17.8° C.) to Boiling Point. The change in heat content of a system is given by the exact thermodynamic equation:

$$dH = C_P\,dT - \left[T\left(\frac{\delta V}{\delta T}\right)_P - V\right]dP \tag{10}$$

For the liquid state, however, calculation reveals that for the pressure range considered here the second member of the equation is insignificant (except near the critical state) and may be disregarded.

Then

$$dH = C_P dT$$

For the liquid state (*4*)

$$C_P = \frac{2.10 - S}{2030}(t + 670) \tag{11}$$

where t = ° F. and S = sp. gr. at 60° F./60° F.

$$H - H_0 = \frac{2.10 - S}{2030}\int_0^t (t + 670)dt$$

$$H - H_0 = \frac{2.10 - S}{2030}\left[\frac{t^2}{2} + 670t\right] \tag{12}$$

where $H_0 = 0$ at $t = 0$° F.

This equation for the total heat content of the liquid from 0° F. to a temperature t, when applied to naphtha becomes

$$H = 6.6502 \times 10^{-4}\left(\frac{t^2}{2} + 670t\right)$$

t = ° F.
H = B. t. u. per lb.

Calculation of Heat of Vaporization. The process of vaporization of a pure compound takes place at constant temperature and constant pressure. In the case of a mixture, however, when vaporization takes place at constant pressure, the temperature increases; and, when vaporization takes place at constant temperature, the pressure decreases (retrograde condensation region excluded) and the heat required for vaporization from saturated liquid to the same final saturated vapor state will vary, depending upon whether the process is carried out at constant temperature or at constant pressure. The heat content of the vapor will, of course, be the same in the two cases.

It does not appear that the heat of vaporization at constant pressure is readily calculable from the physical properties directly. On the other hand, the heat required for vaporization at constant temperature can be so calculated according to the method given below.[2] By combining these values with the heat of the liquid, the total heat of the saturated vapor at any temperature and its corresponding pressure may be obtained. The heat of vaporization at constant pressure can then be computed by substraction of the heat of the liquid up to the temperature of the boiling point at that pressure.

---

[2] The amount of heat that would be absorbed if the vaporization of a mixture were conducted reversibly at constant temperature is greater than the difference in heat content of saturated vapor and boiling liquid at the same temperature. In actual refinery operation this type of vaporization does not occur; however, the change in heat content is more important. There appears to be no generally accepted definition of the heat of vaporization of a mixture. As used in this paper, it means change in heat content of unit weight of the system when the temperature is constant and the pressure decreases from that of the boiling point to that of the dew point.

The method of calculation of the heat of vaporization at constant temperature is as follows: By a combination of the first and second laws of thermodynamics, it can be shown (*5*) that

$$dH = TdS + VdP \tag{13}$$

where H = heat content
S = entropy
T = abs. temp.
V = volume of system
P = pressure

This equation is perfectly general and may be applied to the calculation of the change of heat content when any system undergoes a change.

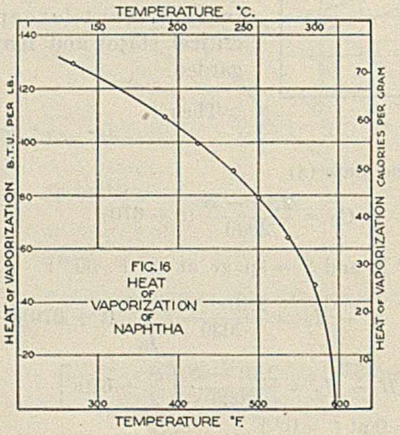


FIG. 16 HEAT OF VAPORIZATION OF NAPHTHA

In its application to the vaporization of a liquid mixture at constant temperature T,

Since

$$(\delta S)_T = \left(\frac{\delta P}{\delta T}\right)_V (\delta V)_T$$

Equation 13 becomes

$$dH = T\left(\frac{\delta P}{\delta T}\right)_V (\delta V)_T + VdP$$

Putting $dH = L$, the latent heat, and $(\delta V)_T = (V_V - V_L)_T$, the difference between the volumes of unit weight of saturated vapor and liquid, respectively, at temperature T, Equation 14 is obtained:

$$L = T\left(\frac{\delta P}{\delta T}\right)_V (V_V - V_L)_T + VdP \tag{14}$$

Since the equilibrium pressure varies continuously throughout, the vaporization $\left(\frac{\delta P}{\delta T}\right)_V$ changes continuously, and it is necessary to determine the average value during the course of the vaporization. This may be done graphically as follows: From a plot of the isotherms similar to Figure 4, the values of the pressure and temperature at constant volume are read off for a number of constant volumes. The pressure-temperature data for each volume are then plotted as $\log_{10} p$ against $1/T$(abs.), and the slope of the lines measured. These slopes are plotted against the corresponding values of the volume to give a curve from which the slope of the line can be obtained for any volume of the system during vaporization.

If s = slope of line,

then

$$\left(\frac{\delta \log_{10} P}{\delta \frac{1}{T}}\right)_V = -s = -0.4343\,\frac{T^2}{P}\left(\frac{\delta P}{\delta T}\right)_V \tag{15}$$

or

$$\left(\frac{\delta P}{\delta T}\right)_V = \frac{sP}{0.4343\,T^2} \tag{16}$$

Using this equation, the values of $\left(\frac{\delta P}{\delta T}\right)_V$ are calculated for a number of different volumes (at constant temperature), and these values plotted against the corresponding values of the volume of the system and a smooth curve drawn through the points. The average value of $\left(\frac{\delta P}{\delta T}\right)_V$ between the saturated volumes of liquid and vapor is then determined graphically.

The value of VdP in Equation 14 is obtained graphically by determining the area under the isotherm between the saturation pressures of the liquid and vapor.

The above-described method for the calculation of the latent heat of a mixture has been applied to the data on naphtha. The calculated latent heats in B. t. u. per pound have been plotted against temperature, and are shown in Figure 16.

Calculation of Total Heat of Vapor State. The thermodynamic equation is:

$$dH = C_P dT - \left[T\frac{(\delta V)}{(\delta T)_P} - V\right] dP \tag{17}$$

Now

$$C_P = C_{P_0} + \frac{12CP}{T^3} + \frac{6EP^2}{T^3}$$

and

$$V = \frac{AT}{P} - \frac{C}{T^3} - \frac{EP}{T^3} + D + FP$$

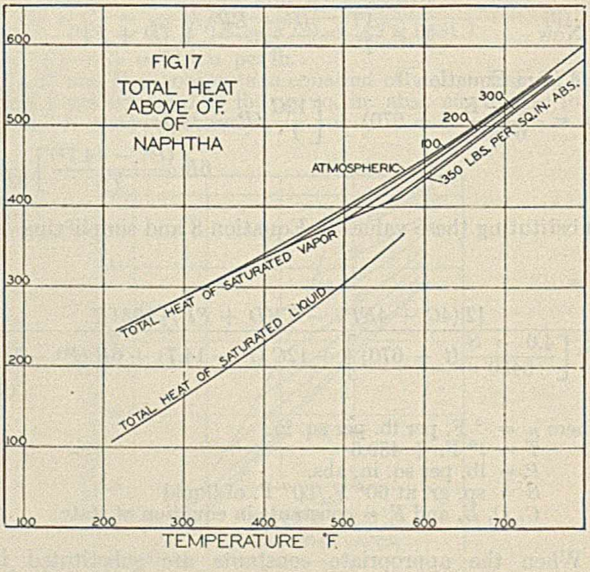


FIG. 17 TOTAL HEAT ABOVE 0° F. OF NAPHTHA

Substituting in the above equation and simplifying:

$$dH = \left[C_{P_0} + \frac{12CP}{T^4} + \frac{6EP^2}{T^4}\right] dT - \left[\frac{4C}{T^3} + \frac{4EP}{T^3} - D - FP\right] dP$$

Since

$$C_{P_0} = \frac{4.0 - S}{6450}\,(t + 670)$$

the above equation when integrated gives

$$H - H_0 = \frac{4.0 - S}{6450}\left[\frac{t^2}{2} + 670t\right] + \frac{1}{9331.7}\left(DP + \frac{FP^2}{2} - \frac{4CP}{T^3} - \frac{2EP^2}{T^3}\right) \tag{18}$$

where S = sp. gr. of liquid 60° F./60° F.
t = ° F.
T = ° F. abs.
H_0 = constant
H = total heat content, B. t. u. per lb.
D, F, C, and E = constants in equation of state when P, T, and V are expressed as lb. per sq. in. abs., ° F. abs., and cu. in. per lb., respectively.

The value of H_0 is determined by substituting a known value of H at some pressure and temperature (for example, at the temperature of the saturated vapor at atmospheric pressure) and by solving the equation for H_0.

Substituting the appropriate values of the constants in the above equation, the following equation is obtained for the heat content of naphtha from 0° F. (−17.8° C.) to any temperature (t° F.) where the distillate exists only in the vapor state:

$$H = \frac{4.0 - 0.7500}{6450}\left[\frac{t^2}{2} + 670t\right] + \frac{1}{9331.7}$$
$$\left[20.47P + 0.258P^2 - \frac{P}{T^3}(28{,}970 + 203.4P) \times 10^7\right] + 167$$

The values of the total heat for various pressures and temperatures have been calculated for naphtha, and the results plotted against temperature in Figure 17.

It will be noted that Figure 17 is not complete in the critical region. This arises partly through the fact that the equations for specific heats of the liquid cannot be guaranteed as exact in this region. In general, however, the total-heat curves along the dew-point and boiling-point curves should be rounded to meet at the critical point.

ACKNOWLEDGMENT

The authors are indebted to E. W. Thiele for valuable suggestions with reference to the calculation of the latent heat, and to E. R. Kirn who aided in the experimental work on gasoline.

LITERATURE CITED

(1) Bahlke and Kay, IND. ENG. CHEM., 21, 942 (1929).
(2) Bureau of Standards, *Circ.* 279, 77 (1926).
(3) Caubet, *Z. physik. Chem.*, 40, 257 (1902).
(4) Fortsch and Whitman, IND. ENG. CHEM., 18, 795 (1926).
(5) Lewis and Randall, "Thermodynamics," p. 133, McGraw-Hill, 1923.
(6) Linde, *Mitt. über Forsch-arbeiten vom Ver. deut. Ing.*, 21, 64 (1905).
(7) Young, Sydney, *J. Chem. Soc.*, 47, 640 (1885).
(8) Young, Sydney, *Phil. Trans.*, 177, Part 1, 135 (1886).
(9) Young, Sydney, *Z. physik. Chem.*, 29, 193 (1899).

RECEIVED November 9, 1931. Presented before the Division of Petroleum Chemistry at the 82nd Meeting of the American Chemical Society, Buffalo, N. Y., August 31 to September 4, 1931.

Tower-Absorption Coefficients—IV

L. M. BENNETCH AND C. W. SIMMONS, Department of Chemical Engineering, Lehigh University, Bethlehem, Pa.

Mole-flow ratio and free-volume concepts are introduced into the derivation of a general absorption equation which is applicable equally to systems obeying either Henry's or Raoult's law

MUCH has been written concerning the mechanism of gas absorption by countercurrent tower processes, and much emphasis has been placed on the graphical solution of tower-design problems. It is the purpose of this paper to give a mathematical analysis of countercurrent tower processes, to derive an absorption equation, and to apply this equation to some experimental data.

DONNAN-MASON CONCEPT

The derivation of a satisfactory equation representing the continuous countercurrent absorption process, such as is used in gas scrubbing, depends chiefly upon the function representing the rate of solution of the solute gas in the extractor. This rate of solution was given by Donnan and Masson (*3*) to be

$$\frac{dm}{dt} = f(m) - n \qquad \text{(A)}$$

where m = gram concentration of solute in carrier gas
n = gram concentration of solute in extractor

At equilibrium, when no absorption occurs, $f(m)$, some function of m, and n are equal. In addition, in a system obeying Henry's law, $f(m)$ equals $k(m)$ where k is Henry's coefficient. Cantelo (*1*) utilized this fact to transform the original equation of the rate of solution to

$$\frac{dm}{dt} = -K(km - n) \qquad \text{(B)}$$

where K = Cantelo dissolution coefficient, which, for strictly specified conditions of gas and extractor flow, etc., will remain a constant

With the aid of a second equation based on the fact that a steady state prevails within a countercurrent absorption unit, Cantelo integrated Equation B obtaining a formula for investigating tower-absorption coefficients.

LEWIS CONCEPT

It was proposed by Lewis (*4*) and Whitman and Keats (*6*) that the rate of solution of soluble gas in extractor can be more accurately represented by

$$\frac{dm}{dt} = -K(P_g - P_l)$$

where $P_g - P_l$ = difference between partial pressure of solute in gas and vapor pressure of solute in extractor

Here equilibrium conditions prevail when $P_g = P_l$. The Lewis form may be equated to the Donnan and Masson form by applying Henry's or Raoult's law and converting the partial pressures to gram concentrations. Thus in

$$P_l = HX$$

P_l = vapor pressure of solute in extractor
X = its mole fraction
H = either Henry's or Raoult's factor

However, the fundamental difference between these equations for the rate of solution is in the units expressing solute concentrations. The first form which uses gram concentrations introduces an inaccuracy, owing to the fact that the concentrations in Henry's and Raoult's laws must be given in mole fractions. The Lewis rate-of-solution equation readily lends itself to evaluation in mole-fractional quantities, and it is therefore used as the basis of the derivation in this article.

Fundamental Assumptions

A countercurrent tower-absorption process is assumed in which there exists a steady state. Thus, at any chosen point in the tower, all factors, such as temperature, pressures, or rates, are constant. Mathematically this means that at any fixed point in the tower all derivatives with respect to time are zero. Moreover, the extractor is taken to exert a negligible vapor pressure, and the carrier gas to be inert. For example, these conditions obtain in a benzene scrubbing unit where coke-oven gas is the inert carrier and the petroleum-oil extractor is nonvolatile at the temperature of the system. The recovery of hydrocarbons from natural gas is a similar process. However, in the case of water, aqueous solutions, and organic solvents being used as the extracting medium, there may be error introduced into the calculations if these extractors exert an appreciable vapor pressure. The magnitude of this error will depend upon the ratio of the vapor pressure of the extractor to the total gas pressure within the tower, and to the partial pressure of extractor in the entering gas, i. e., the degree of saturation of entering gas. Finally, it is assumed that the systems obey Henry's or Raoult's law and that these coefficients are known at the temperatures and pressures involved.

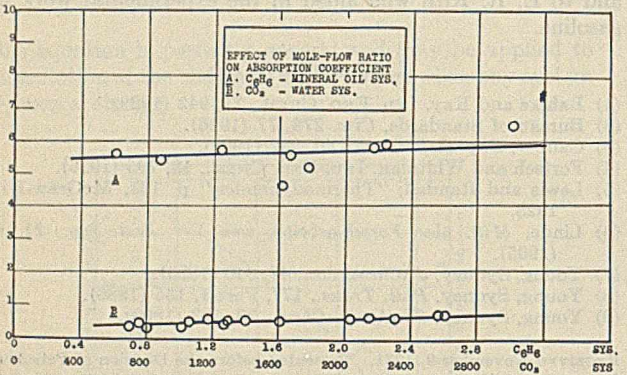


Figure 1

The nomenclature which follows applies to the derivation of tower-absorption coefficients using mole-flow ratios and free volumes, and expressing concentrations or partial pressures in terms of mole fractions.

A = area of cross section × free volume/unit gross volume, sq. dm.
h = height above gas inlet, dm.
Ah = free volume of tower, liters
$\frac{dh}{d\theta}$ = gas rate up tower, dm./min.
ρ = density of carrier gas, grams/liter
m = molecular weight of carrier, grams
M = molecular weight of extractor, grams
w = carrier rate, grams/min.
W = extractor rate, grams/min.
f = mole-flow ratio
P_g = partial pressure of solute in gas, atm.
P_{gas} = total average pressure of gas in tower, atm.
P_l = vapor pressure of solute in extractor, atm.
Z = Henry's or Raoult's coefficient, atm.
K = absorption coefficient
θ = unit of time, min.
y = moles solute/mole carrier at time θ
x = moles solute/mole extractor at time θ
Subscripts (0) refer to conditions at h = zero
No subscripts refer to conditions at h = height of tower

A countercurrent absorption process may be represented by the equation of continuity:

$$A\rho \frac{dh}{d\theta} = w \qquad (1)$$

This equation states that there is no change in the quantity of carrier in its passage through the tower. It can be transformed into terms of partial press:

$$\frac{dh}{d\theta} = \frac{w}{A} \times \frac{22.4}{m}\left(\frac{P_{gas}}{P_{gas} - P_g}\right) \qquad (2)$$

where $\frac{1}{\rho} = \frac{22.4}{m}\left(\frac{P_{gas}}{P_{gas} - P_g}\right)$

It can also be shown that

$$\frac{dP_g}{d\theta} = -K(P_g - P_l) \qquad (3)$$

Equation 3 is the equation adopted as representing the rate of solution, expressed as rate of change of partial pressure of solute in the gas as a function of $(P_g - P_l)$.

$$\frac{P_g}{P_{gas}} = \frac{y}{1+y} = \text{mole fraction of solute in gas} \qquad (4)$$

or
$$y = \frac{P_g}{P_{gas} - P_g}$$
$$dP_g = \frac{P_{gas}\,dy}{(1+y)^2}$$
$$P_{gas} - P_g = \frac{P_{gas}}{1+y}$$

Equation 4 is supported by Avogadro's and Dalton's gas laws.

Now
$$\frac{P_l}{Z} = \frac{x}{1+x} \qquad (5)$$
$$x = \frac{P_l}{Z - P_l}$$

Equation 5 is a statement of Henry's or Raoult's vapor-pressure law, with concentrations expressed in moles per mole.

$$\frac{w}{m}(y_1 - y) = \frac{W}{M}(x_1 - x) \qquad (6)$$

Equation 6 is a solute-balance relationship between carrier and extractor.

Let $\frac{Wm}{Mw} = f$, the mole-flow ratio, and $i = y_1 - fx_1$, a constant depending upon terminal conditions, or Equation 6 becomes $y = i + fx$

and
$$P_l = \frac{(y - i)}{(b + y - i)}$$

Equations 3 and 2 are combined, and the necessary substitutions performed to eliminate Pg, P_l, and x, yielding

$$\frac{(f - i + y)dy}{P_{gas}\,y\,(f - i + y) - Z(y - i)(i + y)} = -\frac{KAm}{22.4\,w\,P_{gas}}\,dh \qquad (7)$$

Let
$$-\frac{KAm}{22.4\,wP_{gas}} = K'$$

and
$$(f - i) = D$$

Equation 7 is integrated according to the form

$$\int\frac{D + y}{a + by + cy^2} = \frac{1}{2c}\ln(a + by + cy^2) + \frac{2cD - b}{2c}\int\frac{dy}{a + by + cy^2}$$

where a, b, and c = coefficients in quadratic denominator of Equation 7.

Integrating and evaluating the constant,

$$\ln\frac{a + by + cy^2}{a + by_0 + cy^2_0} + \frac{2cD - b}{\sqrt{b^2 - 4ac}}\ln\frac{(2cy + b - v)(2cy_0 + b + v)}{(2cy + b + v)(2cy_0 + b - v)} = 2cK'h \qquad (8)$$

$v = \sqrt{b^2 - 4ac}$ and $b^2 > 4ac$ for real results, a fact that is borne out by substituting experimental values.

Also
$$a = iZ$$
$$b = P_{gas}D + Z(i - 1)$$
$$c = P_{gas} - Z$$

and $a + by + cy^2 = \frac{(2cy + b - v)(2cy + b + v)}{4c^2}$ which is substituted into (8), and the result rearranged giving

$$\frac{(2cD - b + v)}{v} \ln \frac{(2cy + b - v)}{(2cy_0 + b - v)} - \frac{(2cD - b - v)}{v} \ln \frac{(2cy + b + v)}{(2cy_0 + b + v)} = 2cK'h \quad (9)$$

Now dividing through by $2c$ and multiplying through by v,

$$\left(D - \frac{b - v}{2c}\right) \ln \frac{\left(y + \frac{b - v}{2c}\right)}{\left(y_0 + \frac{b - v}{2c}\right)} - \left(D - \frac{b + v}{2c}\right) \ln \frac{\left(y + \frac{b + v}{2c}\right)}{\left(y_0 + \frac{b + v}{2c}\right)} = \sqrt{b^2 - 4ac}\, K'h \quad (10)$$

Let
$$\frac{b - v}{2c} = S, \frac{b + v}{2c} = R, \ K' = -\frac{KAm}{22.4\ wP_{gas}}$$

or
$$(D - S) \ln \frac{y + S}{y_0 + S} - (D - R) \ln \frac{y + R}{y_0 + R} = -\frac{KAmhv}{22.4\ wP_{gas}} \quad (11)$$

or
$$K = \frac{22.4 \times 2.303\ wP_{gas}}{Ahm\sqrt{b^2 - 4ac}}\left[(D - R) \log \frac{(y + R)}{(y_0 + R)} - (D - S) \log \frac{(y + S)}{(y_0 + S)}\right] \quad (12)$$

Thus Equation 12 is the final form of the absorption equation which is applied to the following absorption processes.

Applications

The above equation was used in calculating the tower-absorption coefficients for several systems, including volatile and nonvolatile extractors and systems controlled by Raoult's and Henry's laws. Simmons and Long (*5*) used a countercurrent absorption tower, packed with Raschig ring filler for the absorption of benzene by mineral oil, and operated it in accord with the fundamental assumptions of the absorption equation. This is the case in which the extractor is nonvolatile and in which the system conforms with Raoult's law. The absorption coefficient was calculated over a fivefold variation in mole-flow ratio, yielding a substantially constant value as shown in Table I, and in Figure 1, curve *A*. Applying the earlier equation of Cantelo (*1*) to these results, an absorption coefficient is obtained which decreases exponentially as flow ratio or extractor rate increases.

The second case, in which the absorption process followed Henry's law, is given in the data by Cantelo (*2*) on the extraction of carbon dioxide from air by water in a countercurrent system. All the assumptions specified in the equation developed in this article were realized in this system, except that water (the extractor) exerted a vapor pressure. However, the error introduced in calculating the absorption coefficient was slight because the entering gas contained water vapor corresponding to the humidity of the air used. Although no data are given, a minimum humidity of 50 per cent generally prevailed. Then, neglecting any changes in gas volume entailed by vaporization of extractor, the absorption coefficients were calculated with the above formula, using the data in Table II. The resulting absorption coefficient was plotted against mole-flow ratio as shown in Figure 1, curve *B*.

Table I. Absorption of Benzene

Test	Benzene Gas		Rates		Temperatures		Pressure	Mole-Flow	Absorption Coefficient
	Inlet	Outlet	Air	Oil	Gas (in)	Oil (out)	Gas (in)	Ratio *f*	*K*
	%	%	*L./min.*	*L./min.*	° *C.*	° *C.*	*Mm. Hg*		
1	6.00	1.10	5.38	0.04	24.0	29.0	760.7	0.608	5.67
2	6.01	1.20	5.66	0.06	24.0	30.5	757.3	0.875	5.44
3	4.01	0.92	5.66	0.11	27.0	29.5	757.3	1.618	4.65
4	4.38	0.78	5.95	0.09	23.5	28.7	753.1	1.249	5.78
5	3.64	0.67	5.95	0.12	26.4	30.0	758.4	1.669	5.61
6	5.01	0.98	5.66	0.12	28.0	33.0	755.4	1.775	5.23
7	3.88	0.52	5.38	0.14	28.3	34.2	757.0	2.171	5.89
8	3.50	0.48	5.66	0.15	29.2	34.5	748.0	2.245	5.99
9	3.99	0.42	5.66	0.21	25.8	28.5	754.5	3.086	6.56

Table II. Absorption of Carbon Dioxide

Test	CO_2 Gas		Rates		Temperatures		Pressure	Mole-Flow	Absorption Coefficient
	Inlet	Outlet	Gas	Water	Gas (inlet)	Water	Gas Av.	Ratio *f*	*K*
	%	%	*L./min.*	*L./min.*	° *C.*	° *C.*	*Mm. Hg*		
1	17.8	12.4	3.38	2.24	15.6	9.2	758.3	1060	0.523
2	11.8	7.2	3.46	2.94	18.2	8.2	749.0	1297	0.552
3	25.4	18.0	4.02	2.72	11.6	7.0	756.0	1179	0.600
4	21.6	12.0	3.88	5.21	21.2	7.0	755.6	2301	0.658
5	25.6	13.4	4.05	6.06	12.0	7.2	763.0	2600	0.775
6	15.2	8.2	3.40	4.39	18.8	6.8	755.3	2030	0.645
7	18.4	12.3	3.28	2.57	15.4	9.0	758.3	1265	0.434
8	24.6	18.2	3.54	2.04	17.4	9.2	759.0	1010	0.359
9	13.8	10.6	3.85	1.72	17.6	8.4	748.0	696	0.345
10	26.4	20.6	3.48	1.56	16.6	9.2	759.0	804	0.297
11	13.8	9.8	3.57	1.73	18.8	8.6	749.0	757	0.443
12	25.8	16.0	3.63	3.26	17.4	9.2	759.0	1604	0.537
13	13.8	8.6	3.57	3.20	18.4	8.4	749.6	1398	0.535
14	13.6	7.8	3.57	5.05	14.0	6.4	755.0	2152	0.592
15	20.8	10.6	3.91	6.13	10.4	7.4	755.2	2566	0.790

Some increase of the absorption coefficient with increase in mole-flow ratio may be noted from the curves. The reason for this is the experimental difficulty in maintaining a constant free volume under operating conditions. From the equation derived, it may be seen that the coefficient is inversely proportional to the free volume, *Ah*. An increase in the velocity of the absorbing liquid results in a decrease in the free volume of the tower, and hence an increase in the absorption coefficient.

This investigation is being continued, using semi-commercial countercurrent scrubber units and bubble-cap towers. The resulting practical applications of the equation to industrial operation and design will appear in subsequent articles.

Conclusions

1. The experimental results indicate the validity of the above-derived equations when the solute obeys Henry's or Raoult's law, and the extractor is nonvolatile.

2. For a given system, the absorption coefficient is substantially constant, and the magnitude of the coefficient is a characteristic of the system.

3. At elevated mole-flow ratios, an upward trend in the absorption coefficient is observed, an effect explained by the diminution in free tower volume associated with increasing extractor rate.

Acknowledgment

This investigation was carried out under the Henry Marison Byllesby Memorial Research Fellowship in Engineering.

Literature Cited

(1) Cantelo, *Chem. Met. Eng.*, 33, 680 (1926).
(2) Cantelo, Simmons, Giles, and Brill, Ind. Eng. Chem., 19, 989 (1927).
(3) Donnan and Masson, *J. Soc. Chem. Ind.*, 39, 236T (1920).
(4) Lewis, J. Ind. Eng. Chem., 8, 825 (1916).
(5) Simmons and Long, *Ibid.*, 22, 718 (1930).
(6) Whitman and Keats, *Ibid.*, 14, 186 (1922).

Received December 1, 1931.

Chrome Tanning

I. The Role Played by Sodium Chloride in Chrome Liquors upon Chrome Tanning

Edwin R. Theis and A. W. Goetz, Department of Chemical Engineering, Lehigh University, Bethlehem, Pa.

Salt concentration in the wash before tanning and the salt concentration of the chrome liquors are shown to play an important role in the amount of chrome adsorbed by the skin. It is further shown that sodium chloride results in a lessened chrome take-up. The effect of added salt to the chrome liquors is noticeable, regardless of the concentration of chrome used. Added salt not only alters the chemical combinations during actual tannage but also has an effect upon the physical characteristics of the finished leather.

THE role played by salt and salt concentration has in the past been attributed to the action upon the chrome liquor itself, the altered chrome liquor affecting the actual tannage. Wilson and Gallun (*4*) suggest that the cause of a decreased chrome adsorption with increasing salt concentration may be due to the removal of water (from the role of solvent) thus increasing the concentration of the chrome-liquor constituents. Thomas and Foster (*3*) have attributed the retarding effect of salt upon chrome adsorption to complex ion formation. Gustavson's extensive and comprehensive experimental work (*1*) tends to point out just how salt concentration affects the hydrogen-ion concentration, precipitation point, and other factors, which in turn affect chrome tannage. That the factors outlined above play a very important role in chrome tanning, no one can doubt, and these may be termed the chemical reactions occurring and resulting from the addition of salt.

However, there appears to be another phase of this salt effect—namely, that of varying concentration of salt in the chrome liquor itself upon the salt content of the skin and the subsequent effect upon chrome adsorption.

Experimental Procedure

For studying the effects of various concentrations of sodium chloride in tanning liquors (these in turn varying in chrome content) upon the subsequent chrome tanning of pickled calf skin, a commercial tanning agent (Tanolin R) was employed. This tanning agent in the solid form showed a chrome content of 23.5 per cent chromic oxide and 10.2 per cent moisture; when dissolved, this tanning agent gave a basic chromium sulfate solution, which was shown by analysis to be 37.5 per cent basic.

The bends of a pickled (sulfuric acid–sodium chloride) calf skin were cut into small cubes of 1-cm. edge and mixed thoroughly, and 25.0-gram samples were weighed. The samples were then placed in 50 cc. of a tanning solution containing various amounts of chrome and salt, and, with occasional shaking, remained in these solutions for 48 hours. The tanned skin was then rinsed with distilled water. The residual chrome liquors were analyzed for sodium chloride and the leathers for chrome content.

The amounts of both chrome and salt used in the tanning solutions are expressed as per cent, based on the initial weight of the pickled skin; the pickled skin contained 68.2 per cent moisture and 5.75 per cent sodium chloride. Table I shows the amounts and concentration of the tanning agent employed.

Table I. Relation between Amount of Tanning Agent and Concentration of Chrome in Tanning Solutions

Tanning Agent[a] %	Cr_2O_3 *Grams/liter*
3	3.825
6	7.650
9	11.475
12	15.300

[a] Grams per 100 grams pickled stock.

Discussion of Results

If a protein, such as hide powder, is placed in a sodium chloride solution, diffusion of salt into the protein occurs until

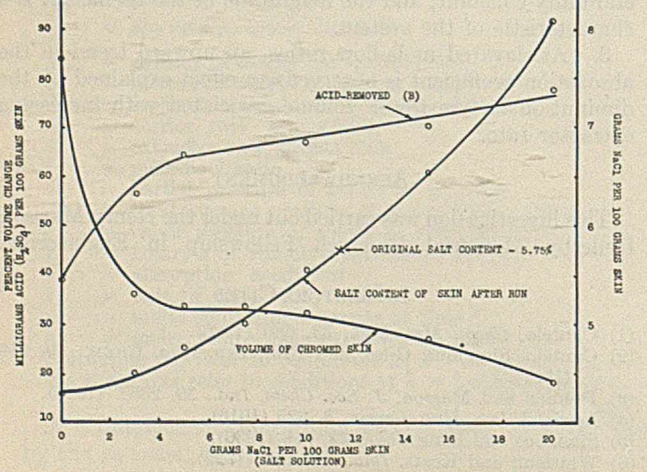


Figure 1. Effect of 20-Minute Run of Pickled Skin in Various Concentrations of Salt Solution

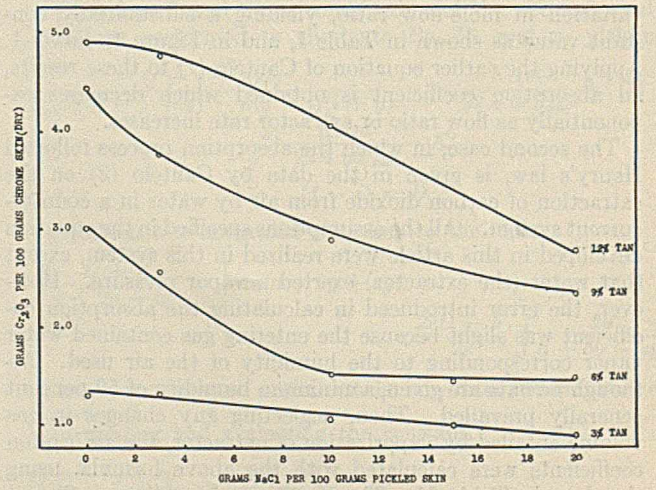


Figure 2. Effect of Various Amounts of Salt upon Chrome Adsorbed for Various Amounts of Chrome in Tanning Liquor

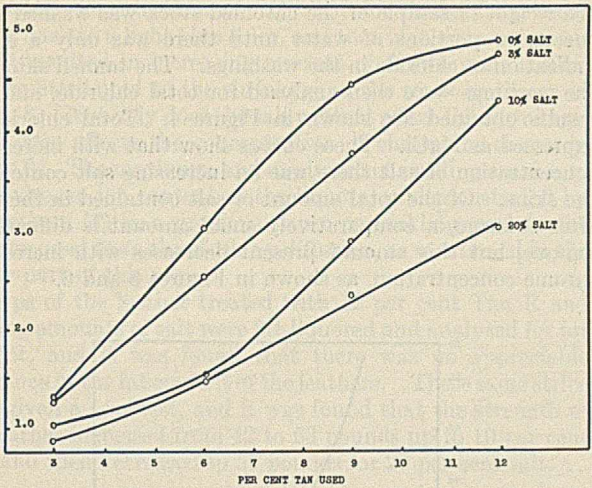


FIGURE 3. EFFECT OF VARIOUS AMOUNTS OF CHROME AND OF SALT IN TANNING LIQUOR UPON CHROME ADSORBED BY SKIN

the molal free energy or solution potential of the salt in the solid and liquid phase are in equilibrium. The reverse occurs if the protein contains diffusible salt ions and is placed in water. This phenomenon is not only appreciable with salts but also with acids. In the customary process of chrome tanning, when pickled skin is placed in a drum containing salt solution, there is an immediate diffusion of salt and acid from within the skin outward into the external solution until the equilibrium is established between the external and internal phases.

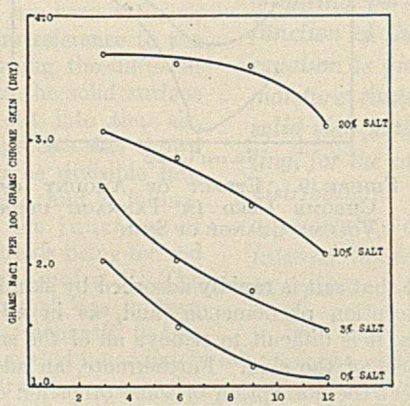


FIGURE 5. EFFECT OF AMOUNT OF CHROME IN TANNING LIQUOR UPON AMOUNT OF SALT FIXED BY CHROME SKIN FOR VARIOUS AMOUNTS OF SALT

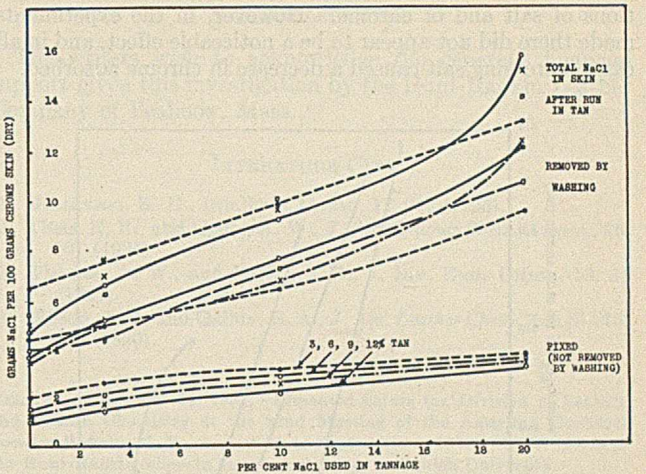


FIGURE 4. RELATION BETWEEN SALT ADSORBED AND FIXED BY SKIN WHEN TANNED WITH VARIOUS AMOUNTS OF CHROME AND SALT

Figure 1 shows graphically the results obtained when samples of pickled skin are drummed for 20 minutes in varying concentrations of salt in solution. The curve showing the salt content of the skin, after 20 minutes, demonstrates the conclusions previously made regarding the diffusion of the salt, either out of or into the skin. Since the original pickled skin contained 5.75 per cent salt, it is to be noted that there was a diffusion of salt from the skin to the external solution for those salt solutions of concentrations less than 11.75 per cent (calculated on weight of pickled skin), and above this salt concentration there was a diffusion of salt from the exterior solution into the skin. Figure 1, curve *B*, clearly demonstrates that the amount of acid removed by the salt solution is not only a function of the acid contained in the skin, but also of that of the concentration of the salt solution. This effect is decidedly pronounced up to 6 per cent salt. In the tanning process, this removal of acid causes an immediate decrease in the basicity of the chrome liquor and a change in the complexity of the chrome salt. The initial acid removed is in all probability that acid which existed as free acid in the pickled skin; therefore it might be suggested that, if skin is pickled in a high-acid pickle, thus resulting in high free-acid content, the effects upon the chrome liquor noted above will be decidedly pronounced.

A still further effect of the concentration of salt within the pickled skin and in the salt solution is that of shrinkage of the skin which, upon subsequent tannage, would result in a drawn grain in the finished leather. This effect of salt concentration is shown by the volume-change curve of Figure 1. The decrease in volume of the skin during the 20-minute run is explained by the removal of the acid from the skin and the increase in salt concentration. Associated with shrinkage is the agglutination of the fibers themselves, diminishing their free surface affinities and thereby decreasing the rate of adsorption of the chrome. This colloidal phenomenon has received little consideration, and in the opinion of the writers an investigation should bear fruitful results.

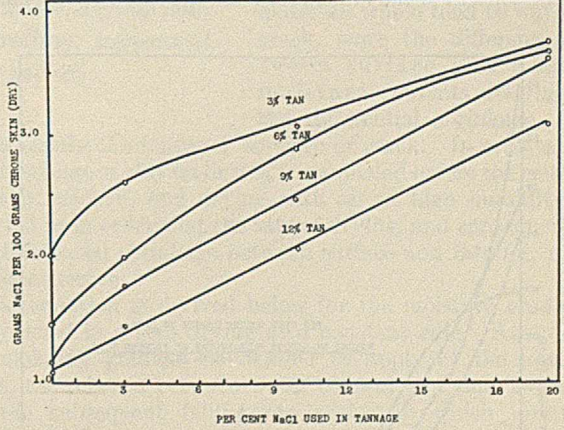


FIGURE 6. EFFECT OF AMOUNT OF SALT IN TANNING LIQUOR UPON AMOUNT OF SALT FIXED BY CHROME SKIN FOR VARIOUS AMOUNTS OF CHROME

The effect of varying amounts of salt in chrome solutions of different chrome content upon the chrome adsorbed is shown in Figures 2 and 3. The low concentrations of Tan R were employed in order to determine whether the concentration effect stated by Wilson and Gallun would result in an increase in chrome adsorbed, at least for the lower concentrations of salt and of chrome. However, in the experiments made there did not appear to be a noticeable effect, and in all cases increasing salt caused a decrease in chrome adsorbed.

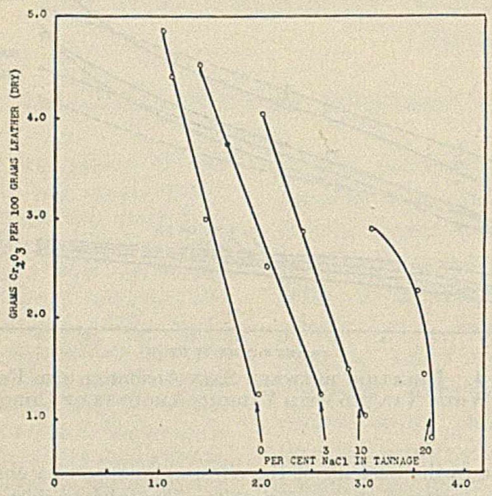


FIGURE 7. RELATION BETWEEN SALT AND CHROME CONTENT OF LEATHERS TANNED WITH VARYING AMOUNTS OF SALT AND CHROME

It is interesting to note from the various curves of Figure 2 that the salt effect is not of the same order for the different amounts of Tan R. For the 3 per cent Tan R the salt effect is comparatively slight, whereas for 6 per cent Tan R there is a marked decrease in chrome adsorbed up to 10 per cent salt and then apparently no effect with increasing amounts of salt. The 9 and 12 per cent Tan R curves are similar except for the tendency for the 9 per cent Tan R curve to approach a constant for the higher salt concentrations. Figure 3 shows similar results with regard to effect of increased salt content upon chrome adsorption.

In order actually to determine the relation between the chrome content of the tanned skin and the salt content, half of the weight of sample of the chromed stock was washed with successive portions of water until there was only a slight indication of chloride in the washings. The tanned skin and the washings were then analyzed for total chloride, and the results obtained are shown in Figure 4. Total chloride is expressed as NaCl. These curves show that with increasing concentration of salt there was an increasing salt content in the skins. Of the total amount of salt contained in the skin after tannage, a comparatively small amount is difficult to remove, but this amount present decreases with increasing chrome concentration, as shown in Figures 5 and 6.

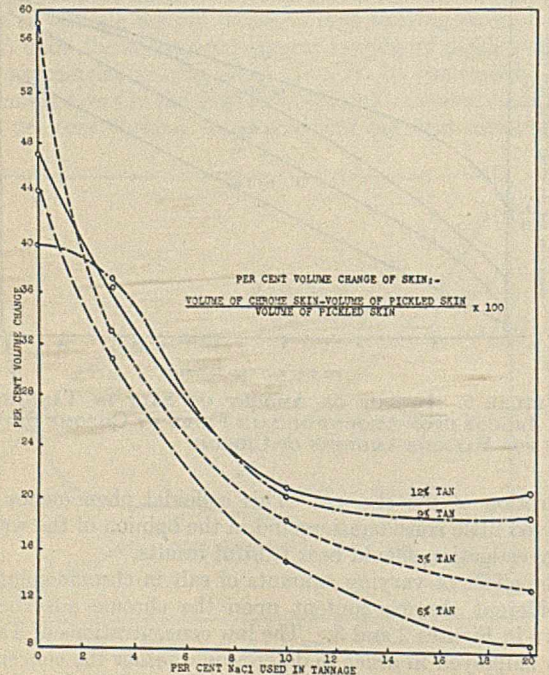


FIGURE 8. EFFECT OF AMOUNT OF SALT USED IN TANNAGE UPON VOLUME CHANGE OF CHROMED SKIN

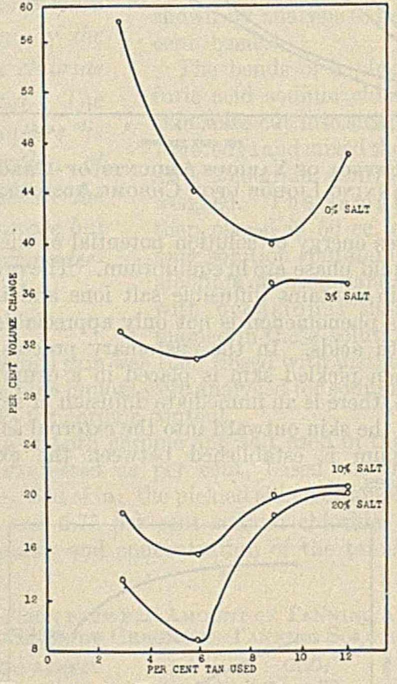


FIGURE 9. EFFECT OF AMOUNT OF CHROME USED IN TANNAGE UPON VOLUME CHANGE OF SKIN

The fact that salt is rapidly adsorbed by skin is indicative of an adsorption phenomenon, and, as in all adsorption phenomena, it is difficult to remove all of the salt from the fiber surfaces of the skin. Furthermore, an adsorbate will always affect the adsorption of some other ion or molecule. Therefore, since in the chrome-tanning process there must first be an adsorption of the chrome upon the fiber before chrome combination, any substance, such as sodium chloride, which is already adsorbed owing to unsaturated chemical affinities, may cause a blocking effect upon chrome adsorption and consequently upon chrome combination; or, owing to the adsorption of salt, there is an increase in the osmotic pressure in the skin, decreasing the diffusion tendency of the chrome salt. This effect whether it be large or small, beyond a doubt plays some role in the effect of neutral salts in chrome tanning; a more comprehensive investigation would be required to ascertain the effect as previously stated. However, a comparison was made in this work between the chrome content of the leather and the amount of salt contained in the leather after a thorough washing as stated above. The relation can be observed from Figure 7, where each curve represents the ratio of chrome and salt in the leathers tanned with various amounts of the tanning agent. From the slope of the curves this ratio was very much the same.

The effect of salt not only alters the chemical combinations during the process of tannage but has a decided effect upon the appearance of the stock. Thus it was found that, with increasing concentrations of salt, the color changed markedly from a dark to a light blue color, and that high concentrations of salt resulted in increasing amount of drawn grain. This may be attributed to the shrinkage of the stock as shown in Figure 8. Not only does the salt content affect the shrinkage, but it also affects the concentration of chrome as shown in Figure 9. The maximum and minimum of swelling are due to the hydrogen-ion content of the liquors, as demonstrated by the authors (*2*) in a previous paper on pickling, and to the acid removed from the stock by diffusion, as mentioned in the earlier part of this paper.

Strips of the leather treated with 12 per cent Tan R and varying amounts of salt were fat-liquored and analyzed for fat content, and it was found that there was no appreciable difference in the fat content of the leathers. These same strips were given a tear test, and it was found that the strength of the leather increased from 42 to 63 pounds up to 10 per cent salt, and then decreased to 52 pounds for 20 per cent salt.

ACKNOWLEDGMENT

The writers wish to acknowledge the generous financial support given this investigation by the Hunt-Rankin Leather Company of Peabody, Mass.

LITERATURE CITED

(1) Gustavson, K. H., IND. ENG. CHEM., 17, 945 (1925).
(2) Theis, E. R., and Goetz, A. W., *J. Am. Leather Chem. Assocn.*, 26, 507 (1931).
(3) Thomas, A. W., and Foster, S. B., J. IND. ENG. CHEM., 13, 31 (1921).
(4) Wilson, J. A., and Gallun, E. A., *J. Am. Leather Chem. Assocn.*, 15, 273 (1920).

RECEIVED September 14, 1931. Presented before the Division of Leather and Gelatin Chemistry at the 82nd Meeting of the American Chemical Society, Buffalo, N. Y., August 31 to September 4, 1931. A. W. Goetz is the Hunt-Rankin fellow in leather technology at Lehigh University.

The Drying of Solids—IV

Application of Diffusion Equations

T. K. SHERWOOD, Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Mass.

In the drying of a solid slab, the moisture distribution approached during the constant rate-of-drying period is represented by a parabolic function of the distance from the surface. The equation is given expressing the relation between moisture content and time in the drying of a solid slab with internal liquid diffusion controlling, for the case of an initial parabolic moisture distribution. Data are presented supporting the applicability of this relation to the drying with internal liquid diffusion controlling, subsequent to a preliminary constant-rate period.

IN THREE previous articles (*3, 4, 5*) the general mechanism of the air-drying of solids has been outlined, with particular reference to the factors governing the diffusion of moisture to the solid surface and thence out into the air. The drying process was shown in general to be divisible into a constant-rate and a falling-rate period, the junction of these two periods being termed the "critical point." The falling-rate period was in turn shown to be frequently in two parts: in the period immediately following the critical point the rate of drying decreases because of a decrease in wetted surface; and in the last stage of the drying process the rate of diffusion of water through the solid controls the rate of drying. In the drying of certain slow-drying materials, however, no constant-rate period occurs, and internal liquid diffusion is controlling from the first. An equation (*3*) was presented for this case, giving the relation between the moisture content and the time of drying for an infinite slab:

$$E = \frac{8}{\pi^2}\left[e^{-\left(\frac{\pi}{2}\right)^2\frac{K\Theta}{R^2}} + \frac{1}{9}e^{-9\left(\frac{\pi}{2}\right)^2\frac{K\Theta}{R^2}} + \frac{1}{25}e^{-25\left(\frac{\pi}{2}\right)^2\frac{K\Theta}{R^2}} + \ldots\right] \quad (1)$$

Recently Newman (*2*) has derived the corresponding relations for other solid shapes.

In the drying of many common materials, a short constant-rate period is followed by a falling-rate period in which internal liquid diffusion controls throughout. During the constant-rate period there may be set up an appreciable difference between the moisture contents at the surface and in the interior of the solid. Since Equation 1 was derived on the assumption of a uniform distribution of moisture in the solid at the start, it cannot be expected to apply to the falling-rate period in such a case, even though internal liquid diffusion is controlling. The moisture gradients in the constant-rate period are determined by the nature of the solid, its dimensions, and the rate of drying. They are of great interest in the drying of materials which tend to warp or crack, since the difference between surface and internal moisture contents determines the differential shrinkage, and consequently the tendency to warp or crack. In most cases the shrinkage of clay on drying is completed before the critical point is reached, and drying with air of high humidity is resorted to in order that the rate of drying, and consequently the differential shrinkage between surface and interior, may not be excessive.

The equation is derived below for the moisture gradient approached in a slab drying at a constant rate. Assuming the moisture gradient so derived to apply at the critical point, the relation between water content and time is given for the subsequent falling-rate period in which internal liquid diffusion controls throughout.

MOISTURE GRADIENTS IN SLAB DURING CONSTANT-RATE PERIOD

The general equation for diffusion of a liquid in a solid is

$$\frac{\delta^2 T}{\delta x^2} = \frac{D}{K'}\frac{\delta T}{\delta \Theta} \quad (2)$$

which may, presumably, be employed in an analysis of the conditions in the solid during the constant rate period. As long as the rate of drying is constant, the moisture gradient at the solid surface will remain constant, as given by

$$\left(\frac{dT}{dx}\right)_s = -\frac{1}{K'}\frac{dW}{Ad\Theta} \tag{3}$$

and for the case of an infinite slab or sheet, the gradient at each surface will be the same.

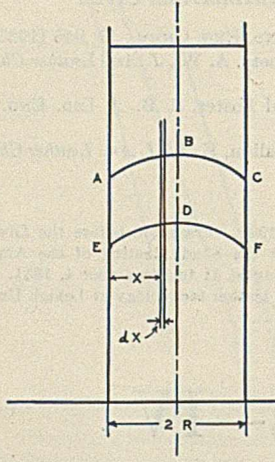


Figure 1. Cross Section of Slab

Figure 1 represents the cross section of a slab, with ordinates representing the moisture concentrations at different times during the constant-rate period. *ABC* represents the gradient at any instant, and *EDF* the new gradient after a finite length of time. Since no moisture crosses the center line, the slope of the concentration curve is zero at that point. Furthermore, since the rate of drying is constant, then from Equation 3 the slopes at *A*, *E*, *C*, and *F* are equal. Now the area *ABCFDE* represents the moisture lost; and, since the rate of drying is constant, the areas between successive concentration curves, corresponding to equal time intervals, will be the same. Humps or high points in the gradient curves will tend to disappear rapidly because $\frac{\delta^2 T}{\delta x^2}$ will be numerically large, and from Equation 2 it follows that the rate of decrease of moisture concentrations at such points will be correspondingly large. The gradient curves will clearly approach a definite shape, after which successive curves will be parallel, and $\frac{\delta T}{\delta \Theta}$ will be a constant. From Equation 2, therefore

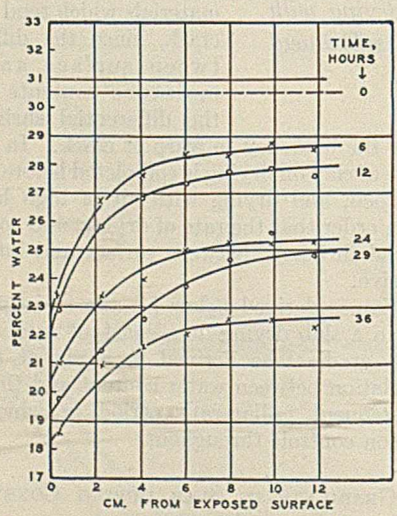


Figure 2. Concentration Curves Obtained by Troop and Wheeler in Dying Clay

$$\frac{\delta^2 T}{\delta x^2} = \text{constant} \tag{4}$$

Integrating and substituting the conditions that $\frac{\delta T}{\delta x} = 0$ when $x = R$; $T = T_m$ when $x = R$; and $T = T_s$ when $x = 0$:

$$T = T_m - \frac{(x - R)^2}{R^2}(T_m - T_s) \tag{5}$$

On differentiating and substituting $x = 0$, the gradient at the surface is found:

$$\left(\frac{dT}{dx}\right)_s = \frac{2(T_m - T_s)}{R} = -\frac{1}{K'}\left(\frac{dW}{Ad\Theta}\right) \tag{6}$$

From Equation 5 it follows that, after drying an infinite slab for an appreciable length of time at a constant rate, the moisture-gradient curve approaches a parabolic form, no matter what the initial moisture gradient may have been.

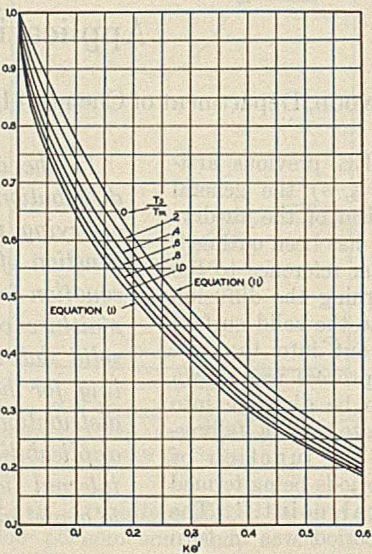


Figure 3. Plot of E' vs. $K\Theta'/R^2$

As a test of the correctness of the above derivation there are available the data of Troop and Wheeler (*6*), who obtained moisture gradients in clay samples dried at various temperatures and humidities. Small clay cylinders, 12.7 cm. long and 2.54 cm. in diameter, were held in copper tubes and placed in a thermostat maintained at a constant temperature. One end face was exposed to air at a controlled temperature and humidity, and, as the drying took place wholly from the single exposed end face, the conditions were similar to the drying of a 25.4-cm. infinite slab and clay. After various time intervals, identical samples were taken at several points along the length of the cylinder, and the moisture concentrations obtained. Figure 2 shows concentration curves obtained with air at 70° C. and 90 per cent relative humidity, these data being typical of the results obtained. The parabolic moisture gradients are clearly indicated, and it is of special interest to note how quickly the initial flat moisture-distribution curve disappears and the parabolic distribution is approximated.

In the test described, the rate of drying of each sample during the constant-rate period was 2.86 grams in 24 hours. From Figure 2 the average value of $(T_m - T_s)$ may be found to be 0.053. Substituting these values together with a value of R of 12.7 in Equation 6, the value of K' is found to be 7.8×10^{-4} grams per second per square centimeter per centimeter thickness per unit dT. It may be noted that $K' = KD$.

Repeating the calculation of K', using the data of Troop and Wheeler for other tests, values of K' were obtained varying roughly with the fluidity of water at the temperature of the thermostat. For example, at 30° C. the value of K', calculated from the value of $T_m - T_s$ after drying for 24 hours, is 1.3×10^{-4}.

DRYING AT CONSTANT RATE FOLLOWED BY LIQUID DIFFUSION CONTROLLING

The theoretical relation for the drying of an infinite slab, when internal liquid diffusion is controlling, is given above (Equation 1). The equation is applicable, however, only when the moisture distribution is uniform throughout the slab at the beginning of the period when internal liquid diffusion controls. Frequently, as in the drying of certain shapes of wood and clay, the period of internal liquid diffusion controlling follows immediately after the constant-rate period, and the moisture distribution at the start of this period is consequently more nearly parabolic than uniform. It is evident then that Equation 1 does not hold for this case. It would appear that an equation similar to (1), but based on the assumption of an initial parabolic moisture distribution, would be useful in the study of the drying of such materials.

Carslaw (*1*) gives the solution of the basic diffusion equation for an infinite slab where the initial concentration gradient is $f\ (x')$ as

$$v = \frac{1}{R}\int_0^{2R} f(x') \sum_1^{\infty} \left(\sin\frac{n\pi x'}{2R}\sin\frac{n\pi x}{2R}\,e^{-\frac{Kn^2\pi^2\Theta}{4R^2}}\right) dx' \qquad (7)$$

Where shrinkage is negligible, TD can replace v. Substituting the parabola (5) for $f\ (x')$, and integrating,

$$T = \frac{2T_s}{\pi}\sum_1^{\infty}\frac{1}{n}\{1-(-1)^n\}\sin\frac{n\pi x}{2R}\,e^{-\frac{Kn^2\pi^2\Theta'}{4R^2}}$$

$$+\frac{16}{\pi^3}(T_m - T_s)\sum_1^{\infty}\frac{1}{n^3}\{1-(-1)^n\}\sin\frac{n\pi x}{2R}\,e^{-\frac{Kn^2\pi^2\Theta'}{4R^2}} \qquad (8)$$

It may be noted that when $\Theta' = 0$, and $x = R$, this reduces to $T = T_m$.

More important than the concentration at any point, however, is the total water content, obtained by integrating the concentration across the slab thickness. Defining E' as the ratio of the free-water content to the free-water content at the end of the constant-rate period (the critical point), then

$$E' = \frac{\int_0^{2R} T\,dx}{\int_0^{2R} f(x')\,dx'} \qquad (9$$

Substituting the two series of Equation 8 for T, and the parabola (Equation 5) for $f\ (x')$, and integrating,

$$E' = \frac{24T_s}{\pi^2(T_s + 2T_m)}\left[e^{-p} + \frac{1}{9}e^{-9p} + \frac{1}{25}e^{-25p} + \ldots\right]$$

$$+\frac{192}{\pi^4}\frac{(T_m - T_s)}{(T_s + 2T_m)}\left[e^{-p} + \frac{1}{81}e^{-9p} + \frac{1}{625}e^{-25p} + \ldots\right] \qquad (10)$$

For the case of $\Theta' = 0$, Equation 10 may be shown to reduce to $E' = 1$. Furthermore, when $T_m = T_s$, the second series disappears and the result checks exactly with (1), the corresponding equation for the case where the initial moisture distribution is uniform. Equation 10 represents the theoretical relation between water content and time, for the drying of an infinite slab with liquid diffusion controlling, for the case of an initial parabolic moisture distribution, as at the end of a constant-rate period.

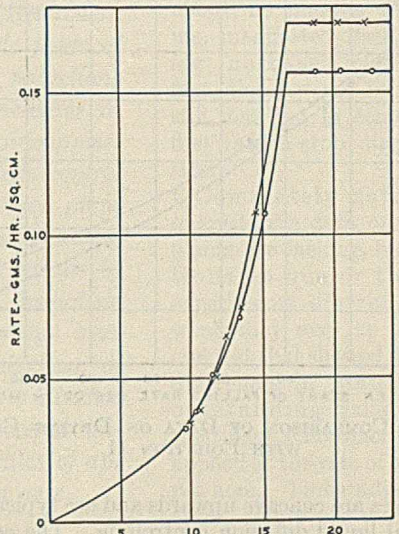


FIGURE 4. RESULTS OF DRYING CLAY SLABS IN HIGH-VELOCITY AIR STREAM

The coefficients of the two series in Equation 10 are both functions of the ratio, T_s/T_m. E' is consequently a function of the two dimensionless ratios, p and T_s/T_m. This fact suggests a method of plotting Equation 10, as shown in Figure 3, where E' is plotted vs. $K\Theta/R^2$, for values of T_s/T_m of 1.0 (Equation 1) to 0 (Equation 11).

EXPERIMENTAL DATA ON DRYING OF BRICK CLAY

In an experimental study of liquid diffusion in solids, it is found advantageous to exaggerate the importance of the period where liquid diffusion controls, by drying in a high-velocity air stream, thus vaporizing the water as fast as it diffuses to the surface. The drying of a clay slab 2.54 cm. thick under such conditions was described in a previous

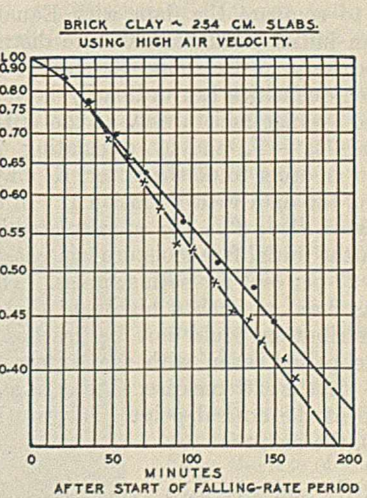


FIGURE 5. COMPARISON OF DATA ON DRYING CLAY SLABS WITH EQUATION 1

article (*3*). The results of two such tests are shown plotted in Figure 4. The rates of drying obtained by measuring the slopes of the curves of weight *vs.* time are shown plotted against the free-moisture content. Each sample dried at a constant rate down to about 16.5 per cent water, after which the rate curves are concave upwards and are typical of drying with internal liquid diffusion controlling. The edges of the slabs were covered with tin foil, and consequently diffusion was possible only in a direction normal to the faces, as in an infinite slab.

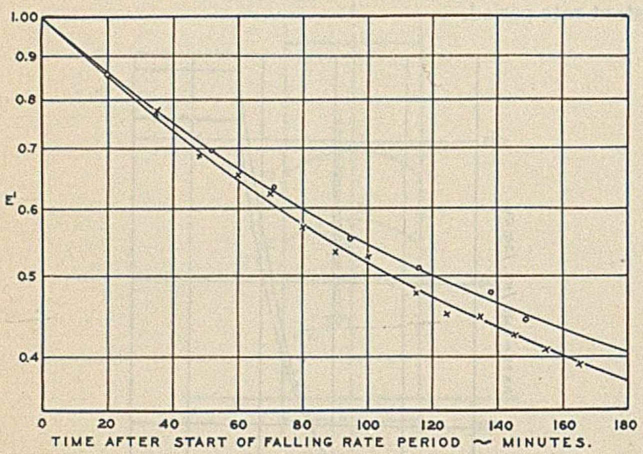


FIGURE 6. COMPARISON OF DATA ON DRYING CLAY SLABS WITH EQUATION 11

The data are first compared with the theoretical relation (1) by means of Figure 5. A special coördinate plot is constructed, the ordinate or E' scale being modified to force the theoretical relation (1) to be linear in E' and $\frac{K\Theta'}{R^2}$. Thus, the data of any single experiment following Equation 1 should fall on a straight line, when plotted as E', the fraction of the critical free moisture vs. $\frac{K\Theta'}{R^2}$, or vs. Θ', the time after the end of the constant-rate period. Figure 5 shows lines having a marked curvature at high values of E', which is to be expected since the derivation of Equation 1 assumes a uniform moisture distribution at the start, i. e., at the critical point.

In order to compare the data with Equation 10 which allows for an initial parabolic moisture distribution in the slab, it is necessary to determine T_m and T_s at the critical point. These quantities can ordinarily be found using the fact that the average moisture T_c at the critical is T_s plus two-thirds of $T_m - T_s$, and by calculating $T_m - T_s$ from Equation 6. In order to do the latter, K' may be estimated by comparing the data with Equation 1. In the case of the present data on clay, $T_m - T_s$ so calculated is considerably greater than the initial free-moisture content, which was approximately 27 per cent for both samples. This means that the clay was dried at such a high rate that the parabolic moisture distribution could not be reached in the short constant-rate period, even with the surface concentration, T_s, at zero. In the extreme case, T_s may be assumed to have reached zero at the critical point. Substituting $T_s = 0$ in Equation 10, the result is

$$E' = \frac{96}{\pi^4}\left[e^{-p} + \frac{1}{81}{}^{-9p} + \frac{1}{625}e^{-25p} + \ldots\right] \qquad (11)$$

Table I shows values of E' calculated from this series, as well as from Equation 1. In order to compare the data with Equation 11, Figure 6 is shown with the ordinate scale modified to make this relation linear. In this case the data fall on lines reasonably straight at high values of E', but slightly concave upwards at the lower ends. Going from a comparison with (1) to a comparison with (11), the lines representing the data have changed from convex to concave upwards, whereas in each case the lines representing the theoretical equations are straight. It may be concluded: that either the data would compare better with the more rigorous solution (10), using suitable values of T_m and T_s than the extreme cases (1) and (11); or the series (10), using $T_s = 0$, is approximated closely, and that the curvature of the lines of Figure 6 is due to a decrease of the diffusion constant, K, with decrease in moisture content.

TABLE I. VALUES OF E AND E' CALCULATED FROM EQUATIONS 1 AND 11

$\frac{K\Theta'}{R^2}$ or $\frac{K\Theta}{R^2}$	E Equation 1	E' Equation 11
0	1.0	1.0
0.02	0.840	0.951
0.05	0.749	0.880
0.10	0.643	0.775
0.15	0.563	0.684
0.20	0.496	0.605
0.30	0.387	0.473
0.50	0.236	0.290
1.00	0.069	0.086

An approximate value of K' for this clay may be obtained by noting from Figure 6 that $E' = 0.605$ at about 75 minutes. Since this E' corresponds to a value of $K\Theta'/R^2$ of 0.20, it follows that

$$K = 0.20 \times 1.27^2/75 \times 60 = 0.72 \times 10^{-4}$$
$$\text{and } K' = KD = 1.6 \times 0.72 \times 10^{-4} = 1.15 \times 10^{-4}$$

This value, for clay-drying at room temperature, agrees reasonably well with the values of 7.8×10^{-4} at 70° and 1.3×10^{-4} at 30° C., calculated from the data of Troop and Wheeler for a different clay.

NOMENCLATURE

A = face area
D = density of dry solid
E = ratio of total free-water content to initial free-water content
E' = ratio of total free-water content to free-water content at end of the constant-rate period, i. e., at critical point
K = diffusion constant of moisture through solid, with concentrations as weight per unit volume
K' = same with concentrations as weight of water per unit weight of dry solid = KD
p = $\frac{K\pi^2\Theta'}{4R^2}$
R = half slab thickness
T = free-moisture concentration, weight of water per unit weight of dry solid
T_m = same at center line of slab at critical point
T_s = same at faces of slab at critical point
v = free-water concentration at any point
W = weight of water
x = distance from slab face
Θ = time
Θ' = time after critical point

LITERATURE CITED

(1) Carslaw, H. S., "Introduction to the Mathematical Theory of Conduction of Heat in Solids," MacMillan, 1921.
(2) Newman, A. B., Interim publication of Am. Inst. Chem. Eng., August, 1931.
(3) Sherwood, T. K., IND. ENG. CHEM., 21, 12 (1929).
(4) Sherwood, T. K., *Ibid.*, 21, 976 (1929).
(5) Sherwood, T. K., *Ibid.*, 22, 132 (1930).
(6) Troop and Wheeler, *Trans. Ceram. Soc.*, 26, 231, 239, 261 (1926–27); 27, 303 (1927–28).

RECEIVED December 9, 1931. Presented before the meeting of the American Institute of Chemical Engineers, Atlantic City, N. J., December 9 to 11, 1931.

Chloropicrin for Nematode Control

M. O. Johnson and G. H. Godfrey

Experiment Station, Association of Hawaiian Pineapple Canners, University of Hawaii, Honolulu, Hawaii

Chloropicrin treatment of root-knot (Heterodera radicicola) infested soils in pineapple fields of Hawaii have brought about striking reductions in infestation and equally striking increases in vigor of plant growth and in yield of pineapples. Whereas no claim is made that nematode control is the only factor involved in the improved plant growth, this paper deals with that factor alone, and includes actual measurements, by means of cowpea indicator crops, of extent of nematode reduction. The most effective treatments were those which consisted of the introduction of chloropicrin in liquid form into holes 5 to 6 inches deep, spaced 18 inches apart and covered immediately with mulching paper, the rates of application being 163 pounds or more per acre.

In 1927 the senior author treated soil from bad failure areas in pineapple fields with chloropicrin and obtained remarkably increased vigor of resulting pineapple-plant growth, as compared with untreated controls. The soils were in root observation boxes, and it was evident that the increased vigor was due to a direct effect on the roots. Among the results was a notable decrease in the amount of nematode root knot in the treated boxes. This was verified repeatedly by similar experiments without, however, any actual measurements being taken of the amount of decrease. These preliminary tests led to carefully conducted field experiments the same year (1927) and subsequent years by the senior author, which showed striking increases in growth and yield of fruit. This paper discusses in detail certain of the field tests which were studied by the junior author, primarily from the point of view of nematode control. Results are reported in terms of actual nematode reduction, measurements being by means of indicator crops.[1]

While chloropicrin has been used more or less extensively for fumigation, its use for soil treatment has been very limited, as indicated by the chloropicrin bibliographies prepared by Roark (*3*) and Gersdorff (*1*). The present authors have not been able to review the original papers cited by these men, but refer to their annotations on the work of Piutti and Bernardini, Spencer, Matthews, Russel, Hasson, Dingler, Fryer, Parker, Feytaud, and Annie Matthews, particularly to Matthews (*2*) who appears to have included nematodes in her studies. None of this work seems to have been followed by practical field applications.

PRELIMINARY EXPERIMENTS ON PINEAPPLE

Most of the preliminary field tests referred to above, in which chloropicrin was introduced into nematode-infested soil in measured doses by means of a Vermorel injector, demonstrated remarkable increase of plant growth over the untreated controls within 2 or 3 months after planting. This increased vigor persisted throughout the growth of the plant, and at plant-crop stage, about 20 months after planting, manifested itself by striking increases in yields. In fact, the increase in vigor was still manifest in some plots at first ratoon-crop stage, 1 year later.

Completely satisfactory quantitative data on effects on plants are lacking, but observations on one or two of the experiments are recorded for what they may be worth. In one test that showed, by striking differences in plant growth, outstanding value from the treatment, chloropicrin had been applied at the rate of 180 pounds per acre. Three adjacent pineapple plants selected as representative were removed intact, roots and all, from this plot, and three from a comparable control plot, just following harvesting the fruit when the plants were approximately 20 months old. Greater extent of root growth, including abundance of fine feeding-branch rootlets in the treated plots, was strikingly evident. The three control plants showed *Heterodera radicicola* infestation in 90 per cent of all roots, while treated plants showed only 30 per cent infestation. These differences in root systems were paralleled by very obvious differences in the aerial parts of the plants. The untreated plants had an average lateral spread or total width of 45 inches and a height of 35 inches; the treated plants showed 55 inches spread, and 45 inches height, a difference of well over 20 per cent in both measurements. Pineapple-yield differences were striking. The 180-pound chloropicrin bed yielded in plant crop 11.8 tons more than the control, a difference of 57.0 per cent. Figure 1 illustrates the condition of these two rows at first ratoon-crop stage, the third summer after planting.

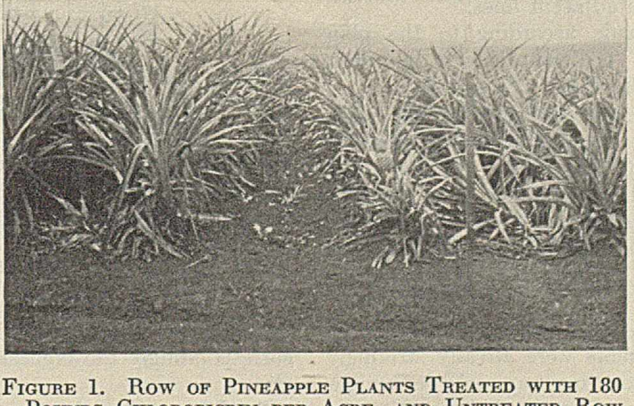


FIGURE 1. ROW OF PINEAPPLE PLANTS TREATED WITH 180 POUNDS CHLOROPICRIN PER ACRE, AND UNTREATED ROW AT FIRST RATOON-CROP STAGE, APPROXIMATELY 3 YEARS AFTER PLANTING

The yield difference between the two was over 20 tons per acre in the two crops

In another experiment chloropicrin applications were made by means of the Vermorel applicator, at rates varying between 45 and 185 pounds per acre, just prior to planting on August 23, 1929. On October 18, 1930, approximately 14 months after planting, two plants chosen by the authors as representative were removed with roots intact from each of several of the treatments which showed above-ground differences in vigor of growth. Since the size of samples was so inadequate (two plants only, out of several hundred in each lot), a detailed classification of results could not be considered as having much significance. It will be recorded only that:

---

[1] The junior author is preparing a paper on the indicator-crop method of determining effects of various soil treatments on nematode infestation of the soil, pointing out its usefulness and its limitations.

(1) of the twelve plants examined, the two from the bed receiving the heaviest application of chloropicrin (bed 17, 180 pounds per acre) ranked first in vigor of top and root growth, and ranked lowest in amount of nematode root knot and of root-lesion nematode infestation (*Tylenchus brachyurus* Godfrey); (2) plants from beds 2 and 16 (controls) ranked last in vigor of growth and among the highest in amount of root knot and *Tylenchus;* other treatments examined, ranging from 120 to 145 pounds per acre, variously applied as regards spacing, etc., gave intermediate results; and (3) yield records showed a difference in plant crop of 7.1 tons per acre over the average of controls, a difference of 21.8 per cent in favor of the best treatment.

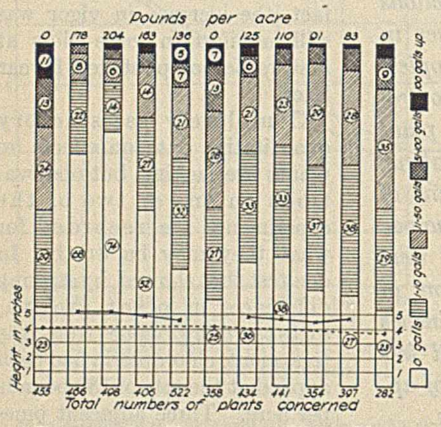


FIGURE 2. HELEMANO TEST NO. 1

Chart shows percentages of plants with different degrees of nematode infestation for each of the several different chloropicrin treatments.

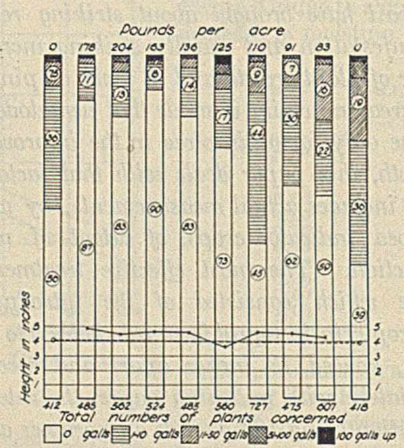


FIGURE 3. HELEMANO TEST NO. 2

Same order of treatments as Figure 2, but additional application of chloropicrin at rate of 110 pounds per acre between beds.

EXPERIMENTS WITH COWPEA INDICATOR

Pursuant to these continuously favorable results, further experiments were initiated and an effort was made to measure more exactly the effects of treatments on nematodes. Treatments were applied in two different localities in the leading pineapple section in the vincinity of Wahiawa, on Oahu. Applications were made by means of the usual Vermorel injector in various dosages in a series of standard plant beds through wide (54-inch) mulching paper. Two weeks after treatment, pineapples were planted according to the four-line system. In this planting system, four lines of plants were set through the one line of 54-inch paper, the lines of plants being 16 inches apart and the plants 16 inches apart in the row, plants and spaces alternating in adjacent lines.

Actual applications were made according to the plan indicated in Table I, the term "bed" applying to the plant bed of four rows of plants under paper.

In cases in which more than one bed received the same application, samples were taken only from the middle one of three or from the one of two which lay adjacent to a bed with a higher rate of application, in order to eliminate in so far as possible contaminations from controls or inadequate lower treatments. Of such cases in Table I, beds 1, 4, 6, 8, 10, 13, 16, 18, 20, 22, 35, and 37 were selected for sampling.

In February, 1931, 4 months after planting, differences in pineapple growth in different plots were already strikingly evident. At this time, in an effort to get an early determination on effects of the treatments on nematode infestation, an indicator crop, rather than pineapple plants which would have to be destroyed, was employed for root examination. For this purpose, Whippoorwill cowpeas were seeded at the edges of the paper and in the three spaces between pineapple rows through the paper. On March 26 to 31, 1931, the indicator plants, being approximately 30 days old from seeding, were removed from the soil by means of trowels with the root systems as complete as possible. These plants were tied in bundles and labeled as to source. There were in all some thirteen thousand of them from the two locations. The plants were taken to the laboratory, and height to the growing point was measured; tops were removed, and plants, still in labeled bundles, were immersed in 2 per cent (commercial) formaldehyde. The roots were then available for examination at leisure as to degree of nematode infestation. Height of plants in each bed and average degree of infestation of the cowpea roots were recorded. Readings on infestation were obtained in the form of numbers of plants in each of several different classes as to degree of infestation, ranging from 0, through trace (1 to 10 galls per plant), slight (10 to 50 galls), medium (50 to 100 galls), and heavy (100 galls up per plant). This was an arbitrary classification which appeared to meet the needs of this particular experiment satisfactorily. The figures from these tabulations were used in the preparation of the charts shown in Figures 2 to 5, which show much more clearly than do tabulations the results of the experiment.

The charts are self-explanatory. They show clearly the benefits, in the way of enhanced plant growth and decreased nematode infestation derived from the applications of chloropicrin, particularly the applications of 163 pounds or more per acre. Without attempting a detailed statistical analysis of results, certain conclusions that would appear to be obvious because of numbers concerned are specified.

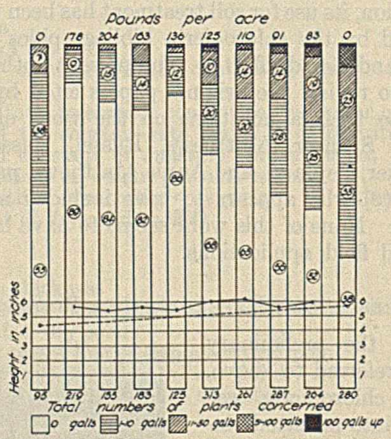


FIGURE 4. KUNIA TEST NO. 1

CONCLUSIONS

1. The control plots (untreated) consistently show the lowest percentages of roots free from nematode root knot, and correspondingly the highest percentages with heavy infestation.

2. The curves for freedom from infestation correlate directly to a fair degree with quantities of chloropicrin applied. Certain seeming inconsistencies in this respect are to be explained in part by differences in method of application,

tests of which were an important part of the experiment. In bed 6 throughout, for example, chloropicrin at the rate of 204 pounds per acre in the plant bed was applied in holes 24 inches apart; in bed 4, receiving only 178 pounds per acre, points of application were 18 inches apart. Figures 3 and 4 show better control with the lighter of the two applications. It would appear that in these two soils the better distribution of the chemical through the soil with the closer points of application more than balanced the benefit derived from the larger quantity. The same relationship existed between the 125- and the 110-pound applications, and Figures 2 and 5 show a distinct advantage for the lighter and closer application. Both applications, however, were irregular in effectiveness, and it was evident that many spots were not reached effectively by the chemical.

3. Curves for higher degrees of infestation are roughly parallel throughout with the curve for freedom from infestation. It should be noted that the differences between lightly and heavily infested plots would be much more accentuated if each figure for percentage were appropriately "weighted" by multiplying by a factor representing average number of galls per plant in its class. For example, the horizontal-lined shading, if assigned the value 5 for each per cent of total number of plants examined, would call for a factor of 30 (average of 10 and 50) for the diagonal shading; of 75 for the cross hatching; and of 150 for the solid black. These figures are arbitrary of course, since they represent not actual but theoretical means. The picture of comparisons would be very much the same, however, if minimum instead of theoretical mean figures were used in each class. On the selected basis the total infection portion of column 1, Figure 2, would be approximately 3600, as compared with 534 for column 2 and 768 for column 3. These figures obviously present a truer picture of relative amounts of infestation left alive than do the total lengths of all shaded portions in the charts. The benefit derived from the heavier applications of chloropicrin in the way of reduced nematode infestation is therefore considerably greater than is at first apparent.

TABLE I. PLAN OF CHLOROPICRIN APPLICATION USED IN EXPERIMENTS I AND II

BEDS	CHLOROPICRIN UNDER PAPER	SPACING OF POINTS OF APPLICATION	REMARKS
	Lb. per acre	*Inches*	
1, 2	0	Controls	
3, 4	178	18 (12 from edge)	
5, 6, 7	204	24 (in 3 lines, center and either edge)	
8, 9	163	18 (in 3 lines)	
10, 11	136	24 (in 2 lines)	
12, 13, 14	0	Controls	
15, 16, 17	125	24 (in 3 lines)	
18, 19	110	18 (in 2 lines)	
20, 21	91	36 (in 2 lines)	
22, 23	83	24 (in 2 lines)	
24, 25	0	Controls	
26	0	Control	Subsequent beds given additional application of 110 lb. per acre in "middles," between plant beds
27, 28	178	18 (in 2 lines)	Total per acre, 288 lb.
29	204	24 (in 3 lines)	Total per acre, 314 lb.
30	163	18 (in 3 lines)	Total per acre, 273 lb.
31	136	24 (in 2 lines)	Total per acre, 246 lb.
32	125	24 (in 2 lines)	Total per acre, 235 lb.
33	110	18 (in 2 lines)	Total per acre, 220 lb.
34	94	36 (in 2 lines)	Total per acre, 204 lb.
35, 36	83	24 (in 2 lines)	Total per acre, 193 lb.
37, 38	0	Control	

4. An expected advantage in favor of those areas receiving an extra application of chloropicrin in the "middles" between beds did not materialize, at least not to an extent commensurate with the quantities involved. Figure 3, as compared with Figure 2, appears to show such advantage, but the control plots show equivalent or greater differences; therefore the better control in Figure 3 cannot be considered as significant. Figure 5 shows no such advantage whatever over 4 in the heavier applications, but a seeming advantage in the lighter, in which the bed-application was inadequate of itself.

5. Measurements of growth of indicator crops were made on all the experimental areas, and results are recorded in the form of graphs at the bottoms of Figures 2 to 5. It is to be noted that a line drawn through the points for height of check plants will almost without exception orient the higher applications with consequent increased growth well above it.

Cost considerations are of course important in connection with any chemical treatment of the soil. A Pacific Coast firm has quoted a tentative price of 65 cents per pound for chloropicrin in large quantities laid down in Honolulu. The agent of an eastern firm is selling locally for 84 cents per pound. At the lower figure an application of 140 pounds per acre, which appeared to give highly satisfactory results in recent field tests, would make the cost something like $90.00 per acre. Improved methods of application which are being developed may lower the quantity required per acre. Likewise increased consumption will probably lower the costs. Cost of application, even with hand applicators, will probably be less than $5.00 per acre, and can be lowered by machine methods. The cost figures given, when compared with yield increases, would appear to justify extensive use of the material on badly infested land.

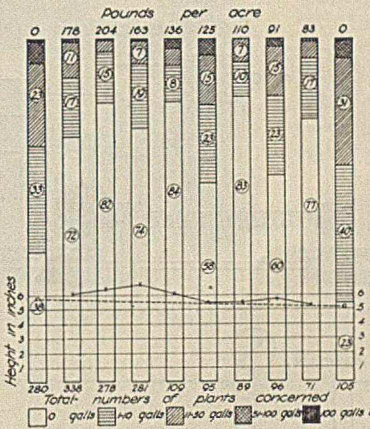


FIGURE 5. KUNIA TEST NO. 2

Same order of treatments as Figure 4, but additional application of chloropicrin at rate of 110 pounds per acre between beds.

Experimental work on chloropicrin for nematode control is continuing at the Pineapple Experiment Station and at various pineapple plantations.

ACKNOWLEDGMENT

Acknowledgment is due Helene M. Hoshino and Holoaumoku Gittel for their extensive routine examinations of plants from these experiments.

LITERATURE CITED

(1) Gersdorff, W. A., U. S. Dept. Agr., Bur. Chemistry and Soils, Supplement to Chloropicrin Bibliography, Oct., 1930 (mimeographed).

(2) Matthews, D. J., Mrs., Exptl. Research Sta., Nursery Market Garden Industries' Devel. Soc., Ltd., Turner's Hill, Cheshunt, *Herts. 5th Ann. Rept.*, 18–21 (1929); *Ibid., 6th Ann. Rept.*, 45–51 (1930).

(3) Roark, R. C., U. S. Dept. Agr., Bur. Chemistry, *Chem. Bibliography* 1 (1926).

RECEIVED October 3, 1931. Published with the approval of the Director as Technical Paper 31 of the Experiment Station of the Association of Hawaiian Pineapple Canners, University of Hawaii.

Reactions of Acetaldehyde over Various Oxide Catalysts

MAURICE E. KINSEY AND HOMER ADKINS

Laboratory of Organic Chemistry, University of Wisconsin, Madison, Wis.

THE reactions of acetaldehyde in ethyl alcohol over a zinc-chromium oxide catalyst at 360° C. under a pressure of approximately 200 atmospheres resulted in the formation of a mixture of alcohols, aldehydes, and esters. The fractionation of these products after hydrogenation and hydrolysis resulted in the isolation, as the principal products boiling below 200° C., of ethyl, *n*-butyl, and hexyl alcohols, and of acetic, butyric, and caproic acids (*2*).

This study has been continued by determining the effect of certain variations in the catalyst upon the ratio of the products.

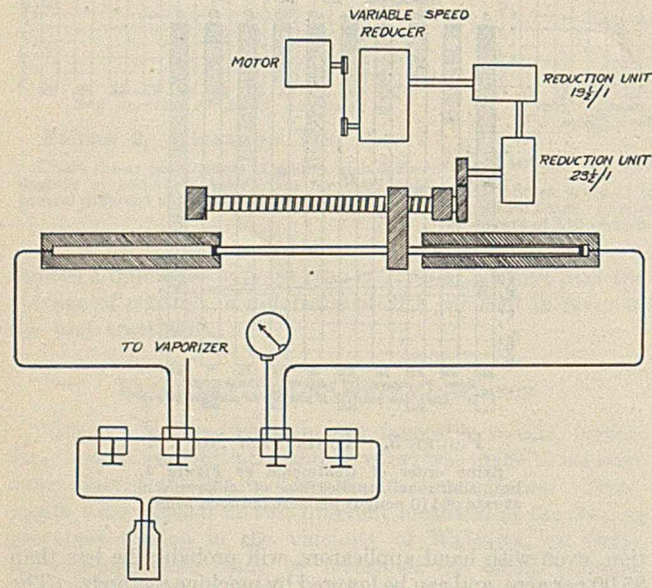


FIGURE 1. PUMP VALVE AND GAGE ASSEMBLY

The essential parts of the apparatus used in carrying out the reactions under pressure were a pump, a vaporizer, a catalyst chamber, a condenser, a receiver, a hydraulic gage, and the necessary valves, tubing, and connections. The pump had two cylinders, each having an internal volume of 150 ml., one of which at any given time was delivering and the other receiving liquid. It was made by the Watson-Stillman Company. The liquid could be delivered at rates from 60 to 600 ml. per hour against pressures up to 1000 atmospheres. The vaporizer was a chrome-vanadium steel bomb, similar in construction to the catalyst chamber but having an internal volume of only 50 ml. It was filled with 1/4-inch (6.4-mm.) steel balls. The catalyst chamber was essentially the same as that supplied by the American Instrument Company, Washington, D. C., as their standard catalyst chamber for ammonia synthesis on a laboratory scale, but modified, in that external heating was used and the catalyst holder had a capacity for about 75 ml. of catalyst. The condenser was a 1/4 × 1/16 inch (6.4 × 1.6 mm.) steel tubing, 3 feet (91.4 cm.) long, inclosed in a jacket through which water was circulated. The receiver was similar in design to the catalyst chamber except that it had an internal volume of 200 ml. and was of somewhat lighter construction. It was provided with an outlet at both top and bottom so that either gas or liquid could be withdrawn from the system. Figures 1 and 2 illustrate diagrammatically the arrangement of the apparatus described above; Figures 3 and 4 are photographs of the apparatus. The motor shown in the diagram is a 0.5 h. p. induction motor made by the General Electric Company. The variable speed reducer is a Reeves No. 000 variable speed transmission. Standard reduction units are indicated, giving the ratio of reduction. The lead screw which drives the pistons had a pitch of four threads per inch.

Approximately 270 ml. per hour of a mixture of two parts of acetaldehyde and one part of ethyl alcohol were pumped over 30 ml. of pellets of catalysts held at 360 ± 5° C. under a pressure of approximately 200 atmospheres of hydrogen. The method of working up the liquid products from these reactions was simplified as follows:

Samples were analyzed for aldehydes by the sodium sulfite method; then 300 ml. of the condensate were subjected to hydrogenation at 100–200 atmospheres at 175° C. over a nickel catalyst. The absorption of hydrogen was noted, and the acid and ester content of the hydrogenated product were determined. Two hundred and ten grams of the hydrogenated product were saponified with alkali. The mixture was then distilled until the distillate, as it came over, separated into two layers. The neutral compounds were then salted out of the distillate with potassium carbonate. The residue in the distillation flask was cooled and extracted with ether. After drying with potassium carbonate, the ether was distilled and the residue combined with the neutral compounds salted out from the original distillate. The combined neutral compounds were again dried over potassium carbonate and fractionated through a Widmer column, having a glass spiral 50 cm. in length. The column was heated externally with a coil of nichrome wire carrying a suitable current. The alkaline residue, after the removal of the alcohols, was evaporated almost to dryness and acidified with sulfuric acid. Any insoluble acid was separated and the residue extracted with ether. The insoluble acids and the ether extract were then

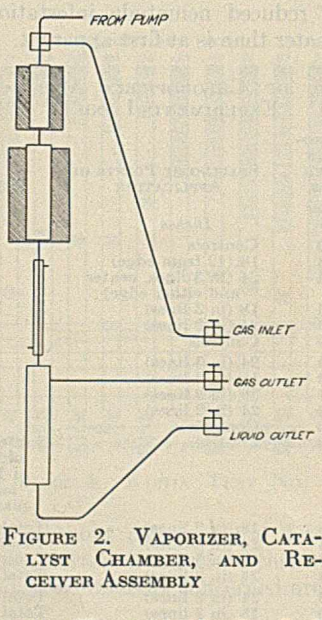


FIGURE 2. VAPORIZER, CATALYST CHAMBER, AND RECEIVER ASSEMBLY

combined and dried over anhydrous magnesium sulfate. After removal of the ether, the acids were fractionated through a Widmer column, externally heated and having a glass spiral 15 cm. in length.

Discussion of Experimental Results

The results of the fractionation of typical mixtures are shown in Figures 5 and 6 for several catalysts, and the data from representative runs on all of the catalysts are summarized in Table I.

The catalysts may be compared on several different bases, for example:

1. Their activity for bringing about the reaction of acetaldehyde.
2. The hydrogen number or unsaturation of the products of the condensation.
3. Their activity for ester formation.
4. Their activity in producing butyl alcohol (including its precursors, crotonic and butyric aldehydes and crotonyl alcohol).
5. Their activity in producing hexyl alcohol (and its precursors).
6. Their effect upon the ratio of acids produced.
7. Their effect upon the production of resinous products boiling above 200° C.

The values in the first column of figures in the table show that the copper-chromium catalyst is the most active in bringing about the reaction of acetaldehyde. There were 15.1 millimoles of acetaldehyde per gram of material passed over the catalyst, and over 94 per cent of it underwent reaction. The cadmium-chromium, the copper-barium-chromium, and the manganese-chromium oxides were all quite active.

The degree of unsaturation of the products is indicated by the differences between the figures in columns 1 and 2 of the table, for a mole of aldehyde would require 1 mole of hydrogen for its hydrogenation. These differences show that copper-chromium and silver-chromium oxides are either least active for the reactions which form alkene linkages, or are most active for catalysis of their hydrogenation.

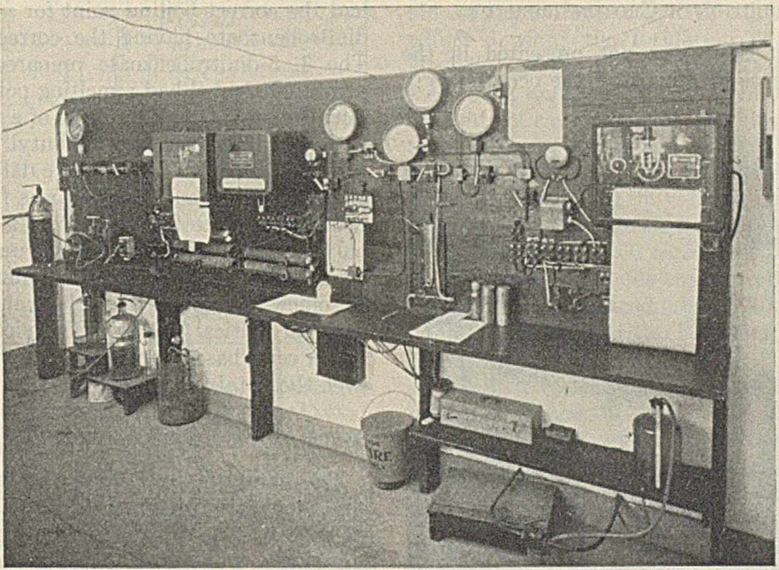


Figure 3. Control Panel for High-Pressure Laboratory

Valves and gage of Figures 1 and 2 are at left-hand end of panel. The layout, pictured here and in Figure 4, was designed and assembled by Howard I. Cramer and the authors.

The copper-chromium oxide catalyst is by far the most active for ester formation, i. e., for bringing about the autoxidation reduction of an aldehyde according to the equation:

$$RCHO + RCHO = RCO_2CH_2R \quad (1)$$

Cadmium-chromium and silver-chromium oxides are also quite active for this reaction.

The catalysts differ less with respect to butyl alcohol formation than when measured by any other standard. This fact, taken in conjunction with the observation that large amounts of butyl alcohol are produced over glass beads and steel balls, indicates that the aldol reaction (Equation 2) on which the formation of butyl alcohol is supposed to depend takes place over almost any surface at 360° C.

$$2CH_3CHO = CH_3CHOHCH_2CHO \quad (2)$$

The formation of hexyl alcohol appears to be much more dependent upon the nature of the contact mass than are any of the other reactions except the formation of esters. Fourteen grams of hexyl alcohol were recently obtained from an experiment involving the passage of twenty times as much acetaldehyde over a zinc-chromium catalyst as was used in the catalyst-testing experiments now reported. Such a yield of hexyl alcohol would not be detected on the scale of operations which is now under consideration so that the yield of hexyl alcohol for comparative purposes is recorded in this paper as zero for the zinc-chromium oxide catalyst. It will thus be obvious that relatively rather large yields of hexyl alcohol were produced on copper-chromium, silver-chromium, and copper-barium-chromium oxides.

There appeared to be little variation in the weights of caproic acid produced over various catalysts, whereas the weights of butyric acid obtained varied from zero to 11.7 grams. The parallelism between the production of butyric

Table I. Products from Reaction of Acetaldehyde over Various Catalysts

Catalysts	Aldehyde	H_2 Absorbed	Ester[a]	Butyl Alcohol	Hexyl Alcohol	Acetic Acid	Butyric Acid	Caproic Acid	Residue
	Millimoles per gram			*Grams per 210 grams of hydrogenated product*					
Cu-Cr oxides	0.88	3.17	4.64	23.0	6.0	27.0	11.7	6.2	10.0
Cd-Cr oxides	1.50	3.93	3.19	14.0	0.0	16.6	4.2	6.0	20.0
Ag-Cr oxides	3.12	5.13	3.16	20.0	7.0	15.0	5.2	5.0	16.0
Cu-Cr-Ba oxides	1.31	4.45	2.26	23.0	7.0	7.0	8.2	7.5	27.0
Co-Cr oxides	2.22	5.46	2.10	15.0	4.0	9.0	3.0	5.2	27.5
Cr oxide	2.67	6.16	1.98	16.0	0.0	7.2	0.0	6.0	27.5
Cu-Mo oxides	3.75	6.51	1.91	17.0	3.0	5.7	2.5	6.2	29.0
Zn-Cr oxides	3.51	6.75	1.80	16.0	0.0	7.4	1.0	6.5	29.0
Zn-Cr oxides (Na_2SO_4)	1.86	5.01	1.76	16.0	2.0	5.1	1.5	8.0	37.0
Cu-V oxides	3.67	6.44	1.60	16.0	3.0	5.0	1.0	6.0	29.0
Mg-Cr oxides	2.85	5.40	1.47	16.0	2.0	2.2	0.0	6.5	40.0
Fe-Cr oxides	3.81	7.13	1.40	17.0	0.0	4.3	0.0	5.5	32.0
Mn-Cr oxides	1.67	5.09	1.36	11.0	2.0	3.0	0.0	6.2	50.5
(Ni-Cr oxides)[b]	(2.74)	(3.84)	(1.35)	(18.0)	(10.0)	(2.6)	(4.2)	(2.2)	(16.0)
Glass beads	3.24	6.53	1.14	14.0	2.0	0.8	0.0	11.0	36.0
Steel balls	7.24	9.86	0.63	20.0	0.0	0.8	0.0	0.0	19.0

[a] The ester determination was made on the hydrogenated product; 28 ± 4 per cent of the ester had been hydrolyzed during the various operations.

[b] The data on the nickel catalyst should not be compared with that on the other catalysts because 35 to 45 per cent of the aldehyde was decomposed into gaseous products.

and acetic acids, the rather constant yield of caproic acid, and the large yield of caproic acid almost free of acetic and butyric acids over glass beads indicate that the acetic and butyric acids are produced by a similar mechanism (i. e., as in Equations 1 and 2) while caproic acid is formed by an entirely different chain of reactions. It may be recalled that a similar conclusion was drawn in the previous paper (*2*) on the basis of the relative yields of hexyl alcohol and caproic acid.

PREFERENTIAL REDUCTION OF CROTONALDEHYDE

Through an oversight, there was not presented in the previous paper any evidence in support of the occurrence of the reaction there listed as VIII. This reaction involved the reduction of an aldehyde group by alcohol as indicated for crotonic aldehyde and ethyl alcohol:

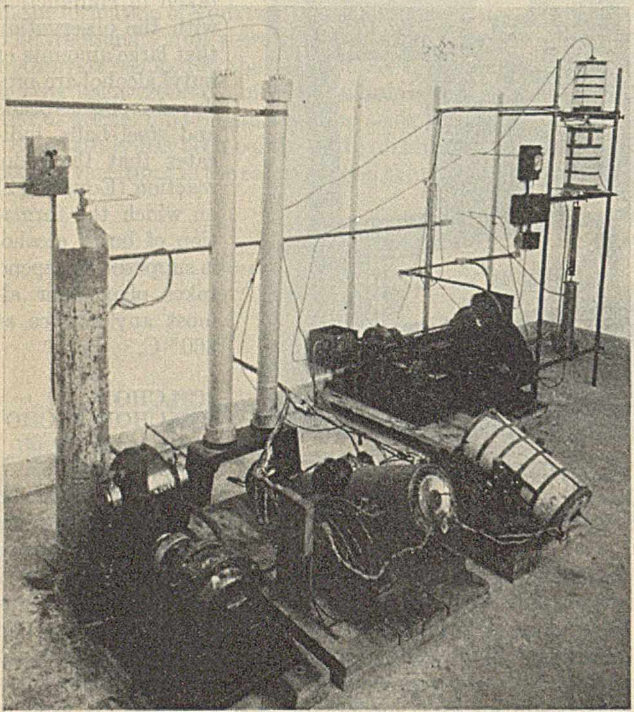


FIGURE 4. HIGH-PRESSURE LABORATORY

Feed pump, vaporizer, catalyst chamber, condenser, and receiver represented in Figures 1 and 2 are in right background. Hydraulic pump for compressing gas in tall cylinders and two outfits for hydrogenation in batch lots shown in foreground.

$$CH_3CH{=}CHCHO + C_2H_5OH = CH_3CH{=}CHCH_2OH + CH_3CHO \quad (3)$$

That this reaction does occur over a zinc-chromium oxide catalyst was shown in the following experiment: A solution containing one part of crotonaldehyde to 2 parts of ethyl alcohol was passed at the rate of 270 ml. per hour over 30 ml. of zinc-chromium oxide pellets at 360° C. under a pressure of 200 atmospheres of hydrogen. The product was fractionated, and in one experiment 27 grams (boiling point 115–120° C.) of a product were obtained. This material had a refractive index, n^{20}_{D} of 1.4235. The value given in the International Critical Tables (*5*) for crotonyl alcohol is 1.4240. This value would indicate that the product (boiling point 115–120° C.) was rather pure crotonyl alcohol. However, when it was subjected to hydrogenation over nickel, the hydrogen absorption was 83.5 per cent as great as it should have been for pure crotonyl alcohol. This determination may well have been several per cent in error, but the value shows conclusively that the product was not pure crotonyl alcohol. The calculated refractive index for crotonyl alcoho is 1.4263 n^{20}_{D}. The value given in the International Critical Tables (*5*) for *n*-butyl alcohol is 1.3993 n^{20}_{D}. If the impurity in the sample of crotonyl alcohol is butyl alcohol, and the variation in refractive indices of mixtures of the two alcohols is a linear function of the percentage composition, then the sample of crotonyl alcohol under consideration was approximately 90 per cent pure. The first premise noted above is justified by the fact that the reduction product of the mixture had the correct boiling point for *n*-butyl alcohol and gave a dinitrobenzoate having the correct melting point—63° C. The 3, 5-dinitrobenzoate prepared from the sample of unsaturated alcohol had a melting point of 58–59° C. A determination of the melting point of a mixture of this compound with the dinitrobenzoate of butyl alcohol showed a melting point of 51–53° C. The above data indicate that the sample of crotonyl alcohol obtained was from 80–90 per cent pure, containing 10 to 20 per cent of *n*-butyl alcohol which boils only 2–3° C. lower than does the unsaturated alcohol. It appears that the true refractive index of pure crotonyl alcohol is somewhat higher than the value recorded in the International Critical Tables. The yield of crotonyl alcohol was 18 per cent, based upon the amount of crotonaldehyde passed over the catalyst.

PREPARATION OF CATALYSTS

The catalysts containing chromium and either copper, zinc, manganese, magnesium nickel, silver, cobalt, or cadmium were prepared by the decomposition of the ammonium chromates as patented by Lazier and described elsewhere (*1*). The ammonium chromates of magnesium, silver, and cadmium did not decompose spontaneously but required continual heating in order to complete the decomposition. Sodium sulfate was incorporated into the zinc-chromium oxide by adding an aqueous solution containing 5 grams of it to 100 grams of the zinc-chromium oxide. The catalyst containing iron-chromium oxide was made according to the general method, except that the solution was heated to 90° C. in order to secure a more completely precipitated chromate. The copper ammonium vanadate was prepared by adding a solution containing 1 mole of copper nitrate to a hot solution of 1 mole of ammonium metavanadate. The dried precipitate was decomposed by heating. The copper ammonium molybdate was precipitated by mixing solutions containing equimolecular quantities of copper nitrate and

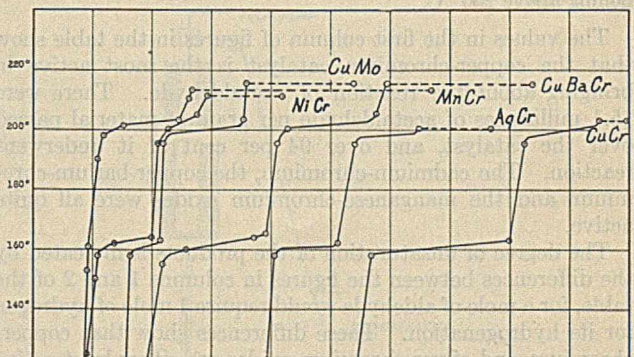


FIGURE 5. DISTILLATION CURVES FOR ACIDS OBTAINED FROM ACETALDEHYDE OVER CERTAIN CATALYSTS

Dotted portions indicate weights of residue not volatile at highest temperature indicated on curve.

ammonium molybdate. The dried, green precipitate was readily decomposed. It was washed with a 10 per cent solution of acetic acid. The catalyst containing barium was prepared as described elsewhere (*3*). Chromium oxide was prepared by the decomposition of ammonium dichromate.

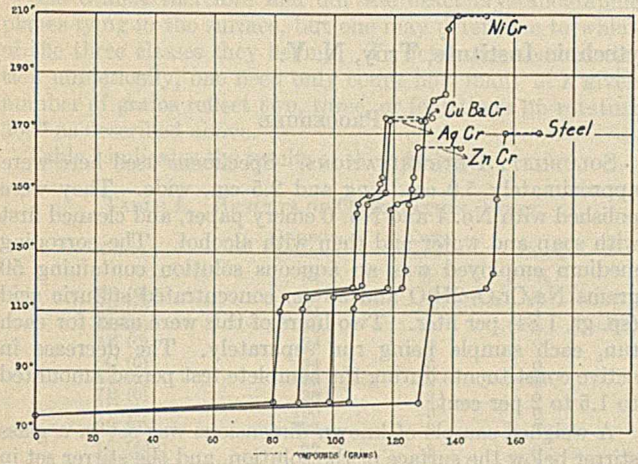


FIGURE 6. DISTILLATION CURVES FOR NEUTRAL COMPOUNDS OBTAINED FROM ACETALDEHYDE OVER CERTAIN CATALYSTS

Dotted portions indicate weights of residue not volatile at highest temperature indicated on curve.

All of the above catalysts were compressed into pellets and so placed in the catalyst chamber. The glass beads used were 6.4 mm. in diameter, while the steel balls were of a similar size and were such as are used for ball bearings. They had been etched with hydrochloric acid and thoroughly washed.

COMPOSITION OF COPPER-CHROMIUM OXIDE CATALYSTS. The copper in the catalysts as placed in the chamber was in the divalent state. However, under the conditions of the reaction it was almost immediately reduced to the metallic state (*4*). It is probable that in some other cases one or more components of the catalyst were reduced during their use.

SUMMARY

A study has been made of the condensation of acetaldehyde at 360° C. and 200 atmospheres pressure, over oxide catalysts containing (1) chromium; (2) chromium and either copper, or (3) cadmium, or (4) silver, or (5) cobalt, or (6) zinc, or (7) magnesium, or (8) iron, or (9) manganese, or (10) nickel; (11) copper and either vanadium, or (12) molybdenum; (13) copper, barium, and chromium; and (14) zinc, chromium, and sodium sulfate. Steel balls and glass beads were also used as contact reagents.

All of these contact reagents bring about the formation of similar amounts of *n*-butyl alcohol so that it appears that almost any surface at 360° C. will cause the aldol reaction on which depends the formation of the precursors of butyl alcohol. All the contact reagents, except the glass beads and steel balls and the catalyst containing nickel, gave similar amounts of caproic acid. The glass beads gave almost twice as much caproic acid as any other contact mass, while steel balls showed no activity in this respect. The amounts of esters produced over the catalyst varied more than seven fold. Disregarding the esters in the nonvolatile portion, the yields of acetic and butyric acid varied from a total of 0.8 to 38.7 grams. The catalyst containing copper and chromium was by far the most active for the production of esters, while those containing cadmium or silver with chromium were rather active in this respect.

The yield of high-boiling resins was particularly large over catalysts containing magnesium or manganese. The introduction of barium or sodium sulfate into a catalyst increased the yield of these high-boiling tars.

It has been demonstrated that an aldehyde group in an unsaturated aldehyde (crotonic) can be reduced to a carbinol group through the use of an alcohol (ethyl) without hydrogenating the alkene linkage to any considerable extent.

LITERATURE CITED

(1) Adkins and Connor, *J. Am. Chem. Soc.*, 53, 1091 (1931).
(2) Adkins, Folkers, and Kinsey, *Ibid.*, 53, 2718 (1931).
(3) Connor, Folkers, and Adkins, *Ibid.*, 54 (March, 1932).
(4) Frolich, P. K., IND. ENG. CHEM., 21, 109 (1929); Cryder and Frolich, *Ibid.*, 21, 1052 (1929); Abom and Davidson, *J. Phys. Chem.*, 34, 522 (1930).
(5) International Critical Tables, Vol. I, p. 276, McGraw-Hill, 1926.

RECEIVED December 12, 1931.

* * *

Percolator Series of Prints

The illustration on page 366 is No. 17 in the series of prints which we have reprinted from the front cover of *The Percolator*. Photographic prints 8 × 10 inches can be supplied at $2.50, and 16 × 20 inches at $5.

Orders, specifying the numbers here indicated and titles as given, should be placed with advance payment with D. D. Berolzheimer, editor of *The Percolator*, The Chemists' Club, 52 E. 41st St., New York, N. Y.

1. Medieval Pharmacy, Castle of Saint Angelo (August 1931, page 966)
2. Le Chimiste, Teniers (London) (August 1931, page 967)
3. The Laboratory, Hunt (August 1931, page 966)
4. Rumford, Gainsborough (August 1931, page 967)
5. L'Alchimiste en Meditation, Wyck (December 1931, page 1333)
6. L'Alchimiste, Teniers (The Hague) (September 1931, page 1074)
7. Lavoisier and His Wife, David (October 1931, page 1175)
8. Impossible, Pynas (October 1931, page 1174)
9. L'Alchimiste, Teniers (self-portrait) (November 1931, page 1310)
10. The Alchemical Making of a Medicine, Diemer (September 1931, page 1074)
11. Joseph Priestley, Humphrey (November 1931, page 1311)
12. The Arrest of Lavoisier, Langenmantel (October 1931, page 1175)
13. The Alchemist, Than (November 1931, page 1311)
14. L'Alchimiste, Teniers (Dresden) (November 1931, page 1310)
15. The Elixir of Life, Lomax (November 1931, page 1316)
16. Rudolph II, Emperor of Germany, in the Laboratory of His Alchymist, 1576, Brozik (February 1932, page 157)
17. The Goldmaker, Breughel (March 1932, page 363)

Effect of Cold-Rolling and Annealing on Solubility of Cartridge Brass in Chromic Acid

JOSEPH D. PARENT, Rensselaer Polytechnic Institute, Troy, N. Y.

IT WAS not until recently that any work had been done on the corrosion of brass with regard to its relation to grain size, or mechanical and thermal treatment. Although a limited amount of information is available, it presents a wide variation both in actual results and in theoretical discussions and conclusions. Probably the most notable work has been carried out by Bassett (*1*, *2*), Lasche (*6*), Haas (*5*), and Davidenkov and Bugakov (*3*). The last-named authors have just published what appears to be the first attempt to correlate physical properties with corrosion losses.

It has been the experience of various investigators on plotting the physical properties of α-brass against the degree of cold work, that there is a critical region in which the curves suddenly change in slope, and then continue again as before. Davidenkov and Bugakov (*3*) have shown that the curve expressing the solubility in nitric acid plotted against the degree of cold-rolling exhibits the same characteristic. Subsequent annealing at 200° C. removed the break in the solubility and hardness curves. These authors also measured the inner stresses and showed that the peculiarity exhibited by the above-mentioned curves is due to this factor.

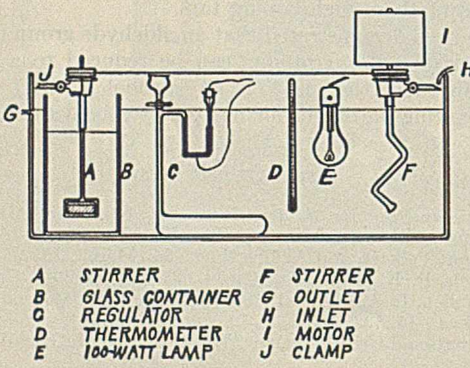


FIGURE 1. ESSENTIAL PARTS OF APPARATUS FOR CORROSION TESTS

The effect of grain size on the corrosion rate has been investigated by Desch and Whyte (*4*) and several others, but in practically all cases the material investigated lay in the (α + β) region. Their results are not concordant. As far as can be ascertained, no investigation has been carried out on the effect of variation of grain orientations. Moreover, the effect of annealing is quite indeterminate, as results from different sources do not agree.

The material used in this investigation was cartridge brass in sheet form, having the following chemical composition: 66.75 per cent copper; 33.09 per cent zinc; 0.12 per cent lead; 0.04 per cent iron. It consisted therefore of a single phase, the α-solid solution. The material had been annealed at 600° C. in order to free it from the effects of working, and was afterwards cold-rolled until the following reductions in thickness were effected in different samples: 0, 6, 10, 19, 27, 37, 49, 60, and 67 per cent. These samples were numbered from 1 to 9, and divided into three series. The first series was not subjected to any further treatment; the second was annealed for 30 minutes at 450° C., and the third for 30 minutes at 800° C.

PROCEDURE

SOLUBILITY DETERMINATIONS. Specimens used here were approximately 5.0 cm. long and 2.5 cm. wide. They were polished with No. 1 and No. 0 emery paper, and cleaned first with soap and water and then with alcohol. The corroding medium employed was an aqueous solution containing 50 grams $Na_2Cr_2O_7 \cdot 2H_2O$ and 35 cc. concentrated sulfuric acid (sp. gr. 1.84) per liter. Two liters of this were used for each run, each sample being run separately. The decrease in active constituents during the complete test period amounted to 1.5 to 2 per cent.

A weighed sample of known dimensions was set in a glass stirrer below the surface of the solution, and the stirrer set in motion by a motor. The sample was cleaned, dried, and weighed after exposures of 20, 40, 60, and 80 minutes. The temperature was kept at 20.0° ± 0.1° C.

The essential parts of the apparatus used are shown in Figures 1 and 2. The regulator reservoir was filled with toluene and the U-tube with mercury. The heating element was a 100-watt lamp. The stirrer in the corroding solution was made of glass, and that in the outer bath, of copper tubing. The glass stirrer, in which the sample was set, had small glass prongs to keep the sample from slipping out.

The Rockwell hardness, grain size, and grain orientations were then determined for each sample. The first two were ascertained by the usual methods. The grain orientations were determined by one of Tammann's methods (*8*–*11*) as subsequently described.

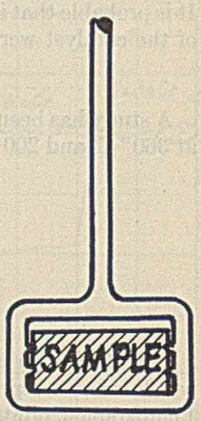


FIGURE 2. STIRRER

GRAIN-ORIENTATION DETERMINATIONS. Lattice planes of different indices lie in the polished surface of a metal conglomerate if the grains are oriented at random. On etching this surface there arise very minute etching pits or hills whose boundaries are squares on cube planes, triangles on octahedral planes, and furrows on dodecahedral planes. If one illuminates this surface under the microscope with oblique incident diffuse light, some grains appear dark and others light. On rotating the specimen about the axis of the microscope tube, the positions of these bright and dark areas interchange. All grains are found to reflect either two, three, or four times on one complete revolution, depending on whether there are dodecahedral, octahedral, or cube planes lying in the surface.

On etching, the planes of higher indices are quickly cleared off, leaving lattice planes which are more densely packed. On these, almost the same etch figures result so that the reflection produced on rotation is the same as for cube, octahedral, or dodecahedral planes. Thus, etch figures of cube planes would arise on all tetrahexahedral planes with the indices varying from (100) to (210), whereas on those between (210) and (110) the etch figures of the dodecahedral plane would be formed. All the planes would be distributed among the three chief classes as follows:

	Planes		
Thickly packed	Cube (001)	Octahedron (111)	Dodecahedron (011)
Less thickly packed	Tetrahexahedron Trapezohedron	Trapezohedron Trigonal trisoctahedron Hexoctahedron	Trigonal trisoctahedron Hexoctahedron Tetrahexahedron

One cannot therefore find out the exact crystallographic planes lying in the surface, but one may determine to which of the three classes they belong. To determine the orientation numerically, one need only count how many of a given number of grains reflect two, three, or four times on rotating 360° as described above.

Table I indicates the results of these tests.

Table I. Results of Orientation Tests

Sample	Dodecahedron	Octahedron	Cube
	%	%	%
1B (0)[a]	98	2	0
2B (0)	94	2	4
3B (0)	90	10	0
4B (0)	94	6	0
5C (0)	94	6	0
6B (0)	96	2	2
7B (0)	98	2	0
8C (0)	100	0	0
9C (0)	100	0	0
1C (450)	92	8	0
2B (450)	92	4	4
3C (450)	90	10	0
4C (450)	94	6	0
5B (450)	98	2	0
6C (450)	100	0	0
7C (450)	100	0	0
8B (450)	100	0	0
9B (450)	100	0	0
1C (800)	96	4	0
2B (800)	90	6	4
3C (800)	86	14	0
4C (800)	92	8	0
5B (800)	94	6	0
6C (800)	96	4	0
7B (800)	98	2	0
8C (800)	100	0	0
9C (800)	100	0	0

[a] The numbers in parentheses indicate temperature of annealing in ° C.; 0 indicates no annealing.

The results of the corrosion tests are embodied in Figure 3, while Figure 4 shows the hardness and grain-size measurements as well as those of the corrosion. From the graphs it is evident that the series annealed at 800° C. is more resistant to corrosion than the two other series. Also, the critical range in the unannealed series, as mentioned by Davidenkov and Bugakov (*3*), is noted here in the solubility and hardness curves. Likewise it may be seen that below the critical range of 20 to 30 per cent reduction, the series annealed at 450° C. is more soluble than that which was not annealed; beyond this range the order is reversed, so that in this region the higher the temperature of annealing, the greater is the resistance to corrosion.

There is no break in the grain-size curve in the critical region, so that there must be a change of some sort in the physical nature of the grains. Moreover, there is no break in the curves of the annealed series in this range.

The solubility and hardness curves of the series annealed at 450° C. show a change in direction in the range of 5 to 10 per cent reduction. From the grain-size curve and from microscopic observation it is seen that recrystallization has barely started in this region, but that beyond this it is complete. The increase in solubility here may be attributed to an electrochemical acceleration due to the voltaic effects arising from the difference in solution pressures of the large and small grains, the latter being the equiaxed grains formed on recrystallization. This is not due intrinsically to the shape or size of the grains, but rather to the fact that the small grains are unstressed and the large ones are stressed.

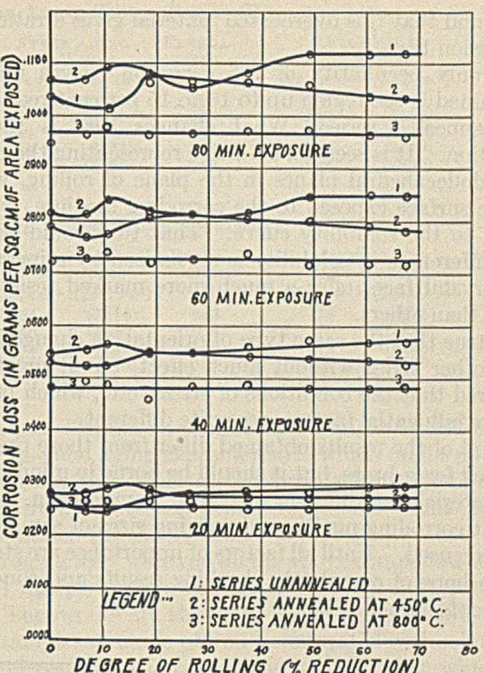


Figure 3. Corrosion Loss *vs.* Degree of Rolling

The proof that the large ones are stressed lies in the fact that annealing at a higher temperature causes further grain refinement. It is quite logical to assume that the stressed material, having a higher energy content, would be more soluble. This is why the solubility decreases beyond the critical range with the increase in annealing temperature.

There are no breaks in the curves for the series annealed at 800° C. The values on the solubility curve are inclined to be somewhat erratic. This is possibly due to overheating, the sample not being chemically homogeneous because of the appearance of the β-phase at that elevated temperature. The mode of corrosion noted here is different from that noted elsewhere; there is considerable surface pitting and a small amount of dezincification. It is the experience of von Schwarz (*12*) that coarse grains in α-brass are favorable to this type of corrosion. Likewise, several other investigators

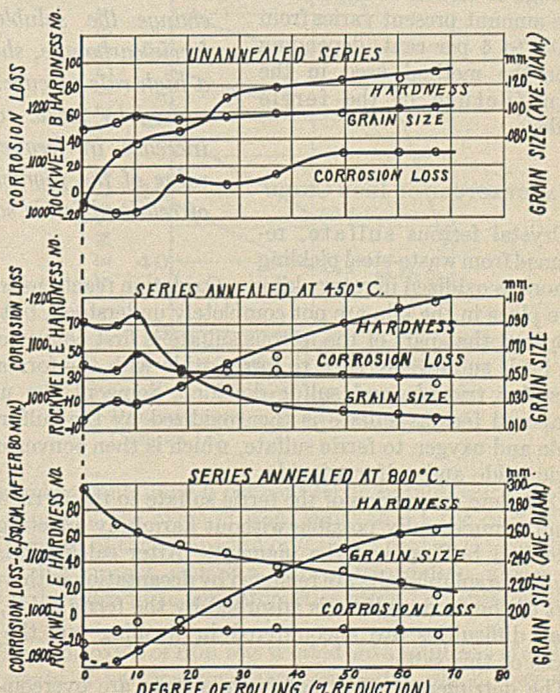


Figure 4. Measurements of Hardness, Grain Size, and Corrosion

have found that this overheated material gives erratic results in corrosion tests.

The only peculiarity of the corrosion curves remaining unexplained is the region up to 10 to 15 per cent reduction in the unannealed series. What changes here is the grain orientation. It is seen that a curve representing the percentage of dodecahedral planes in the plane of rolling, which is also the surface exposed to the corroding medium, would be parallel to the solubility curve. That this would suffice to cause differences in solubility is recognized by mineralogists. Some crystal faces offer a much more marked resistance to etching than others.

It is true that the same type of orientation change is noted in the other series without much effect, but it must be remembered that the conditions of stress, etc., which probably are more influential factors, are quite different.

Several of the results obtained differ from those previously published for α-brass, but it should be borne in mind not only that materials of different chemical composition, but also different corroding media, and varying sizes of samples, etc., have been used. Until all factors of importance are standardized, no hope of completely checking results and conclusions can be entertained (7).

In conclusion, it may be stated, regarding corrosion work of this sort, that the grain size in itself gives no indication of the corrosion loss to be expected. The factors of importance are: inner stresses; chemical homogeneity; physical homogeneity; and orientation of the grains.

Literature Cited

(1) Bassett and Bedworth, Ind. Eng. Chem., 17, 346 (1925).
(2) Bassett and Davis, *Am. Inst. Mining Met. Eng.*, 71, 745 (1925).
(3) Davidenkov and Bugakov, *Metallwirtschaft*, 10, 1 (1931).
(4) Desch and Whyte, *J. Inst. Metals*, 11, 235 (1914).
(5) Haas, *Metals & Alloys*, 1, 183 (1929).
(6) Lasche, "Konstruction und Material im Bau von Dampfturbinen und Turbodynamos," pp. 127–144.
(7) Portevin, *Rev. mét.*, 26, 606 (1929).
(8) Tammann, *Z. tech. Physik*, 7, 531 (1926).
(9) Tammann and Heinzel, *Z. anorg. allgem. Chem.*, 167, 173 (1927).
(10) Tammann and Meyer, *Z. Metallkunde*, 18, 176 (1926).
(11) Tammann and Meyer, *Ibid.*, 19, 82 (1927).
(12) von Schwarz, *Korrosion u. Metallschutz*, 2, 152 (1926).

Received October 30, 1931. From a thesis submitted to the Rensselaer Polytechnic Institute in partial fulfilment of the requirements for the degree of master of science. The author's present address is 823 Newton St., N. E., Washington, D. C.

Impure Iron Oxide as a Rubber Pigment

I. Effect of Ferric Sulfate on Cure and Aging of Rubber

Joseph W. Ayers, C. K. Williams and Company, Easton, Pa.

The traces of free ferric sulfate present in oxide of iron are shown by experiment to cause accelerated aging of rubber. This impurity markedly retards the rate of cure. Oxide of iron, treated with sodium carbonate in solution to change the soluble ferric sulfate to insoluble ferric carbonate, shows good aging properties and a high rate of cure. Aggregates of oxide of iron caused by ferric sulfate during its manufacture increase in frequency and size, and the color value of the pigment decreases as the percentage of retained ferric salt increases.

Commercial ferric oxide, commonly used as a coloring agent of red, tan, and brown rubber stock, invariably contains a small percentage of soluble ferric sulfate. The amount present varies from 0.005 to 4 per cent, depending upon the method used in the manufacture of the ferric oxide.

Manufacture of Iron Oxide

Crystal ferrous sulfate, reclaimed from waste-steel pickling liquors, is oxidized in rotary kilns. Oxidation reactions which take place in the kiln are not completely understood, but it is supposed that part of the ferrous sulfate is first converted to the basic sulfate and then to ferric oxide with the formation of sulfur trioxide and sulfur dioxide. Some of the undecomposed ferrous sulfate is then oxidized by the sulfur trioxide and oxygen to ferric sulfate, which is then converted to ferric oxide and sulfur trioxide.

Complete conversion of the ferric sulfate to the ferric oxide is not commercially possible without harmfully affecting the color and brilliance of the pigment. After calcination, the remaining soluble salts are removed by decantation with water. Part of the ferric sulfate is adsorbed by the ferric oxide, and great difficulties are encountered in washing out the last traces of this salt.

The detrimental effects of ferric sulfate are overcome by treating the oxide with sodium carbonate as shown in the following experiments.

Methods of Test

All compounds were milled on a Farrell-Birmingham laboratory experimental mill. Care was taken that each batch was milled for exactly the same length of time and also cut back the same number of times on the rolls.

Master batches of all compounds were first milled, to which the color and accelerator were added just previous to cure.

A standard 6 × 6 inch four-cavity mold was used in curing the test slabs. An insulated press with cast-iron platens with automatic recording temperature and pressure gages was used, the surface of the platens having previously been tested for uniform heat transfer with a thermocouple.

All cured slabs were kept at an even temperature and humidity for 24 hours before breaking on a Scott testing machine. The elongation was taken visually from a measuring tape, the rate of elongation being 20 inches (50.8 cm.) per minute.

Aging Tests. Uniform oxygen pressure 300 pounds per square inch (21.1 kg. per sq. cm.) was supplied from an oxygen cylinder to a standard Bierer-Davis bomb, completely submerged in a thermostatically controlled circulating water bath at 60° C.

Circulating air was supplied to a standard Geer oven by an electric fan, the oven being electrically heated to 70° C. and thermostatically controlled.

Control Tests. Cure curves were run on all compounds

Table I. Effect of Ferric Sulfate in Bomb Aging Tests (Series I)

Ferric Sulfate	Before Aging		Elongation	After Aging 24 Hours		Elongation	After Aging 48 Hours		Elongation	After Aging 72 Hours		Elongation
%	*Kg./cm.²*	*(Lb./in.²)*	%	*Kg./cm.²*	*(Lb./in.²)*	%	*Kg./cm.²*	*(Lb./in.²)*	%	*Kg./cm.²*	*(Lb./in.²)*	%
Normal	206	(3075)	770	224	(3282)	730	231	(3278)	667	206	(2930)	650
0.50	201	(2885)	765	249	(3535)	706	220	(3120)	636	250	(3550)	653
1.00	209	(2970)	718	250	(3547)	686	249	(3540)	636	243	(3460)	580
2.50	197	(2800)	751	199	(2820)	686	236	(3355)	673	240	(3410)	646
6.00	158	(2250)	686	203	(2885)	630	215	(3055)	640	208	(2950)	636

Table II. Effect of Sodium Carbonate in Bomb Aging Tests (Series I)

Sodium Carbonate	Before Aging		Elongation	After Aging 24 Hours		Elongation	After Aging 48 Hours		Elongation	After Aging 72 Hours		Elongation
%	*Kg./cm.²*	*(Lb./in.²)*	%	*Kg./cm.²*	*(Lb./in.²)*	%	*Kg./cm.²*	*(Lb./in.²)*	%	*Kg./cm.²*	*(Lb./in.²)*	%
0.03	205	(2910)	770	254	(3730)	740	254	(3610)	683	278	(3955)	683
0.10	205	(2910)	750	257	(3650)	736	268	(3810)	693	270	(3835)	683
0.60	221	(3143)	755	244	(3475)	743	265	(3760)	686	275	(3900)	683
2.00	210	(2980)	778	252	(3580)	713	262	(3715)	680	267	(3790)	653

used in this work to determine the optimum point of each. The hand-tear test was not applied. Curing times sufficient to bring the stock to the point just below the optimum were chosen.

The aging tests were grouped into two series—namely, the sulfate series and the carbonate series.

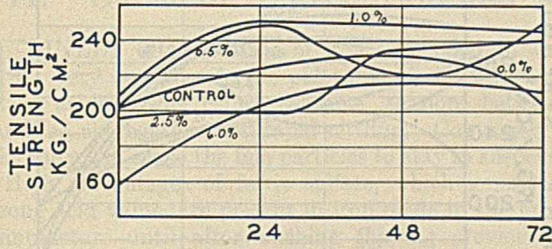


Figure 1. Effect of Increasing Percentages of Ferric Sulfate (Series I)

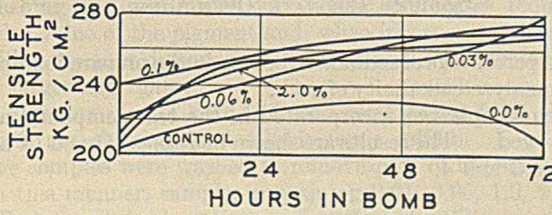


Figure 2. Effect of Increasing Percentages of Sodium Carbonate (Series I)

The control samples were run through the laboratory at the same time as the prepared samples so that all associated test batches were subjected to the same conditions.

A standard red oxide of iron of the following analysis was chosen for the experiments:

	%		%
Oxide of iron	99.15	Manganese	0.0227
Silicon dioxide	0.29	Calcium oxide	0.146
Alumina	0.10	Magnesium oxide	0.02
Total soluble sulfates[a]	0.13	Water	0.28
Copper	0.0042		

[a] Includes salts of magnesium and calcium from wash water.

Series I

The following standard blanc-fixé red oxide of iron tube compound was chosen for the first series of experiments:

	Grams		*Grams*
Pale crepe	66.00	Stearic acid	0.50
Zinc oxide	3.50	Sulfur	1.625
Lithopone	3.00	Captax	0.75
Blanc fixé	24.00	Oxide of iron	2.00

Cure, 8 minutes: 4.2 kg. per sq. cm. (60 lb. per sq. in.).

The use of Captax as an accelerator might be criticized because of its good aging characteristics which might offset any slight deteriorating effect of the ferric sulfate present in the oxide of iron. This compound represents plant practices and was chosen for this reason.

Bomb aging tests were run on the above compound at 60° C. and 21.1 kg. per square centimeter (300 pounds per square inch). The results are shown in Table I and Figure 1.

Four samples of oxide of iron were treated with solutions of increasing concentrations of ferric sulfate, after which they were dried, repulverized, and compounded into the above tube stock. The amount of ferric sulfate present in each oxide, as indicated in Table I, was calculated on the weight of the oxide of iron present in the compound, and includes the amount of ferric sulfate present in the oxide of iron as shown in the analysis above.

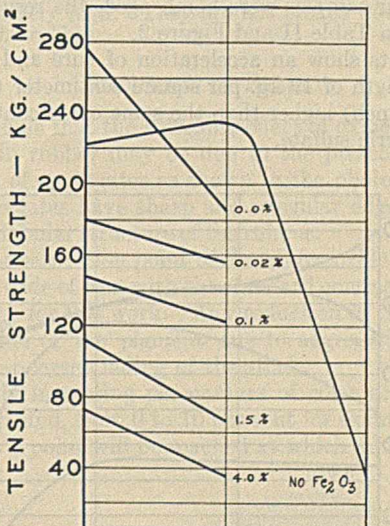


Figure 3. Effect of Increasing Percentages of Ferric Sulfate (Series II)

Sample 4 containing 6 per cent ferric sulfate, calculated on the weight of the oxide of iron, equal to 0.1 per cent of the total weight of the compound or 0.18 per cent of the weight of the rubber present, caused a marked retardation of cure and also a decrease in tensile properties after 72 hours of bomb aging.

The same oxide of iron was treated with solutions of sodium carbonate of varying concentrations, after which they were washed, dried, repulverized, and incorporated in the tube compound. In this manner the soluble ferric sulfate was

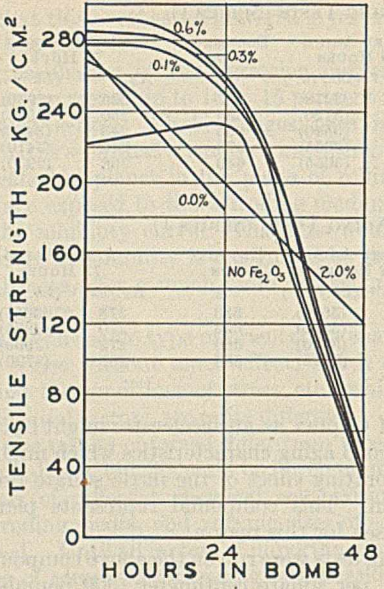


FIGURE 4. EFFECT OF INCREASING PERCENTAGES OF SODIUM CARBONATE (SERIES II)

converted to insoluble ferric carbonate. The percentage of sodium carbonate in the prepared samples is the analyzed alkalinity of each. Excess sodium carbonate is unquestionably responsible for some of the accelerated cure shown in the data. High percentages of sodium carbonate were used in samples 3 and 4 to determine the effect of a large excess of this material.

These four samples were bomb aged, the results of which are shown in Table II and Figure 2.

The results show an acceleration of cure and an average tensile strength of 19 kg. per square centimeter (270 pounds per square inch) higher than the same oxide containing only traces of ferric sulfate.

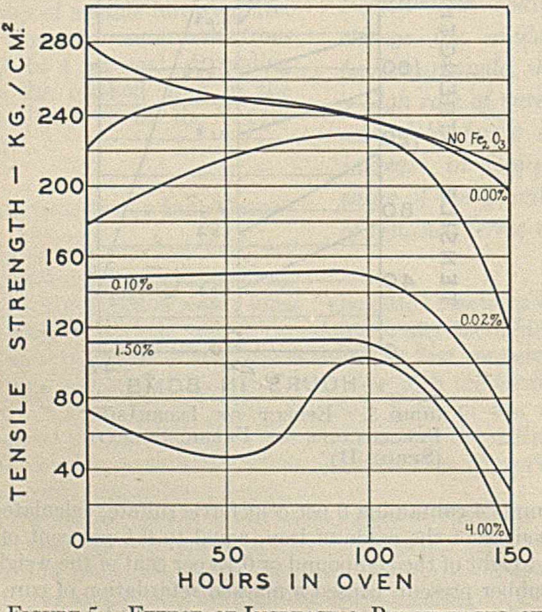


FIGURE 5. EFFECT OF INCREASING PERCENTAGES OF FERRIC SULFATE (OVEN AGING)

The oxide treated with sodium carbonate moved towards the stress axis of the stress-strain curve as indicated by the comparative elongation figures in Tables I and II.

SERIES II

A second series of tests was run, using a standard D. P. G. test compound having poor aging characteristics to exaggerate the deteriorating properties of ferric sulfate:

	Grams
Rubber	100.00
Zinc oxide	5.00
Sulfur	4.00
D. P. G.	0.75
Oxide of iron	25.00

Cure, 60 minutes: 2.7 kg. per sq. cm. (38 lb. per sq. in.).

This compound was first bomb aged, leaving out all oxide of iron. No attempt was made to substitute another filler for the oxide.

Four samples of oxide were treated with ferric sulfate and four with sodium carbonate as in series I. The amount of ferric sulfate present in each oxide sample as indicated in Table III was calculated on the weight of the oxide of iron present in the compound and includes the amount of ferric sulfate present in the oxide of iron as shown in the analysis above.

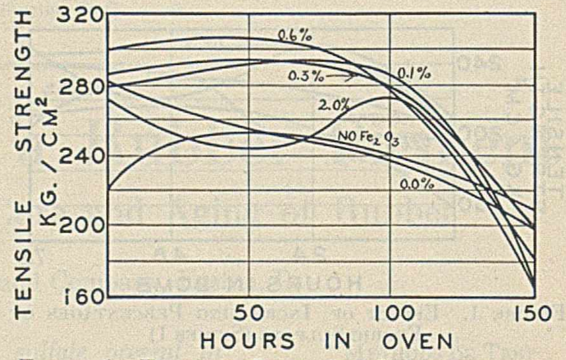


FIGURE 6. EFFECT OF INCREASING PERCENTAGES OF SODIUM CARBONATE (OVEN AGING)

The percentage of sodium carbonate in the prepared samples is the analyzed alkalinity of each.

Each sample was incorporated in the test compound and bomb aged. The results are shown in Tables III and IV and Figures 3 and 4.

TABLE III. EFFECT OF FERRIC SULFATES IN BOMB AGING TESTS (SERIES II)

FERRIC SULFATE	BEFORE AGING		ELONGATION	AFTER AGING 24 HOURS		ELONGATION	AFTER AGING 48 HOURS		ELONGATION
%	*Kg./cm.²*	*(Lb./in.²)*	%	*Kg./cm.²*	*(Lb./in.²)*	%	*Kg./cm.²*	*(Lb./in.²)*	%
No ferric oxide	322	(3154)	755	235	(3340)	765	33	(430)	450
Ferric oxide compound	278	(3995)	720	185	(2635)	700	..	...	...
0.02	179	(2535)	665	156	(2213)	660	..	...	...
0.10	148	(2100)	675	122	(1735)	665	..	...	...
1.50	112	(1590)	700	67	(950)	615	..	...	...
4.00	73	(1035)	715	36	(510)	670	..	...	...

TABLE IV. EFFECT OF SODIUM CARBONATE IN BOMB AGING TESTS (SERIES II)

SODIUM CARBONATE	BEFORE AGING		ELONGATION	AFTER AGING 24 HOURS		ELONGATION	AFTER AGING 48 HOURS		ELONGATION
%	*Kg./cm.²*	*(Lb./in.²)*	%	*Kg./cm.²*	*(Lb./in.²)*	%	*Kg./cm.²*	*(Lb./in.²)*	%
0.03	285	(4055)	712	256	(3630)	705	32	(430)	295
0.10	278	(3950)	705	250	(3555)	695	50	(720)	395
0.60	290	(4255)	697	262	(3720)	675	36	(510)	280
2.00	271	(3850)	615	200	(2850)	585	121	(1720)	490

The results show marked retardation of cure and accelerated aging with increasing percentages of ferric sulfate. The oxide of iron treated with sodium carbonate is similar in age resistance to the stock containing no oxide of iron, and the acceleration of cure was very apparent after 72 hours in the bomb.

The same tests were repeated in the Geer oven at 70° C. for 50, 100, and 150 hours. The results are shown in Tables V and VI, and closely parallel the bomb tests.

Table V. Effect of Ferric Sulfate in Oven Aging Tests

Ferric Sulfate	Before Aging		Elongation	After Aging 50 Hours		Elongation	After Aging 100 Hours		Elongation	After Aging 150 Hours		Elongation
%	*Kg./cm.*²	(*Lb./in.*²)	%	*Kg./cm.*²	(*Lb./in.*²)	%	*Kg./cm.*²	(*Lb./in.*²)	%	*Kg./cm.*²	(*Lb./in.*²)	%
No ferric oxide	221	(3145)	755	254	(3615)	715	240	(3540)	675	210	(2980)	625
Ferric oxide compound	280	(3995)	720	256	(3640)	730	238	(3770)	740	198	(2810)	710
0.02	178	(2535)	665	214	(3045)	685	229	(3230)	670	121	(1715)	620
0.10	148	(2100)	675	151	(2145)	665	150	(2140)	640	69	(980)	565
1.50	112	(1590)	700	113	(1600)	685	112	(1590)	660	27	(386)	520
4.00	73	(1035)	715	45	(640)	540	105	(1500)	570	2.6	(37)	385

Table VI. Effect of Sodium Carbonate in Oven Aging Tests

Sodium Carbonate	Before Aging		Elongation	After Aging 50 Hours		Elongation	After Aging 100 Hours		Elongation	After Aging 150 Hours		Elongation
%	*Kg./cm.*²	(*Lb./in.*²)	%	*Kg./cm.*²	(*Lb./in.*²)	%	*Kg./cm.*²	(*Lb./in.*²)	%	*Kg./cm.*²	(*Lb./in.*²)	%
0.03	286	(4055)	712	294	(4040)	735	278	(3950)	630	198	(2810)	660
0.10	378	(3950)	705	291	(4125)	697	286	(4050)	675	166	(2360)	610
0.60	300	(4255)	697	301	(4280)	680	276	(3925)	640	165	(2350)	575
2.00	271	(3850)	615	242	(3440)	620	273	(3880)	680	183	(2600)	530

◆ ◆ ◆ ◆ ◆

II. Cause of Aggregation and Poor Dispersion of Oxide of Iron in Rubber

FINELY divided oxide of iron suspended in water is very sensitive to the pH value of the water. Slight acidity will cause cohesive tension between the particles, aggregation, and rapid settling. Conversely, slight alkalinity will cause the fine particles to stay in suspension.

High percentages of ferric sulfate, which ionizes with a strong acid value, are present in iron oxide in the process of manufacture until after washing (having previously gone through the processes of grinding and elutriation).

Experimental Procedure

Oxide of iron not thoroughly washed will aggregate in the washing and settling tanks. These aggregates reduce the color value of the pigment and, when incorporated in rubber, will cause poor dispersion and act as nuclei for the formation of larger aggregates.

Five samples of oxide of iron were taken from process. Each sample contained soluble ferric sulfate. Four of the five samples were washed to remove part of the soluble salt. In this manner, samples containing 0.01, 0.05, 1.0, 2.5, and 6.0 per cent ferric sulfate were retained. They were dried and pulverized, and incorporated into the blanc-fixé tube compounds given in Part I. Microsections were taken from each stock by the Allen method (*1*) and examined microscopically. The results of the investigation are shown by the photomicrographs in Figure 1.

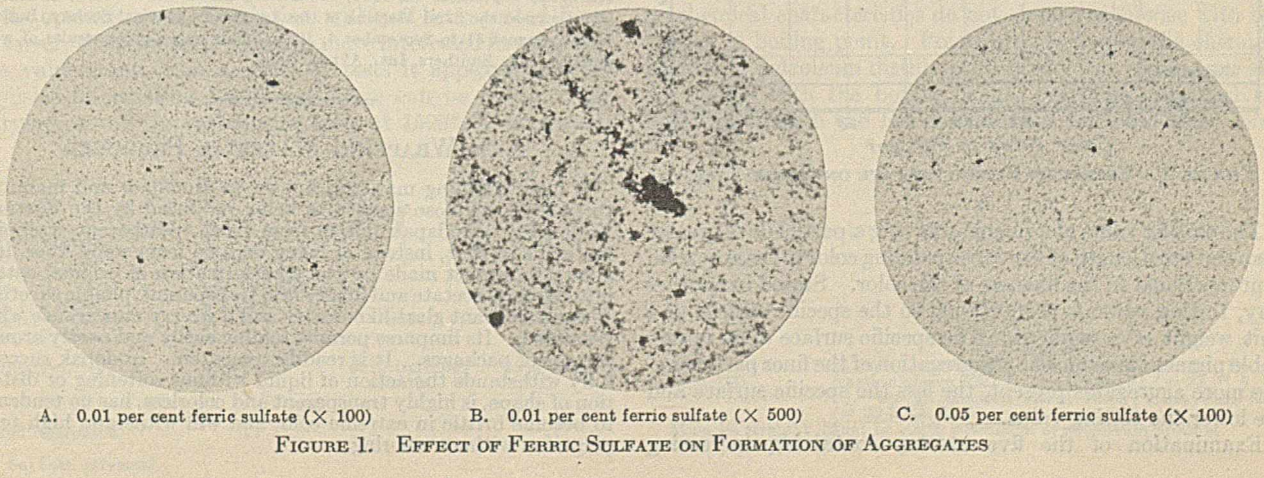
A shows oxide of iron containing 0.01 per cent ferric sulfate. The frequency of aggregates is high, but their relative size is small. B is the same as A at 500 diameters. This gives a clear picture of the character of the aggregates present. C, D, E, and F show the effect of increasing percentages of ferric sulfate. The number of aggregates in F is more than twice as great as in A; the aggregates in F are much larger than those in A. This is clearly shown by comparing B and G. The sharp definition of the edges of the aggregates, particularly those in G, indicate that they act as individual particles and that the cohesive tension between the small particles making up the aggregate is very high. They are not broken down during the milling of the rubber.

Discussion of Results

It is possible that the softening effect of oxide of iron when milling it in rubber may be due to the presence of a large percentage of aggregates as shown in the photomicrographs. These aggregates have sharp and irregular edges which tear apart the globular structure of the rubber.

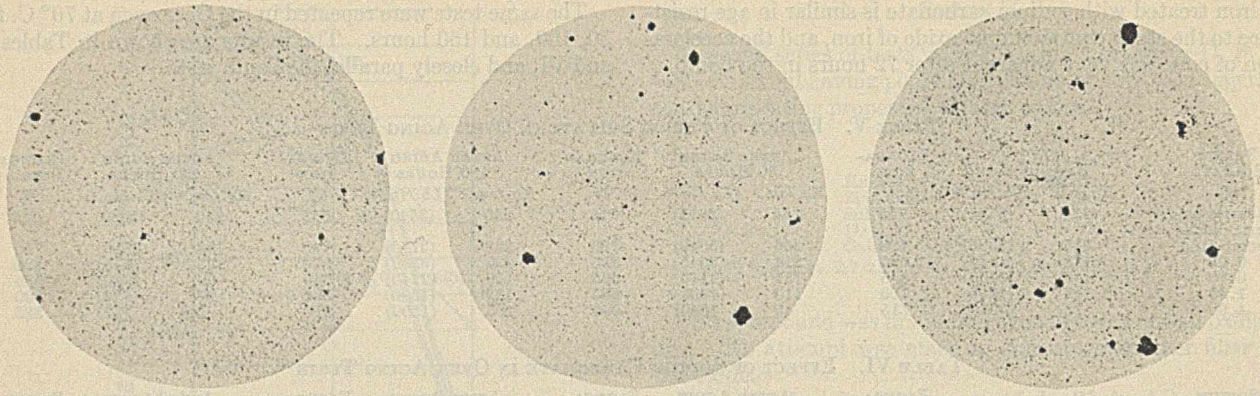
The color-saturation point of the above oxide is reached at 2 per cent oxide of iron with the standard commercial grade of oxide chosen for this work. Any reduction in the coloring or tinting value of the pigment due to aggregation would be shown by apparent fading of the stock.

If slightly increasing percentages of color are added to a given compound, from 0 to 10 per cent for example, it will be found that a point will be reached at which addition of more

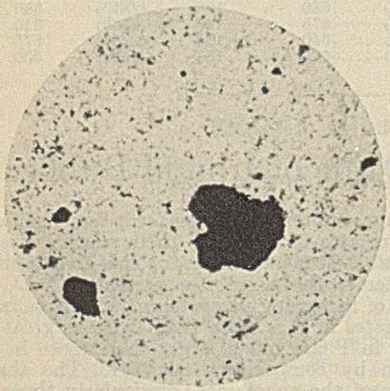


A. 0.01 per cent ferric sulfate (× 100) B. 0.01 per cent ferric sulfate (× 500) C. 0.05 per cent ferric sulfate (× 100)

Figure 1. Effect of Ferric Sulfate on Formation of Aggregates



D. 1.0 per cent ferric sulfate (× 100) E. 2.5 per cent ferric sulfate (× 100) F. 6.0 per cent ferric sulfate (× 100)



G. 6.0 per cent ferric sulfate (× 500)

FIGURE 1. EFFECT OF FERRIC SULFATE ON FORMATION OF AGGREGATES (*Concluded*)

color will not improve the overtone and brilliance of the rubber stock. This point is conveniently called the saturation point. It may be at 2, 3, or 8 per cent oxide of iron, depending on the hiding power of the other compounding pigments, on the color of the rubber, or reclaim, or the tinting value of the oxide of iron itself.

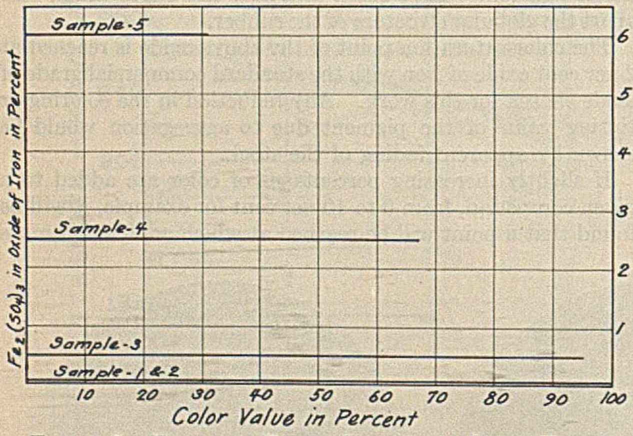


FIGURE 2. EFFECT OF FERRIC SULFATE ON COLOR VALUE

The tinting value of a pigment having a particle size greater than the wave length of the corresponding color in the spectrum is proportional to the fineness of the color. Stated in another way, tinting value is proportional to the specific surface of a unit weight of a pigment. The specific surface of an impalpable pigment is reduced by aggregation of the finer particles—the more aggregates present, the less the specific surface and the lower the tinting value.

Examination of the five stocks, containing increasing amounts of ferric sulfate, for color showed the color to fade in proportion to the amount of ferric sulfate present in the oxide. Sample 5 faded to such an entent that the stock was only a faint pink. The results are shown graphically in Figure 2.

SUMMARY

1. Traces of ferric sulfate in oxide of iron will accelerate aging of rubber.
2. Traces of ferric sulfate in oxide of iron will cut down the rate of cure of rubber.
3. The Bierer-Davis bomb aging tests and the Geer oven tests lead to the same conclusions, although the stocks perform differently in each case.
4. By changing the ferric sulfate to ferrous carbonate with sodium carbonate in solution and washing out the residual sodium sulfate, the ferric sulfate is neutralized to an inactive salt.
5. Iron oxide aggregated by ferric sulfate will not break down on milling in rubber.
6. Increased aggregation reduces the specific surface and the coloring or tinting value of the pigment.

LITERATURE CITED

(1) Allen, R. P., IND. ENG. CHEM., Anal. Ed., 2, 311 (1930).

RECEIVED September 10, 1931. Presented before the Division of Rubber Chemistry at the 82nd Meeting of the American Chemical Society, Buffalo, N. Y., August 31 to September 4, 1931. This paper gives results of work done at V. L. Smithers, Inc., Akron, Ohio.

NEW WRAPPING MATERIAL PRODUCED

A new wrapping material, known as Kodapak and manufactured from cellulose acetate, is being produced by the Eastman Kodak Co. Kodapak differs from most transparent wrapping materials in that, instead of being derived from wood fiber, it is a cotton product made by the transformation of original cotton into cellulose acetate and finally into transparent, pliable sheeting. It has a brilliant glass-like clarity and a silvery appearance when crumpled. Its limpness permits folding easily and neatly around corners of packages. It is readily cemented. Kodapak successfully withstands the action of liquid without softening or distortion of shape, is highly transparent and colorless, has no tendency to become brittle in extreme cold, and will withstand high temperatures without coloring.

Carbureting Values of Gas Oils and a New Method for Their Evaluation

A. Holmes, Standard Oil Co. of New Jersey, Elizabeth, N. J.

The attempts by the gas manufacturers to define the qualities which a gas oil should have in order to be suitable for carbureting water gas have not proved entirely satisfactory so far and, moreover, have resulted in the placing of restrictions which tend to prevent the use of entirely satisfactory oils for this purpose. In lieu of a satisfactory chemical method of analysis, the carbureting values of the oils are, in some instances, determined in a small carbureting apparatus in the laboratory, which is somewhat time-consuming. A simpler method has been proposed for evaluating the carbureting value of a gas oil based upon specific gravity d, average boiling point T, and light dispersion H, of the oil. These factors combined in the form,

$$\frac{T(1-d)d}{H}$$

give values which form a straight line on logarithmic paper when plotted against the gallons of oil required per 1000 cubic feet of finished gas.

PRIOR to the introduction of cracking processes into the petroleum industry, little difficulty was experienced by the gas companies in securing gas oils satisfactory for the carburetion of water gas. Subsequently, however, a definite competition developed between gas companies and refiners operating cracking equipment for the paraffinic gas oils, the stocks best suited for gas-making purposes being in greatest demand for cracking. This demand for oils of the same general quality by the two interests resulted in the formulation of specifications by the gas companies covering the quality of gas oil to be delivered for gas-making purposes. Several such specifications are illustrated in Table I.

It will be noted that the quality of gas oil is in most cases described by gravity and boiling-point range. This does not give the control desired, and in many cases works a hardship on both the gas manufacturers and the petroleum refiner.

The present work was undertaken in order to develop a method which would more definitely reflect the quality in a gas oil desired by gas manufacturers, thus permitting the selection of satisfactory stocks which are barred by present specifications, and would be of mutual benefit to all concerned. As a basis for this work, there existed a laboratory carbureting method developed by the Brooklyn Union Gas Company and recently described in detail by Murphy (*2*) for evaluating gas oils by using them in actual carburetion under laboratory conditions closely paralleling those existing in the plant.

Since the experience obtained with this apparatus in the present work has revealed no additional information in regard to its operation, its description will not be repeated here. However, the petroleum refiner is more interested in comparative values, and from a series of tests it appears that the requisite information for this purpose can be obtained by carrying out all the carbureting tests at 1500° F., correcting the results to the use of a 300 B. t. u. blue gas when the heating value of this gas varies from this figure, and expressing the gasification value of the oil as the number of gallons required per 1000 cubic feet of finished gas having a heating value of 530 B. t. u. per cubic foot.

Gravity and Boiling Range

Of the various qualities which have been cited in specifications of gas oil, the gravity and the boiling range are the most indicative of its chemical composition, and therefore of its carbureting value. Gravity alone has but little value in classifying gas oils, and the reason for attempting to limit to above 28° A. P. I. is not clear, since there are many good oils having a much lower gravity. This is seen from the data given in Table II.

The boiling range, on the other hand, has much greater significance. This must become apparent when it is considered that, in carbureting, it is sought to break the oil down into the maximum total heating value of gaseous products consistent with the gain in the heating value of the finished gas. This implies that the cracking is not extended so far as to produce appreciable amounts of hydrogen but stops with the production of the gaseous hydrocarbons. Obviously, in any one group of hydrocarbons, the larger the molecule, the greater should be the volume of the gaseous products capable of being produced from a given amount of material. Since for any one series of homologous compounds the boiling point increases with the size of the molecule, then the higher the boiling point of an oil, the more desirable it should be for carbureting purposes; that is, of course, provided its chemical characteristics do not change otherwise with the change in boiling point. Practically, however, the chemical natures of petroleum distillates from any one stock generally do change with the boiling point, becoming progressively unsaturated with the heavier fractions. This is even more

Table I. Gas-Oil Specifications

	A	B	C	D	E
Gravity, ° A. P. I. (min.)	32	28	28	..	..
Sulfur, % (max.)	1	1	0.75	0.5	0.1
Color	Dark	..	..	..	..
Viscosity, sec.	40[a]	..	..	..	..
Flash	150 PM closed	..	..	..	..
B. S. and water	1% (max.)	..	..	None	None
Carbon, % (max.)	0.1	0.3	0.25	0.5	..
Pour, ° F. (max.)	..	..	..	..	0 (winter) 40 (summer)
Distillation, ° F.	400–700	95% (min.) at 400–700	95% (min.) at 700	85% (min.) at 400–700	70% (min.) at 400–700. I. b. p. above 400° F. Sp. gr. fraction above 600° F. less than 0.91 (= 24.0° A. P. I.). Sp. gr. fraction above 700° F. less than 0.92 (= 22.3° A. P. I.)
Added restriction	..	..	..	Must be straight run uncracked	Must be 100% petroleum or petroleum product

[a] Saybolt universal.

noticeable with cracked distillates and is exemplified by data in Table III under the heading of 98 per cent acid residue.

The latter fact would naturally lead to the conclusion that a boiling restriction, such as has been prepared, would insure the gas companies of receiving the most satisfactory oils from any given source, irrespective of the considerations mentioned above—namely, that they should boil as high as possible. A series of experiments was carried out to determine the value of a boiling-range limitation as an index of gas-oil quality for carbureting purposes. A few representative data are illustrated in Table III in which a cycle gas oil, obtained from cracking West Texas gas oil, was distilled into four equal fractions, and their several carbureting values determined.

TABLE II. DATA AT CARBURETING TEMPERATURE 1500° F.

RUN	SAMPLE	DESCRIPTION	GRAVITY ° A. P. I.	SP. GR. $\frac{60°}{60°}$	GAL./M FOR 530 B. T. U. GAS
29	PGOB-30	Paraffin gas oil	25.7	0.9001	2.85
30	PGOB-50	Paraffin gas oil	27.5	0.8899	2.84
35	PUB-OO	24 + gas oil	24.2	0.9088	2.94
43	OZL	Medicinal oil	26.6	0.8950	2.75
51	WT-CS-FB	Cracked gas oil	28.1	0.8866	3.27
44	PA-OO-SE	SO_2 extract	27.8	0.8883	3.15

TABLE III. CARBURETING VALUE *vs.* FRACTION OF CRACKED STOCK

		DISTILLATION						98% ACID RESIDUE	GAL./M FOR 530 B. T. U. GAS
RUN	SAMPLE	Gravity	I. b. p.	Temp. at 50%	At 650 ° F.	F. b. p.	Av. b. p.		
		° *A. P. I.*	° *F.*	° *F.*	*Vol. %*	° *F.*	° *F.*	*Vol. %*	
20	WT-CS	25.3	350	561	80	760	571	61	3.33
50	WT-CS-FA	32.7	324	470	100	598	470	74	3.46
51	WT-CS-FB	28.1	473	517	100	578	520	68	3.27
52	WT-CS-FC	23.9	542	588	93	690	592	62	5.10
53	WT-CS-FD	16.0	600	697	8	750	693	52	3.90

It will be noted from these results that none of the fractions would be considered as acceptable if it were required that a satisfactory oil should not exceed 3 gallons per 1000 cubic feet for a 530 B. t. u. gas, although the oils used in runs 50 and 51 are well within the generally accepted limits of gravity and boiling range.

From what has been said, it appears that, instead of relying upon a gravity and boiling-range restriction, a more satisfactory gas oil is apt to be obtained if the range of gravity is restricted, and if only a minimum boiling point is required. This results from the fact that for a given gravity the best oil is the one which has the highest boiling point. This will be seen in Table IV in which oils are compared which have approximately the same gravity but different boiling ranges.

TABLE IV. CARBURETING VALUES *vs.* BOILING RANGE WITH CONSTANT GRAVITY

		DISTILLATION						GAL./M FOR 530 B. T. U. GAS
RUN	SAMPLE	Gravity	I. b. p.	Temp. at 50%	At 650° F.	F. b. p.	Av. b. p.	
		° *A. P. I.*	° *F.*	° *F.*	*Vol. %*	° *F.*	° *F.*	
54	SO-OO	43.0	562	684	0.5	...	685	2.09
34	PA-OO-XFAT	43.2	450	564	91	725	566	2.21
33	PA-OO	41.9	345	543	95	702	542	2.38
40	COL-CS2-XFAT	41.5	370	450	100	565	453	2.45
41	MRL	35.6	575	683	10	757	688	2.24
39	COL-CS1-XFAT	35.8	440	531	92	708	541	2.45
56	BLTO-OO	33.6	390	466	100	596	471	3.27
57	BLTO-CS	33.5	400	460	100	575	462	3.62
32	PGOE-52	32.7	165	655	47.5	746	652	2.45
50	WT-CS-FA	32.7	324	470	100	598	470	3.46
31	PGOE-30	30.8	454	689	10	738	684	2.45
27	COL-CS-2	30.9	380	457	100	541	458	3.69
44	PA-OO-SE	27.8	355	548	91	718	545	3.15
51	WT-CS-FB	28.1	473	517	100	578	520	3.27
29	PGOB-30	25.7	296	720	1.5	777	716	2.85
45	WT-OO-SE	25.7	385	575	69	740	578	3.34
55	V-OO	19.2	592	706	6	738	706	3.16
46	COL-OO-SE	19.0	234	540	76	703	543	4.60

These figures clearly indicate that, for a given gravity, oils having the highest average boiling point are almost invariably the most efficient for water-gas enrichment. A closer inspection of the above data shows that oils with a low gravity and a high boiling range are often better than those having a higher gravity and lower boiling range. In fact, if the average boiling point of an oil is above 700° F., it appears that the gravity of the oil can be around 22° A. P. I. and still show a consumption of not more than 3 gallons for a 530 B. t. u. gas.

Nevertheless, the gravity and average boiling point are of great use to those who are attempting to grade gas oils by means of a few physical tests. For those who have avoided the difficulties involved by the use of physical properties in the evaluation of these oils through actual carbureting tests in the laboratory, the discussion so far may be of only passing interest, but carbureting tests in the laboratory consume considerable time and are otherwise more or less expensive, so that efforts are constantly being made to devise more economical methods for gas-oil evaluation. In attempting to work out a different analytical procedure for determining the carbureting value of a petroleum distillate, it is realized that one is entering an assiduously investigated field. Since the writer has not endeavored to make a survey of the literature on this subject, what follows will undoubtedly be considered incomplete; but from contacts with various workers in the field it appears that the present chemical methods of gas-oil analysis are not entirely satisfactory. The realization of this situation led to an investigation on the part of the authors, which had for its object the development of either a more accurate method of analysis or one having the same accuracy as those now current, yet which would be more rapid and therefore more economical.

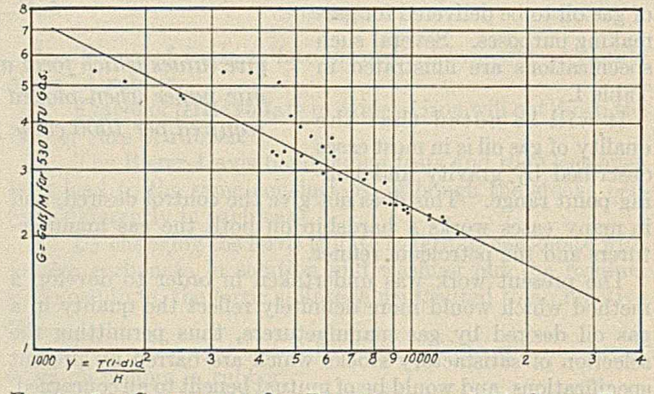


FIGURE 1. GALLONS OF OIL REQUIRED PER 1000 CUBIC FEET OF GAS VS. *y*

Any chemical method of analysis of petroleum oils generally endeavors to estimate the relative amounts of the four main groups of hydrocarbons which are normally present—namely, paraffins, naphthenes, unsaturates or olefins, and aromatics. For carbureting purposes the sulfur, nitrogen, and oxygen compounds are of negligible importance. In order to determine the relative amounts of the four groups of hydrocarbons, the following qualities have been considered at various times: gravity or specific gravity, viscosity, heating value, aniline point, refractive index, extraction with acids, extraction with solvents, boiling point, and molecular weight.

No one of these factors, with the possible exception of the treatment with acids, is sufficient by itself for the separation of the four groups of hydrocarbons; therefore recourse must be had to various combinations of these qualities. The establishment of what may be deemed the most suitable combination generally resolves itself into a more or less tedious task of "cut and try," assisted to a certain extent by the worker's conception of the behavior of the various groups of hydrocarbons under the conditions of carbureting. The present investigation followed the usual procedure to a certain degree.

DISPERSION TOWARDS LIGHT

In reviewing the utility of the various qualities possessed by hydrocarbons, such as those listed above, for determining their carbureting value, it appears that the dispersion towards light is the most useful. The dispersion as used in this work is the difference in the refractive indices of the oil for the C and F lines of the solar spectrum (the red and blue lines of hydrogen) at 100° F., which the standard refractometers are equipped to determine. This property is not only very easily determined, but, by properly combining it with specific gravity, factors can be obtained which are characteristic for the four main groups of hydrocarbons. Table V, based upon values given in the International Critical Tables, will serve to illustrate the nature of these factors.

TABLE V. DISPERSION FACTORS FOR VARIOUS HYDROCARBONS

HYDROCARBON	(T) BOILING POINT	(d) DENSITY $\frac{20^\circ \text{ C.}}{4}$	(H) DISPERSION $N_F - N_C$ AT 20° C.	(COL. A) $\frac{d}{\text{DISPERSION}}$	(COL. B) $\frac{(1 - d)d}{\text{DISPERSION}}$
	° C.				
Paraffins					
2,2,3-Trimethylbutane	81	0.691	0.0068	101.7	31.4
4-Methylheptane	118	0.722	0.0070	103.1	28.7
n-Octane	125	0.712	0.0069	103.0	29.6
4-Ethylheptane	139	0.741	0.0071	104.3	27.0
n-Decane	174	0.747	0.0075	99.7	25.2
Dipropylethylmethane	221	0.761	0.0075	101.5	24.2
Mean of available data	...	...	....	101.6	..
Naphthenes					
Cyclohexane	81	0.779	0.0072	108.0	23.8
Hexahydrotoluene	103	0.764	0.0076	100.3	23.7
o-Dimethylcyclohexane	129	0.779	0.0076	102.3	22.6
Mean of available data	...	...	....	103.3	..
Olefins and acetylenes					
2,4-Hexadiene	82	0.718	0.0167	43.0	12.1
Dipropargyl	85	0.805	0.0122	66.0	12.9
n-Amylacetylene	111	0.738	0.0087	84.8	22.2
n-Hexylacetylene	125	0.756	0.0089	85.0	20.7
α-Decylene	172	0.749	0.0090	83.1	20.9
α-Hexadecylene	274	0.789	0.0084	93.9	19.8
Unsaturated naphthenes					
1,3-Cyclohexadiene	81	0.842	0.0131	64.3	10.2
1,2,3,4-Tetrahydrobenzene	83	0.810	0.0095	85.3	16.2
1,3,3-Dihydro-*p*-xylene	136	0.830	0.0116	71.5	12.2
1,2,3,4-Tetrahydronaphthalene	207	0.971	0.0169	57.5	1.7
Aromatics					
Benzene	80	0.878	0.0167	52.5	6.4
m-Xylene	139	0.865	0.0158	54.7	7.4
Pseudocumene	170	0.870	0.0158	55.0	7.2
Hydrindene	177	0.965	0.0168	57.5	2.0
Hemimellitene	177	0.895	0.0157	57.0	6.0
1,2,3,4-Tetramethylbenzene	204	0.901	0.0157	57.4	5.7
α-Methylanthracene	200	1.101	0.0541	20.4	−2.1
Naphthalene	218	1.145	0.0287	39.9	−5.8
Dibenzyl	284	0.984	0.0187	52.6	0.8
Acenaphthene	278	1.024	0.0293	35.0	−0.8

A detailed discussion of the various deductions which have been made by the use of the above-mentioned data is beyond the scope of this paper, but it is felt that an inspection of these figures will justify the conclusion that they are sufficiently significant to form the basis for evaluating gas oils. Since the carbureting efficiency of an oil should increase with its boiling point, the average boiling point has been combined with the expression under heading column B to give the relation which is a function of the carbureting value. This takes the form,

$$y = \frac{T\,(1 - d)\,d}{H}$$

where y = a number which is a function of the number of gallons of oil required per 1000 cu. ft. of finished gas, having a desired B. t. u. (530 in this investigation) per cu. ft. when using a 300 B. t. u. blue gas
d = specific gravity (at 100° F.)
H = light dispersion of oil (at 100° F.)
T = av. boiling point of oil, usually in ° F.

By plotting y vs. gallons of oil required per 1000 cubic feet of finished gas, having 530 B. t. u. per cubic foot, on logarithmic paper, a straight line is obtained, as can be seen in Figure 1. The straight line in this plot can be expressed with sufficient accuracy by

$$G = 238\,y^{-1/2}$$

where G = gallons of oil required per 1000 cubic feet of 530 B. t. u. gas.

It will not be attempted to give the large amount of experimental data collected in order to produce the results represented by this curve. A similar curve will be obtained when producing a finished gas having any other desired B. t. u. than that used in these experiments.

CHEMICAL METHOD

Of the various chemical methods which have been used for the analysis of gas oils for carbureting purposes, that by Mighill (*1*) apparently has attained the most extensive application so far in this country. In order to compare this method with the one which has been proposed in this paper, the analyses of a series of oil by the Mighill method were obtained. The results from the two methods can be seen in Table VI.

From these figures it appears that the proposed method is not only as accurate as the chemical method, but that from the data on oil COL-CS.2 it is more applicable to the poorer stocks. Since the proposed method comprises only three short determinations—namely, the specific gravity, dispersion, and average boiling point, it has an advantage over the chemical method from the standpoint of ease and time required.

CONCLUSION

1. The introduction of the boiling range of 400° to 700° F. into gas-oil specifications imposes unnecessary limitations, since a gas oil having a given gravity improves as the boiling point increases, and there are suitable gas oils available which boil outside of the stated limits.

2. Gas oils cannot be selected universally upon the basis of a gravity and boiling-range requirement.

3. The carbureting value is best determined by means of a laboratory carbureting equipment.

4. In lieu of the actual evaluation of gas oils in a laboratory apparatus, their values can be ascertained either by the Mighill method of chemical analysis or by the new dispersion method which has been developed.

TABLE VI. COMPARISON OF CHEMICAL AND DISPERSION METHODS OF GAS-OIL ANALYSIS

		PROPOSED METHOD				CHEMICAL ANALYSIS (MAGHILL METHOD)					GAL./M FOR 530 B. T. U. GAS				
RUN	SAMPLE	Sp./gr. at 100° F. = d	Dispersion at 100° F. = H	Av. b. p. = T	$y = \frac{T(1-d)\,d}{H}$	Unsaturates	Aromatics	Naphthenes	Paraffins	Available for enrichment	Found	Calcd., $G = 238y^{-1/2}$	Difference	Calcd. from chem. analysis	Difference
				° F.						%					
28	BYY	0.838	0.0084	476	7690	12.0	22.9	19.7	45.4	73.0	2.94	2.71	−0.23	2.86	−0.08
23	COL-OO	0.862	0.0105	585	6630	14.0	18.1	46.2	21.7	65.1	2.85	2.92	+0.07	3.07	+0.22
27	COL-CS.2	0.857	0.0114	458	4930	12.0	33.4	18.6	36.0	68.1	3.69	3.39	−0.30	2.94	−0.75
45	WT-OO-SE	0.886	0.0125	578	4670	23.3	24.5	22.9	29.3	62.6	3.34	3.48	+0.14	3.20	−0.14
16	WT-OO	0.861	0.0080	571	8540	17.3	19.0	30.6	33.1	67.3	2.80	2.57	−0.23	2.98	+0.18
33	PA-OO	0.801	0.0089	542	9710	2.0	7.8	12.6	77.6	90.4	2.38	2.42	+0.04	2.25	−0.13
38	COL-OO-XFAT	0.826	0.0078	590	10870	3.3	0.0	34.8	61.8	85.8	2.28	2.28	0.00	2.37	+0.09

5. The dispersion method evaluates an oil from three quantities—specific gravity d, dispersion H, and average boiling point T. The gasification value of the oil apparently takes the form of

$$G = 238 \left[\frac{T\,(1 - d)d}{H}\right]^{-1/2}$$

G being the gallons of oil required per 1000 cubic feet of a 530 B. t. u. finished gas, d and H being determined at the same temperature (100° F.), and T expressed in ° F.

6. The dispersion method is equally as accurate as the chemical method and has the advantage of being more easily carried out and of requiring considerably less time.

Literature Cited

(1) Mighill, T. A., *Proc. Am. Gas Assocn.*, 1927, 1454.
(2) Murphy, E. J., *Gas Age-Record*, 65, 389 (1930).

Received March 17, 1931. Presented before the Division of Petroleum Chemistry at the 81st Meeting of the American Chemical Society, Indianapolis, Ind., March 30 to April 3, 1931.

Fluorination of Hexachloroethane under Pressure

H. S. Booth, W. L. Mong, and P. E. Burchfield

Morley Chemical Laboratory, Western Reserve University, Cleveland, Ohio

Hexachloroethane has been fluorinated under elevated pressures and temperatures by the Swarts reaction, using sublimed SbF_3 with $SbCl_5$ as catalyst; this yields a solid $CFCl_2{\cdot}CCl_3$ boiling at 136.8° C.; a liquid $CFCl_2{\cdot}CFCl_2$, boiling at 91.0° C.; a liquid C_2Cl_4, boiling at 119° C.; a liquid $CF_2Cl{\cdot}CFCl_2$, boiling at 46.5° C.; and relatively smaller amounts of three gases, probably C_2F_6, C_2F_5Cl, and $C_2F_4Cl_2$.

The physical and chemical properties and the solubilities of a number of substances in these new liquid and solid derivatives have been determined.

Moisture in traces seems to catalyze the fluorination, at least at atmospheric pressure.

The substitution of fluorine for the other halogens in organic compounds has been thoroughly studied by Frederic Swarts over a long period of years. He has developed several methods (*9*) for replacement of chlorine by fluorine, of which the method using antimony trifluoride is perhaps the best. In this method an organic halide is heated with sublimed antimony trifluoride in the presence of bromine or antimony pentachloride as a catalyst. He has found it impossible to introduce more than two fluorine atoms by this method on a single carbon atom of an aliphatic chain, except in the case of trichloromethyl benzene ($C_6H_5CCl_3$). As far as can be judged from his writings, he has never tried the antimony trifluoride reaction at pressures greater than atmospheric. It seemed probable that this reaction at higher pressures and higher temperatures would yield compounds containing three fluorine atoms on a single carbon atom of an aliphatic chain.

The simplest and stablest aliphatic-chain compound containing the CCl_3 grouping which might be amenable to fluorination under pressure is hexachloroethane (CCl_3CCl_3). A careful survey of the literature failed to reveal any study of the fluorination of hexachloroethane. Furthermore, hexachloroethane is a by-product of little use, and it was thought that fluorination might convert it into lower-boiling liquids of use as solvents and into inert and noncombustible gases which might have value as anesthetics or refrigerants.

Swarts (*7*) fluorinated tetrachloroethane and obtained $CHCl_2CHF_2$ among other products. This compound was then chlorinated in the presence of $AlCl_3$, yielding CCl_3CF_2Cl. This is the only compound of this series found in the literature, and it has been prepared indirectly and only in very small amounts.

Another potent reason for studying this reaction was the possibility of obtaining C_2F_6, which, up to the time of beginning this study, had not been prepared in a state of purity. This should be a gas of high stability, reasoning from the analogy of CF_4 to CCl_4. Lebeau and Damiens (*5*) and Ruff and Keim (*6*) each found, in the higher-boiling fractions from the preparation of CF_4 by direct fluorination of charcoal, some evidence for believing in the presence of C_2F_6, C_3F_8, etc., but neither has yet satisfactorily isolated and established these compounds. On the other hand, Humiston (*4*) claims to have obtained C_2F_4 by the direct action of fluorine on filtchar at −80° C. Since the experimental work reported in this article was completed, Swarts (*8*) has prepared C_2F_6 by electrolyzing trifluoroacetic acid, the gas being evolved at the anode.

Preliminary Experiments at Atmospheric Pressure

For the sake of comparison this reaction was first studied at atmospheric pressure. In the first experiment moisture was avoided scrupulously, and accordingly 40 grams of hexachloroethane were well mixed with the equivalent of sublimed antimony trifluoride and placed in a flask fitted with an air-reflux condenser which had been thoroughly dried by the passage through it for some time of air dried over P_2O_5. The apparatus was again flamed while dry air was passing through it for half an hour before the antimony pentachloride catalyst was added. After refluxing at 160° C. for several hours with only slight evolution of gas, the temperature suddenly rose accompanied by vigorous evolution of a considerable quantity of silicon tetrafluoride. Feathery crystals of sublimed antimony fluoride were found in the generator, but no evidence of reaction with the hexachloroethane.

The experiment was then repeated without any attempt to dry the apparatus. Forty grams of hexachloroethane were heated alone in the flask until they began to sublime. Antimony trifluoride (68 grams) was then added, and the temperature of the oil bath raised to 210° C. with no evidence of reaction. Antimony pentachloride (2 cc.) was added, and the bath heated to 170–5° C. Reaction took place, and a thin liquid began condensing and refluxing. A small amount of SiF_4 was evolved, probably derived from the glass by action of the hydrofluoric acid formed by hydrolysis of the antimony trifluoride.

Gradually the boiling point of the liquid refluxing dropped from 175° to 117° C. during 15 hours of refluxing. An additional 4 hours of refluxing lowered the boiling point no farther. Addition of more antimony trifluoride and pentachloride generated more product but produced no further lowering of the boiling point.

FRACTIONATION OF THE PRODUCT. The product began distilling rapidly at 91° C., and the distillation was finished at 110° C. The distillate consisted of a slush of coarse white crystals in a colorless liquid, which on fractionation gave as the chief product a liquid boiling at approximately 91° C. which later study showed to be $C_2F_2Cl_4$, with a smaller amount of a crystalline product (C_2FCl_5 and unchanged C_2Cl_6) boiling at a higher temperature.

FLUORINATION UNDER PRESSURE

In the hope that more complete fluorination could be obtained, the reaction was next carried out in a 200-cc. steel bomb at much higher temperatures and pressures. The bomb was heated in a bath of low-melting alloy to a temperature of from 300° to 325° C. On cooling and opening the bomb it was found to be still under pressure, and the gaseous products were lost in this first experiment. The bomb contained a thin limpid liquid of vile odor, and a white solid.

The liquid was first distilled to separate the nonvolatile components, and the distillate fractionated through a Vigreux column and distilling head. Several refractionations finally gave four fractions boiling at 46.5°, 91.0°, 119°, and 136.8° C. at 740.3 mm. pressure, with total immersion of the thermometer stem. The thermometer was checked at these temperatures against a standard thermometer calibrated by the Bureau of Standards. Later experiments showed the need of cooling the receiver with carbon dioxide snow when collecting the first fraction. Fractionation eliminated the bad odor, but the quantities of each compound were too small for further study.

TABLE I. TYPICAL RUN IN LARGE BOMB

TIME	TEMPERATURE	PRESSURE	
	° *C.*	*Lb./sq. in.*	*(Kg./sq. cm.)*
9:20	245	0	
9:50	270	130	9.14
10:10	290	360	25.31
10:30	290	510	35.85
11:00	300	650	45.70
11:30	300	700	49.21
12:30	315	700	49.21
1:30	300	730	51.32
2:30	305	770	54.13
3:30	320	840	59.05
4:30	300	800	56.24

PREPARATION ON LARGER SCALE. A *D* cylinder (*1*) was filled with a mixture of 2.6 kg. of SbF_3, 1.7 kg. of hexachloroethane, and 80 cc. of antimony pentachloride. A 4-foot steel pressure pipe was screwed into the neck of the cylinder and fitted with a pressure gage and a valve. The bomb was then placed in a large metal bath, maintained at approximately 300° C. The observed time, temperatures, and pressures of a typical run are given in Table I. Upon removal of the bomb from the metal bath immediately at the end of the run, it was connected to a smaller cylinder and equalized into it. This cylinder was then replaced by a second, and finally by a third chilled with carbon dioxide snow in order to collect the gases from the reaction.

The gases were then bled off from these cylinders and collected in a gas-fractionating apparatus (*1*) by condensation with liquid air. The liquid contents of the cylinders were then collected, washed by thorough shaking with an equal volume of partly saturated sodium bicarbonate solution several times, and finally with pure water. It was found that weak alkali solution had no effect on the organic fluorides but removed some antimony compounds which had distilled out of the bomb with the fluorides. Little or no water was retained dissolved in the chlorofluorides. The washed product had only a faint camphor-like odor. This process was repeated until about 5 liters of the product were obtained.

FRACTIONATION ON LARGER SCALE. After some experimentation a very successful fractionating tower was devised. A 5-liter round-bottom Pyrex flask was surmounted by a glass tube, 100 cm. tall and 2 cm. in diameter, packed with iron jack chain. Above this was placed a 60-cm. Vigreux column. The side tube of the latter led down into a water-jacketed condenser which emptied into receiving bottles packed in carbon dioxide snow.

The distillation was carried on very slowly in order that a sharp cut could be made between fractions. The yield of the various fractions from fractionating about 2.5 kg. in one run is shown in Table II.

TABLE II. YIELD FROM ONE FRACTIONATION OF LIQUIDS

MAIN COMPONENT	BOILING POINTS	PRODUCT	
	° *C.*	*Grams*	*%*
$C_2Cl_3F_3$	46.5–47	411	17.1
	47 –90	46	1.9
	90 –90.5	40	1.7
$C_2Cl_4F_2$	90.5–91	1373	57.2
	91 –118.5	10	0.4
C_2Cl_4	118.5–120.4	202	8.4
	120 –135	55	2.3
	135 –136.8	36	1.5
C_2Cl_5F	136.8–140	157	6.5
	140 –149	7	0.3
C_2Cl_6	Residue	65	2.7
Total	....	2402	100.0

The various fractions were identified by determination of their molecular weights by the Victor Meyer apparatus with a closed system and an accurate gas buret, and by determination of their chlorine content.

Before determination the various fractions were purified by distillation to constant boiling point (0.005° C.), using a Beckman thermometer. It was found that for the fractions boiling at 46.5 + °, 119 + °, and 136 + ° C., three such fractionations sufficed, but the fraction boiling at 91° C. proved more difficult to purify. It was finally purified by numerous distillations alternated by crystallizations.

ANALYSIS

In the procedure for the determination of chlorine in organic chlorides described by Chablay (*2*), sodium is added to a solution of the organic halide in liquid ammonia, the system being cooled in a mixture of acetone and carbon dioxide snow. The ammonia is allowed to evaporate, the excess free sodium destroyed with ethyl alcohol, and the amount of chloride determined by one of several standard methods. In certain cases, however, the decomposition of the organic compound gives rise to the formation of cyanides, as was pointed out by Dains and Brewster (*3*). The compounds which were of interest for the purposes of the present experiment were found to be members of the latter class.

Accordingly it was thought possible to oxidize the cyanide to cyanate by destroying the excess of free sodium with an excess of ammonium nitrate, driving off the ammonia, and fusing the mixture of compounds at a comparatively low temperature. The cyanate may react with silver nitrate, but silver cyanate is decomposed by the action of dilute nitric acid with the evolution of carbon dioxide and the formation of silver nitrate and ammonium nitrate.

In all instances in which the above fusion with ammonium nitrate was carried out, low results were obtained as shown in the following values for the determination of the percentage of chlorine in $C_2Cl_3F_3$:

THEORETICAL CHLORINE	FOUND CHLORINE
%	%
56.77	46.29
56.77	47.50
56.77	46.20

Evidently sodium chloride and ammonium nitrate form an equilibrium,

$$NaCl + NH_4NO_3 \rightleftharpoons NaNO_3 + NH_4Cl$$

and the ammonium chloride volatilizes at the low temperature to which the mixture is heated. If the oxidation was omitted from the procedure, a very high figure was obtained for the percentage of chlorine in $C_2Cl_3F_3$, the theoretical value being 56.77 per cent, and the found value 90.00 per cent.

After many modifications were tried, the following procedure yielded satisfactory results. The sample to be analyzed was introduced into a thin-walled, weighed bulblet, drawn out at each end into a small capillary tube, the tubes being sealed before the final weighing. A sample weighing 0.25 to 0.30 gram was taken. The bulblet was crushed under the surface of 25 cc. of ethyl ether contained in a Kjeldahl flask while the flask and contents were cooled in a bath of acetone and carbon dioxide snow (*10*).

Enough liquid ammonia was added to half fill the flask. When the system had reached the temperature of the bath, an excess of bright metallic sodium was introduced. The system was allowed to stand overnight, during which time the ether and ammonia completely evaporated. The excess sodium was carefully neutralized with absolute alcohol, and the contents of the flask then washed into a 300-cc. nickel crucible. After evaporation to dryness, the solid residue was covered with a thin layer of sodium peroxide and the mixture slowly heated to quiet fusion. The fused mass was taken up in water and acidified with nitric acid, and the amount of chloride ion was volumetrically determined by the method of Volhard.

The results for the analysis and molecular-weight determinations are shown in Table III.

TABLE III. ANALYSES AND MOLECULAR WEIGHT DETERMINATIONS

FRACTION	B. P. AT 740.3 MM.	MOLECULAR WEIGHT Observed	MOLECULAR WEIGHT Formula	CHLORINE Found	CHLORINE Theoretical	FORMULA
				%	%	
1. Liquid	46.5	190.6; 191.6	187.4	56.57 56.44	56.77	$C_2F_3Cl_3$
2. Solid (low melting)	91.0	207.3; 206.0	203.8	69.76 69.78	69.58	$C_2F_2Cl_4$
3. Liquid	119.0	173.5; 172.2	165.84	85.36 85.48	85.53	C_2Cl_4
4. Solid	136.8	219.2; 226.0	220.3	80.41 80.58	80.48	C_2FCl_5

The unsaturated nature of the liquid product boiling at 119° C. was evidenced by its slow reaction with bromine yielding a crystalline solid having the physical properties of $C_2Cl_4Br_2$. The C_2Cl_4 was obviously a thermal decomposition product of C_2Cl_6.

PROPERTIES

These fluorochloroethanes are characterized by faint odors, decreasing in intensity from the monofluoropentachloroethane which somewhat resembled camphor, to the almost imperceptible odor of the trifluorotrichloroethane.

SURFACE TENSION. This was determined approximately by the rise in a capillary tube held in its container in a thermostatic bath. The surface tension of $C_2Cl_3F_3$ is approximately 0.2 of that of water, and that of $C_2Cl_4F_2$ is about 0.3 that of water. Accurate data on these constants will be reported later.

SPECIFIC GRAVITY. A pycnometer was filled with the liquid below the temperature of the bath, then placed in the thermostat, and allowed to rise to the temperature of the bath, and the excess liquid due to expansion was removed. It was then dried and weighed, and calibrated with distilled water in the same bath. Results are as follows:

FORMULA	BOILING POINT	SPECIFIC GRAVITY	TEMPERATURE
	° C.		° C.
$C_2F_3Cl_3$	46.5	1.42	25.0
$C_2F_2Cl_4$	91.0	1.64	30.0
C_2FCl_5	136.8	1.74	25.0

VISCOSITY. This was determined in a glass U-tube type of viscometer held in a thermostatic bath. The viscosity was determined by comparison with pure water; the viscosity of the C_2Cl_5F was not taken on account of its high melting point. The results are as follows:

FORMULA	VISCOSITY COEFFICIENT	TEMPERATURE
		° C.
$C_2Cl_3F_3$	0.00502	21.2
$C_2Cl_4F_2$	0.01154	30.0

REFRACTIVE INDEX. This was obtained by means of an Abbé refractometer. The results are as follows:

FORMULA	REFRACTIVE INDEX	TEMPERATURE
		° C.
$C_2Cl_3F_3$	1.3530	23.0
$C_2Cl_2F_4$	1.4264	23.0

MELTING POINTS. The melting points were kindly determined by M. J. Bahnsen of this laboratory by time-temperature cooling (or warming) curves, using a multiple thermoelectric copper-constantan couple, accurately calibrated. Results are as follows:

FORMULA	MELTING POINT	B. P. AT 740.3 MM.	LIQUID RANGE
	° C.	° C.	° C.
$C_2Cl_3F_3$	−37.00	46.5	83.5
$C_2Cl_4F_2$	26.5	91.0	64.5
C_2Cl_5F	100.00	136.8	36.8

SOLVENT ACTION. The solubilities of a wide range of compounds and elements were tried in each of the three liquids. The solubility of solids was determined with small quantities of solute and solvent under the microscope at room temperatures only. The rate of solution and the amount of residue left after evaporation of the solution on the slide gave an excellent qualitative idea of the solubility. The solubility of liquids was determined in test tubes as usual.

TABLE IV. SOLVENT ACTION

SOLUTE	$C_2Cl_3F_3$	$C_2Cl_4F_2$
INORGANIC COMPOUNDS		
Ammonium nitrate	Insol.	Insol.
Ammonium fluosilicate	Insol.	Insol.
Ammonium thiocyanate	Insol.	Insol.
Asbestos	Insol.	Insol.
Barium dioxide	Insol.	Insol.
Boric acid	Insol.	Insol.
Cadmium iodide	Insol.	Insol.
Chromium oxalate	Insol.	Insol.
Chromium chloride (violet)	Insol.	Insol.
Iodine	Insol.	Slightly sol.
Potassium antimonyl tartrate	Slightly sol.	Insol.
Potassium chromate	Insol.	Insol.
Potassium permanganate	Insol.	Insol.
Silver nitrate	Insol.	Insol.
Sodium carbonate	Insol.	Insol.
Water	Insol.	Insol.
ORGANIC ACIDS AND ACID ANHYDRIDES		
Anthranilic acid	Very slightly sol.	Insol.
Benzoic acid	Moderately sol.	Very sol.
Malic acid	Very slightly sol.	Insol.
Malonic acid	Insol.	Insol.
Mandelic acid	Insol.	Insol.
Monochloroacetic acid	Insol.	Insol.
Phthalic anhydride	Moderately sol.	Moderately sol.
Salicylic acid	Very slightly sol.	Moderately sol.
Stearic acid	Moderately sol.	Slightly sol.
Succinic acid	Very slightly sol.	Very slightly sol.
Tartaric acid	Very slightly sol.	Very slightly sol.

TABLE IV. SOLVENT ACTION (*concluded*)

SOLUTE	$C_2Cl_3F_3$	$C_2Cl_4F_2$
RESINS, GUMS, FATS, AND OILS, ETC		
Amberol F7 light	Slightly sol.	Slightly sol.
Bakelite XR821	Insol.	Insol.
Damar	Moderately sol.	Very sol.
Ester gum	Moderately sol.	Insol.
Glyptol 1102	Insol.	Insol.
Shellac	Insol.	Insol.
Agar	Insol.	Insol.
Gelatin	Very slightly sol.	Very slightly sol.
Gum arabic	Insol.	Insol.
Gum mastic	Slightly sol.	Insol.
Casein	Insol.	Insol.
Egg albumen	Insol.	Insol.
Cocoa butter	Very sol.	Soluble
Castor oil	Very sol.	Miscible
Cottonseed	Very sol.	Miscible
Anisol	Miscible	Miscible
Citral	Miscible	Miscible
Clove oil	Miscible	Miscible
ALIPHATIC SOLUTES		
n-Hexane	Miscible	Miscible
n-Heptane	Miscible	Miscible
Kerosene	Miscible	Miscible
Carbon tetrachloride	Miscible	Miscible
Chloroform	Miscible	Miscible
Dichloromethane	Miscible	Miscible
Hexachloroethane	Sol.	Sol.
Bromoform	Miscible	Miscible
Iodoform	Slightly sol.	Slightly sol.
Ethyl bromide	Moderately sol.	Very sol.
Methylene iodide	Insol.	Insol.
Ether	Miscible	Miscible
Ethyl alcohol	Miscible	Miscible
Methanol	Miscible	Miscible
Ethylene glycol monobutyl ether	Miscible	Miscible
Glycerol	Insol.	Insol.
Acetone	Miscible	Miscible
Cane sugar	Insol.	Very slightly sol.
Cellulose acetate	Insol.	Insol.
Nitrocellulose (1/2 sec.)	Insol.	Insol.
Urea	Slightly sol.	Slightly sol.
Thiourea	Insol.	Insol.
Acetamide	Very slightly sol.	Very slightly sol.
Theobromine	Very sol.	Slightly sol.
Sulfonal	Slightly sol.	Moderately sol.
Trional	Slightly sol.	Very sol.
Dimethylglyoxime	Insol.	Insol.
AROMATIC AND RING COMPOUNDS		
Benzene	Miscible	Miscible
Diphenyl	Moderately sol.	Very sol.
Naphthalene	Very sol.	Very sol.
Anthracene	Very slightly sol.	Very slightly sol.
Xylene	Miscible	Miscible
Chlorobenzene	Miscible	Miscible
Iodobenzene	Miscible	Miscible
a-Chloronaphthalene	Miscible	Miscible
a-Bromonaphthalene	Miscible	Miscible
Tribromophenol	Very sol.	Slightly sol.
Nitrobenzene	Miscible	Miscible
Azobenzene	Very sol.	Very sol.
Aniline	Insol.	Miscible
Acetanilide	Moderately sol.	Very slightly sol.
Antipyrine	Very slightly sol.	Slightly sol.
Diphenylamine	Insol.	Very sol.
Quinaldine	Miscible	Miscible
Methylene blue	Insol.	Insol.
Indigo	Very slightly sol.	Insol.
Phenol	Very slightly sol.	Very slightly sol.
Benzyl alcohol	Miscible	Miscible
Resorcinol	Insol.	Insol.
Benzil	Moderately sol.	Moderately sol.
Diphenyl carbinol	Moderately sol.	Very sol.
Thymol	Very sol	Very sol.
Camphor	Very sol.	Very sol.
Benzophenone	Very sol.	Very sol.
Anthraquinone	Insol.	Slightly sol.
Phenolphthalein	Insol.	Insol.
p-Nitrobenzoylacetoacetic ester	Moderately sol.	Very sol.

CHEMICAL PROPERTIES. No chemical action was observed between any of the compounds made and any of the solutes upon which they were tested. Apparently none of these compounds are appreciably hydrolyzed by water at room temperature. They are stable over a period of time, but, when sprayed into a Bunsen flame, they decompose, reacting with the burning hydrocarbon to give hydrogen chloride and hydrogen fluoride. They may be readily decomposed by dropping into a liquid ammonia solution of metallic sodium. The stability of these compounds apparently increases with increase in fluorine content as would be expected.

CONSTITUTION. The structure of these compounds may be deduced from the work of Swarts and from other investigations completed in this laboratory. Swarts (*7*) has found that the introduction of one fluorine atom facilitates the replacement of another chlorine atom by fluorine on the same carbon atom. However, he states that he has never been able to introduce more than two fluorine atoms on a single carbon atom of a chain. It has been shown by other investigators[1] in this laboratory that the reduction of $C_2Cl_3F_3$ by zinc dust in alcohol yields $CFCl:CF_2$; that the reduction of $C_2Cl_4F_2$ in the same way yields $C_2F_2Cl_2$; and that the reduction of C_2Cl_5F similarly yields $CCl_2:CFCl$. This suggests that the structure of the compounds found in this investigation are $CCl_2F\cdot CClF_2$, $CCl_2F\cdot CCl_2F$, and $CCl_3\cdot CCl_2F$. Swarts (*7*) has shown that the isomer $CF_2Cl\cdot CCl_3$ melts at 52° C., while the compound found in this investigation melts at 26.5° and apparently is not Swarts' isomer. On the assumption that Swarts' compound has the formula $CF_2Cl\cdot CCl_3$, the one found here is probably the isomer $CCl_2F\cdot CCl_2F$.

GASEOUS PRODUCTS. The gaseous products were contaminated with hydrofluoric acid, hydrochloric acid, volatile antimony compounds, carbon dioxide, water vapor, etc., and were therefore scrubbed with weak caustic solution, dried over barium oxide and condensed and fractionated (*1*), yielding a fraction boiling at approximately the subliming point of carbon dioxide snow, one boiling between −35° to −40° C., and another fraction boiling at slightly above 0° C. These gases were odorless, noncombustible, and nonsupporters of combustion. Their properties suggest that they should be useful as refrigerants. They were somewhat soluble in water, and considerable gas was lost before this was realized. The yield of gas in the fluorination of hexachloroethane even under pressure is low, and coupled with the loss in fractionation yielded finally only relatively small amounts. Preliminary density determinations indicate that these gases are probably the rest of the series of fluorinated products, C_2F_6, C_2F_5Cl, and $C_2F_4Cl_2$. The gas accumulated from a number of charges in the large-scale preparation are now being purified and studied, and will be reported in detail later.

The physiological studies of these products will be reported in another paper. The physical constants of the compounds described in this paper are being redetermined in this laboratory with great accuracy and will also be reported later.

ACKNOWLEDGMENT

The authors gratefully acknowledge the assistance of the Ohio Chemical and Manufacturing Company in carrying out the fluorination under pressure.

LITERATURE CITED

(1) Booth, H. S., *J. Chem. Education*, 7, 1259 (1930).
(2) Chablay, *Ann. chim.*, [9] 1, 510 (1914).
(3) Dains and Brewster, *J. Am. Chem. Soc.*, 42, 1573 (1920).
(4) Humiston, *J. Phys. Chem.*, 23, 572 (1919).
(5) Lebeau and Damiens, *Compt. rend.*, 183, 1340 (1926); 191, 939 (1930).
(6) Ruff and Keim, *Z. anorg. allgem. Chem.*, 192, 251 (1930).
(7) Swarts, F., *Centralblatt*, 1, 13 (1903).
(8) Swarts, F., *Bull. sci. acad. roy. Belg.*, 17, 27 (1931).
(9) Swarts, F., *Bull. soc. chim.*, [4] 35, 1533 (1924).
(10) Vaughn and Nieuwland, IND. ENG. CHEM., Anal. Ed., 3, 274 (1931).

RECEIVED September 3, 1931. P. E. Burchfield is the holder of one of the Ohio Chemical and Manufacturing Company graduate fellowships in chemistry, 1931–2.

---

[1] Results obtained by Booth, Bixby, McKelvey, and Burchfield to be reported later.

before the close of the experiment, showed no detectable antiscorbutic potency in the dosage fed. The pigs in this group were all dead of scurvy by the thirty-ninth day of the experimental diet. Whereas this is a few days beyond the life period of the control scurvy animals, the tooth histology showed no evidence of prevention.

These results demonstrated first that the fruit itself stored at refrigerator temperature retains its vitamin C content at least for 3 months; second, that the orange juice, unstrained, expressed from these oranges, loses its antiscorbutic potency so rapidly that a test which extends over 4 weeks demonstrates that loss, and that at the end of 3 months the destruction appears to be practically complete; third, that a heavy Crush sirup made from this orange juice, unstrained, by adding sugar and preservative and acidifying with lemon citric acid retains the original vitamin C as satisfactorily as does the fruit itself during refrigerator storage for 3 months; and fourth, that this Crush sirup, when diluted to twelve volumes with carbonated water again loses its antiscorbutic action so rapidly that storage in that condition for 4 to 5 weeks is not feasible.

Since it is in this final diluted form that Orange Crush is dispensed to the public, it is highly important to know the rate of destruction of vitamin C under these conditions. The retailer is required to dilute and bottle Orange Crush weekly. Ten to fourteen days should, therefore, be the maximum lapse of time between dilution and consumption of this product. A final set of experiments was run in which one group of pigs was given 1 cc. of orange juice, equivalent per pig of a new supply of freshly prepared Crush sirup diluted daily. Another group of animals was given the same amount of Crush sirup which had been diluted, bottled, and allowed to stand in the refrigerator 10 days before feeding. A control scurvy group was run parallel to these. By the thirty-fifth day one of the scurvy pigs was dead. The other had lost 135 grams in weight and had swollen tender joints, red gums, and loose yellow teeth. The autopsy findings were those of advanced scurvy. The pigs in the other two groups were either holding their maximum weight or gaining slowly. They were fairly strong and active, and their fur was smooth and well-kept. The autopsy findings were those of mild scurvy. The antiscorbutic potency of this sample of Crush sirup was undoubtedly higher than that of the original lot supplied for the earlier experiments reported above. The important consideration in this experiment, however, was that the 10-day storage period at refrigerator temperature did not produce sufficient deterioration of the antiscorbutic potency to be detected by such biological tests. It must be borne in mind, nevertheless, that in making this dilution there was a minimum of exposure to air and room temperature.

These observations tend to the conclusion that the preservation of antiscorbutic activity in the Crush sirup is due to the high acidity and possibly to the sugar content, and that the loss of potency following dilution is the result of decreased protective action and takes place gradually. It may be that traces of chlorine or other constituents of tap water have slight destructive action. These factors appear to be insignificant, however, for it apparently makes no difference whether the dilution is made with ordinary tap water, carbonated water, or carbonated distilled water. Removel of carbon dioxide from the diluted sirup by suction was of no significance.

Since the orange juice, unstrained, from which the Crush sirup is prepared contains appreciable amounts of pulp and skin as compared with the hand-expressed orange juice, it seemed logical to expect somewhat less vitamin C potency in the Crush sirup than in the freshly expressed juice. This was not the case however; in fact, the difference, if any, was in favor of the Crush sirup. This result raised the question of whether the added citric acid, which is prepared from lemons, does not carry some vitamin C. Samples of citric acid prepared from lemons and also by fermentation were secured and added to a sugar solution so that 20 cc., the daily intake, contained 0.2 gram of acid. This amount was four times the intake of citric acid when 1.7 cc. of Crush sirup were administered. However, in neither case did the citric acid solution have the slightest effect in delaying the onset of acute scurvy. Obviously then, the vitamin C of the Crush sirup is derived entirely from the orange juice, unstrained, and probably is preserved by the addition of citric acid, or in part, perhaps, by the high sugar content. In 3 months there was no apparent loss of this potency unless the Crush sirup was diluted again to a low acidity.

CONCLUSIONS

Experiments conducted to determine whether the commercial orange-juice drink called Orange Crush retains the vitamin C originally present in the fruit have resulted in the following conclusions:

1. The orange juice, unstrained, commercially expressed from freshly gathered oranges was as potent in vitamin C as ordinary hand-expressed juice.
2. When stored either frozen or at refrigerator temperature in this form, it lost that potency so rapidly that the loss was marked during a 4-week test period, and practically complete at the end of 3 months.
3. When this orange juice, unstrained, was diluted to 1.7 times its volume of Crush sirup by the addition of sugar, lemon citric acid, and a small amount of preservative and coloring, it retained the original vitamin C practically undiminished for a period of 3 months.
4. The antiscorbutic potency of the Crush Sirup was not a result of any vitamin having been added with the citric acid. The vitamin of the original juice appeared to be preserved by the high acidity and possibly high sugar content of the sirup. The preservative action of the acid sirup is of academic and commercial interest.
5. When the final beverage, Orange Crush, was prepared commercially from the crush sirup by diluting 12.3 times with carbonated water, the resulting product gradually lost its vitamin C potency.
6. When the same dilution was made in the laboratory with a minimum opportunity for exposure to air and room temperature, and the diluted bottled product was stored in the refrigerator 10 days before feeding, there was no detectable loss of antiscorbutic potency.
7. The results show that if the final dilution of Crush sirup is done in accordance with the precautions stipulated by the company and dispensed within 10 days, the final bottled Orange Crush retains essentially the original vitamin C activity; that is, it contains the vitamin C from 1 cc. of orange juice per 21 cc. of Orange Crush. It appears, therefore, that a maximum interval of 10 to 14 days between dilution and consumption of the finished product assures the presence of antiscorbutic potency in Orange Crush as it is dispensed to the public.

ACKNOWLEDGMENT

The authors wish to express to R. R. Bensley, William Bloom, and I. Shouer, of the department of anatomy, University of Chicago, appreciation for their generous assistance in preparing and interpreting the various tooth sections.

RECEIVED October 19, 1931. The expense of this investigation was in part borne by the Orange Crush Company through the courtesy of W. D. Bost.

Comparative Study of Juices from Frozen Fruits

T. A. Pickett, Georgia Experiment Station, Experiment, Ga.

DURING the last few years there has been a great deal of controversy concerning the optimum temperatures at which to freeze and store foodstuffs. Some data have already been obtained on fruits, using organoleptic tests. These tests, however, are subject to great individual differences, and it is desirable to have data not influenced by these variations.

The fruits used in this work were blackberries, cherries, dewberries, peaches, pears, plums, raspberries, and strawberries. One principal variety of each fruit was used, except for peaches where several varieties were used. Altogether, eight different fruits and twelve varieties of these fruits were used.

After the fruit was picked, it was sorted very carefully and as quickly as possible put into quart paper-board containers. The peaches were stored both whole and cut into slices. The other fruits were stored whole. Nothing else was added to any of the containers.

Method of Freezing and Testing

One sample of each fruit was tested immediately, and the other samples were divided into two groups. Some samples were put into a room at +10° F. (−12.2° C.) and thus were slow-frozen; the others were subjected to contact with either carbon dioxide snow or small fragments of carbon dioxide ice. These last samples were considered to be quick-frozen at approximately −100° F. (−73.3° C.). After they had been in contact with the solid carbon dioxide for 24 hours, one sample was tested and the others were placed at +10° F. (−12.2° C.) until they were examined.

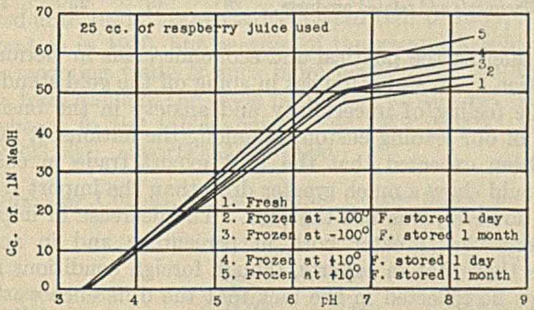


Figure 1. Titration Curves for Raspberry Juice

The fruits were taken out of the refrigerator room at intervals, and the juices expressed by the use of a hydraulic press. A pressure of 10,000 pounds per square inch (703 kg. per sq. cm.) was used. The juices were centrifuged to remove any solid materials that might come through the pressing cloths. The freezing-point depression, conductivity, and total solids were determined on some of the juices, and the hydrogen-ion concentration and titratable acidity were run on all of them. Total solids were determined by the Abbé refractometer, using the sugar scale. The hydrogen-ion concentrations and titratable acidities were obtained by using a hydrogen electrode against a saturated potassium chloride–calomel cell. The titratable acidities are tabulated in terms of cubic centimeters of 0.1 *N* sodium hydroxide per 100 cc. of juice. The end point is pH 8.3, approximately the turning point of phenolphthalein.

Effect of Freezing and Storing Period

The total solids and conductivities of the juices do not show very important differences among the samples. Some results (typical of many others) for the freezing-point depressions, hydrogen-ion concentrations, and titratable acidities are shown in Table I.

Table I. Results of Tests on Fruit Juices

Fruit	Temp. Frozen	Length of Storage at 10° F. (−12.2° C.)	Initial pH	0.1 *N* NaOH to Bring 100 cc. of Juice to pH 8.3	Freezing-Point Depression
	° F. (° C.)			*Cc.*	*° C.*
Strawberries	... ...	Fresh	3.50	190	0.65
	+ 10 (−12.2)	1 day	3.36	202	0.77
	+ 10 (−12.2)	1 month	3.35	210	0.84
	+ 10 (−12.2)	4 months	3.35	236	0.85
	−100 (−73.3)	1 day[a]	3.38	182	0.71
	−100 (−73.3)	1 month	3.35	190	0.78
	−100 (−73.3)	4 months	3.35	216	0.80
Red raspberries	... ...	Fresh	3.35	208	1.00
	+ 10 (−12.2)	1 day	3.30	234	1.16
	+ 10 (−12.2)	1 month	3.40	256	1.19
	−100 (−73.3)	1 day[a]	3.40	216	1.12
	−100 (−73.3)	1 month	3.40	226	1.15
Dewberries	... ...	Fresh	3.16	269	..
	+ 10 (−12.2)	1 day	3.15	302	..
	+ 10 (−12.2)	1 month	3.15	326	..
	−100 (−73.3)	1 day[a]	3.23	275	..
	−100 (−73.3)	1 month	3.40	296	..
Plums	... ...	Fresh	3.19	266	..
	+ 10 (−12.2)	1 day	3.16	282	..
	+ 10 (−12.2)	1 month	3.10	300	..
	−100 (−73.3)	1 day[a]	3.05	273	..
	−100 (−73.3)	1 month	3.16	292	..
Cherries	... ...	Fresh	3.35	260	..
	+ 10 (−12.2)	1 week	3.41	268	..
	+ 10 (−12.2)	2 weeks	3.40	276	..
	+ 10 (−12.2)	1 month	3.40	296	..
Mayflower peaches	... ...	Fresh	4.19	78	..
	+ 10 (−12.2)	1 day	4.13	80	..
	+ 10 (−12.2)	2 weeks	4.10	86	..
	+ 10 (−12.2)	1 month	4.00	88	..
	+ 10 (−12.2)	3 months	3.97	92	..
Early Rose peaches	... ...	Fresh	4.28	99	..
	+ 10 (−12.2)	1 day	4.15	108	..
	+ 10 (−12.2)	2 weeks	4.10	112	..
	−100 (−73.3)	1 day[a]	4.10	98	..
	−100 (−73.3)	2 weeks	3.95	100	..
Elberta peaches	... ...	Fresh	3.76	82	..
	+ 10 (−12.2)	1 week	3.95	96	..
	+ 10 (−12.2)	1 month	3.78	96	..
	−100 (−73.3)	1 week	3.80	92	..
	−100 (−73.3)	1 month	3.75	104	..
Blackberries	... ...	Fresh	3.22	230	..
	+ 10 (−12.2)	1 day	3.15	242	..
	+ 10 (−12.2)	1 month	3.20	250	..
	−100 (−73.3)	1 day[a]	3.26	235	..
	−100 (−73.3)	1 month	3.40	244	..

[a] Stored at −100° F. (−73.3° C.).

According to Nelson (*1*) in 1925, the acids of the red raspberry are mixtures of approximately 97 per cent citric acid and 3 per cent malic acid. The titration curves (Figure 1) for the juices from the fresh raspberry, raspberry frozen at +10° F. (−12.2° C.), and raspberry frozen at −100° F. (−73.3° C.) are similar to one another, and also to the curves of citric and malic acids. This indicates that the same type of acid is present in all of the juices, and therefore the gains in titratable acidity appear to be due, probably, to an increase in concentration of those particular acids present in the fresh berry—namely, citric and malic. Similar results were obtained with other fruit juices.

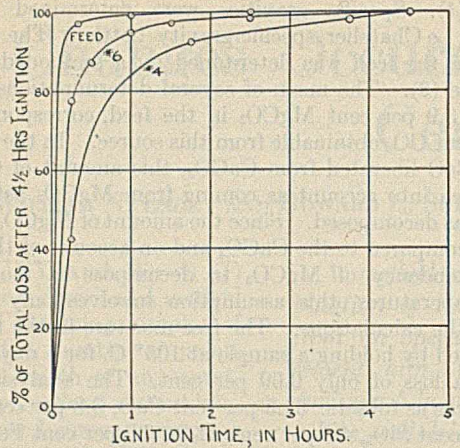


Figure 4. Rate of Loss during Ignition

This smaller discrepancy might be explained by the fact that the nitrogen was produced from liquid air and was not purified from oxygen before use. No great difference was found for the sample from station 8 whether air or nitrogen was used. The higher value for loss on ignition of the feed has been used in Figure 2 and in subsequent calculations.

A series of determinations of loss on ignition was made by the customary method of heating the sample in a platinum crucible over a blast burner, no change in gas supply being made during a run. The object of this series was a study of the rate of weight loss during ignition. The rates for three samples are shown in Figure 4, the total loss at the end of $4^1/_2$ hours of ignition being called in each case 100 per cent to give an easier basis of comparison. It will be seen that the samples vary in the rapidity with which volatile matter is given off. Two of the samples shown had evidently not reached constant weight at the end of $4^1/_2$ hours. Twelve hours of continuous igniting of four samples resulted in greater losses than those found in 4 hours in the furnace tube as shown in Table II. The fairly constant increase in loss during the last 8 hours, irrespective of the variation of magnitude of the total loss from one sample to another, might indicate a gradual volatilization of alkalies. This gradual increase in loss on ignition makes it very difficult to know when to stop the process when highly accurate results are desired.

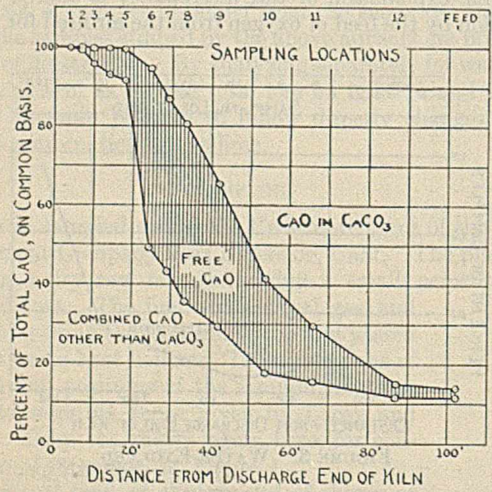


Figure 5. State of Combination of CaO in Kiln Charge at Various Points in the Kiln

Table II. Data on Loss on Ignition

Sample	Loss on Ignition[a] 4 hours in tube	12 hours in crucible
	%	%
12	30.7	31.2
10	23.1	23.5
8	9.4	9.9
6	3.2	4.1

[a] Percentage of original sample.

Figure 3 shows that the combined water was driven out of the charge rapidly. As stated above, only 0.1 per cent water was free moisture, removable by drying at 105° C. The slight increase in water remaining in the samples from stations 7 and 8, although not large enough to be much beyond experimental accuracy, might be attributed to the great tendency of samples from this section of the kiln to absorb moisture. This tendency is illustrated in Table III. The samples cited therein were stored in tightly covered tin cans but were not sealed with paraffin. In a similar set of samples stored for a year, stations adjacent to No. 7 showed water-remaining values of about 9 per cent, while the feed gave only 1.5 per cent.

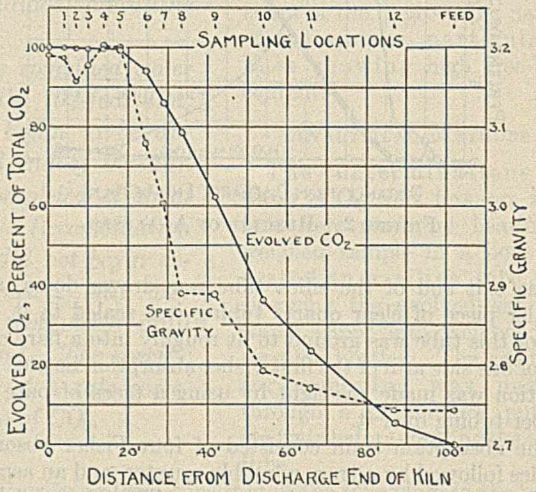


Figure 6. Relation of Increase in Specific Gravity and CO_2 Evolution

Table III. Tendency of Samples to Absorb Moisture

Sample	Loss on Ignition Initial	4 months later	Difference	Free Lime Content
	%	%	%	%
Feed	31.8	31.7	−0.1	0.9
10	23.1	23.4	0.3	11.7
9	15.4	17.2	1.8	19.6
8	9.4	12.0	2.6	26.1
7	6.4	10.3	3.9	26.3
6	3.2	8.2	5.0	28.2
4	0.3	1.7	1.4	4.2
2	0.3	0.4	0.1	0.3
Clinker	0.1	0.6	0.5	0.1

Discussion of Results

Before considering the changes occurring in the charge as it progresses through the kiln, it becomes necessary to bring the analytical results to some common basis for comparison. It has been assumed that the nonvolatile material (i. e., 100 per cent minus the percentage of loss on ignition) of the feed passes through the kiln without loss or gain in weight. This involves the assumption that the material volatilized by igniting the feed in a crucible is the same in amount as that volatilized by a partial ignition in the kiln followed by final ignition in the crucible. This constant amount of nonvolatile material then serves as a "tracer" to assist in the determination of the amounts of the samples taken at different stations which correspond to a given-size sample of original feed. Such calculations have been made on a basis of a sample of 100 pounds of feed, and the amounts of certain constituents present at various stages of the process found. In these calculations the loss on ignition of the feed has been taken as 32.2 per cent, which is the value obtained by ignition in an atmosphere of nitrogen, as described above. The initial free lime plus all the CaO liberated from $CaCO_3$ during the process is less than the total CaO present, the difference representing CaO which was originally in combination with other acidic constituents than CO_2.

Figure 5 shows three fields indicating the state of combination of the CaO in the kiln charge at various points in the kiln. It will be noted that $CaCO_3$ persisted in appreciable quantity to within 20 feet of the discharge end of the kiln. Free lime was not reduced to a satisfactory value until the clinker was within 10 feet of the discharge end. Only small amounts of lime were recombined while the charge was in the upper half of the kiln. The most rapid recombination of lime occurred near the 20-foot point where the last of the CO_2 disappeared from the charge. The last of the lime recombination was a comparatively slow process.

The data presented in Figure 6 show that, although no strict correlation exists, the increase in specific gravity of the charge follows in a general way the evolution of CO_2 from the charge. The decided drop in the specific-gravity curve at stations 3 and 2 might be explained by the presence of β-dicalcium silicate which changed, upon premature removal from the kiln, into the γ form which has about 10 per cent greater volume. There is no direct evidence in favor of this explanation, and it is merely suggested.

Acknowledgment

The authors wish to express their indebtedness to the members of the research department of the Riverside Cement Company of Los Angeles, Calif., who greatly assisted in the taking of samples, and who made the free-lime determinations as well as the analysis of the clinker.

Literature Cited

(1) Lacey and Woods, Ind. Eng. Chem., 21, 1124 (1929).
(2) Meade, R. K., "Portland Cement," pp. 526–9, Chemical Publishing Co., 1926.

Received October 26, 1931.

Displacement of Crude Oil and Benzene from Silica by Aqueous Solutions

F. E. Bartell and F. L. Miller, Chemistry Department, University of Michigan, Ann Arbor, Mich.

The object of this investigation has been to obtain data which would give information concerning the function of "flooding agents" used in the displacement of oil from oil-bearing sands. The results obtained indicate that neither the surface-tension values of the liquids nor the interfacial-tension values of the liquid-liquid system are the dominant factors. Effective displacing agents appear to be those that alter the aqueous solution–silica interface either through a high degree of adsorption or through chemical reaction at the interface.

IN AN earlier paper the authors (*2*) reported some results obtained in a study of the displacement of different crude oils from finely powdered and compressed silica by water. A determination of the percentage of oil which could be recovered from oil-wetted silica was not attempted, but the magnitude of the pressures developed in the displacement of the oils from silica was determined. In the present paper the problem of the displacement of oil by aqueous solutions is considered.

It is well known that water will displace organic liquids and crude petroleum oils from silica. It has been observed, however, that water itself is comparatively ineffective as a displacing agent when used in actual oil-field work. The water, whose displacing ability is originally very effective, soon becomes sluggish in its action, and the rate of displacement of the oil becomes low. This effect may be due in part to the saturation of water with some of the more soluble constituents of the oil or to highly adsorbed constituents of the oil on the silica surface which are not easily removed by the water. Experience has shown that certain aqueous solutions are more effective than pure water in removing the oil from the silica. Such solutions are generally known as flooding agents. The salt solution most commonly referred to in this connection is sodium carbonate, or soda ash. Practically, the use of this salt has apparently not met with success. Uren (*15*) and Beckstrom and Van Tuyl (*8*) have used a number of different salt solutions in their researches and have determined the relative percentages of oil recovered by each. Uren and Fahmy (*16*) have also recently published data showing the effect of different salt solutions upon the recovery of crude oils by displacement. It is the opinion of the above-mentioned workers that only the salts of strong bases and weak acids are effective as flooding agents. Acidic salts or neutral salts are not suitable.

Theories Relating to Function of Flooding Agents

A number of theories have been advanced to explain the behavior of such aqueous solutions, but as yet none of them is generally accepted. It has been suggested that the oil is displaced from the sand because of a differential capillary effect; i. e., since the water has a higher surface tension than the oil, it was thought that the difference in these capillary forces might result in the displacement of the oil. Salts, which when added to water cause an increase in the surface tension of the water, would, then, produce a greater difference between the two surface tensions and would thus effect a greater displacement of the oil from the sand. This explanation is hardly acceptable in view of the fact that many different salts will increase the surface tension of water, and yet only a few of them are efficient as flooding agents. It is also true that the increase in surface tension of the water is slight.

Other investigators have attributed the displacement tendency to a chemical reaction. Nutting (*11–14*) is one who has advanced this idea. He suggested that an attraction exists between the silica particles (SiO_2) and the hydrogen ions of the water, so that a layer of siloxyl (SiOOH) radicals is formed. These radicals would be acidic in character and would have one free bond by means of which they might unite with some other substance. A reaction between the siloxyl radicals and the basic constituents of the oil then would occur, so that over the surface there would be a chemical combination of the oil with silica which is quite stable. If pure water alone were used as a flooding agent, the displacement of oil would not be efficient because of the formation of this compound. If, however, some alkaline salt were added, the oil would be much more completely displaced; the strong base would displace the weaker one from the acidic siloxyl radical, and the oil, being weakly basic, would thus be removed. This would leave on the surface of the silica grains a coating of $MHSiO_3$ (M = Na, K, etc.) instead of the oil compound.

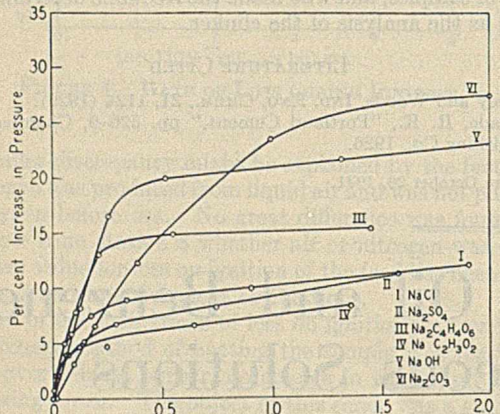


Figure 1. Increase in Pressure, Benzene-Aqueous Solutions

Another theory, which depends upon a physical interpretation, has been advanced to explain the displacement of oil by water and its solutions. It is assumed that the oil removal is accomplished by means of a rearrangement of the interfacial-tension relationships between water, oil, and silica. Certain simple relationships between the interfacial forces will determine the direction of the displacement. Let S_{12} represent the interfacial tension, oil-solid; S_{13} the interfacial tension, water-solid; and S_{23} the interfacial tension, water-oil. Consider that the following relationship holds when

$$S_{12} > S_{13} + S_{23}$$

that is, when S_{12} is greater than the sum of the other two interfacial tensions, the oil-solid (S_{12}) interface will be the one to disappear. This is found to be the case with silica as the solid; the organic liquids and oils are displaced by water. There are no reliable methods for measuring either S_{12} or S_{13}, but there are a number of different methods for determining accurately the value of the interfacial tension, liquid-liquid (S_{23}), and it is known also that it is possible to alter its value. Uren (*15, 16*) noted that the addition of sodium carbonate would lower the interfacial tension of a water-oil system from about 18 dynes per cm. to 6 dynes per cm. or less, as measured by the ring method. While the relationship given above is theoretically sound, it cannot be applied on a quantitative basis, owing to the lack of interfacial-tension data relating to solid-liquid systems.

It is believed by some investigators that the displacement is really the result of the combination of the two factors—chemical combination and interfacial tension. In this case, reaction is considered to occur between the silica and the alkali (sodium hydroxide, potassium hydroxide, etc.) which is added or which is formed by the hydrolysis of strongly basic salts. Uren (*15, 16*) has recently expressed the belief that the reaction between the silica and sodium hydroxide forms a silicate which is soluble, and the factor S_{13} in the equation above consequently becomes zero. It seems impossible to determine the correctness of this view inasmuch as so little is known concerning the true value of the interfacial tension of the solid-liquid system. The above author also believes it possible that a reaction between the base and the oil is the cause of the reduction of the interfacial tension, oil-aqueous solution, so that both of the interfacial tensions, S_{13} and S_{23}, may be considered to have been decreased as a result of chemical reactions. Thus it is believed that salt solutions are effective as flooding agents in proportion to the amount of base they are able to furnish the solution.

In order to obtain further information regarding the displacement of oils from sands, it seemed desirable to carry out an investigation with silica and crude oils, in which would be measured the maximum displacement pressure of oil by different aqueous solutions over a wide range of concentrations and also the interfacial tension values of these same solutions against the oil. In addition, it seemed desirable to use some pure organic liquid (one non-reactive with alkali) in the place of the oil, and to make similar measurements with the aqueous solutions. In this manner it should be possible to observe the similarities or the dissimilarities in the behavior of systems in which a chemical reaction was possible, and one in which no reaction was known to occur. A comparison of results obtained with the crude oil and with the organic liquid should, it seemed, give worthwhile information concerning the displacement of oils from sands.

Materials and Methods Used

In carrying out the measurements indicated above, a crude oil, referred to as crude oil M in a previous paper (*2*), and benzene were the two liquids used. The crude oil appeared to be representative of crude oils in general, and its properties were admirably suited to this type of work. The salts chosen for this investigation were NaCl, Na_2SO_4, $NaC_2H_3O_2$, $Na_2C_4H_4O_6$, Na_2CO_3; and the base, NaOH. These were used in concentrations ranging from about 0.1 to 10 per cent by weight. The silica used in this investigation was air-float Tripoli silica of about 350-mesh particle size which had been purified by hydrochloric acid treatment until it analyzed less than 0.4 per cent impurities.

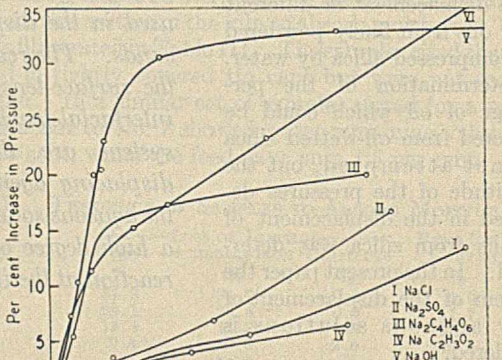


Figure 2. Increase in Pressure, Crude Oil-Aqueous Solutions

The interfacial tensions of the aqueous solutions against benzene and against the crude oil were determined by means of a method developed by the authors which has been described in previous papers (*2, 3*). This method is based upon a modification of the capillary-tube method and is well suited to work with oil which may be dark and not transparent. The measurements were carried out in a thermostat which was maintained at 25° C.

For measuring the displacement of benzene and the oil by the aqueous solutions, the cell designed by Bartell and Osterhof (*5*) was used. This method has been described in a number of recent papers (*1*, *2*, *4*, *5*, *6*, *7*), so that it will be unnecessary to give further details at this time. With the apparatus it is possible to measure the maximum pressure developed when water or an aqueous solution tends to displace another and immiscible liquid from silica. The actual amount of oil or benzene displaced was not measured.

NOTE. The cells were packed by means of a hydraulic press under a gage pressure of 3000 pounds per square inch (210.9 kg. per sq. cm.). Recent work in this laboratory has shown, however, that under such conditions the effective pore size of the membrane may vary somewhat with progressive displacement of liquid. No attempts, therefore, have been made to use the displacement data obtained in this work in calculating the adhesion tension values for these solutions. Since the conditions are probably quite comparable with those found in the actual oil sands, the pressure data are given to show the effect of the different salt solutions upon the displacement of the oil.

TABLE I. DISPLACEMENT OF CRUDE OIL M AND BENZENE BY AQUEOUS SOLUTIONS

CONCENTRATION		BENZENE			CRUDE OIL		
% by wt.	*Equiv./M grams H_2O*	Pressure *Grams/cm.²*	Increase in pressure *%*	S_{23}	Pressure *Grams/cm.²*	Increase in pressure *%*	S_{23}
			$NaCl$				
0.00	0.0000	346.5	0.0	34.65	255.3	0.0	24.54
0.05	0.0085	349.3	0.8	34.71	255.3	0.0	24.93
0.10	0.0171	353.3	2.1	34.75	255.3	0.0	25.07
0.50	0.0859	366.9	5.9	34.91	256.8	0.6	25.49
1.00	0.1728	372.4	7.5	35.10	258.0	1.0	25.67
2.00	0.3395	377.3	8.9	35.40	262.3	2.7	25.87
5.00	0.9014	380.5	9.8	36.20	268.5	5.2	26.13
10.00	1.9010	387.3	11.8	37.40	288.1	12.8	26.27
			Na_2SO_4				
0.00	0.0000	346.5	0.0	34.65	255.3	0.0	24.54
0.10	0.0141	346.5	0.0	34.71	255.3	0.0	24.54
0.20	0.0282	353.5	2.1	34.80	255.3	0.0	24.54
0.50	0.0708	360.1	3.9	34.95	256.8	0.6	24.54
1.00	0.1423	364.2	5.1	35.10	260.0	1.8	24.54
2.00	0.2874	369.7	6.7	35.25	264.0	3.4	24.55
5.00	0.7422	375.1	8.2	35.78	272.0	6.5	24.60
10.00	1.5650	384.6	11.2	36.70	296.4	16.1	24.73
			$NaC_2H_3O_2$				
0.00	0.0000	346.5	0.0	34.65	255.3	0.0	24.54
0.50	0.0613	360.1	3.9	34.62	256.9	0.6	23.58
1.00	0.1232	362.9	4.7	34.68	258.2	1.1	23.10
2.00	0.2489	362.9	4.7	34.71	260.9	2.2	22.36
5.00	0.6427	368.3	6.3	34.68	265.0	3.8	18.99
10.00	1.3550	375.1	8.2	34.75	270.4	5.9	12.85
			$Na_2C_4H_4O_6$				
0.00	0.0000	346.5	0.0	34.65	255.3	0.0	24.54
0.50	0.0518	364.2	5.1	34.45	260.9	2.2	24.54
1.00	0.1041	373.7	7.8	34.33	269.0	5.4	24.54
2.00	0.2104	391.8	13.1	34.11	305.8	19.8	24.45
5.00	0.5432	398.2	14.9	34.02	299.0	17.1	23.99
10.00	1.1454	399.5	15.3	34.27	304.2	19.6	22.24
			Na_2CO_3				
0.00	0.0000	346.5	0.0	34.65	255.3	0.0	24.54
0.01	0.0019	346.5	0.0	34.10	255.3	0.0	23.29
0.05	0.0094	346.5	0.0	34.12	256.8	0.6	15.62
0.10	0.0189	346.5	0.0	34.17	258.0	1.0	13.69
0.50	0.0948	357.9	3.2	34.33	273.4	7.1	9.32
1.00	0.1906	369.1	6.5	34.51	284.0	11.2	7.06
2.00	0.3850	389.2	12.3	34.64	293.5	15.0	2.54
5.00	0.9942	428.1	23.5	34.75	313.9	23.0	1.19
10.00	2.0960	441.7	27.4	34.85	346.5	35.8	1.02
			$NaOH$				
0.00	0.0000	346.5	0.0	34.65	255.3	0.0	24.54
0.052	0.01	...	..	33.76	...	..	...
0.50	0.1256	375.1	8.2	34.10	281.3	10.2	9.08
1.00	0.2525	403.6	16.5	34.40	313.6	22.9	8.52
2.00	0.5102	415.9	20.0	35.05	332.9	30.4	8.26
5.00	1.3170	421.3	21.6	35.90	338.4	32.6	8.10
5.24	1.380	...	..	35.95	...	..	...
10.00	2.7780	432.2	24.7	36.05	339.8	33.2	6.91

DISPLACEMENT PRESSURES

From the displacement-pressure measurements with the oil and benzene against the different aqueous solutions, some interesting relationships were observed. With dilute solutions of salts such as NaCl and Na_2SO_4, the maximum displacement pressures were only slightly different from those obtained with pure water. When solutions of 10 per cent concentration were used, the total pressure increase was 11.8 and 12.8 per cent (Table I) for benzene and crude oil, respectively, with NaCl; and 11.2 and 16.1 per cent for the same pair of liquids with Na_2SO_4. There was very little increase in pressure when $NaC_2H_3O_2$ solutions were employed. With a 10 per cent solution of this salt the pressure increase amounted to 8.2 per cent for benzene and 5.9 per cent for the oil. When $Na_2C_4H_4O_6$ was used, however, somewhat greater pressure differences were obtained. The increases in pressures were 15.3 and 19.6 per cent for the benzene and oil, respectively, with a 10 per cent solution. With Na_2CO_3 and NaOH solutions the greatest effects were obtained. A 10 per cent solution of Na_2CO_3 caused an increase in pressure of the benzene displacement of 27.4 per cent and an increase of 35.8 per cent in the pressure of displacement of the oil. A similar concentration of NaOH caused increases of 24.7 and 33.2 per cent, respectively, for the same two liquids. It is interesting to note that the percentage increase of pressures is very similar with both benzene and the crude oil against the various solutions. This series of pressure measurements also shows an agreement with the views of other workers—namely, that alkaline solutions are the most effective in displacing oils from oil-bearing sands. Graphs showing the relation of concentration of salt solutions to percentage increase in pressure are given in Figures 1 and 2.

INTERFACIAL-TENSION VALUES

The results of the interfacial-tension measurements of the different solutions against crude oil and against benzene are more striking than those of pressure measurements. With solutions of the neutral salts, such as NaCl and Na_2SO_4, no great difference in the liquid-liquid interfacial-tension values were observed. Against benzene, both salt solutions increased the interfacial-tension values until at a concentration of 10 per cent the values were 37.4 and 36.7 dynes per cm. for NaCl and Na_2SO_4 solutions, respectively, which compare with 34.65 dynes per cm. for the water-benzene interface (Table I). With the crude oil, similar increases were obtained although they were not quite so great as those found with benzene. With $NaC_2H_3O_2$, however, the benzene and crude oil behaved quite differently (Table I). Against benzene there was little if any change in the interfacial-tension values even at rather great concentrations of solute. Against the crude oil the salt solution reduced the interfacial-tension value almost 50 per cent when a 10 per cent salt solution was used. $Na_2C_4H_4O_6$ solutions seemed to behave almost the same against both of the liquids. A small decrease in the interfacial tension against both benzene and the crude oil was observed (Table I). With the NaOH and Na_2CO_3 solutions, however, there was no similarity between the effect upon the benzene-water tension and upon the crude oil–water tension. Against the crude oil a 10 per cent solution of NaOH reduced the interfacial tension from a value of 24.54 dynes per cm. to 6.91 dynes per cm. With Na_2CO_3 a still greater decrease was obtained. The interfacial tension of a 10 per cent solution against the crude oil was found to be around 1 dyne per cm. In both of these systems the interfacial-tension values dropped very rapidly with increasing concentration of the salt or base (curves V and VI, Figure 3). Against benzene, quite different results were obtained. At low concentrations, only slight decreases in the interfacial tensions of the solutions against benzene were found. With a Na_2CO_3 solution of 0.010 per cent concentration, the interfacial tension was found to be 34.10 dynes per cm. compared with 34.65 for benzene-water. With higher concentration the values increased regularly until at a concentration of 10 per cent the value was 34.85 dynes per cm. With NaOH a similar result was obtained. With a concentration of 0.052 per cent the value found was 33.76 dynes per cm., but, as the concentration was increased, the interfacial-tension values increased until at a concentration of 5.24 per cent the value found was 35.95 dynes per cm. These measurements agree fairly well with those obtained by Harkins and co-workers (*9*) in which they found with the drop-weight method that at low concentrations a decrease of 1 to 2 per cent was observed in the sodium hydroxide–benzene interfacial tension, although increasing the concentration soon caused the tension to go higher than that of water-benzene. In Figures 3 and 4 curves are presented to show the effect of the different salt solutions upon the interfacial tensions of the benzene-water and crude oil–water interface.

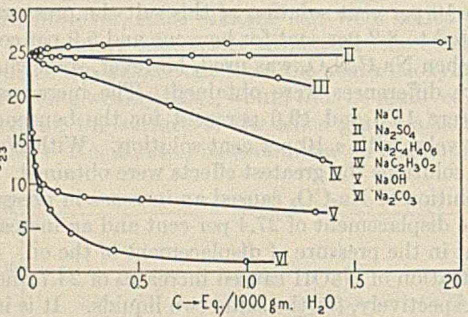


FIGURE 3. INTERFACIAL TENSION, CRUDE OIL–AQUEOUS SOLUTIONS

NOTE. The NaOH used for the above measurements was prepared by allowing water vapor to come into contact with metallic sodium. The resulting concentrated solution was caught in a platinum dish below a monel-metal gauze upon which the sodium was suspended. This NaOH gave excellent results which were easily reproducible. Measurements which were attempted with some of the purified compound obtained from various commercial sources did not give satisfactory results, nor results which could be duplicated.

DISCUSSION

From the results obtained above it appears that several relationships exist between the effect of aqueous solutions upon benzene and crude oil, and their displacement from silica by these solutions. As a result of the displacement-pressure determinations, one obtains evidence that the different salt solutions behave similarly against both benzene and crude oil. This is difficult to explain in the light of some of the earlier theories. It is also obvious that the alkaline solutions are more effective in bringing about this displacement.

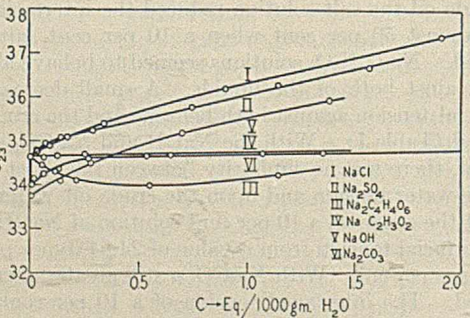


FIGURE 4. INTERFACIAL TENSION, BENZENE-AQUEOUS SOLUTIONS

Interfacial-tension measurements show that the effect of the neutral salt solutions against benzene and oil is similar, but that with alkaline solutions the effect upon the two liquids is very different. Alkaline solutions greatly reduce the interfacial tension of the water–crude oil interface whereas they increase slightly the water-benzene interfacial tension. This would indicate that the alkaline substances must react with some constituent of the crude oil, so that a compound is formed which is highly adsorbed at the liquid-liquid interface. This then would cause the great decrease in the interfacial tension which has been observed. It would appear, however, that this reaction between the oil and alkali does not have an appreciable effect upon the displacement of oil from the sand, since the alkaline solutions appear to displace the benzene from the sand just as effectively as they do the oil. It seems probable that the increased effectiveness of the alkaline solutions in displacing liquids from silica is due to a reaction between the silica and the aqueous solution. Either the base reacts chemically with the silica or is highly adsorbed by it. The factor determining the efficiency of flooding agents then appears to be associated with the aqueous solution–silica portion of the system. In this respect the views of Nutting (*10, 13, 14*) receive, at least, partial substantiation. According to his theory, effective oil displacement by aqueous solutions is brought about by chemical reactions which occur at the solid-liquid interface. His views were discussed earlier in this paper.

As a result of the present investigation, it may be concluded that whatever the nature of the displacement no definite relationship between the change in pressure of displacement and the change in the liquid-liquid interfacial-tension values can be found. Effective displacing agents appear to be those that alter the aqueous solution–silica interface, either through a high degree of adsorption or through chemical reaction at the interface.

LITERATURE CITED

(1) Bartell and Greager, IND. ENG. CHEM., 21, 1248 (1929).
(2) Bartell and Miller, *Ibid.*, 20, 738 (1928).
(3) Bartell and Miller, *J. Am. Chem. Soc.*, 50, 1961 (1928).
(4) Bartell and Osterhof, *Fourth Colloid Symposium Monograph*, 1926, 234–45.
(5) Bartell and Osterhof, IND. ENG. CHEM., 19, 1277 (1927).
(6) Bartell and Osterhof, *Z. physik. Chem.*, 130, 715 (1927).
(7) Bartell and Smith, IND. ENG. CHEM., 21, 1102 (1929).
(8) Beckstrom and Van Tuyl, *Bull. Am. Assocn. Petroleum Geol.*, 11, 223 (1927).
(9) Harkins, Davies, and Clark, *J. Am. Chem. Soc.*, 39, 541 (1917).
(10) Nutting, P. G., IND. ENG. CHEM., 17, 1035 (1925).
(11) Nutting, P. G., *Econ. Geol.*, 21, 234 (1926).
(12) Nutting, P. G., *J. Franklin Inst.*, 203, 313 (1927).
(13) Nutting, P. G., *Oil Gas J.*, 25, 76 (March 31, 1927).
(14) Nutting, P. G., *Ibid.*, 25, 32 (May 5, 1927).
(15) Uren, L. C., *Natl. Petroleum News*, 19, No. 31, 50 (1927).
(16) Uren and Fahmy, *Oil Field Eng. (Phila.)*, 3, No. 4, 11 (1928).

RECEIVED October 30, 1931. This paper contains results obtained in an investigation on "The Displacement of Petroleum Oils from Oil-Bearing Sands by Means of Selected Aqueous Solutions," listed as Project 27 of American Petroleum Institute Research. Financial assistance in this work has been received from a research fund of the A. P. I. donated by the Universal Oil Products Company. This fund is being administered by the Institute with the coöperation of the Central Petroleum Committee of the National Research Council. F. E. Bartell is the director of Project 27, and F. L. Miller is an A. P. I. research assistant.

UNITED STATES LEADS IN PRODUCTION OF ALUMINUM. Considering aluminum and bauxite production by countries, the United States leads all others in production of the metal, and France leads in production of bauxite, according to the United States Bureau of Mines. Six countries supply about 88 per cent of the total aluminum produced in the world; in order of output they are the United States, Canada, Germany, France, Switzerland, and Norway. Three countries—France, Hungary, and the United States—supply 66 per cent of the total bauxite produced; four other countries—Dutch Guiana, Italy, British Guiana, and Yugoslavia—supply 32 per cent. Of the seven chief producers of bauxite and six chief producers of aluminum only two countries—the United States and France—appear in both groups. Aluminum is the most abundant metal in the earth's crust.

Corrosion of Metals by Milk

Effects of Operating Conditions on Corrosion in Various Parts of Pasteurizing Equipment

H. A. Trebler, National Dairy Products Corp., Baltimore, Md., and W. A. Wesley and
F. L. LaQue, International Nickel Co., Inc., New York, N. Y.

The corrosion of nickel, copper, nickel-silver, an experimental chromium-nickel alloy, and a chromium-nickel-iron alloy in sweet milk was studied.

It was found that in milk being heated to the pasteurizing temperature and held at that temperature nickel was corroded only slightly. The normal increase in the rate of corrosion which accompanies a rise in temperature of most corrosives was found to be prevented in a positive manner by the formation of a protective film on nickel favored by air supersaturation and high velocity of the milk. During the process of cooling milk from the pasteurizing temperature, there was no protective film formation so that the corrosion of nickel was normal, depending on aëration, temperature, and velocity. Corrosion was appreciable during the initial stages of cooling, and decreased steadily as the temperature was lowered. The dual effect of high aëration and high velocity in increasing the rate of corrosion under certain conditions and decreasing the corrosion rate by accelerating protective-film formation under other conditions, accounted for the difficulty in applying the results of former investigations to explain the practical behavior of nickel in milk.

Nickel-silver showed somewhat the same behavior as nickel, but copper was not noticeably protected on heating. The chromium-nickel alloy was resistant under all conditions, as was the chromium-nickel-iron alloy in the limited number of tests in which it was included.

Galvanic corrosion, due to differences in metal, aeration, or temperature, was unimportant, as was also the metal content of the milk.

The results are directly applicable to plant operations and will enable the manufacturer and operator to use nickel with assurance in the larger part of pasteurizing equipment and to avoid the difficulties which would be associated with its use in the particular pieces of equipment where corrosion is appreciable.

THE use of new types of equipment for the continuous pasteurization of large volumes of milk at high rates of flow has become common. Rapid corrosion of nickel in regenerative coolers in some of these systems was in apparent disagreement with the satisfactory performance of the metal in internal tubular heaters and other units. Conditions of service in heaters seemed more severe than in regenerators, because of the higher temperatures maintained at the metal walls; nevertheless the corrosion in heaters was very slight.

Several explanations of this supposed abnormality were offered. They will be discussed in detail elsewhere in this paper. However, a further development of the data given by McKay, Fraser, and Searle (*5*) seemed sufficient to account for the rapid corrosion of the regenerators. They also pointed out that freedom from corrosion of heater tubes might be explained by the formation of protective films, but did not suggest why film formation was confined to heaters and similar equipment. They enumerated the principal factors to be considered in laboratory corrosion tests—namely, acidity, temperature, aëration, velocity, film formation, and galvanic effects. To these should possibly be added the effect of more noble metals in solution such as copper.

Space is not available for a complete review of the literature on metals in milk. A comprehensive bibliography is, however, contained in the above-mentioned paper. Some recent contributions by Hunziker, Cordes, and Nissen (*4*) and Guthrie, Roadhouse, and Richardson (*3*) should be added.

Unfortunately most laboratory investigations on corrosion of metals by milk and the effects of metals on flavor have been carried out under special conditions usually very different from those actually encountered in most plants. While the pasteurizing process itself is simple enough, there are about as many different flow sheets as there are plants; consequently, pasteurizing conditions in respect to corrosion vary greatly.

In the present investigation, corrosion tests were made in both plant and laboratory. The laboratory tests served to study the variables encountered in the plants and finally to develop a laboratory procedure which was believed to reproduce plant conditions and to explain satisfactorily the peculiar behavior of milk in its corrosion of metals.

The following metals and alloys were included in the tests:

Metal	Approximate Analysis				
	Ni	Cu	Cr	Fe	Zn
	%	%	%	%	%
Nickel	99.5	..	..	..	..
Copper	..	99.9	..	..	..
Nickel-silver	20	75	..	..	5
Chromium-nickel alloy	83	..	12	5	..
Chromium-nickel-iron alloy	8	..	18	74	..

These will all be recognized as materials in common use, except the chromium-nickel alloy which is an experimental composition now being developed.

Laboratory Study of Normal Corrosion of Metals

In studying corrosion by milk in the laboratory, it was not considered advisable to prolong the individual tests because of the changes which might occur in the milk. In addition it was found that, even in tests as short as 1.5 hours, weighable losses were obtained; the results were reproducible and checked those obtained by weight-loss determinations in 7- to 8-hour plant tests.

In some experiments the acidity of the milk was determined by titration before and after the tests. The changes found were so slight that the practice was discontinued in favor of simple tasting, which served to demonstrate that no important changes in acidity had occurred.

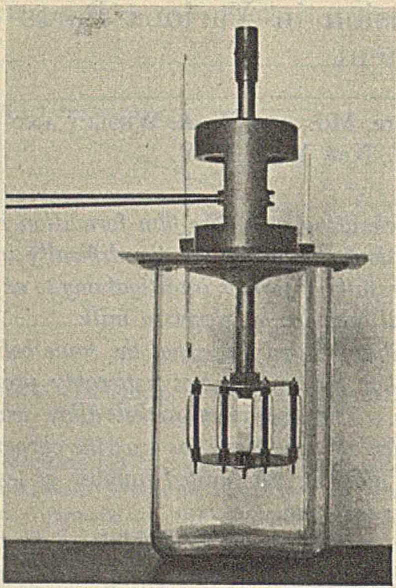


Figure 1. Rotating Spindle Apparatus for Corrosion Testing

The bacterial content of the milk samples used was not determined. However, all the samples were taken from the same pasteurizing plant, and all had the same age when used. The bacteria content would presumably still show great variations, but very little is known about the importance of this factor in regard to corrosion of metals by milk. It is conceivable that a large number of dead or living bacteria might influence the results because of their effect on the available oxygen content, but no important error would be expected from this source because the milk was kept, as far as possible, saturated with oxygen during all the experiments.

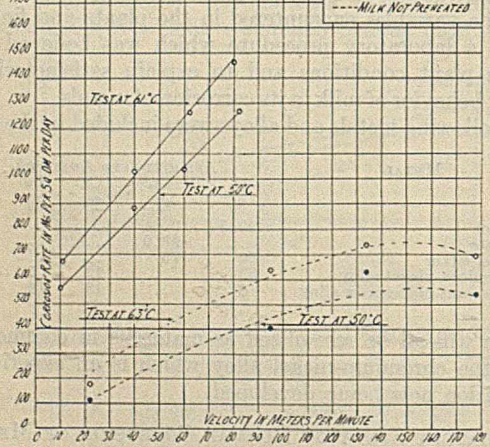


Figure 2. Effect of Velocity on Corrosion of Nickel by Milk as Determined with Rotating Spindle Machine

Tests at 63° C. Most plants have one thing in common; that is, that milk is heated quickly to about 63° C., held at this temperature for 30 minutes, and then cooled down again to about 4° C. Therefore it seemed desirable to determine the rates of corrosion of metals at 63° C. in fully aërated milk at the convenient, arbitrarily chosen velocity of 4.7 meters per minute, available in the standard vertical circular-path corrosion machine described by Fraser, Ackerman, and Sands (*2*). Such determinations would serve as a convenient basis of comparison for tests made under other conditions. However, in most of the later tests control specimens were used whenever possible to facilitate direct comparison, independent of unavoidable variations in conditions.

In most of the experiments sheet-metal test pieces, 2.5 by 5 cm., were suspended in glass stirrups attached to the moving arm of the corrosion machine. The specimens were first resurfaced with No. 0 French emery and then scrubbed with pumice, wiped off with a clean cloth, and weighed. After exposure the pieces were cleaned with tripoli soap by rubbing with the fingers only, using no brush or harsh abrasives. This treatment proved satisfactory for removing any adherent corrosion product or film without removing any of the metal itself.

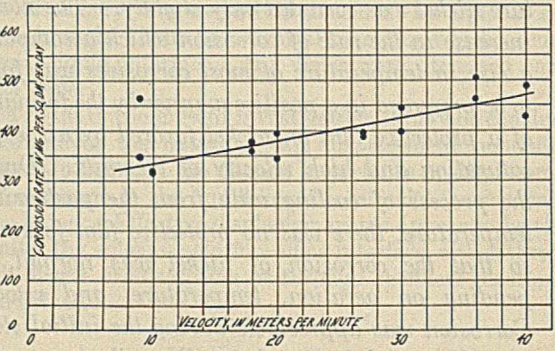


Figure 3. Effect of Velocity on Corrosion of Nickel by Milk as Determined with Continuous-Flow Apparatus

Open storage-battery jars served as containers for the milk. Aëration was effected by the introduction of filtered compressed air through glass tubes ending in fine tips near the bottom of the jars. A better distribution of the air was attempted by means of porous cups but had to be abandoned because of excessive foaming. The temperature of the milk was regulated by adjusting the temperature of the water bath in which the jars were placed.

The results obtained with nickel, copper, and chromium-nickel in 4-hour tests are given in Table I. There was a noticeable spread between the highest and lowest values found both for nickel and copper but not more than would be expected in corrosion tests. In the case of copper the checks within a single test were very good, while the differences between the results from the different tests were somewhat larger.

Effect of Various Factors

Temperature and Velocity. In order to determine the effects of temperature and velocity on corrosion of nickel in fully aërated milk, a number of tests were made with the rotating spindle machine shown in Figure 1. With this apparatus the velocities of the test pieces depended on their speed of rotation and their distances from the axis of rotation.

The results of these tests are shown in Figure 2. At lower temperatures than those covered by the graph, the results were not sufficiently consistent to permit plotting. The reason for this behavior at lower temperatures was probably connected with lack of uniform aëration of the milk and the development of protective films to some extent. In order to obtain the maximum rates of corrosion, it was necessary to heat the milk above the temperature to be investigated and then cool it to the desired value. When this was not done,

TABLE I. CORROSION OF NICKEL, COPPER, AND CHROMIUM-NICKEL IN FULLY AËRATED MILK AT 62–64° C.

EXPT.	AV. TEMP.	CORROSION OF NICKEL			CORROSION OF CHROMIUM-NICKEL			CORROSION OF COPPER		
		Test 1	Test 2	Av.	Test 1	Test 2	Av.	Test 1	Test 2	Av.
	° *C.*	*M. d. d.*[a]	*M. d. d.*	*M. d. d.*	*M. d. d.*	*M. d. d.*	*M. d. d.*	*M. d. d.*	*M. d. d.*	*M. d. d.*
14	63	501	550	525	0	2	1	...	...	...
20	63	519	533	526	0	0	0	130	130	130
20	63	478	523	500	..	..	..	125	134	130
22	64	524	527	525	0	0	0	152	131	142
22	64	538	543	540	0	0	0	164	169	166
23	62	499	504	502	..	..	..	...	...	...
Grand average	..	...	...	520	..	..	0	...	...	142
Average deviation from the mean			...	±3%	..	..	..	...	...	±11%

[a] Mg. per sq. dm. per day.

TABLE II. EFFECT OF AËRATION ON CORROSION OF NICKEL BY MILK AT 63° C.

EXPT.	RATE OF CORROSION OF NICKEL IN MILK AËRATED WITH: AIR			NITROGEN			REMARKS
	Test 1	Test 2	Av.	Test 1	Test 2	Av.	
	M. d. d.[a]	*M. d. d.*	*M. d. d.*	*M. d. d.*	*M. d. d.*	*M. d. d.*	
13	501	550	525	132	126	129	Nitrogen sweeping over surface of milk
17	440	442	441	53	109	81	....
17	267	364	316	71	131	101	Test made using raw milk
19	555	629	591	15	23	19	Milk aërated and deaërated for long time prior to test

[a] Mg. per sq. dm. per day.

and the milk was brought just to the testing temperature and held there, much lower rates were obtained, as shown in the two lower curves in Figure 2. This point will be discussed in greater detail in connection with protective films elsewhere in this paper.

Because of the uncertainty in regard to velocity and aëration in the above experiments, another experimental procedure was tried which, however, was capable of producing results only at low velocities.

Four holders similar to Figure 5, except that each contained two nickel specimens, were joined together in series and placed in a water bath. The diameters of the four glass tubes of the holders were so chosen that the velocities of the milk past the test pieces would be in ratio 1:2:3:4. The milk came from a small storage jar and was heated up to about 58° C. while flowing through a glass coil submerged in water at 62° C. From the coil the milk flowed through a glass tube, 1 meter long, and the four specimen holders in a water bath at 58° C. The temperature of the milk dropped to about 57° C. before entering the first holder, and reached 56° C. after passing through all four. The milk was aërated and returned to the storage jar by means of an air lift 2.5 meters long. The runs lasted 2 hours each. The results of two experiments are given in Figure 3. The corrosion rates would presumably have been higher if more of a temperature drop or a longer cooling time had been allowed before the milk reached the pieces. A possible disturbing effect of the slight temperature drop from piece to piece was taken into consideration by making two runs; in one the milk entered at the widest tube and in the other at the narrowest.

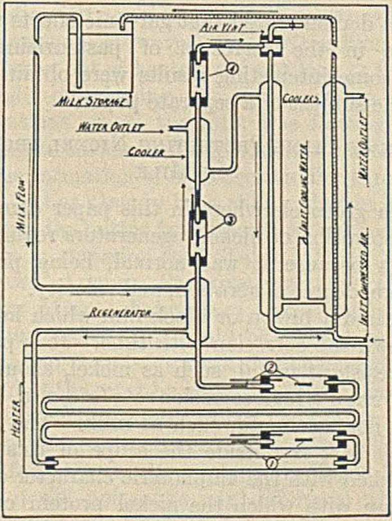


FIGURE 4. APPARATUS FOR MAKING CORROSION TESTS IN FLOWING MILK

Further data on the effects of temperature and velocity on the corrosion of nickel and copper may be obtained from the curves in Figure 6 and from Tables VIII and IX, covering laboratory results with flowing milk, and in Figure 17 which gives the grand average of the results obtained in plant tests.

The rate of corrosion of nickel by milk decreased about 15 mg. per sq. dm. per day per ° C. at the average plant velocity. Good checks were obtained in plant and laboratory tests run at corresponding temperature, velocity, and degree of aëration.

AËRATION. The importance of aëration in the corrosion reactions has been mentioned. Some experiments were made to compare the rates of corrosion of nickel in fully aërated milk with those found in milk more or less completely freed of air by the substitution of nitrogen for air in the aërating system. The usual test pieces, 2.5 by 5 cm., were employed, suspended in glass stirrups from the moving arm of the corrosion machine. The tests were of 3 hours' duration. The results are given in Table II. It was quite evident that the rate of corrosion was materially decreased when the oxygen content was reduced. The results of experiment 19 in particular demonstrated that, if the efficiency of the deaëration were improved by increasing the length of time the milk was exposed to nitrogen, the rate of corrosion of nickel by milk would approach zero, and that therefore oxygen must play a very important role in the corrosion reaction.

The chromium-nickel alloy was included in two series of tests and showed no corrosion in aërated or deaërated milk.

TABLE III. EFFECT OF BUTTER FAT ON CORROSION OF NICKEL BY FULLY AËRATED MILK AT 63° C.

TEST	CORROSION RATE	TYPE OF MILK
	M. d. d.[a]	
1	440	4 liters homogenized and pasteurized milk
2	456	225 cc. whipping cream in 4 liters homogenized and pasteurized milk
3	451	4 liters pasteurized milk
4	421	225 cc. whipping cream in 4 liters pasteurized milk

[a] Mg. per sq. dm. per day.

EFFECT OF BUTTER-FAT CONTENT ON NORMAL CORROSION OF NICKEL. The fat content of the samples used was presumed to be fairly constant, as was also the number and size of the fat globules. However, it was thought advisable to make some comparative studies using raw and pasteurized milk (Table II), and pasteurized and homogenized milk with and without the addition of cream (Table III). The results indicated that the effect of the quantity and distribution of butter fat in the milk was not important.

TABLE IV. EFFECT OF STEAM STERILIZATION ON CORROSION OF NICKEL SPECIMENS IN PLANT I

TEST STATION	LOCATION OF TEST STATION	CORROSION OF SPECIMENS INTRODUCED: BEFORE STERILIZATION, Test 1	BEFORE STERILIZATION, Test 2	BEFORE STERILIZATION, Av.	AFTER STERILIZATION, Test 1	AFTER STERILIZATION, Test 2	AFTER STERILIZATION, Av.
		M. d. d.[a]	*M. d. d.*	*M. d. d.*	*M. d. d.*	*M. d. d.*	*M. d. d.*
7	12th tube of heater	30	23	27	71	68	70
8	19th tube of heater	67	..	67	99	..	99
12	3rd tube of regenerator	1150	1090	1120	1167	1103	1135
15	7th tube of regenerator	888	888	888	940	1100	1020
16	9th tube of regenerator	825	..	825	917	..	917

[a] Mg. per sq. dm. per day.

This finding was not in conflict with the results obtained by McKay, Fraser, and Searle (*5*) concerning the effect of butter fat on the corrosion of nickel in lactic acid solutions, because it is now generally assumed that sweet milk does not contain any free lactic acid.

PRETREATMENT OF METAL. It was observed in some plant tests that the rates of corrosion, determined with specimens introduced before the equipment was sterilized with steam, differed noticeably from those found when the specimens were installed after the sterilizing process (Table IV). To check this point in the laboratory a number of the usual nickel strips were treated in different ways and then exposed to fully aërated milk at 58° C. for 2 hours in the corrosion machine. The treatment given the various pieces and the results obtained are shown in Table V. The treatment with steam and air afforded definite protection to the metal. Steam alone or heat (in air) alone did not cause any appreciable reduction in the rate of corrosion. The ammonia treatment, which usually renders nickel passive, had less effect than might be expected.

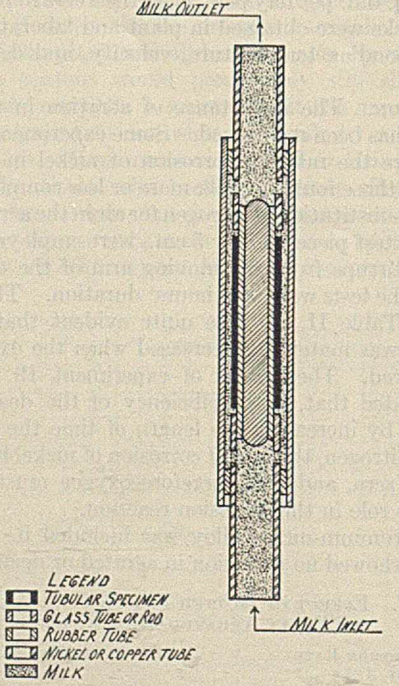


FIGURE 5. SPECIMEN HOLDER USED WITH CONTINUOUS-FLOW APPARATUS

DISSOLVED AND METALLIC COPPER. Colin G. Fink in a discussion of the paper by McKay, Fraser, and Searle (*5*) suggested that dissolved copper might have an effect on the corrosion of nickel by milk, and that nickel apparatus might remove copper from milk. Certain tests were made on this point, the results of which may be published separately since they are aside from the subject matter of the present paper. It should, however, be noted that the present authors have not found that the presence of dissolved or metallic copper affected corrosion rates appreciably, or that nickel equipment changed the normal copper content of milk.

GALVANIC EFFECTS. The possible galvanic corrosion of nickel, due solely to the difference of solution pressure of the metal in contact with milk on the outside of regenerator tubes at one temperature and on the inside of the tubes at a higher temperature, was investigated. The study was complicated to some extent by the galvanic currents set up by the differences in concentration of dissolved oxygen in the milk at the two temperatures. Tests were also made on galvanic effects obtained by coupling of different metals.

TABLE V. EFFECT OF PRETREATMENT OF THE SPECIMENS ON CORROSION OF NICKEL BY FULLY AËRATED MILK[a]

PRETREATMENT OF NICKEL SURFACE	TEST 1	TEST 2	AV.
	M. d. d.[b]	*M. d. d.*	*M. d. d.*
Control specimens resurfaced with emery and scrubbed with pumice	494	538	516
Specimens resurfaced with emery and washed with soap	476	538	507
Specimens resurfaced and exposed to steam at 97° C. for 1 hour	482	500	491
Specimens resurfaced and exposed to steam and air at 95° C. for 1 hour	125	180	152
Specimens resurfaced and exposed to air at 80° C. for 1 hour	482	507	494
Specimens resurfaced and treated with cold 1% ammonia solution for 1 hour	356	363	360

[a] The specimens treated at high temperatures were allowed to cool down before placing them in the milk.
[b] Mg. per sq. dm. per day.

The data demonstrated that galvanic effects were of minor importance in the corrosion of pasteurizing equipment. However, some interesting results were obtained which will be made the subject of a separate paper.

FORMATION OF FILMS PROTECTING NICKEL FROM CORROSION IN MILK

The data given elsewhere in this paper demonstrate that the rapid corrosion of nickel regenerators required no special explanation because it was normal, being proportional to temperature, degree of aëration, and velocity. The corroding metal acquired a brown or black film which had a tendency to slow down the corrosion with time. It is peculiar that a corrosion-resistant metal, such as nickel, should, under any conditions, show a high corrosion rate (see, e. g., Table X) in an essentially neutral liquid, such as milk. The final explanation of this fact is outside the scope of this paper. It is possibly linked with the amphoteric character of the protein, and the ease with which the nickel protein complex in its monomolecular state is dispersed in milk.

The fact requiring explanation was that nickel equipment did not corrode wherever the milk was being heated.

It was realized early that a protective film was formed in heaters distinctly different from the black or brown corrosion tarnish mentioned above. In some cases this protective film was practically invisible, but it could usually be recognized by a distinct iridescence. These films seemed to harden and take on a whitish color on exposure to air. They could be removed from the test pieces by washing with tripoli soap before weighing. If the pieces were incompletely washed, they would show gains in weight up to 1 or 2 mg. per square decimeter of surface, presumably because of the weight of the film. Nickel test pieces were also installed for a complete pasteurizing run in an internal tubular heater and inside a regenerative cooler in plant I (Figure 7). Some of the pieces were used as controls for direct weight-loss determinations, while others were taken to the laboratory for use in corrosion tests to determine the durability of the protective coatings. The experiments showed that a definite and lasting protection was afforded by the previous exposure of the samples in the heater. Previous exposure in the regenerator also developed good protection of the specimens, which, however, could be traced to the adhering corrosion products rather than to films of the type formed in the heater.

Possible Effect of Butter Fat. It seemed reasonable to assume that the butter fat in milk might be effective in the formation of protective films, since fat would give the metal excellent protection if it could become sufficiently well attached to the metal surface. However, the surface films observed on test pieces taken out of heaters did not look or feel greasy, although a slight oily feeling was developed on specimens exposed in locations where the milk was flowing at a low velocity. It looked rather as if deposition of butter fat were secondary to the formation of a protective film through some other agency. It has already been shown that in laboratory tests an increase in the butter-fat content was not accompanied by any decrease in corrosion rate (Table III).

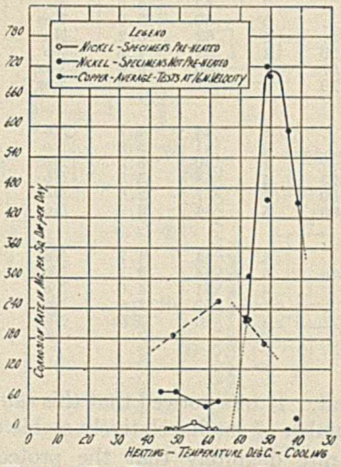


Figure 6. Results of Laboratory Tests on Corrosion of Metals in Flowing Milk

Formation by Anodic Precipitation of Colloidal Particles from Milk. Laboratory experiments showed that corrosion-protective films could be formed on nickel by anodic precipitation, but later work demonstrated that any such effect would at the most be of only secondary importance, because perfect protection could be obtained both in plant and laboratory on test pieces which were electrically well insulated. As a matter of fact, the results as shown in Table VI showed definitely that it did not make any difference whether the pieces were grounded or not.

Table VI. Comparison of Corrosion Rates of Insulated[a] and Grounded Nickel Test Pieces in Plant I

	Insulated Specimens			Grounded Specimens			
Station	Test 1	Test 2	Av.	Test 1	Test 2	Av.	Remarks
	M. d. d.[b]	*M. d. d.*	*M. d. d.*	*M. d. d.*	*M. d. d.*	*M. d. d.*	
6	7	1	4	8	11	9	Iridescent film
8	51	27	39	42	40	41	Iridescent film
12–13	913	958	936	918	984	951	Heavy black film

[a] Insulated specimens were mounted on holders (Figure 13) in the center of the tubes; grounded specimens were in contact with the tube walls.
[b] Mg. per sq. dm. per day.

Effect of Direction of Heat Flow. Since plant experience had shown that nickel corroded wherever the milk was being cooled and did not corrode where the milk was being heated, the possibility that the direction of flow of heat between the metal and the milk might affect the rate of corrosion of nickel was investigated.

It was improbable that the protection on heating was due to some sort of "baking on" effect, since in most plants the heating medium was only a degree or two hotter than the maximum temperature of the milk, and because protection occurred at temperatures as low as 15° C. However, the experiments were not conclusive in establishing a means of producing protective films at will.

Table VII. Corrosion of Nickel in Samples of Milk Taken from Various Locations in an Operating Plant

Source of Milk	Temp. When Taken	Temp. of Test	Corrosion of Nickel Test 1	Corrosion of Nickel Test 2	Corrosion of Nickel Av.	Duration of Run
	° *C.*	° *C.*	*M. d. d.*[a]	*M. d. d.*	*M. d. d.*	*Hours*
Raw milk from mixers	3	47	477	440	459	2.0
Regenerator trough	4	47	473	464	469	2.0
Regenerator trough	47	58	511	570	541	2.0
Regenerator trough	49	58	450	576	513	1.5
6th tube of heater	35	51	387	416	402	2.0
6th tube of heater	63	58	440	480	460	2.0
20th tube of heater	55	53	492	432	462	2.0
20th tube of heater	59	59	460	534	497	2.0
20th tube of heater	59	60	488	544	516	1.5
Outlet of holder	60	61	195	257	226	1.5
7th tube of regenerator	45	58	440	465	453	2.0
7th tube of regenerator	45	57	340	413	377	1.5

[a] Mg. per sq. dm. per day.

Several types of apparatus were used to study this point. The experiments showed that, if the metal were kept hotter than the milk, or if the milk were heating up, low corrosion rates would usually be obtained; if the metal were cooler than the milk, or if the milk were cooling down, normal corrosion rates could be expected. The conclusion was reached that the direction of heat flow was not important in determining the extent of protective-film formation except in so far as it caused either heating or cooling of the milk in contact with the metal. This was still more conclusively proven by the plant results listed in Table VI, which demonstrated that specimens placed in the center of heater tubes were afforded protection as well as those placed in contact with the metal walls.

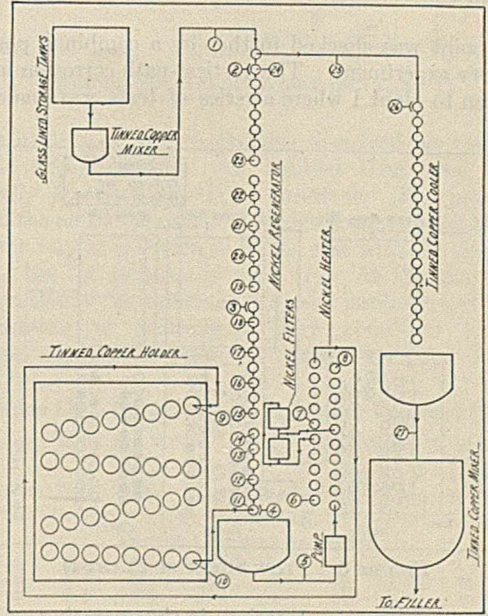


Figure 7. Flow Sheet of Plant I

Importance of Air. It was evident that up to this point no laboratory procedure had been developed to produce protective films on nickel at will, and that some factor operating in the plant was not being covered adequately by the laboratory test. It was thought that this missing factor might be connected with the condition of the air in the milk being heated.

Table VIII. Corrosion of Nickel in Flowing Milk

Velocity 16 M. per Min.						Velocity 7–10 M. per Min.						Velocity 0.1–0.7 M. per Min.					
Expt.	Temp. ° C.	Time Hours	Pre-treatment	Temp. dif. ° C.	Wt. loss M. d. d.[a]	Expt.	Temp. ° C.	Time Hours	Pre-treatment	Temp. dif. ° C.	Wt. loss M. d. d.[a]	Expt.	Temp. ° C.	Time Hours	Pre-treatment	Temp. dif. ° C.	Wt. loss M. d. d.[a]
STATION 1, 1ST STEP OF HEATER																	
4	47	3.3	Yes	+18	0	...	..	...	...	..	...	9	46	3.0	Yes	+16	0
9	46	3.0	Yes	+16	0	...	..	...	...	..	...	8	47	1.7	Yes	+12	28
8	47	1.7	Yes	+12	0	...	..	...	...	..	...	5	58	3.2	No	+35	75
1	44	2.6	No	+13	74	...	..	...	...	..	...	4	47	3.3	Yes	+18	81
3	49	4.6	No	+20	75	...	..	...	...	..	...	7	50	3.0	Yes	+38	104
..	..	...	...	..	..	5	58	3.2	No	+35	120	6	45	1.5	Yes	+39	160
..	..	...	...	..	..	...	..	...	...	..	...	1	44	2.6	No	+13	212
STATION 2, 2ND STEP OF HEATER																	
4	62	3.3	Yes	+33	0	...	..	...	...	..	...	8	55	1.7	Yes	+20	28
9	60	3.0	Yes	+30	0	...	..	...	...	..	...	3	63	4.6	No	+34	42
8	55	1.7	Yes	+20	14	...	..	...	...	..	...	9	60	3.0	Yes	+30	56
1	59	2.6	No	+28	46	...	..	...	...	..	...	5	62	3.2	No	+39	90
3	63	4.6	No	+34	57	7	60	3.0	Yes	+48	120	1	59	1.5	No	+28	111
..	..	...	...	..	..	5	62	3.2	No	+39	157	7	60	3.0	Yes	+48	144
..	..	...	...	..	..	6	61	1.5	Yes	+55	270	6	61	1.5	Yes	+55	160
STATION 3, 1ST STEP OF COOLER																	
3	58	4.0	No	−5	216	...	..	...	...	..	...	8	44	1.7	No	−11	85
4	58	3.3	No	−4	222	...	..	...	...	..	...	9	41	3.0	No	−19	121
1	57	2.6	No	−2	305	...	..	...	...	..	...	7	50	3.0	No	−10	152
9	41	3.0	No	−19	450	7	50	3.0	No	−10	423	4	58	3.3	No	−4	177
8	44	1.7	No	−11	593	6	44	1.5	No	−17	450	1	57	2.6	No	−2	212
..	..	...	...	..	...	5	54	3.2	No	−8	600	5	54	3.2	No	−8	240
STATION 4, 2ND STEP OF COOLER																	
8	44	1.7	No	−11	0	...	..	...	...	..	...	8	44	1.7	No	−11	70
9	40	3.0	No	−20	24	5	44	3.2	No	−18	416	5	44	3.2	No	−18	135
3	51	4.0	No	−12	456	...	..	...	...	..	...	3	51	4.0	No	−12	198
4	50	3.3	No	−12	700	...	..	...	...	..	...	1	50	2.6	No	−8	305
1	51	2.6	No	−8	720	...	..	...	...	..	...	9	40	3.0	No	−20	415

[a] Mg. per sq. dm. per day.

In order to determine if milk previously heated and supersaturated with air would develop protective films, four experiments were made by heating fully aërated milk quickly in a closed coil, from which it flowed directly into a jar in which the specimens were moved as usual at a velocity of 4.7 meters per minute. In one of the experiments good protection was obtained, but this could not be reproduced in the three following experiments. Although the milk might be supersaturated with air as it left the coil, apparently that condition was not maintained in the milk in contact with the test specimens in the jar.

This point was checked further by a combined plant and laboratory experiment. The vertical-path corrosion machine was taken to plant I where a series of tests was made, using milk taken from various locations in the operating equipment directly to the jars of the corrosion machine. The results are covered by Table VII. They showed that, if the formation of protective films was due to the air in the milk, the favorable condition did not persist after the milk was removed from the closed equipment. In each case care was taken to prevent a drop in temperature of the milk while it was being transferred from the equipment to the corrosion machine. The only sample which gave any protection in these tests was that taken from the stopcock connected with the final tube of the long-flow holding unit. It was noticed that this sample contained a very large number of small, relatively stable air bubbles.

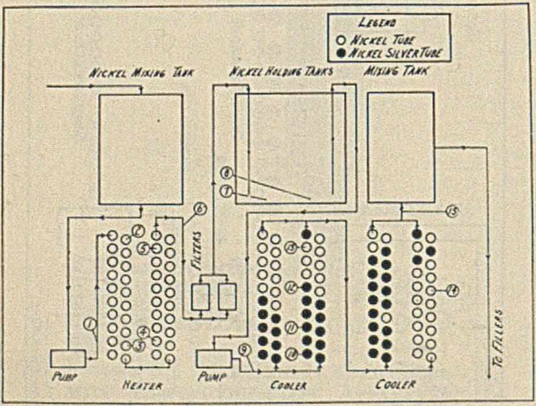


Figure 8. Flow Sheet of Plant II

To demonstrate definitely that the protection afforded nickel in heaters and the high rates of corrosion of regenerators depended solely on the condition of the milk, the apparatus shown in Figure 4 was constructed entirely of glass. Milk at about 30° C. flowed through a siphon from a 2-liter storage jar into the jacket of a Liebig condenser which served as a regenerative cooler for the milk from the heating coils. From the jacket the preheated milk flowed through a coil in a water bath kept at 64° C. Test pieces were installed within the glass tubes, as indicated in the sectional drawing, Figure 5, at the locations shown in Figure 4. The velocity of movement of the milk over the surface of the test pieces could be varied by changing the diameters of the tubular metal specimens and of the glass tubes in which they were supported, since the milk had to flow through the annular space between the specimens and the tube walls. In a typical run the milk reached a temperature of 47° C. at test location 1, and of 61° C. at location 2. The milk started to cool as soon as it left the heating coil so that at location 3 its temperature was 58° C.; and at location 4, after the first water cooler, the temperature dropped to 51° C. The milk was finally returned to the storage jar through two more water coolers, the last one serving as an air lift simultaneously circulating and aërating the milk by the introduction of compressed air. The velocity of flow of the milk could be adjusted to some extent by regulating the amount of air and the height of the lift.

The results obtained when using this apparatus are shown in Table VIII for nickel and Table IX for copper. The tendency for corrosion rates to decrease with time should be taken into consideration in comparing the results of the various experiments. The values obtained for the corrosion of nickel and copper at a velocity of 16 meters per minute have been plotted in Figure 6. A comparison of these curves with the grand average curves of all the plant tests (Figure 17) shows a striking similarity, indicating that the apparatus described gave a satisfactory means of duplicating plant conditions in the laboratory. These tests showed clearly that, wherever the milk was being heated, the nickel specimens were protected; whereas, where the milk was cooling, the nickel corroded at appreciable rates.

The data of Table VIII demonstrate that the efficiency of the protection on heating was not nearly so marked at low rates of flow of the milk as it was at the highest velocity. This relation is evident in the results of the plant tests in Tables X to XV, and can be detected even in the data secured in the rotating spindle machine and presented in Figure 2. In that figure the difference between the dotted and the straight-line curves is greater at the higher velocities, signifying relatively better protection from corrosion as the velocity increases. The conclusion can therefore be drawn that a high velocity of flow, or the provision of intimate contact of the metal with the aërated milk by some other means, is essential for complete protection of nickel in heaters.

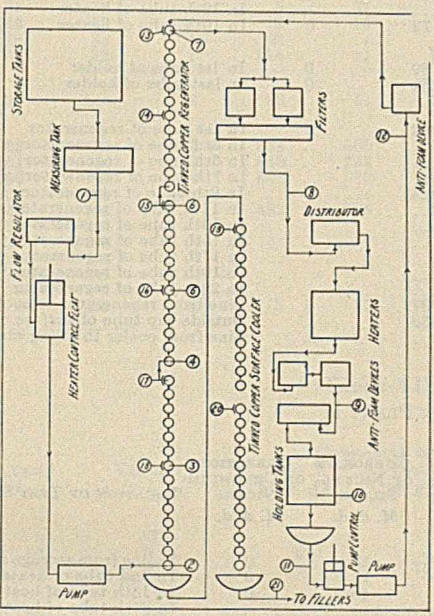


FIGURE 9. FLOW SHEET OF PLANT III

Temperature differences in Table VIII indicate the difference between the temperatures maintained at the test stations and the lowest (+) or highest (−) temperature reached by the milk as it circulated through the apparatus. The magnitude of these temperature changes did not seem important in determining the extent of protection of nickel. Protection could be expected where the milk was passing though a closed tube at an appreciable velocity so long as the temperature of the milk was increasing or even constant. Evidently a drop in temperature of some 6 or 7 degrees is necessary to develop the maximum rate of corrosion of nickel by cooling milk. Plant experience had previously shown this effect which was now demonstrated by the laboratory tests and by plant tests to be described. The very low corrosion rates obtained in experiments 8 and 9 at station 4, as shown in Table VIII and in Figure 11, might have been due to the fact that in these experiments there was a very large temperature drop between stations 2 and 3, and little or no drop from station 3 to 4. Consequently the milk was not really cooling at station 4 but was at a constant temperature with conditions possibly favorable to protective-film formation, especially at the highest velocity.

The location of the points of maximum corrosion can be expected to vary from plant to plant, according to the velocity of the milk and the rapidity of the cooling. It is probable that at lower velocities the temperature drop required to develop the maximum rate of corrosion of nickel is less than at high velocities.

Where the metal specimens were pretreated so that they were hotter than the milk at the time of the initial contact, there was a decrease in the rate of corrosion in every case at the high velocity, as is evident from Figure 6. At the lower velocities the effect of this pretreatment was indefinite.

The results of the tests on copper shown in Table IX and Figure 6 showed that copper was not afforded any positive protection on heating, and that the rates of corrosion were governed by the usual factors—velocity, temperature, and aëration. As the copper showed no difference in behavior whether it was exposed to milk being heated or to milk being cooled, only the actual temperatures at the test pieces and not the temperature differences were recorded in Table IX.

MECHANISM OF FORMATION OF PROTECTIVE FILM ON NICKEL. The mechanism of the formation of the protective film is no more definitely known than the mechanism of corrosion. However, it seems rather probable that protein, because of its surface tension–lowering activity, will collect at the gas-liquid interface (in this case at the exposed surface of the milk) at the surface of all the air bubbles in the milk, and possibly even at the air-coated metal wall itself.

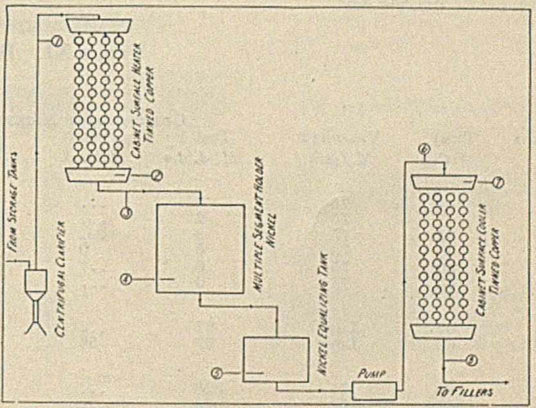


FIGURE 10. FLOW SHEET OF PLANT IV

The heating of milk containing dissolved air causes it to become supersaturated. Air bubbles then tend to form, especially at the metal-liquid interface. The protein film around the air bubbles may be rendered unstable on heating in the same way as is known to be the case with the protein film coating the fat globules in milk (*1*). At the same time it becomes slowly "denaturated" (*6*) and insoluble (probably by condensation of molecules). Any condition promoting intimate contact between the protein-enriched interfaces

TABLE IX. CORROSION OF COPPER IN FLOWING MILK

Velocity 16 M. per Min.					Velocity 0.7 M. per Min.				
Expt.	Temp.	Time	Pre-treatment	Wt. loss	Expt.	Temp.	Time	Pre-treatment	Wt. loss
	° *C.*	*Hours*		*M. d. d.*[a]		° *C.*	*Hours*		*M. d. d.*[a]
STATION 1, 1ST STEP OF HEATER									
4	47	3.3	Yes	140	..	..	...	...	..
3	49	4.5	No	144	3	49	4.0	No	41
2	47	2.5	Yes	278	2	47	2.5	Yes	96
STATION 2, 2ND STEP OF HEATER									
3	63	4.5	No	171	..	..	...	...	..
4	62	3.3	Yes	266	4	62	3.5	Yes	136
2	62	2.5	Yes	326	2	62	2.5	Yes	126
STATION 3, 1ST STEP OF COOLER									
3	58	4.0	No	168	3	49	4.0	No	55
4	58	3.3	Yes	192	..	..	...	...	..
2	56	2.5	Yes	298	2	56	2.5	Yes	96
STATION 4, 2ND STEP OF COOLER									
4	51	3.3	Yes	111	4	51	3.3	Yes	57
3	51	4.0	No	162	..	..	...	...	..
2	54	2.5	Yes	240	2	54	2.5	Yes	67

[a] Mg. per sq. dm. per day.

Table X. Results of Tests in Plant I

(7.6-hour run)

Station	Temp.	Velocity	Corrosion of Nickel			Corrosion of Copper	Corrosion of Nickel-Silver	Corrosion of Chromium-Nickel	Location of Test Stations
	° C.	M./min.	Test 1 M. d. d.[a]	Test 2 M. d. d.	Av. M. d. d.	M. d. d.	M. d. d.	M. d. d.	
						HEATING			
1	7	5	0	..	0	40	18	7	Line from storage to regenerator
2	9	6	30	22	26	11	31	8	Outside 2nd tube from top regenerator
3	26	6	25	15	20	0	11	..	Outside 14th tube from top regenerator
4	49	6	0	0	0	69	0	0	Outside bottom tube regenerator
5	49	50	55	82	69	...	...	..	Line from regenerator to heater
6	50	50	89	58	73	156	110	0	In 2nd tube of heater
7	56	50	30	23	27	...	...	..	In 12th tube of heater
8	62	50	43	66	55	185	78	0	In 19th tube of heater
						HOLDING			
9	63	3	40	..	40	127	89	0	In 1st tube of holder
10	63	3	265	..	265	101	151	0	In last tube of holder
						COOLING			
11	62	50	552	..	552	210	202	0	In 1st tube of regenerator
12	58	50	1150	1090	1120	...	...	..	In 3rd tube of regenerator
13	55	50	1076	1095	1085	...	...	..	In 5th tube of regenerator
15	51	50	888	882	885	...	...	..	In 7th tube of regenerator
16	48	50	825	..	825	81	124	9	In 9th tube of regenerator
17	45	50	747	700	724	...	...	..	In 11th tube of regenerator
18	42	50	658	663	660	...	...	..	In 13th tube of regenerator
19	38	50	497	..	497	...	...	..	In 15th tube of regenerator
20	35	50	490	..	490	...	...	..	In 17th tube of regenerator
21	32	50	307	..	307	...	...	..	In 19th tube of regenerator
24	17	50	195	..	195	...	...	..	In 29th tube of regenerator
25	15	50	370	..	370	32	37	0	Line from regenerator to cooler
26	15	6	129	132	130	40	33	..	Outside top tube of surface cooler
27	4	50	4	0	2	...	...	..	Line from cooler to filling machines

[a] Mg. per sq. dm. per day.

Table XI. Results of Tests in Plant II

(7.5-hour run)

Station	Temp.	Velocity	Corrosion of Nickel			Corrosion of Copper	Corrosion of Nickel-Silver	Corrosion of Chromium-Nickel	Location of Test Stations
	° C.	M./min.	Test 1 M. d. d.[a]	Test 2 M. d. d.	Av. M. d. d.	M. d. d.	M. d. d.	M. d. d.	
						HEATING			
1	4	75	0	...	0	48	18	0	In line from storage tank to heater
2	7	75	2	...	2	55	17	0	In 2nd tube of heater
3	20	75	2	...	2	52	45	0	In 18th tube of heater
4	37	75	0	0	0	...	...	..	In 24th tube of heater
5	60	75	0	...	0	130	11	0	In 38th tube of heater
6	63	75	0	...	0	142	49	0	In line from heater to filters
						HOLDING			
7	62	Low	97	...	97	106	150	0	In holding tank
8	62	Low	97	56	76	...	...	..	In holding tank
						COOLING			
9	61	75	328	...	328	238	395	0	In line from holders to coolers
10	57	32	379	...	379	225	404	0	In 2nd tube of cooler
11	52	32	610	721	666	...	...	..	In 6th tube of cooler
12	43	32	426	474	450	...	...	..	In 12th tube of cooler
13	35	32	119	...	119	60	48	0	In 18th tube of cooler
14	18	32	19	26	22	...	...	..	In 31st tube of cooler
15	4	75	4	...	4	42	17	0	In line from coolers to fillers

[a] Mg. per sq. dm. per day.

and the metal will presumably favor the formation of protective films.

After the milk has reached the holding stage and no further rise in temperature occurs, the protein film at the air-milk interfaces starts to become stabilized. This process is not ordinarily completed during the holding period, and consequently some protection can take place even in the first stages of the cooling process. When the milk is cooling down, the tendency will be for the air to redissolve in the milk and for the metal walls to be perfectly wetted by the milk. No new air bubbles will form, and the old ones will contract and become stabilized so that corrosion may proceed unhindered.

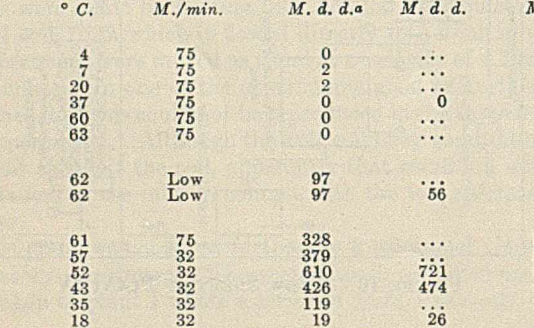


Figure 11. Flow Sheet of Plant V

In addition to the collection and denaturation of protein at the air-liquid interfaces, the formation of a protective film depends, of course, upon a high specific adsorption of protein or denaturated protein by nickel. Otherwise, it would be expected that copper, for example, would receive exactly the same protection. This the laboratory and plant tests show definitely not to be the case.

Plant Corrosion Tests

There is a considerable variation from plant to plant in the types and layout of equipment used for pasteurizing milk. This will be evident upon inspection of the flow sheets for six different plants shown in Figures 7 to 12. Of course, the condition of the milk, as it affects corrosion, varies markedly from plant to plant, owing especially to effects of the design and operating characteristics of the equipment on the temperature, degree of aëration, and velocity of the milk. The approximate velocities and temperatures at the various points in each plant have been listed in Tables X to XV. Since milk entering a plant is usually well aërated, the degree of aëration can be estimated at different stages of the pasteur-

TABLE XII. RESULTS OF TESTS IN PLANT III

(7.6-hour run)

STATION	TEMP.	VELOCITY	Pieces	CORROSION OF NICKEL Min.	Max.	Av.	Pieces	CORROSION OF COPPER Min.	Max.	Av.	CORROSION OF CHROMIUM-NICKEL	LOCATION OF TEST STATIONS
	° *C.*	*M./min.*		*M. d. d.*[a]	*M. d. d.*	*M. d. d.*		*M. d. d.*	*M. d. d.*	*M. d. d.*	*M. d. d.*	
							HEATING					
1	6–14	32	1	7	..	7	1	22	..	22	5	In raw milk line
2	8–15	32	3	5	21	13	2	62	85	73	10	Inside regenerator tube 1
3	15	32	2	5	7	6	1	79	..	79	..	Inside regenerator tube 8
4	22	32	2	0	86	28	2	40	74	57	7	Inside regenerator tube 15
5	28	32	2	17	34	25	1	83	..	83	..	Inside regenerator tube 20
6	35	32	3	5	37	24	4	52	77	62	4	Inside regenerator tube 26
7	49	32	7	8	16	11	3	90	115	105	8	Inside regenerator tube 38
8	48	32	1	49	..	49	2	91	95	93	8	In line to heater
9	62	32	1	114	..	114	1	174	..	174	11	In line to holder
							HOLDING					
10	63	Low	3	30	51	37	1	42	..	42	5	In holding tank
							COOLING					
11	62	32	3	634	663	649	3	183	199	191	7	In line to regenerator
12	61	60	3	640	717	660	3	212	222	217	9	In line to regenerator
13	60	6	4	592	886	751	7	159	190	168	..	Outside regenerator tube 38
14	50	6	..	...	...	...	2	113	120	116	..	Outside regenerator tube 32
15	40	6	4	482	785	604	7	74	83	78	..	Outside regenerator tube 26
16	33	6	..	...	...	...	2	58	86	72	..	Outside regenerator tube 20
17	27	6	..	...	...	...	8	33	49	41	..	Outside regenerator tube 14
18	20	6	..	...	...	...	2	23	30	26	..	Outside regenerator tube 8
19	13	6	..	...	...	...	5	17	21	20	..	Outside surface cooler top tube
20	8	6	..	...	...	...	4	13	18	16	..	Outside surface cooler middle
21	3	32	3	3	11	7	6	15	37	24	13	Inside line to filling machine

[a] Mg. per sq. dm. per day.

TABLE XIII. RESULTS OF TESTS IN PLANT IV

(7.5-hour run)

STATION	TEMP.	VELOCITY	CORROSION OF NICKEL Test 1	Test 2	Av.	CORROSION OF COPPER	CORROSION OF CHROMIUM-NICKEL-IRON	LOCATION OF TEST STATIONS
	° *C.*	*M./min.*	*M. d. d.*[a]	*M. d. d.*	*M. d. d.*	*M. d. d.*	*M. d. d.*	
					HEATING			
1	5	67	14	21	17	30	...	In line from clarifier to heater
2	63	?	0	0	0	70	...	In trough underneath surface heater
3	62	70	0	15	8	61	...	In line from heater to holder
					HOLDING			
4	62	Low	50	70	60	70	0	In holder
					COOLING			
5	61	Low	425	...	425	140	0	In equalizing tank after holder
6	60	70	364	370	367	203	...	In line from equalizing tank to cooler
7	59	?	302	314	308	184	...	In trough over surface cooler
8	4	67	4	44	24	18	...	In line from surface cooler to fillers

[a] Mg. per sq. dm. per day.

izing process by considering the opportunity presented for air to leave the milk as it is heated and to redissolve in milk as it is cooled. Surface heaters and open holders, of course, favor loss of dissolved air on heating; closed heaters and holders favor retention of air; and combinations of such equipment give intermediate degrees of aëration of the cooling milk. Plant I is a typical example of a closed system where the degree of aëration is high; plant IV of an open system where the degree of aëration is low; and plant VI, with a closed heater and open holders, of a system where an intermediate degree of aëration can be expected. Similarly, surface coolers favor more rapid solution of air than closed coolers.

During the progress of this work, a large number of plant tests were run to determine the rates of corrosion of different metals in the plants, to check the results of the laboratory work, and to investigate conflicting reports on the behavior of the metals in service.

Cleaned and weighed samples of the various metals were exposed to milk within the operating equipment during regular runs in six plants.

The metal specimens were supported and insulated from each other and from the equipment by the holder illustrated in Figure 13, which accommodated four U-shaped specimens about 7 by 1.25 cm., the area of each being 0.17 sq. dm. The collar-shaped specimens were formed by rolling up metal strip of the proper size. The outside of the collars, in contact with the tube walls, was covered with an insulating lacquer baked on to provide the necessary electrical insulation and to confine corrosion to the inner surface of the specimens. In certain cases the lacquer insulation was supplemented by the use of Bakelite cloth or Cellophane between the specimens and the tube walls. These collars were 5 cm. long and had an exposed area of about 0.75 sq. dm. They were purposely rolled up slightly oversize so that they could be held in place by the slight spring action. The bent specimens for use on the outside of tubes were simply rolled up so as to fit snugly. They were insulated from the equipment by the use of lacquer and other materials. They were 8.25 by 6 cm., and had an exposed area of 0.5 sq. dm.

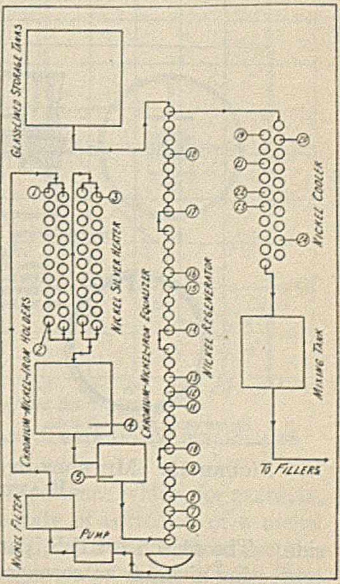


FIGURE 12. FLOW SHEET OF PLANT VI

The results obtained are covered by Tables X to XV and shown graphically in Figures 14 to 17. In view of the limited number of points in certain cases, the connecting lines should not be used for interpolation of corrosion rates between the points, but simply for identification purposes. The

Table XIV. Results of Tests in Plant V

(5.25-hour run)

Station	Temp.	Velocity	Corrosion of Nickel Test 1	Corrosion of Nickel Test 2	Corrosion of Nickel Av.	Corrosion of Copper Test 1	Corrosion of Copper Test 2	Corrosion of Copper Av.	Location of Test Stations
	° C.	M./min.	M. d. d.[a]	M. d. d.	M. d. d.	M. d. d.	M. d. d.	M. d. d.	
						HEATING			
1	6	60	13	16	14	56	...	56	In raw milk line from storage tank to regenerative heater
2	48	60	13	15	14	90	...	90	In line from regenerator to heater
3	50	60	20	34	27	111	...	111	In 1st tube of heater
4	63	60	12	17	15	205	...	205	In last tube of heater
						HOLDING			
5	62	Low	86	92	89	64	102	83	In holding tank
5	62	Low	73	86	79	96	102	99	In holding tank
						COOLING			
6	61	60	918	958	938	291	...	291	In line from equalizing tank to regenerator
7	60	6	790	...	790	207	211	209	Outside top tube of regenerator
8	38	6	468	...	468	45	95	70	Outside 13th tube from top of regenerator
9	18	30	332	470	401	56	...	56	In line from regenerator to surface cooler
10	18	6	185	...	185	26	27	27	Outside top tube of surface cooler
11	13	6	...	...	...	14	...	14	Outside 9th tube from top of surface cooler
12	7	6	...	...	...	24	...	24	Outside 17th tube from top of surface cooler

[a] Mg. per sq. dm. per day.

Table XV. Results of Tests in Plant VI

(4.8-hour run)

Station	Temp.	Velocity	Pieces	Corrosion of Nickel Min.	Corrosion of Nickel Max.	Av.	Corrosion of Copper	Corrosion of Chromium-Nickel	Corrosion of Chromium-Nickel-Iron	Location of Test Stations
	° C.	M./min.		M. d. d.[a]	M. d. d.	M. d. d.	M. d. d.	M. d. d.	M. d. d.	
						HEATING				
1	49	43	4	132	178	155	73	8	..	Inside heater tube 1
2	54	43	2	15	42	29	121	3	..	Inside heater tube 10
3	62	43	4	56	110	81	141	5	..	Inside heater tube 20
						HOLDING				
4	63	Low	4	194	250	214	90	2	..	Inside holding tank
						COOLING				
5	62	Low	2	99	134	117	...	..	0	Inside equalizing tank
6	59	34	4	450	508	477	115	0	8	Inside regenerator tube 2
8	56	34	2	513	534	523	...	..	19	Inside regenerator tube 4
9	53	34	2	550	558	554	96	18	..	Inside regenerator tube 6
11	47	34	2	472	473	473	78	0	..	Inside regenerator tube 10
13	43	34	3	427	458	447	...	..	..	Inside regenerator tube 12
15	34	34	2	426	431	428	...	0	11	Inside regenerator tube 18
19	16	34	2	226	240	233	31	23	..	Inside cooler tube 2
21	13	34	2	118	123	120	...	..	..	Inside cooler tube 6
22	10	34	1	82	...	82	23	27	6	Inside cooler tube 10

[a] Mg. per sq. dm. per day.

station numbers referred to in the tables are indicated on the flow sheets by numbers inside circles designating the locations of the test specimens.

The graph in Figure 14 covers the results obtained with nickel. A marked difference will be noted between the corrosion rates obtained in the cooling part of the process and those associated with similar temperatures on the heating side. The reason for this, particularly the effect of films in protecting nickel from corrosion in heaters, has already been discussed in detail. The rates of corrosion of nickel during the heating and holding steps of the pasteurizing process fell within a narrow range in all the plants. In the cooling processes, however, a much wider spread was observed, owing chiefly to differences in aëration and velocity from plant to plant.

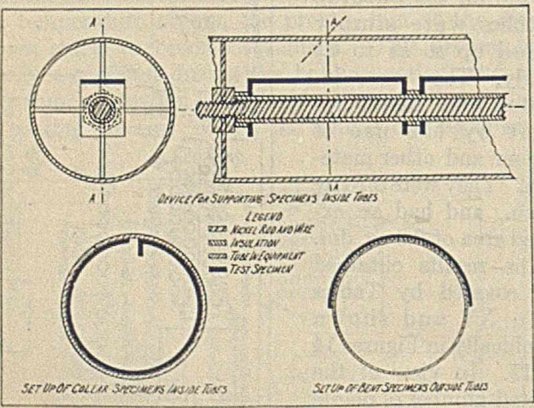


Figure 13. Methods of Supporting Specimens in Plant Tests

For instance, the corrosion rate of 1120 mg. per square decimeter per day in the third tube of the regenerator in plant I (milk at 58° C., velocity of flow 50 meters per minute) could be compared with the rate of 367 mg. per square decimeter per day in the inlet to the surface cooler in plant IV (milk at 60° C., velocity of flow 70 meters per minute). The probable reason for the much higher corrosion rate in plant I, in spite of the lower velocity and temperature, is that in plant I the milk was pasteurized, using closed heaters and holders; and therefore there was no chance for dissolved air to leave the milk as the temperature was raised. As a result the milk entering the regenerator was supersaturated with air, since it contained the concentration of dissolved air soluble in milk at the temperature at which it entered the heaters. In plant IV all the equipment was open to the air, and the concentration of dissolved air at the entrance to the coolers was no greater than that normally dissolved in milk at the pasteurizing temperature. While it is possible that the maximum rate of corrosion in plant IV was not reached at the temperature at which the test was made, it is not at all likely that the maximum rate approached the high rates found in plant I.

The laboratory and plant tests which have been described demonstrated certain general principles, the proper application of which will serve to explain differences in corrosion rates from plant to plant or at different points in any one plant.

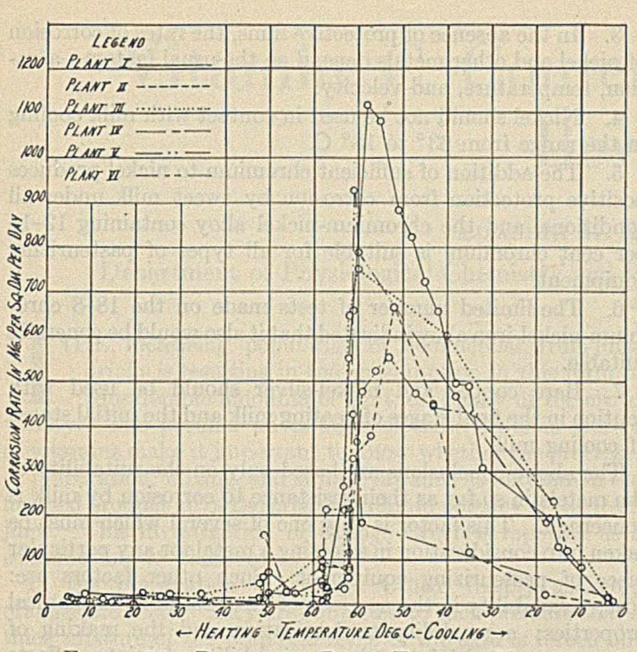


FIGURE 14. RESULTS OF PLANT TESTS ON NICKEL

The following factors were found to favor high rates of corrosion of nickel in the cooling process:

High temperature.
High rates of flow.
A high degree of aëration or supersaturation with air, such as occurs with closed heating and holding equipment.
A short pasteurizing run. Since the rate of corrosion of nickel was found to decrease with time, the rate of corrosion measured over a 5-hour period would be greater than that measured over an 8-hour period.

Similarly, in the heating process the factors conducive to the formation of protective films and hence to low corrosion rates of nickel were found to be:

Increase in temperature of milk or maintenance of a steady temperature.
High rates of flow.
Complete aëration or supersaturation of the milk.

An examination of Figure 15, covering the rates of corrosion of copper in the several plants, will show that, while there was some variation in rates from plant to plant and between the heating and cooling processes, there was no tendency for the copper to be protected on the heating side. The governing factors in the corrosion of copper were found to be temperature, velocity of flow, and degree of aëration. A consideration of these factors will indicate the probable reasons for the variations in corrosion rates determined.

The rates of corrosion of nickel-silver in plants I and II are shown in Figure 16. There was some tendency for nickel-silver to be protected on the heating side. This protection was not as positive as with nickel, so that the corrosion of nickel-silver in heaters and holders was apt to vary widely owing to slight changes in operating conditions. On the cooling side, nickel-silver behaved normally, in that the rate of corrosion was a function of the temperature, velocity, and degree of aëration of the milk. The higher corrosion rates obtained in plant II were probably due to the greater velocity at the points of test—75 meters per minute as compared with 50 meters per minute in plant I.

To facilitate comparison of the various metals, the graph shown in Figure 17 was prepared. The points plotted were the grand averages of the corrosion rates of each metal in the different temperature ranges in all plants. In selecting figures for the grand average, only those corrosion rates determined in milk flowing at a reasonably high velocity were used; furthermore, in order to avoid giving too much weight to those plants in which a large number of tests were made, an average figure for each plant was determined in each temperature range and these average figures used in making up the grand average.

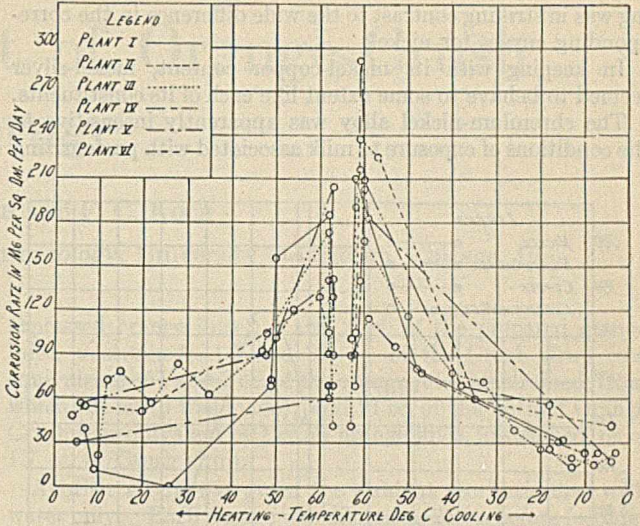


FIGURE 15. RESULTS OF PLANT TESTS ON COPPER

These grand average curves demonstrate quite clearly the fundamental differences in the behavior of the various metals. It should be noted especially that the maximum rate of corrosion of nickel did not occur at the highest temperature on cooling and was not developed until the milk had cooled from 5 to 10 degrees below the holding temperature. This fact was in accord with plant experience which, for example, had shown that the maximum rate of corrosion of a nickel regenerator was found in the middle of the bottom section, whereas the first tube in the regenerator and the tube from the holder to the regenerator suffered relatively less corrosion.

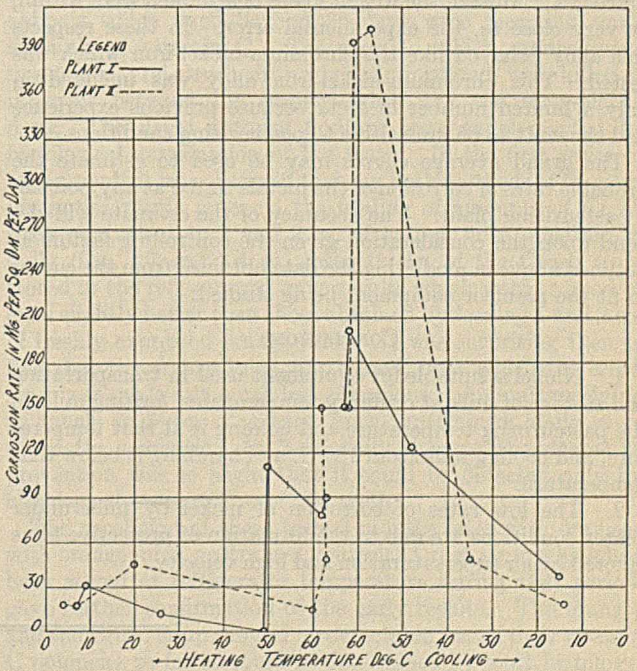


FIGURE 16. RESULTS OF PLANT TESTS ON NICKEL-SILVER

The similarity of the curves for copper on heating and cooling was in striking contrast to the wide difference in the corresponding curves for nickel.

In keeping with its nickel-copper content, nickel-silver seemed to behave to some extent like each of its constituents.

The chromium-nickel alloy was apparently insensitive to the conditions of exposure to milk associated with pasteurizing processes. Most of the weight losses determined were within, or very close to, the experimental error. In these respects this alloy behaved like the chromium-nickel-iron which was tested. This chromium-nickel-iron alloy was included in only a limited number of tests because previous experience had shown it to be insensitive to pasteurizing conditions.

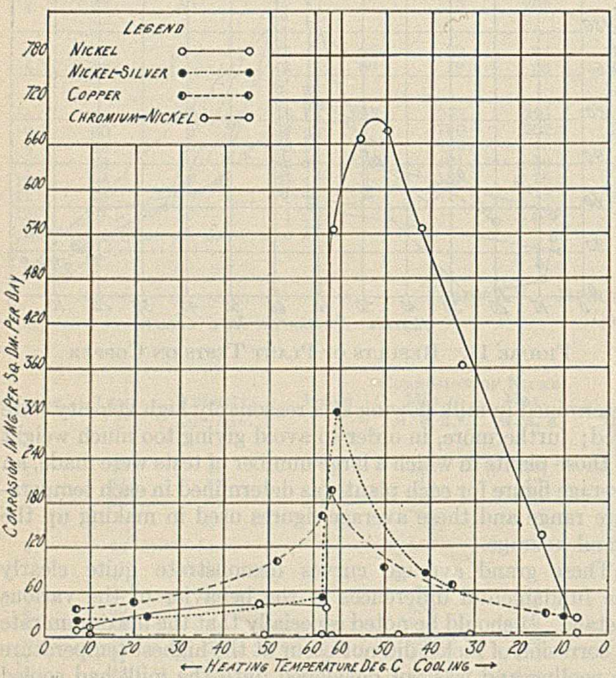


FIGURE 17. AVERAGE RESULTS OF TESTS IN ALL PLANTS

The grand average curves may be used to estimate the probable rates of corrosion of the metals tested at any point in a pasteurizing plant. The accuracy of the estimate will depend upon the consideration given the controlling factors as outlined above in modifying the data obtained from the curves to fit the plant or equipment being studied.

CONCLUSIONS

1. Nickel is suitable for equipment used in transportation and storage of milk at ordinary temperatures, heating milk to the pasteurizing temperature and holding it at that temperature, and cooling milk from 18° C. and handling it below that temperature.

2. The low rates of corrosion of nickel by milk under heater conditions are due to the formation of protective films favored by air supersaturation and high velocity.

3. In the absence of protective films, the rates of corrosion of nickel and other metals depend on the usual factors—aëration, temperature, and velocity.

4. Nickel should not be used in contact with milk cooling in the range from 63° to 18° C.

5. The addition of sufficient chromium to nickel produces positive protection from corrosion by sweet milk under all conditions, and the chromium-nickel alloy containing 12–15 per cent chromium is suitable for all types of pasteurizing equipment.

6. The limited number of tests made on the 18–8 chromium-nickel-iron alloy indicated that it also would be generally suitable.

7. Bare copper and nickel-silver should be used with caution in the final stages of heating milk and the initial stages of cooling milk.

The above conclusions are based only on the suitability of the metals in so far as their resistance to corrosion by milk is concerned. This factor is only one of several which must be taken into consideration in selecting a metal for any particular piece of pasteurizing equipment. Such other factors are: cost; availability in the necessary forms; suitable mechanical properties; amenability to fabrication and the making of common types of joints; the serviceability of joints; effects on the flavor and keeping quality of milk; and resistance to corrosion by cooling media, cleansing, and sterilizing agents.

ACKNOWLEDGMENT

The authors wish to express their gratitude for the friendly coöperation and the helpful criticism of R. J. McKay and O. B. J. Fraser of the International Nickel Company, and J. H. Schrader and F. M. Scales of the National Dairy Products Corporation. The assistance of G. L. Cox of the International Nickel Company, who performed some of the experiments to determine the temperature-velocity-corrosion rate relations for nickel, is greatly appreciated.

LITERATURE CITED

(1) Bogue, R. H., "Theory and Application of Colloidal Behavior," Vol. II, pp. 785–6, McGraw-Hill, 1924.
(2) Fraser, O. B. J., Ackerman, D. E., and Sands, J. W., IND. ENG. CHEM., 19, 332–50 (1927).
(3) Guthrie, E. S., Roadhouse, C. L., and Richardson, G. A., *Hilgardia*, 5, 425–553 (1931).
(4) Hunziker, O. F., Cordes, W. A., and Nissen, B. H., *J. Dairy Sci.*, 12, 140–81 (1929).
(5) McKay, R. J., Fraser, O. B. J., and Searle, H. E., Am. Inst. Mining Met. Eng., *Tech. Pub.* 192 (1929).
(6) Rogers, L. A. (Associates of), "Fundamentals of Dairy Science," pp. 138–9, Chemical Catalog, 1928.

RECEIVED August 26, 1931. Presented before the Division of Industrial and Engineering Chemistry at the 82nd Meeting of the American Chemical Society, Buffalo, N. Y., August 31 to September 4, 1931. The study upon which this paper was based was a coöperative effort between the technical staffs of a large user of dairy equipment and a producer of metal used in its construction. Consultation was handled during the tests with executives and engineers of an equipment manufacturer.

PROCESS GIVES SOFT METALS STRENGTH OF STEEL. At the meeting of the American Institute of Mining and Metallurgical Engineers recently held in New York City, Paul D. Merica stated that many metals and alloys hitherto mechanically inferior to steel may be brought to the standard of steel, as far as mechanical properties are concerned, because of the development within the past decade of the age-hardening process. Until recently steel has been practically the only metal capable of hardening and strengthening by heat treatment. Now all of the common metals may be so alloyed. Copper-nickel alloys, for instance, may be heat-treated to exhibit tensile strength of 175,000 pounds per square inch. After certain heat treatment, Doctor Merica explained, these alloys harden as they grow older, sometimes at room temperature and sometimes at higher temperatures. A single day is often sufficient to bring about the desired changes in the mechanical properties, although slight changes may continue for a month. Doctor Merica predicted that the next ten years will undoubtedly witness a substantial realization of the promise contained in the development of the hardening process.

Vitamin C Content of Orange-Crush Beverage

Elizabeth M. Koch and F. C. Koch

Department of Physiological Chemistry and Pharmacology, University of Chicago, Chicago, Ill.

THE increasing popularity of commercial fruit-juice drinks is resulting in the consumption in this form of considerable amounts of fruit, especially of the citrus variety. The peculiar advantages of these fruits as sources of vitamins make it important to know whether the processes of preparation, mixing, and storage are such as to retain in the finished product all of the original vitamin potency of the fresh juice. This investigation of Orange Crush is reported as a contribution to these questions.

In the preparation of Orange Crush, freshly gathered oranges are used. They are subjected to such pressure that a thick mixture of the pulp and some of the skin is forced out with the juice. To this mixture of juice and pulp are added sugar, lemon citric acid, small amounts of preservative, and a color, consisting of a mixture of Sunset Yellow F. C. F. and No. 150 (85) Orange I. The resulting Crush sirup is stored in bulk at refrigerator temperature until it is to be diluted for the finished drink. Carbonated or plain tap water is used for the final dilution. It is added to the sirup by the retail dealer, who is instructed to prepare not more than a week's supply at one time.

The following materials, freshly prepared from one lot of oranges, were supplied:

1. Orange juice, unstrained, pressed from freshly gathered oranges.
2. Crush sirup, made from 1 by the addition of sugar, lemon citric acid, and small amounts of sodium benzoate and color.
3. Bottled Orange Crush, prepared by dilution of the sirup with carbonated tap water.
4. Bottled carbonated tap water and distilled water.

The antiscorbutic potency of these orange preparations was compared with equivalent amounts of the juice of some of these same oranges expressed daily.

EXPERIMENTAL PROCEDURE

The diet first used, consisting of oatmeal, autoclaved hay, and 20 cc. of whole milk daily, was one previously employed in this laboratory. Preliminary feeding experiments were run to determine how much of the Crush sirup and dilute Orange Crush the guinea pigs could be induced to consume. It was a simple matter to give the orange juice, unstrained, in 5-cc. amounts mixed with the liquid milk, but the Crush sirup with the added citric acid curdled the milk, making a thick mixture which was left almost untouched. Of the dilute Orange Crush, pigs weighing 300 to 350 grams took readily 21 cc., the equivalent of 1 cc. of original orange juice unstrained. Some of the pigs would drink as much as 30 to 40 cc., but these results could not be relied upon for all of the experimental animals.

In view of these preliminary findings, it was obvious that the total volume of liquid must be kept within 20 to 25 cc. Dried whole milk was therefore substituted for the liquid milk and mixed thoroughly with the oatmeal. The various orange-juice preparations were diluted with water to the desired volume—21 cc. total. Seven groups of four pigs each were given daily the following preparations: 1 and 2 cc. of freshly expressed orange juice; 1 and 2 cc. of the prepared orange juice, unstrained; 1.7 and 3.4 cc. of the Crush sirup (the equivalents of 1 and 2 cc. of the orange juice, unstrained, from which the sirup was made); and 21 cc. of the bottled Orange Crush the equivalent of 1 cc. of orange juice, unstrained, or of 1.7 cc. of Crush sirup.

Another group was given the straight scorbutic diet with water only. Each dosage was diluted to 21 cc. before feeding. The diluted fruit juice was ordinarily consumed within 4 to 5 hours after feeding. After the consumption of the diluted juice, fresh water was placed in the cage.

Three months later these experiments were repeated to ascertain what loss of vitamin C had occurred during storage of the fruit and juice preparations at refrigerator temperature. A portion of the orange juice, unstrained, was also frozen within 48 hours after it was expressed and kept in that condition for three months.

RESULTS

Some of the pigs which developed acute scurvy were killed on the twenty-eighth day of the experimental period. Others were permitted to live until death occurred some time between the twenty-eighth and the forty-eighth days. The animals which lived beyond 36 days were receiving small amounts of vitamin C. The pigs to which orange juice, unstrained, and Crush sirup were administered, were killed at intervals between the twenty-eighth and the forty-eighth days. The usual autopsy findings were supplemented by histological examination of the teeth. In the first series of experiments it was observed that, by both methods of measuring antiscorbutic potency, the feeding of amounts of Crush sirup equivalent to 1 and 2 cc. of orange juice, unstrained, daily (i. e., 1.7 and 3.4 cc., respectively, of the Crush sirup stored in the refrigerator) gave results which were as good or even slightly better than those obtained by feeding 1 and 2 cc. of freshly expressed orange juice. It was surprising then to find that the orange juice, unstrained, from which the crush sirup was made was much less efficacious. Animals receiving as much as 5 cc. of orange juice, unstrained, daily were distinctly scorbutic. In 2-cc. daily dosages the degree of prevention was so slight that it could be detected only by histological examination of the teeth.

The repetition of these tests 3 months later with oranges, with orange juice, unstrained, and with Crush sirup which had been stored at refrigerator temperature during that period, gave further confirmation of the early results. The oranges and the Crush sirup showed no detectable loss of their vitamin C potencies so far as could be determined by tooth histology. The orange juice unstrained, on the other hand, showed no antiscorbutic action in the dosages fed. The same loss of antiscorbutic potency was observed in the orange juice, unstrained, which had been frozen within 48 hours after it was expressed and kept in that condition for 3 months.

In view of these observations with orange juice, unstrained, it was not surprising to find that the diluted Orange Crush which was bottled and stored in the refrigerator for 50 days before the close of the experiment, showed no detectable antiscorbutic potency in the dosage fed. The pigs in this group were all dead of scurvy by the thirty-ninth day of the experimental diet. Whereas this is a few days beyond the life period of the control scurvy animals, the tooth histology showed no evidence of prevention.

These results demonstrated first that the fruit itself stored at refrigerator temperature retains its vitamin C content at least for 3 months; second, that the orange juice, unstrained, expressed from these oranges, loses its antiscorbutic potency so rapidly that a test which extends over 4 weeks demonstrates that loss, and that at the end of 3 months the destruction appears to be practically complete; third, that a heavy Crush sirup made from this orange juice, unstrained, by adding sugar and preservative and acidifying with lemon citric acid retains the original vitamin C as satisfactorily as does the fruit itself during refrigerator storage for 3 months; and fourth, that this Crush sirup, when diluted to twelve volumes with carbonated water again loses its antiscorbutic action so rapidly that storage in that condition for 4 to 5 weeks is not feasible.

Since it is in this final diluted form that Orange Crush is dispensed to the public, it is highly important to know the rate of destruction of vitamin C under these conditions. The retailer is required to dilute and bottle Orange Crush weekly. Ten to fourteen days should, therefore, be the maximum lapse of time between dilution and consumption of this product. A final set of experiments was run in which one group of pigs was given 1 cc. of orange juice, equivalent per pig of a new supply of freshly prepared Crush sirup diluted daily. Another group of animals was given the same amount of Crush sirup which had been diluted, bottled, and allowed to stand in the refrigerator 10 days before feeding. A control scurvy group was run parallel to these. By the thirty-fifth day one of the scurvy pigs was dead. The other had lost 135 grams in weight and had swollen tender joints, red gums, and loose yellow teeth. The autopsy findings were those of advanced scurvy. The pigs in the other two groups were either holding their maximum weight or gaining slowly. They were fairly strong and active, and their fur was smooth and well-kept. The autopsy findings were those of mild scurvy. The antiscorbutic potency of this sample of Crush sirup was undoubtedly higher than that of the original lot supplied for the earlier experiments reported above. The important consideration in this experiment, however, was that the 10-day storage period at refrigerator temperature did not produce sufficient deterioration of the antiscorbutic potency to be detected by such biological tests. It must be borne in mind, nevertheless, that in making this dilution there was a minimum of exposure to air and room temperature.

These observations tend to the conclusion that the preservation of antiscorbutic activity in the Crush sirup is due to the high acidity and possibly to the sugar content, and that the loss of potency following dilution is the result of decreased protective action and takes place gradually. It may be that traces of chlorine or other constituents of tap water have slight destructive action. These factors appear to be insignificant, however, for it apparently makes no difference whether the dilution is made with ordinary tap water, carbonated water, or carbonated distilled water. Removel of carbon dioxide from the diluted sirup by suction was of no significance.

Since the orange juice, unstrained, from which the Crush sirup is prepared contains appreciable amounts of pulp and skin as compared with the hand-expressed orange juice, it seemed logical to expect somewhat less vitamin C potency in the Crush sirup than in the freshly expressed juice. This was not the case however; in fact, the difference, if any, was in favor of the Crush sirup. This result raised the question of whether the added citric acid, which is prepared from lemons, does not carry some vitamin C. Samples of citric acid prepared from lemons and also by fermentation were secured and added to a sugar solution so that 20 cc., the daily intake, contained 0.2 gram of acid. This amount was four times the intake of citric acid when 1.7 cc. of Crush sirup were administered. However, in neither case did the citric acid solution have the slightest effect in delaying the onset of acute scurvy. Obviously then, the vitamin C of the Crush sirup is derived entirely from the orange juice, unstrained, and probably is preserved by the addition of citric acid, or in part, perhaps, by the high sugar content. In 3 months there was no apparent loss of this potency unless the Crush sirup was diluted again to a low acidity.

CONCLUSIONS

Experiments conducted to determine whether the commercial orange-juice drink called Orange Crush retains the vitamin C originally present in the fruit have resulted in the following conclusions:

1. The orange juice, unstrained, commercially expressed from freshly gathered oranges was as potent in vitamin C as ordinary hand-expressed juice.
2. When stored either frozen or at refrigerator temperature in this form, it lost that potency so rapidly that the loss was marked during a 4-week test period, and practically complete at the end of 3 months.
3. When this orange juice, unstrained, was diluted to 1.7 times its volume of Crush sirup by the addition of sugar, lemon citric acid, and a small amount of preservative and coloring, it retained the original vitamin C practically undiminished for a period of 3 months.
4. The antiscorbutic potency of the Crush Sirup was not a result of any vitamin having been added with the citric acid. The vitamin of the original juice appeared to be preserved by the high acidity and possibly high sugar content of the sirup. The preservative action of the acid sirup is of academic and commercial interest.
5. When the final beverage, Orange Crush, was prepared commercially from the crush sirup by diluting 12.3 times with carbonated water, the resulting product gradually lost its vitamin C potency.
6. When the same dilution was made in the laboratory with a minimum opportunity for exposure to air and room temperature, and the diluted bottled product was stored in the refrigerator 10 days before feeding, there was no detectable loss of antiscorbutic potency.
7. The results show that if the final dilution of Crush sirup is done in accordance with the precautions stipulated by the company and dispensed within 10 days, the final bottled Orange Crush retains essentially the original vitamin C activity; that is, it contains the vitamin C from 1 cc. of orange juice per 21 cc. of Orange Crush. It appears, therefore, that a maximum interval of 10 to 14 days between dilution and consumption of the finished product assures the presence of antiscorbutic potency in Orange Crush as it is dispensed to the public.

ACKNOWLEDGMENT

The authors wish to express to R. R. Bensley, William Bloom, and I. Shouer, of the department of anatomy, University of Chicago, appreciation for their generous assistance in preparing and interpreting the various tooth sections.

RECEIVED October 19, 1931. The expense of this investigation was in part borne by the Orange Crush Company through the courtesy of W. D. Bost.

Comparative Study of Juices from Frozen Fruits

T. A. Pickett, Georgia Experiment Station, Experiment, Ga.

During the last few years there has been a great deal of controversy concerning the optimum temperatures at which to freeze and store foodstuffs. Some data have already been obtained on fruits, using organoleptic tests. These tests, however, are subject to great individual differences, and it is desirable to have data not influenced by these variations.

The fruits used in this work were blackberries, cherries, dewberries, peaches, pears, plums, raspberries, and strawberries. One principal variety of each fruit was used, except for peaches where several varieties were used. Altogether, eight different fruits and twelve varieties of these fruits were used.

After the fruit was picked, it was sorted very carefully and as quickly as possible put into quart paper-board containers. The peaches were stored both whole and cut into slices. The other fruits were stored whole. Nothing else was added to any of the containers.

Method of Freezing and Testing

One sample of each fruit was tested immediately, and the other samples were divided into two groups. Some samples were put into a room at +10° F. (−12.2° C.) and thus were slow-frozen; the others were subjected to contact with either carbon dioxide snow or small fragments of carbon dioxide ice. These last samples were considered to be quick-frozen at approximately −100° F. (−73.3° C.). After they had been in contact with the solid carbon dioxide for 24 hours, one sample was tested and the others were placed at +10° F. (−12.2° C.) until they were examined.

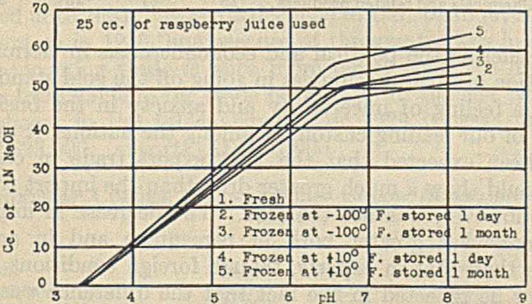


Figure 1. Titration Curves for Raspberry Juice

The fruits were taken out of the refrigerator room at intervals, and the juices expressed by the use of a hydraulic press. A pressure of 10,000 pounds per square inch (703 kg. per sq. cm.) was used. The juices were centrifuged to remove any solid materials that might come through the pressing cloths. The freezing-point depression, conductivity, and total solids were determined on some of the juices, and the hydrogen-ion concentration and titratable acidity were run on all of them. Total solids were determined by the Abbé refractometer, using the sugar scale. The hydrogen-ion concentrations and titratable acidities were obtained by using a hydrogen electrode against a saturated potassium chloride–calomel cell. The titratable acidities are tabulated in terms of cubic centimeters of 0.1 *N* sodium hydroxide per 100 cc. of juice. The end point is pH 8.3, approximately the turning point of phenolphthalein.

Effect of Freezing and Storing Period

The total solids and conductivities of the juices do not show very important differences among the samples. Some results (typical of many others) for the freezing-point depressions, hydrogen-ion concentrations, and titratable acidities are shown in Table I.

Table I. Results of Tests on Fruit Juices

Fruit	Temp. Frozen °F. (°C.)	Length of Storage at 10° F. (−12.2° C.)	Initial pH	0.1 *N* NaOH to Bring 100 cc. of Juice to pH 8.3 Cc.	Freezing-Point Depression ° C.
Strawberries	... ...	Fresh	3.50	190	0.65
	+ 10 (−12.2)	1 day	3.36	202	0.77
	+ 10 (−12.2)	1 month	3.35	210	0.84
	+ 10 (−12.2)	4 months	3.35	236	0.85
	−100 (−73.3)	1 day[a]	3.38	182	0.71
	−100 (−73.3)	1 month	3.35	190	0.78
	−100 (−73.3)	4 months	3.35	216	0.80
Red raspberries	... ...	Fresh	3.35	208	1.00
	+ 10 (−12.2)	1 day	3.30	234	1.16
	+ 10 (−12.2)	1 month	3.40	256	1.19
	−100 (−73.3)	1 day[a]	3.40	216	1.12
	−100 (−73.3)	1 month	3.40	226	1.15
Dewberries	... ...	Fresh	3.16	269	..
	+ 10 (−12.2)	1 day	3.15	302	..
	+ 10 (−12.2)	1 month	3.15	326	..
	−100 (−73.3)	1 day[a]	3.23	275	..
	−100 (−73.3)	1 month	3.40	296	..
Plums	... ...	Fresh	3.19	266	..
	+ 10 (−12.2)	1 day	3.16	282	..
	+ 10 (−12.2)	1 month	3.10	300	..
	−100 (−73.3)	1 day[a]	3.05	273	..
	−100 (−73.3)	1 month	3.16	292	..
Cherries	... ...	Fresh	3.35	260	..
	+ 10 (−12.2)	1 week	3.41	268	..
	+ 10 (−12.2)	2 weeks	3.40	276	..
	+ 10 (−12.2)	1 month	3.40	296	..
Mayflower peaches	... ...	Fresh	4.19	78	..
	+ 10 (−12.2)	1 day	4.13	80	..
	+ 10 (−12.2)	2 weeks	4.10	86	..
	+ 10 (−12.2)	1 month	4.00	88	..
	+ 10 (−12.2)	3 months	3.97	92	..
Early Rose peaches	... ...	Fresh	4.28	99	..
	+ 10 (−12.2)	1 day	4.15	108	..
	+ 10 (−12.2)	2 weeks	4.10	112	..
	−100 (−73.3)	1 day[a]	4.10	98	..
	−100 (−73.3)	2 weeks	3.95	100	..
Elberta peaches	... ...	Fresh	3.76	82	..
	+ 10 (−12.2)	1 week	3.95	96	..
	+ 10 (−12.2)	1 month	3.78	96	..
	−100 (−73.3)	1 week	3.80	92	..
	−100 (−73.3)	1 month	3.75	104	..
Blackberries	... ...	Fresh	3.22	230	..
	+ 10 (−12.2)	1 day	3.15	242	..
	+ 10 (−12.2)	1 month	3.20	250	..
	−100 (−73.3)	1 day[a]	3.26	235	..
	−100 (−73.3)	1 month	3.40	244	..

[a] Stored at −100° F. (−73.3° C.).

According to Nelson (*1*) in 1925, the acids of the red raspberry are mixtures of approximately 97 per cent citric acid and 3 per cent malic acid. The titration curves (Figure 1) for the juices from the fresh raspberry, raspberry frozen at +10° F. (−12.2° C.), and raspberry frozen at −100° F. (−73.3° C.) are similar to one another, and also to the curves of citric and malic acids. This indicates that the same type of acid is present in all of the juices, and therefore the gains in titratable acidity appear to be due, probably, to an increase in concentration of those particular acids present in the fresh berry—namely, citric and malic. Similar results were obtained with other fruit juices.

Discussion

The juices (frozen and tested immediately) from blackberries, cherries, dewberries, peaches, pears, plums, raspberries, and strawberries have a greater titratable acidity than juices from the fresh fruits. These differences appear to be due to a breaking down or increased permeability of the cells upon freezing, so that a more complete extraction takes place.

The juices from these fruits increase in titratable acidity as the length of storage at +10° F. (−12.2° C.) increases. This increase is due to some extent to dehydration of the fruit. Available data show, however, that dehydration is not sufficient to account for the entire increase in titratable acidity.

The juices of the fruits frozen and stored at +10° F. (−12.2° C.) have a greater titratable acidity than those frozen at −100° F. (−73.3° C.) and stored at +10° F. (−12.2° C.). This indicates that the juices of the fruits frozen at the lower temperature are more nearly like the fresh juices in titratable acidity than those frozen at the higher temperature.

The results from the freezing-point depressions for the juices studied—strawberries and raspberries—are similar to the results from the titratable acidities, in that the juices from the fruits frozen at the lower temperature are more like the fresh ones in freezing-point depressions than those frozen at a higher temperature.

The increases in acidity of the juices of the fruits upon freezing and storage are due to a concentration of the same type of acids present in the fresh juices.

Literature Cited

(1) Nelson, E. K., *J. Am. Chem. Soc.*, 47, 1177 (1925).

Received November 25, 1931. Published with the approval of the Director as Paper No. 34, Journal Series, Georgia Experiment Station.

Our Foreign Trade in Chemicals in 1931

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

Last year in this review the point was made that a full year of depression had served as a test for the chemical industries, determining whether the immense expansion of the preceding ten years was soundly based. So far as foreign-trade figures were significant, the returns showed that chemical manufacture was in a gratifyingly strong position. A second full year of hard times has furnished a still more severe test, and the results again show up well. Compared with other general industries, chemical manufacture and trade appear to be weathering the extended period of stagnation and low business morale in a highly encouraging fashion.

Last year, while the total foreign trade of the country was being cut down 35 per cent as compared with 1930, the foreign trade in chemicals and related products was falling off only 24 per cent. In the last two years, covering approximately the period of dull times, the United States has seen its commerce with other countries reduced 53 per cent, but in the buying and selling of chemicals the loss was only 38 per cent. The outgoing trade in chemicals, moreover, has fallen off considerably less than the incoming, exports losing only about one-third in the two years, and imports about 43 per cent. But the chief index to the standing of chemicals in our trade world and the comparative extent to which they have suffered is afforded by setting their record alongside that of other great groups of commodities. In compiling its foreign-trade returns, the government distinguishes ten broad classes of commodities. Out of these, the group covering chemicals and related products has suffered a loss in imports during the depression smaller than any other group save one, and its loss last year as compared with 1930 was also lower than all others save one. In the export trade the falling off was lower for the chemical trade than for any other, both last year and during the whole depression. The difference, moreover, was such as to make the trade in chemicals stand out noticeably, as the percentage of loss was considerably below the average for the other seven groups.

Comparative figures for these ten groups, showing both the decrease in import and export trade in 1931 as compared with 1930, and the decrease between 1931 and the banner year of 1929 will be of interest.

Decrease in U. S. Foreign Trade by Great Groups

No.	Commodity Group	Decrease in Imports 1930–1	Decrease in Imports 1929–31	Decrease in Exports 1930–1	Decrease in Exports 1929–31
		%	%	%	%
..	Total trade of U. S.	32	53	37	54
00	Animals and animal products, edible	37	57	37	52
0	Animals and animal products, inedible	34	58	32	47
I	Vegetable food products and beverages	22	43	28	50
II	Vegetable products, inedible, except fibers and wood	38	59	29	38
III	Textiles	31	59	34	57
IV	Wood and paper	26	37	36	54
V	Non-metallic minerals	37	50	42	50
VI	Metals and manufactures, except machinery and vehicles	45	63	49	66
VII	Machinery and vehicles	45	60	42	60
VIII	Chemicals and related products	26	43	22	34

Considering the political and economic crisis in Germany, the action of several countries in going off the gold standard, and the feeling of uncertainty and anxiety in the business circles of our leading customers among the nations, it might have been expected that the 1931 export trade in chemicals would show a much greater drop than the import trade. Such, however, was not the case. The decrease in imports was somewhat greater both in percentage and in actual dollars than that in exports, though foreign conditions may perhaps be reflected in the fact that the difference was not so great as in the previous year, the decrease in exports being larger than in 1930 and that in imports somewhat smaller. The balance of trade in favor of the United States is slightly higher than in 1930, showing a continuation of the tendency that has been in evidence over many years.

For the three years 1929–31, the total value of the import and export trade of the United States in chemicals and related products was as follows:

Year	Imports	Exports	Balance of Trade
1929	$144,062,000	$152,109,000	+$8,047,000
1930	112,070,000	127,855,000	+15,785,000
1931	82,738,000	100,133,000	+17,395,000

CHEMICALS AND RELATED PRODUCTS

Analyzing the 1931 returns for chemicals and related products, we find that all the subgroups under this classification, as was to be expected, suffered losses as compared with 1930. For most of them the rate of decrease was much the same as the average for all chemicals. Coal-tar products and explosives showed very heavy declines, both in the incoming and the outgoing trade. Imports of the former dropped off more than 30 per cent and of the latter more than 40 per cent, as compared with 26 per cent for the whole group of chemicals; in the export trade both classes of commodities dropped about 40 per cent as against 22 per cent for all chemicals. The best showing among the imports was that of medicinals, which decreased less than 20 per cent; and among the exports that of industrial specialties, comprising many articles of everyday use, which fell off less than 12 per cent. Most of the other groups exhibited about the average reduction of 20 to 30 per cent for imports and 15 to 25 per cent for exports. Leading commodities in the various groups likewise followed the general trend, although in a number of cases actual increases were registered. The 1931 trade by large groups as compared with that of the previous year is shown in the following table:

FOREIGN TRADE IN CHEMICALS AND RELATED PRODUCTS BY GROUPS

GROUP	IMPORTS		EXPORTS	
	1930	1931	1930	1931
Coal-tar products.....	$16,273,000	$11,163,000	$17,556,000	$10,347,000
Medicinal and pharmaceutical preparations	4,948,000	3,973,000	17,801,000	15,104,000
Industrial chemical specialties..........	[a]	[a]	15,589,000	13,754,000
Industrial chemicals...	23,300,000	17,199,000	23,015,000	19,774,000
Pigments, paints, and varnishes...........	2,613,000	2,017,000	21,689,000	15,127,000
Fertilizers and materials................	59,151,000	44,733,000	15,284,000	13,011,000
Explosives, fuses, etc...	911,000	520,000	2,950,000	1,734,000
Soap and toilet preparations.............	4,719,000	3,028,000	13,970,000	11,283,000

[a] Not separately stated.

COAL-TAR PRODUCTS

The marked falling off in the trade in coal-tar products was due to heavy decreases in both imports and exports. The drop in exports was larger, but it was probably due in part to the fact that the decrease in the preceding year had been comparatively slight in the face of a much larger decline in general exports, and a natural slump was merely delayed until 1931. Imports declined in 1931 to about the same extent as in 1930, but because of the greater loss in exports the incoming trade is once more larger than the outgoing. The total value of the trade both ways for the last two years is shown in the table above. For 1929 it was: imports, $22,823,000; exports, $18,061,000.

IMPORTS OF COLORS, DYES, STAINS, COLOR ACIDS, AND COLOR BASES

	1930		1931	
From:	*Pounds*	*Value*	*Pounds*	*Value*
Belgium	63,000	$81,000	49,000	$59,000
France	44,000	57,000	68,000	105,000
Germany	3,103,000	3,318,000	2,827,000	3,065,000
Italy	21,000	25,000	15,000	19,000
Switzerland	1,557,000	1,637,000	1,832,000	2,105,000
United Kingdom	114,000	119,000	107,000	117,000
Other countries	50,000	47,000	46,000	42,000
Total	4,952,000	5,284,000	4,944,000	5,512,000

The falling off in imports was due to a steep drop in our purchases of crudes and intermediates, as contrasted with an actual gain in those of finished coal-tar products. The largest item in the incoming trade is creosote oil. It decreased 54 per cent in value in 1931, dropping from $7,806,000 to $3,598,000, though the quantity held up better with 36,885,000 gallons as against 66,922,000 gallons in 1930. Intermediates likewise declined, the 1931 total being $679,000 as compared with $1,075,000 in the preceding year. In the trade in finished products, the slight gain of 1 per cent in imports stands out sharply against a 33 per cent loss in the year before. It was due to heavier shipments of colors, dyes, stains, etc., from Switzerland and France, which more than offset decreases from Germany (the leading source of supply) and other countries. The trade in these articles in 1929 amounted to 7,611,000 pounds valued at $8,470,000, and in 1930 and 1931 was as shown in the preceding table.

The value of our imports of coal-tar medicinals held up well last year, their total of $252,000 being only 8 per cent under that of the year before, whereas the quantity (39,000 pounds) represented a drop of 45 per cent.

In the export trade the 40 per cent slump is to be ascribed chiefly to a precipitous drop in sales of benzene. This may have been a compensation for unusually heavy shipments in 1930, when the trade exceeded even that of the highly prosperous year 1929. Quantities and value of benzene exports in the last three years were as follows: 1929, 33,346,000 gallons valued at $8,537,000; 1930, 44,600,000 gallons valued at $9,566,000; 1931, 21,861,000 gallons valued at $3,795,000. Although a considerable number of countries share in this trade, much the largest part of our shipments go to Germany and the United Kingdom, and the heavy decrease was due to a falling off in the demands from those countries. Whereas in 1930 benzene exports to Germany were valued at $4,656,000 and in 1929 to $4,460,000, in 1931 they were only $1,292,000. Although the trade with the United Kingdom was cut less severely, it was also sufficient to bring down the total noticeably; exports which registered $2,530,000 in 1930 and about the same in 1929 were reduced to $1,102,000 in 1931.

Exports of coal-tar colors, dyes, stains, and color lakes also dropped sharply, totaling 20,313,000 pounds valued at $4,739,000, as against 28,267,000 pounds valued at $6,246,000 in 1930. Coal-tar pitch, on the other hand, marked up a substantial increase, exports of 50,667 tons valued at $493,000 in 1931 representing a gain of 86 per cent in quantity and 70 per cent in value over 1930, when shipments were 27,221 tons valued at $51,000. Exports of crude coal tar (71,000 barrels valued at $207,000) were about one-fifth less than in 1930. Creosote oil amounting to 1,873,000 gallons valued at $254,000 was sold in 1931; it was not separately listed in 1930.

MEDICINALS AND PHARMACEUTICALS

Considering the general state of trade, imports of medicinals and pharmaceuticals stood up fairly well in 1931 with a loss of only about 20 per cent in value. Trade in one important commodity—quinine sulfate—showed an increase, the 1931 figures of 1,499,000 ounces valued at $498,000 comparing with 1,253,000 ounces valued at $449,000 in 1930. Imports, however, were still some 40 per cent below those of 1929. Menthol, the leading article in the medicinals group, also registered increased shipments in 1931, the total of 326,000 pounds comparing with 308,000 pounds in 1930, although lower prices kept the value down to $878,000 as against $1,017,000 in the previous year.

In the export trade about one-third of the items under medicinals and pharmaceuticals showed increases in value in 1931 as compared with 1930. The gains were small, but in such a year as 1931 they loomed up as very encouraging. The leading item in this group, a class of druggists' preparations listed as tablets, pills, capsules, powders, and similar manufactures, was one of those enjoying an increase, shipments abroad being valued at $2,160,000 as against $2,008,000 in 1930. Druggists' preparations in liquid form, such as elixirs, cordials, tinctures, and extracts, rose from $988,000 in 1930 to $1,049,000 in 1931, and glandular products, organo therapeutics, enzymes, ferments, and culture media from $746,000 to $817,000. Milk of magnesia dropped from $272,000 in 1930 to $195,000 in 1931. Castor oil valued at

Imports and Exports of Industrial Chemicals

Imports	1930 *Pounds*	1931 *Pounds*
Acetylene, butylene, ethylene, and propylene derivs.	282,000[a]	567,000
Acids and anhydrides:		
Acetic or pyroligneous	22,377,000	15,292,000
Arsenious (white arsenic)	21,559,000	15,531,000
Formic	510,000	140,000
Oxalic	574,000	489,000
Sulfuric (oil of vitriol)	918,000	2,344,000
Tartaric	2,912,000	2,246,000
All other	2,330,000	1,333,000
Alcohols, n. e. s. [c] including fusel oil, value	$30,000	$11,000
Ammonium compounds, n. e. s.:		
Chloride (muriate)	6,628,000	5,672,000
Nitrate	8,165,000	6,706,000
All other	661,000	526,000
Barium compounds	6,706,000	4,186,000
Calcium compounds, n. e. s.	1,978,000	413,000
Cellulose products, n. e. s.:		
Acetate	6,000[a]	48,000
All other:		
Sheets, more than 0.003 inch thick and other forms	143,000[a]	175,000
Sheets, bands, and strips more than 1 inch wide, not more than 0.003 inch thick	203,000[a]	40,000
Cobalt oxide	426,000	318,000
Copper sulfate (blue vitriol)	5,964,000	2,644,000
Glycerol:		
Crude	10,906,000	9,951,000
Refined	3,177,000	1,976,000
Iodine, crude	494,000	279,000
Lime, chlorinated, or bleaching powder	2,370,000	2,017,000
Magnesium compounds	10,942,000	11,926,000
Potassium compounds, n. e. s.:		
Argols, tartar, and wine lees	18,083,000	19,314,000
Carbonate	18,241,000	15,167,000
Chlorate and perchlorate	15,106,000	12,416,000
Cream of tartar	60,000	93,000
Cyanide	91,000	94,000
Hydroxide (caustic potash)	9,323,000	8,629,000
Nitrate, crude (saltpeter), tons	12,799	14,520
Other, n. e. s.	3,943,000	7,067,000
Sodium compounds, n. e. s.:		
Sulfate, crude (salt cake)	[b]	145,493,000
Cyanide	26,401,000	18,695,000
Ferrocyanide (yellow prussiate)	1,590,000	1,185,000
Nitrite	61,000	2,000
Phosphate (except pyrophosphate)	1,445,000[a]	1,467,000
Other, n. e. s., value	$2,103,000	$650,000
Radium salts, grains	260	207
Radium salts, value	$925,000	$731,000
Other industrial chemicals, value	$5,046,000	$3,633,000

Exports	1930 *Pounds*	1931 *Pounds*
Acids and anhydrides:		
Organic (exclusive of coal-tar acids)	[b]	559,000
Inorganic:		
Nitric	[b]	679,000
Sulfuric	5,471,000	3,202,000
Hydrochloric (muriatic)	[b]	3,999,000
Boric (boracic)	2,804,000	4,221,000
Other	12,126,000	3,572,000
Alcohols:		
Methanol, gallons	952,000	583,000
Glycerol	608,000	328,000
Butyl	[b]	861,000
Other	3,358,000	1,862,000
Acetone	3,645,000	3,846,000
Carbon tetrachloride	[b]	492,000
Carbon disulfide	[b]	2,091,000
Formaldehyde (formalin)	3,769,000	2,905,000
Ethylene compounds	[b]	718,000
Other synthetic organic products	1,326,000	2,235,000
Nitro or aceto cellulose solutions, collodion, etc.	1,828,000	2,200,000
Ammonium compounds (except sulfate, phosphate, and anhydrous ammonia)	2,365,000	1,263,000
Aluminum sulfate	50,509,000	55,335,000
Other aluminum compounds	2,018,000	1,749,000
Calcium compounds:		
Carbide	3,987,000	2,834,000
Chlorinated lime, or bleaching powder	2,949,000	1,721,000
Chloride	42,699,000	48,703,000
Citrate of lime	[b]	5,044,000
Other, except arsenate and cyanide	4,991,000	1,626,000
Copper sulfate (blue vitriol)	5,062,000	7,191,000
Hydrogen peroxide (or dioxide)	1,917,000	1,320,000
Potassium compounds (not fertilizers)	2,512,000	2,318,000
Sodium compounds:		
Bichromate and chromate	4,933,000	4,407,000
Cyanide	1,242,000	1,121,000
Borate (borax)	165,863,000	173,876,000
Silicate (water glass)	60,494,000	58,577,000
Soda ash	65,873,000	55,277,000
Sal soda	13,073,000	9,058,000
Bicarbonate (acid soda or baking soda)	19,818,000	18,711,000
Sulfate	8,872,000	9,305,000
Bisulfate (niter cake)	[b]	26,703,000
Hydroxide (caustic soda)	126,379,000	131,189,000
Sulfide	[b]	687,000
Fluorides	[b]	131,000
Sodium phosphates (mono-, di-, and tri-)	[b]	6,129,000
Other	51,696,000	7,498,000
Tin compounds	562,000	653,000
Zinc compounds	3,117,000	2,022,000
Gases, compressed and liquefied:		
Ammonia, anhydrous	2,272,000	1,892,000
Chlorine	7,532,000	8,843,000
Other n. e. s.	2,369,000	2,398,000
Other industrial chemicals, value	$4,367,000	$2,690,000

[a] Beginning June 18, 1930.
[b] Not separately stated.
[c] Not elsewhere specified.

$117,000 in 1931 was slightly higher than in the year before, but white mineral oil dropped from $491,000 to $329,000. Biologics for animal and veterinary use fell off from $547,000 to $444,000, serums and antitoxins for human use from $861,000 to $836,000, and household pharmaceuticals in small packages from $760,000 to $540,000.

Proprietary medicinal preparations dropped off in total value about 20 per cent, the 1931 sales aggregating $8,300,000 as against $10,489,000 in 1930. Salves and ointments were the best sellers in this group, reaching a value of $1,925,000 slightly less than in the year before. The various articles classed as tonics, blood purifiers, emulsions, and appetizers stood second in the group with $1,387,000, a considerable decrease from the 1930 figure of $2,211,000. Laxatives, purgatives, and cathartics, however, showed a small gain, their value being recorded as $1,049,000 in the year under review as against $990,000 in the preceding year.

Industrial Chemical Specialties

Only exports are listed under this heading, which covers a number of products of chemical processes of manufacture in common use. These American-made articles enjoy a great popularity abroad, as is shown by the fact that the total of their foreign sales rose from $4,776,000 in 1925 to more than three times that much five years later. This was the only group of chemicals and related products to show increased sales in 1930 as compared with 1929, the totals being, respectively, $15,589,000 and $14,457,000 for the two years. But the second year of world-wide depression had its effect, and the 1931 sales dropped some 12 per cent below those for the previous year, registering a value of $13,754,000.

Household insecticides and exterminators make up the leading item of this group in point of value. It dropped 42 per cent as compared with 1930, sales totaling $2,185,000 as against $3,789,000 in the earlier year. A much smaller reduction was to be noticed in the sales of baking powder, the value of which reached $1,269,000 in 1931 as compared with $1,434,000 in 1930 and $1,730,000 in 1929. A popular article abroad was one which appeared on this list for the first time in 1931—rubber-compounding agents (accelerators, retarders, etc.), which sold last year to a total of $1,157,000. Cementing preparations for repairing, sealing, and adhesive use were likewise separately noted for the first time in 1931, their sales amounting to $502,000. A third new item, textile specialty compounds, had a value of $287,000. Agricultural insecticides and fungicides, and similar materials were valued at $1,199,000 in 1931 as against $1,458,000 in 1930; and household disinfectants, deodorants, germicides, etc., at $283,000 as against $289,000. Petroleum-jelly exports totaled $788,000 in value, a decrease of 14 per cent from the year before; shoe polishes and shoe cleaners, $406,000, a decrease of 37 per cent; leather dressings and stains, $362,000, a decrease of 11 per cent; and automobile polishes, $299,000, about 18 per cent less than in 1930.

Industrial Chemicals

The full list of industrial chemicals (of basic importance to manufacture) sold or purchased abroad by the United States in the last two years, is given in the accompanying table.

As will be noted, the largest import item in point of bulk was salt cake, or crude sodium sulfate. The volume of our purchases of this commodity was many times as great as that of any other of the group. The value, however, which stood at $804,000, was less than one-half that of another sodium compound—sodium cyanide—which led the whole list of industrial chemicals with a total of $1,711,000. This figure represented a decrease of 16 per cent from 1930. Sodium ferrocyanide, with a total value of $102,000, was 25 per cent below the 1930 figure.

Among the potassium compounds the leading import both in quantity and in value was the item, argols, tartar, and wine lees, whose value of $1,605,000 represented a 13 per cent decrease. Potassium nitrate, or saltpeter, was one of the few items in this group to show a gain, the 1931 value of $708,000, comparing with $620,000 in the year before. Carbonate of potassium fell off about 22 per cent in value, totaling $664,000 as against $848,000. Chlorate and perchlorate, $439,000, showed about the same rate of decrease; caustic potash, $452,000, dropped only about 8 per cent.

Most important among the acid imports was that of acetic acid, whose total value fell from $1,498,000 in 1930 to $803,000 in 1931. The only others of importance were tartaric, whose $447,000 total was about 40 per cent below that of the previous year, and arsenious, or white arsenic, which, with $450,000 worth of 1931 imports, recorded about a similar percentage of loss. Other prominent industrial chemicals were crude iodine, the 1931 value of which was $998,000, comparing with $1,798,000 in 1930 and $2,249,000 in 1929 and thus registering a loss of about 60 per cent in two years; crude glycerol, valued at $515,000 in 1931 and $633,000 in 1930, and refined glycerol, $142,000 last year and $272,000 the year before; and cobalt oxide, whose 1931 value of $387,000 was barely half that of 1930.

The export trade in industrial chemicals is dominated by the sodium compounds which together accounted in 1931 for $9,959,000 out of the total of $19,774,000 for the whole group, or slightly more than one-half. Sales of these compounds were well maintained in 1931, their total almost coming up to that of the year before which was $10,627,000. Two-thirds of the total value of the sodium group of commodities was contributed by two chemicals—caustic soda and borax. Caustic soda exports, although heavier in bulk, were about 7 per cent below the 1930 trade in value, the 1931 figure of $3,465,000 comparing with $3,706,000 in the preceding year. The 1929 value was $3,516,000. Borax, on the other hand, marked up a good gain of 10 per cent in value, attaining a total of $3,359,000 as compared with $3,058,000 in 1930 and $2,935,000 in 1929. Last year's imports were higher in value than for any other year since the war except 1928, when they totaled $3,454,000.

Soda ash, third most important of the sodium group, dropped about 25 per cent in value, registering $858,000, as against $1,139,000 in 1930. Water glass showed a much smaller reduction, its $523,000 being about 9 per cent less than in 1930. Bicarbonate, with 1931 exports of $330,000 and bicarbonate and chromate with $288,000, recorded losses of 10 per cent and 12 per cent as compared with the previous year's trade.

Outside of the list of sodium compounds, no commodity classed as an industrial chemical is exported in sufficient volume to reach $1,000,000 in value, and only a few reach $500,000. Citrate of lime was sold abroad to a value of $584,000 (no data for 1930); aluminum sulfate reached $568,000 or practically the same as in 1930; calcium chloride exports were valued at $567,000, a gain of 13 per cent; those of nitro or aceto cellulose solutions, collodion, etc., totaled $536,000, likewise a small increase over 1930; and the alcohols together made up $571,000, hardly half the total of the previous year. Methanol was the principal alcohol export, its value dropping from $483,000 in 1930 to $241,000 in 1931, partly because of a reduction in volume of exports of nearly 40 per cent and partly because of lower prices received which brought the average valuation of exports down from 51 to 41 cents per gallon. This is the lowest recorded valuation of methanol exports and is about one-half that of the last five or six years. Compressed and liquefied gases were sold abroad to a value of $826,000, some 17 per cent less than in 1930. Anhydrous ammonia was formerly the chief of these exported gases, and its 1931 value, $235,000, was 30 per cent below that of the year before. Chlorine, with $248,000, was first in importance in 1931, but it also suffered a slight reduction from 1930.

Pigments, Paints, and Varnishes

The falling off in all lines of import trade noted in 1930 continued during 1931. The decrease in imports of chemical pigments was more noticeable than that in mineral-earth pigments, the former losing 24 per cent and the latter 14 per cent of their 1930 values. Iron oxide and iron hydroxide fell from $375,000 to $259,000, and ochers and siennas from $274,000 to $191,000. The most important articles entering into this trade are lithopone and zinc pigments. These fell off in value 36 per cent, from $670,000 to $429,000, although the quantity, 11,354,000 pounds in 1931, was only 24 per cent below that of the year before. Comparative figures are not available for the 2,914,000 pounds of zinc oxide and leaded zinc oxide, valued at $189,000, imported in 1931. Imports of paints, stains, and enamels fell from a value of $405,000 to $246,000 and varnishes from $51,000 to $31,000.

In the outgoing trade the decline was not quite so much in evidence, but the returns do not indicate an encouraging year. The value of our exports of mineral-earth pigments dropped from $535,000 to $429,000, or about 20 per cent. The larger part of this trade is made up of ocher, umber, sienna, and other forms of iron oxide, whose 1931 value was $272,000. Among the chemical pigments, carbon black continues to occupy the dominant position. Sales in 1931 were heavier in volume than in the year before, but the value was considerably smaller, the figures being: 1931, 96,714,000 pounds valued at $5,079,000; and 1930, 84,260,000 pounds valued at $5,789,000. As compared with 1929, the value of this important export dropped almost 40 per cent, returns for that year showing sales amounting to $8,271,000.

Both in volume and in value the 1930 trade in zinc oxide was cut in half, last year's totals being 10,262,000 pounds with a value of $717,000, and those of the year before, 21,507,000 pounds with a value of $1,447,000. White lead, 10,017,000 pounds valued at $562,000, felt the dull times to a lesser degree, although the 40 per cent loss in value was enough to be felt severely. Red lead, litharge, and orange mineral dropped from $590,000 to $385,000; and lithopone, which maintained its sales better than any other important chemical pigment, from $380,000 to $341,000.

There was an encouraging gain in the foreign sales of pyroxylin lacquers. Pigmented lacquers totaling 333,000 gallons with a value of $950,000 were sent to foreign parts last year, as compared with 256,000 gallons valued at $862,000 in 1930; and clear lacquers amounting to 94,000 gallons valued at $198,000 in 1931, compared with 71,000 gallons valued at $149,000 the year before. A large item in the 1931 trade, not separately reported before, was thinners for pyroxylin lacquers, which were sold to the extent of $370,000. Ready-mixed paints, stains, and enamels continue to go abroad in large volume, but sales were drastically reduced from 1930, the total value dropping from $5,757,000 to $3,309,000. Varnishes, including oil or spirit varnishes and liquid driers, suffered even more severely. The flourishing trade of 1930, amounting to a value of $1,442,000 and exceeding even that of 1929, was cut to $547,000, a loss of 62 per cent. Paste paint, on the other hand, showed up with a surprisingly large increase. As against 1930 shipments of 1,785,000 pounds, last year's returns totaled 4,054,000 pounds, a gain of 127 per cent. The value, which rose from $354,000 to $529,000, returned a smaller percentage gain, but one which distinguished this commodity from nearly all others of the chemical group.

Fertilizers and Fertilizer Materials

The outstanding feature of the import trade in fertilizers last year was the manner in which the trade in Chilean nitrate was maintained. In the face of unprecedented low prices for farm products in this country and a decline of more than 20 per cent in the total value of imported fertilizers, imports of Chilean nitrate practically equaled those of 1930 in value and fell but little below them in quantity. The figure for total value was $21,112,000, and this compared with $21,445,000 in 1930, while the quantity 551,000 tons, compared with 569,000 tons in 1930. The 1931 import value, however, is the lowest in more than fifteen years and is less than half of that of five or six years ago, the 1925 total being $52,531,000 and that for 1926, $42,781,000. The average value of Chilean nitrate imports in 1931 was about $38, higher than for any year since 1927, but much lower than the usual valuation prevailing in earlier years.

The effect of the removal of a tariff duty of $5.60 per ton on ammonium sulfate in June, 1930, is clearly shown in the heavy increases in shipments since that time. Before the duty was removed on June 18, 1930, imports in that year had amounted to only 2845 tons. In the latter half of the year they amounted to 30,939 tons and, in comparison with the total 1930 shipments of 33,784 tons, shipments in 1931 reached a figure of 112,215 tons. The figures showing value of imports tell a similar story except that the rate of increase was somewhat smaller, the 1931 total of $3,142,000 comparing with $1,160,000 in 1930. A fairer comparison would be with the returns of 1929, in which year only 19,000 tons valued at $763,000 were imported. Belgium and the Netherlands were the heaviest exporters of ammonium sulfate to this country in 1931. Germany sent a considerable proportion and in the first part of the year several thousand tons were received from Japan.

Of the other nitrogenous fertilizers, calcium cyanamide was the most important. Imports of this material showed a heavy falling off, the 1930 shipments of 145,000 tons valued at $4,874,000 being reduced to 51,000 tons valued at $1,537,000. Calcium nitrate dropped from a value of $1,560,000 in 1930 to $927,000 in 1931, and guano from $1,656,000 to $504,000. The decline noted last year in imports of ammonium sulfate nitrate continued through 1931, and the total for the year was only $231,000 as against $391,000 in 1930.

Phosphate fertilizers followed the tendency of the times and decreased from $1,909,000 in 1930 to $1,371,000 in 1931. Potash imports likewise returned heavy decreases of 30 to 50 per cent, the figures for the separate commodities standing as follows for the last two years:

Imports of Potash

Fertilizer	1930		1931	
	Tons	*Value*	*Tons*	*Value*
Chloride, crude	273,000	$9,930,000	181,000	$6,518,000
Kainite	112,000	979,000	55,000	505,000
Manure salts	362,000	5,048,000	179,000	2,583,000
Sulfate, crude	86,000	3,947,000	57,000	2,628,000
Other potash-bearing substances	547	5,000	488	4,000

Fertilizer exports fell off much less than the average for other chemical commodities, and a few items showed an actual gain. Ammonium sulfate shipments of 67,000 tons valued at $2,220,000 compared with 82,000 tons valued at $2,910,000 in 1930, a drop of 18 per cent in quantity and 23 per cent in value. Other nitrogenous fertilizer materials, chiefly chemical but including some organic waste materials, were exported to a value of $2,611,000, which more than doubled the 1930 figure of $1,159,000. Phosphate-rock exports of the higher grades totaled 105,000 tons as against only 66,000 tons in 1930, and the value, $614,000, showed a similar gain over the $447,000 of the previous year. Land pebbles, however, dropped from a value of $5,183,000 in 1930 to $3,663,000 in 1931, and superphosphates from $1,595,000 to $941,000. Exports of potash fertilizers and materials doubled in value, the 1931 total of $1,267,000 comparing with $643,000 in the year before. Fertilizers classed as concentrated chemical fertilizers, and including nitrogenous, phosphatic, and potassic materials, were sold abroad to a value of $1,281,000 in 1931 as against $1,869,000 in 1930. Prepared fertilizers decreased from $1,477,000 to $224,000 last year.

Explosives, Fuses, etc.

Imports under this heading were of small importance and consisted, as usual, mainly of firecrackers. This trade was cut in half, amounting to $349,000 as compared with $754,000 in 1930. The chief item of export continued to be dynamite, which fell from a total of 9,090,000 pounds valued at $1,280,000 in 1930 to 5,656,000 pounds valued at $789,000 in 1931. Smokeless powder sold abroad in 1931 was less than one-half in value of that of the year before—$196,000 as against $439,000. Blasting-powder exports increased somewhat in total value, which was $73,000 as against $69,000 in 1930, but the quantity, 748,000 pounds, was about 11 per cent under the mark of the year before.

Soap and Toilet Preparations

All the separate items under this heading suffered substantial decreases in the import trade in 1931. Cosmetics, powders, creams, etc., which reached a value in 1930 of $563,000 fell to $423,000, about 25 per cent less; perfume materials valued at $2,143,000 dropped off to $1,101,000, a 50 per cent loss; toilet soap registered a value of $376,000 as against $556,000 in 1930, a loss of one-third; castile soap fell from $347,000 to $254,000, a 27 per cent decrease; and perfumery, bay rum, and toilet water imports were valued at $681,000 in 1931 as against $921,000 in 1930, a drop of 26 per cent.

Exports likewise furnished but two or three exceptions to the general rule of substantially lower shipments. The best-selling article of the group—dental creams—achieved a total value of $2,080,000 in 1931, a fairly good showing as compared with the $2,274,000 of 1930. Laundry soap was second in value, total sales for the year amounting to $1,756,000, a 30 per cent decrease from 1930. Toilet- or fancy-soap exports were valued at $1,020,000 in 1931 and $1,235,000 in 1930; scouring soaps and powders at $528,000, about 36 per cent under 1930; and shaving soaps, creams, powders, and sticks at $421,000, about 13 per cent less than in the year before.

Talcum powder sold abroad in 1931 to a value of $691,000, nearly 20 per cent less than in the year before, but sales of face powder, $396,000, were practically the same in the two years. Creams, rouges, and other cosmetics reached a total value in the export trade of $1,890,000, the principal items being: cold creams, $512,000; vanishing creams, $367,000; other creams, lotions, and balms, $361,000; and rouges, $209,000. In 1930 the total for these goods was $2,074,000, last year's sales thus showing a decrease of only about 9 per cent. Manicuring preparations fell off 30 per cent to a total of $376,000; depilatories and deodorants, $382,000, were nearly three times the 1930 trade; and hair preparations, $375,000, were slightly above the total for the previous year.

MATERIALS RELATED TO CHEMICAL INDUSTRIES

All the articles and groups of articles mentioned above are included in group 8 of the government statistics, which covers chemicals and related products. In addition to them a number of commodities classified with other industries are of commercial or industrial interest to chemical manufacture and trade. Last year's trade in the more important of these articles is considered below.

Mineral Oils

As was to be expected, world trade in petroleum and its products felt the full force of the business depression last year. Both in imports and in exports the trade of the United States saw heavy reductions, decreases occurring in every branch.

Imports of petroleum last year witnessed not only a drop of about one-fifth in quantity but a considerable price reduction as well, which brought the decrease in value up to much larger proportions. Advanced and refined oils, including gasoline, naphtha, kerosene, etc., were as usual well ahead of crude petroleum in total value, constituting about 57 per cent of the total imports. Practically the same proportion ruled in 1930. The decrease in the quantity of refined oils, from a 1930 importation of 43,381,000 barrels to 38,702,000 barrels last year, or 10 per cent, was much lighter than the decrease in value, which amounted to 34 per cent, the 1931 figure being $52,149,000 as against $78,739,000 in the preceding year. Gasoline, naphtha, and other finished light products were valued at $35,069,000, 40 per cent less than in 1930. About 90 per cent of these oils came from Venezuela but were credited to Curaçao, the Dutch island just off the coast of Venezuela.

Crude petroleum imports, as in previous years, came almost entirely from Mexico and northern South America. Through direct shipments and shipments through the island of Curaçao, more than one-half of last year's imports came from Venezuela. The amounts and value of our imports from the chief sources of supply in the last two years were as follows:

Imports of Crude Petroleum

From:	1930 Barrels	1930 Value	1931 Barrels	1931 Value
Mexico	10,093,000	$8,232,000	8,207,000	$6,062,000
Netherlands West Indies	9,780,000	7,442,000	4,103,000	3,159,000
Colombia	14,204,000	19,860,000	12,329,000	12,509,000
Peru	1,281,000	2,878,000	225,000	491,000
Venezuela	25,299,000	24,519,000	21,122,000	15,633,000
Other countries	1,472,000	1,941,000	1,264,000	1,367,000
Total	62,129,000	64,872,000	47,250,000	39,221,000

In the export trade the influence of the lower prices was everywhere apparent. Decreases in total value were in all cases much larger than those in quantities shipped, and in the case of crude petroleum exports an actual 8 per cent increase in quantity was accompanied by a 35 per cent decrease in value. Exports of petroleum and its important derivatives in the last two years are shown in the table which follows.

In the trade in crude petroleum the much lower prices indicated by the figures in this table were in evidence chiefly in the exports to Europe, where the total value was cut in half while the quantity remained about the same (1,152,000 barrels in 1930 having a value of $1,995,000, and 1,005,000 barrels having a value of $993,000 in 1931), and to Canada, which took 18,967,000 barrels valued at $25,689,000 in 1930 and 19,209,000 barrels valued at $14,765,000 in 1931. Japan increased its purchases from 2,926,000 barrels valued at $3,223,000 in 1930 to 3,606,000 barrels valued at $3,518,000 last year. Cuba was the only other large buyer, its purchases of 769,000 barrels representing a 50 per cent gain.

Exports of Petroleum and Products

Product	1930 Barrels	1930 Value	1931 Barrels	1931 Value
Petroleum, crude	23,704,000	$32,153,000	25,535,000	$20,828,000
Refined oils:				
Gasoline, naphtha, and other finished light products	63,195,000	250,647,000	43,787,000	109,301,000
Illuminating oil (kerosene)	16,690,000	63,325,000	12,534,000	34,796,000
Gas and fuel oil	32,378,000	33,220,000	26,588,000	23,966,000
Lubricating oil	9,752,000	88,931,000	7,994,000	62,986,000

In the export trade in gasoline, naphtha, and other light products, drastic reductions were the rule among all the large buyers except Japan. That country increased its purchases about 4 per cent in value and 18 per cent in quantity, the increase coming entirely in the last six months. As compared with 1930 purchases of 1,067,000 barrels valued at $4,018,000, total purchases for 1931 amounted to 1,256,000 barrels valued at $4,185,000. By way of contrast, shipments to the United Kingdom fell from 19,208,000 barrels to 13,151,000 barrels and in value from $67,013,000 to $28,938,000; to France from 9,331,000 barrels to 6,132,000 barrels, and in value from $35,355,000 to $12,009,000; and to Canada from 4,282,000 barrels to 2,963,000 barrels and in value from $15,261,000 to $8,592,000. The greatest drop was in the trade with Cuba. That country took 1,179,000 barrels valued at $4,073,000 in 1930 and only 288,000 barrels valued at $617,000 in 1931, last year's purchases being far below the normal of earlier years.

The United Kingdom continued to be our best customer for bulk kerosene. Shipments to that country were almost as large as in 1930, but the value was lower by nearly 40 per cent, last year's figures of 2,881,000 barrels valued at $5,006,000 comparing with 2,937,000 barrels valued at $8,144,000 in the year before. (These refer to bulk shipments only. Shipments to Europe in containers were very small and were not separately stated.) The largest buyer of kerosene shipped both in bulk and in containers was China, Hong Kong, and Kwantung (considered as one country), exports to which fell from 3,172,000 barrels to 2,249,000 barrels and from a value of $12,485,000 to $7,255,000. Japan's purchases, 370,000 barrels with a value of $1,413,000, were about two-thirds less than in 1930, while shipments to British India, 553,000 barrels valued at $2,007,000, dropped off about one-third.

Japan's purchases of gas and fuel oil, for which that country is our best customer, were almost the same in 1931 as in the year before, last year's total being 5,437,000 barrels with a value of $4,595,000. Trade with the United Kingdom fell off heavily, shipments totaling 1,397,000 barrels valued at $1,536,000, a drop of 53 per cent in quantity and 65 per cent in value. The value of shipments to Germany, $1,421,000, was only about one-half that of the year before, and exports to other leading customers, including Panama, Chile, Canada, and Mexico, showed decreases ranging from 20 to 50 per cent.

In addition to the exports of these oils given in the table above, bunker oil was supplied to vessels engaged in foreign trade to the extent of 43,714,000 barrels valued at $38,845,000, as compared with 50,773,000 barrels valued at $53,576,000 in 1930. About 46 per cent of the total was sold to American vessels.

Lubricating oil exports were almost uniformly lower than in 1930, with the United Kingdom, France, Germany, Italy, Belgium, and Canada the leading customers. Japan's purchases were an exception to the rule, showing a small increase. That country in 1931 took red and pale lubricating oil to the amount of 171,000 barrels and cylinder oil to the extent of 54,000 barrels, these quantities comparing with 182,000 barrels and 37,000 barrels, respectively, for 1930.

Sulfur

Sulfur exports fell off about 30 per cent in 1931, the total for the year being 407,586 tons of crude sulfur in lumps, valued at $8,837,000, and 13,599 tons of crushed, ground, refined, sublimed, and flowers of sulfur, valued at $432,000. The three leading buyers of crude sulfur continue to be Canada, Germany, and France. Canada's purchases decreased about one-third in value as compared with 1930 and those of Germany about 30 per cent, but France increased its purchases, taking 73,000 tons as against 56,000 in 1930. All other countries took decreased quantities, trade with Australia showing the largest loss. Only 21,000 tons went to that country in 1931 as against 65,000 tons in 1930. Total exports of crude sulfur in 1931 were just about one-half those of two years ago in 1929.

Vegetable, Animal, and Essential Oils

Coconut oil from the Philippines, most important of the vegetable oil imports, enjoyed a trade somewhat heavier in volume but about one-fourth less in total value than in 1930, the 1931 returns standing at 325,175,000 pounds valued at $15,272,000 as against 317,919,000 pounds valued at $19,901,000 in the year before. Palm oil, however, declined both in quantity and value, the imports of 258,156,000 pounds last year being 10 per cent less than in 1930 and the value, $10,792,000, 34 per cent less. Inedible olive oil imported for mechanical or manufacturing purposes fell off one-half in value and more than 40 per cent in quantity, the 1931 imports amounting to 36,924,000 pounds with a value of $1,652,000. Carnauba wax registered increased shipments—7,447,000 pounds as against 7,416,000 pounds in 1930—but the total value, $1,070,000, was 25 per cent less. There was a very marked decrease in the value of imports of tung oil, due apparently to lower prices, since the volume dropped much less than the value, the 1931 imports totaling 79,311,000 pounds valued at $4,426,000 as against 126,323,000 pounds valued at $12,487,000 in the year before. Among the edible vegetable oils, olive oil was the only one to be imported in very large volume, shipments reaching 70,394,000 pounds as against 92,964,000 pounds in 1930. The value, $8,252,000, compared with $11,221,000 in 1930. Most of this oil came from Italy, with Spain second. The large decrease noted last year in the trade in palm-kernel oil continued in 1931, the total amounting to only 12,928,000 pounds as compared with 29,104,000 pounds in 1930 and 69,909,000 pounds in 1929. The value showed an even greater decline, figures for the three years being: 1931, $637,000; 1930, $1,771,000; 1929, $5,301,000.

Among the exports, cottonseed oil (edible) was of greatest value. Shipments were somewhat heavier—12,845,000 pounds as against 11,903,000 pounds, but the 1931 value, $1,162,000, was slightly under that of the year before. Cuba, as usual, was the largest buyer.

Imports of essential and distilled oils dropped sharply in total value, amounting to $3,654,000 as compared with $5,643,000 in 1930. Last year's trade was only one-half as large in value as that of 1929. Imports for the last two years were as follows:

Imports of Essential and Distilled Oils

Oil	1930		1931	
	Pounds	*Value*	*Pounds*	*Value*
Cassia and cinnamon	372,000	$373,000	306,000	$218,000
Geranium	189,000	593,000	140,000	416,000
Otto of roses, ounces	18,000	216,000	20,000	209,000
Bergamot	176,000	440,000	81,000	136,000
Citronella and lemon grass	1,097,000	542,000	1,027,000	389,000
Lavender and spike lavender	376,000	722,000	280,000	500,000
Lemon	624,000	588,000	347,000	216,000
Orange	166,000	362,000	132,000	230,000
Sandalwood	19,000	80,000	10,000	49,000
All other	3,064,000	1,727,000	2,925,000	1,291,000
Total		5,643,000		3,654,000

Peppermint oil exports were lower in both quantity and value than in 1930, shipments reaching 230,000 pounds valued at $438,000, as compared with 233,000 pounds valued at $700,000.

Dyeing and Tanning Materials

Imports under this heading again declined, the total value, $5,126,000, representing a loss of almost 30 per cent from 1930. In the quebracho trade, however, the loss was only in value, as both wood and extracts showed a gain in quantity of shipments, the returns being as follows: quebracho wood, 55,396 tons valued at $587,000 in 1931 as against 44,114 tons valued at $640,000 in 1930; and quebracho extract, 90,237,000 pounds valued at $2,490,000 as against 87,377,000 pounds valued at $3,838,000. Logwood, valued at $384,000, was third in the list and was slightly more than in 1930, while valonia, $282,000, was nearly 40 per cent under 1930 imports.

Exports of dyeing and tanning materials dropped in value from $1,898,000 in 1930 to $1,589,000 in 1931, the chief export being logwood extract, shipments of which were valued at $165,000 as against $193,000 in 1930.

Rubber

In the face of a depression which presumably bears down especially on such luxury industries as automobile manufacture, the importation of rubber (used chiefly in tires) showed highly encouraging results in 1931. American importers bought slightly more crude rubber than in 1930 but paid for it only one-half as much. This indeed is but a continuation of a tendency which has been noticeable since 1926, when post-war import values reached their peak. Since that year the quantity of rubber imports has remained fairly steady, surpassing the 1926 total by about 36 per cent in 1929 and about 20 per cent last year, but the values have descended steeply until in 1931 the total was only about one-seventh that of five years before. The following table shows this decrease year by year:

Imports of Crude Rubber

Year	Pounds	Value
1926	925,878,000	$505,818,000
1927	954,750,000	339,859,000
1928	978,107,000	244,855,000
1929	1,262,939,000	240,966,000
1930	1,089,830,000	140,642,000
1931	1,124,003,000	73,803,000

Shipments decreased in 1931, as compared with 1930, from all the chief sources except British Malaya, which was credited with 804,152,000 pounds as against 763,411,000 pounds in 1930, and the United Kingdom, whose total was 55,481,000 pounds as against 8,962,000. From the Netherlands East Indies, American importers received 157,656,000 pounds as compared with 185,743,000 pounds.

Naval Stores, Gums, and Resins

Chicle, most important of imported gums in point of trade value, showed no exception to the general rule of decreased trade in 1931. In spite of the fact that chicle was placed on the free list in the middle of 1930, free importations for the whole of 1931 were hardly any higher than for the first half of the year before, when it was subject to a duty of 10 cents per pound. Last year's imports reached a total of 8,931,000 pounds valued at $4,195,000, and those of 1930 were 13,957,000 pounds valued at $7,022,000. Shellac, chief varnish gum imported, suffered a severe cut in total value which was only $1,953,000 as against $5,190,000 in 1930, but the quantity made a better showing—11,962,000 pounds as against 18,982,000.

Natural camphor scored notably in competition with synthetic, as both the crude and the refined products entered in greater quantities than in 1930, while shipments of synthetic were cut down one-fourth. Imports of natural crude camphor were doubled—2,010,000 pounds as compared with 1,058,000 in 1930—with the total value rising from $419,000 to $716,000, and those of refined rising from 1,032,000 pounds valued at $557,000 in 1930 to 1,152,000 pounds valued at $546,000 in 1931. Trade in synthetic camphor fell from 2,405,000 pounds valued at $851,000 to 1,798,000 pounds valued at $588,000.

The value of our exports of naval stores, gums, and resins fell off by 37 per cent, totaling only $14,304,000 as compared with $22,698,000 in the year before. The decrease was in evidence both in the trade in rosin and in that of turpentine. Exports of wood rosin, amounting to 154,000 barrels with a value of $1,136,000, were reduced 21 per cent in quantity and 52 per cent in value from 1930; those of gum rosin, 907,000 barrels valued at $6,923,000, were less by 15 per cent and 42 per cent, respectively, in quantity and value. All the large buyers of gum rosin took reduced quantities, the United Kingdom buying 20 per cent and Germany 15 per cent less. These are our best two customers for this product. Turpentine exports were 12,214,000 gallons last year as against 15,142,000 gallons the year before, the total value showing a somewhat larger decrease, from $6,612,000 to $4,813,000. The United Kingdom is much the largest buyer of this product, taking 5,020,000 gallons valued at $1,839,000 in 1930. This represented a decrease of about one-third in quantity and 40 per cent in value from the purchases of the preceding year.

Received February 4, 1932. All 1931 figures are preliminary, but the final figures usually show few changes of importance. Further details regarding the trade in any particular group of articles may be obtained through this publication or by addressing the author.

NOTES AND CORRESPONDENCE

Toxicity of Ethylene and Propylene Glycols

Editor's Note. The following letter was received in June, 1930, but the publication was delayed in the hope that further experiments would be made by the author. Doctor Hunt states that he has not been able to pursue his studies further, and, since the subject is of considerable interest at the present time, the letter is now published.

Editor of Industrial and Engineering Chemistry:

Although comparatively little experimental work with ethylene glycol has been reported, the view has long been held that the substance is practically nonpoisonous; its use as a substitute for glycerol in some food and pharmaceutical preparations has been suggested. Recently two deaths in man have been reported [*J. Am. Med. Assocn.*, 94, 1940 (1930)] from the drinking of an antifreeze mixture consisting of ethylene glycol. Hence it seems desirable to call attention to certain undesirable and dangerous properties of this compound.

It has long been recognized that ethylene glycol, like other polyvalent alcohols, has little or no narcotic or other immediate obvious actions. It is this lack of immediate effects of even comparatively large doses which has caused a number of experimenters to overlook the inherently dangerous character of the compound.

A few years ago I performed a number of experiments with this substance upon rats, mice, guinea pigs, rabbits, cats, and dogs. The compound was administered in various ways—by intraperitoneal and intravenous injections, and by mouth. It was also added to the drinking water of the animals, and the effects of small doses, continued for several days or weeks, were observed. The compound was found to be distinctly poisonous. The toxic action was not due to the glycol itself but to one of the products of its oxidation in the body—oxalic acid. The kidneys were very severely injured by the oxalic acid, and this seemed to be the usual cause of death. Experiments on man have also shown that some of the glycol is oxidized to oxalic acid.

Ethylene glycol proved to be as poisonous as methanol, but in a different way. Of course from a practical standpoint it is a much less dangerous substance than methanol; it is so slightly volatile that there is no danger of poisonous doses being inhaled, and there is no evidence that it is absorbed from the skin. Those who are so foolish as to endeavor to quench their thirst by drinking antifreeze mixtures would probably find other means of committing suicide, but manufacturers should (and apparently do) abstain from adding ethylene glycol to any food product. Used legitimately, this compound is a far less dangerous substance than aniline, benzene, carbon disulfide, turpentine, carbon tetrachloride, and many other chemicals extensively employed in the industries.

A considerable number of experiments were performed with propylene glycol; the results were strikingly different from those obtained with the ethylene compound. I could find no indications of a poisonous action. Thus, young rats grew at the normal rate and reached maturity when the only liquid they received was a 5 per cent solution of propylene glycol; rats receiving a similar solution of ethylene glycol died in two or three days, and those receiving a 1 per cent solution frequently died within a week. The propylene compound was well tolerated by animals whose livers and kidneys had been injured by various poisons. It is possible that this glycol may have a true food value in the sense that ethyl alcohol does, and without the drug action of the latter.

Reid Hunt

Harvard Medical School
Boston, Mass.
June 19, 1930

AMERICAN CONTEMPORARIES

Charles Lathrop Parsons

"WELL, how about a little trip down the river to Portsmouth in our one-lunger and some broiled live lobsters at Ham's?" said Charlie Parsons to Mrs. Bogert and me one summer afternoon at Durham, N. H., nearly thirty years ago, when he was professor of chemistry at the New Hampshire College there and we were his guests. "If you insist upon it," we replied, "lead us to the lobsters and we will show you how mean a knife and fork two hungry New Yorkers can wield." So he and Mrs. Parsons led the way to the creek where the boat, a small open-launch, awaited us. Although not a speed boat or much to boast about in the way of looks, she carried us safely, albeit not very rapidly, down the creek and the Piscataquis River to Portsmouth, where the lobsters " 'n' everythin' " were disposed of with gusto, for in those days Ham's lobsters were famous throughout that region. The night being a beautiful one, we did not leave Portsmouth until quite late, and, when we started, a stiff ebb tide was running against us. But our little put-put kept plugging along valiantly until we got about one-third of the way home, when after one or two despairing consumptive coughs the motor inconsiderately died. Fortunately, we were not very far from the north shore of the river at the time, so that we paddled her in and beached her in a little cove near a group of cottages. While Charlie attacked the engine with his best tools and most persuasive arguments under the admiring but somewhat sleepy eyes of our wives, I climbed up the bank to reconnoiter. Unfortunately it was near midnight, the houses were all dark, and every one apparently was in bed and sound asleep. While deliberating as to the next move, I was cheered by hearing a few feeble coughs from the motor, and, by the time I got back to the boat, the future Secretary of the American Chemical Society had her going again and we limped slowly home, where we arrived in the "wee sma' hours" of the morning, after getting stuck in the mud once or twice as we struggled along in the low water and darkness up the creek.

This was my first chance to get better acquainted with the new professor at Durham and was the beginning of a close and warm friendship which I hope will continue to the end.

One of the outstanding characteristics of Doctor Parsons and his charming wife is their generous, unselfish, and neverwearying hospitality. Every one who knows the Parsons even slightly, knows this. No matter where their home may be, Durham as it was, or Washington as it is now, the door to that home, as to their hearts, is always open to their friends, and no one ever knocks on either without receiving a cordial and cheery welcome. I have seen them time and again, when friends happened to drop in unexpectedly, put themselves to all kinds of trouble and inconvenience to see that these guests were made happy, not considering for a moment their own comfort. When distinguished foreign chemists visit our capital, the hospitable Parsons home is one of the first to entertain them, and in my wanderings in Europe I have had many of my foreign colleagues who have visited Washington tell me that some of the happiest recollections of their trips to our country were the evenings they spent as guests of the Parsons.

Intensely loyal to his friends and always willing and eager to do everything in his power to show that friendship, whether through this abounding hospitality or in other ways, nothing hurts or grieves him more than indifference or coldness on the part of those from whom he has the right to expect sympathy and responsiveness. A man of independent thought, confident in his own judgment tenacious in his opinions and vigorous in their defense, he nevertheless maintains an open mind and is ever willing to discuss any question, to weigh critically the arguments advanced, and to surrender good naturedly when convinced that his position is no longer tenable. People may and do differ with him, but they always respect his judgment and the sincerity of his position. Strong in his dislikes, as in his likes, he can be, when occasion demands it, an active and resourceful antagonist, and two of his pet aversions are pomposity and snobbishness; but, if he is a hard and fair fighter, he is also a good loser and never harbors any grudge as a result of such differences of opinion. Undoubtedly to those who do not know him well, he may now and then give the impression of being too dogmatic. He is endowed with a keen sense of humor, and enjoys a good joke immensely, even when it happens to be on himself. In his own home life he is very happy and an easy mark for his grandchildren. In spare moments he loves to putter around his automobile and to slip away with Mrs. Parsons for a little tour whenever a chance occurs. To him, Washington is the finest place in the world to live, and a stranger hearing one of his ardent boosting orations on the subject might think that he was listening to a real estate agent with property to sell in the vicinity of Cleveland Park. To the American Chemical Society, its officers, and governing boards, he has always shown the staunchest kind of fealty; and no matter how energetically he may debate a question in the Council, when the question is once decided, it always receives his whole-hearted support, whether or not he originally favored it. Not infrequently he may have appeared meticulous and unreasonable upon some matters of Society business, when actually he was only carrying out explicit instructions received from the Council.

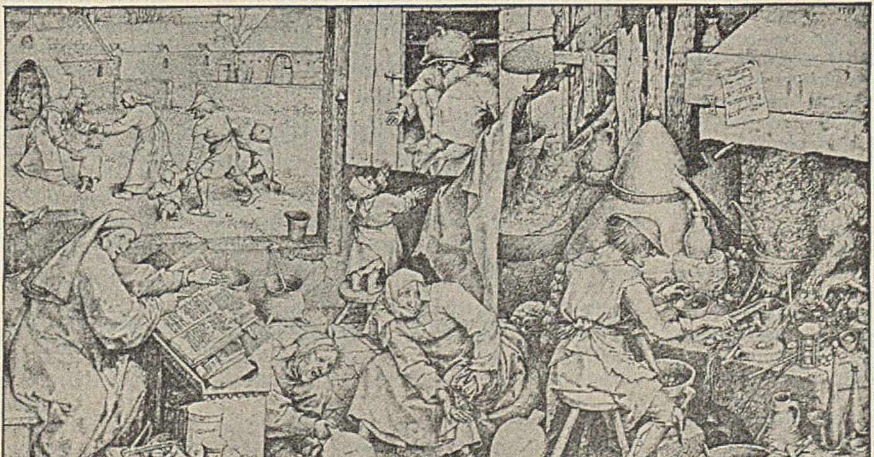
I well remember when the question first came up of his becoming Secretary of our American Chemical Society, in succession to Albert C. Hale, who felt that the burden was growing too heavy for one of his years to carry. Professor Parsons was then deeply engrossed with his scientific work and very happy in it. With his staff and students he was occupied with many interesting researches and was particularly enthusiastic about the work in rare earths which his colleague, the late Professor James, was developing so deftly and yet so modestly. It was a real sacrifice to give up all this as well as his beautiful home in Durham, and move to Washington where the friends now without number were then but a handful. I know from many intimate conferences with him that he came to his decision because he was convinced that as Secretary of the American Chemical Society he would have a better opportunity to advance the cause of chemistry in the United States than as professor of chemistry at New Hampshire College. In all honor be it said that, having put his hand to the plow, he has never once turned back but has continued to put into the cause of the AMERICAN CHEMICAL SOCIETY everything that he had to give of time, energy, and ability; in season and out, early and late, in fair weather and foul, he has striven tirelessly and undiscouraged for the upbuilding and development of our national society until, after nearly a quarter century of the hardest and most loyal kind of service, he has the satisfaction of seeing that organization grow from a membership of about three thousand to nearly twenty thousand, and rise from comparative obscurity to the exalted position it now occupies as the greatest chemical society the world has ever known. Having closely followed the progress of our SOCIETY for the past forty years, I say unhesitatingly and without fear of successful contradiction, that what the AMERICAN CHEMICAL SOCIETY is today it owes more to Charles Lathrop Parsons than to any other American chemist. Isn't that a monument of which any man may well feel proud? Who is there among us who has done more for the cause of American chemistry than what he has accomplished in the building of this great organization? I appreciate that he is not the only one who has contributed to this result, but that many have participated. Presidents have come and gone, and each has contributed what he could; but it has been the accumulated experience of Secretary Parsons, his intimate knowledge of the many problems of the SOCIETY and of the chemists of our country, his frank and fearless advice, which has been our chief guide throughout these many years of development. As a past president I know whereof I speak.

There are those who seem to believe that original research is not only the highest form of service which any chemist can render to his profession, but that everything else is so far inferior as not to be worthy of mention in the same breath. The discovery of new knowledge is undoubtedly of immense importance, but so also is the dissemination of the knowledge we have already gained, for discoveries become valuable only as they become useful, either practically or for the assistance of other workers. The AMERICAN CHEMICAL SOCIETY is today the most potent agency existing for this dissemination of chemical information and discovery. The investigator must keep fully posted and up to date on the rapid advances in his chosen field, and his research results would lose much of their value without an opportunity to bring them in published form to the attention of the chemical profession and of others likely to be interested. Think what *Chemical Abstracts* and our other journals mean to the progress of research, and how much that research is aided and stimulated by the inspiration and encouragement which comes from the contacts with one's fellow investigators provided by the frequent meetings of the SOCIETY and of its sections. That brilliant investigator, Sir William Crookes, is quoted as having said that he felt that his founding of the *Chemical News* and its editing for half a century had been fully as important a contribution to the progress and advancement of chemistry as his research work.

This outstanding service has been recognized clearly in other countries where Doctor Parsons has been the recipient of decorations, of honorary memberships in national chemical societies, and of similar tokens of appreciation and esteem. In his own country he has received the Nichols Medal of the AMERICAN CHEMICAL SOCIETY (1905), and the honorary degrees of D.Sc. from the University of Maine (1911), and of D. Chem. from the University of Pittsburgh (1914).

Born in New Marlboro, Mass., and educated partly in Massachusetts and partly at Hawkinsville, Ga., to which city the family moved while he was still a youngster, his collegiate training was obtained at Cornell University, from which he received his B. S. in 1888. Nothing brings him more joy now than to steal away for a few days of turkey hunting around his old home town of Hawkinsville, where his brother Will still lives. Those who have been so fortunate as to have been his guests on these hunts will not soon forget them or their warm-hearted host. When the wild turkeys down there hear that Charlie is on the warpath again and is going to pay them a visit, they all "beat it" for the deep woods, for they know to their sorrow that today he is as much interested in roast turkey as he used to be about whether a certain element should be called "beryllium" or "glucinum." In fact these turkeys feel as nervous, apprehensive, and ill at ease, when they know that he is scouting around, as though they were chemists who didn't belong to the AMERICAN CHEMICAL SOCIETY.

MARSTON TAYLOR BOGERT



THE GOLDMAKER

by

Pieter Breughel, the Elder

Breughel, a famous Flemish painter and a student of Koek, worked in Antwerp and Brussels and died in the latter city about 1590 at the age of 60. He drew a number of pen and ink sketches, most of them of a humorous nature. The original of the "Goldmaker" is in the Staatliches Museum in Berlin.

[See page 317]

BOOK REVIEWS

INDUSTRIAL ELECTROCHEMISTRY. *By C. L. Mantell.* 528 pages. McGraw-Hill Book Company, Inc., New York, 1931. Price, $5.00.

In his preface the author states, "..... Furthermore, the engineering side of the subject is neglected. ..... This volume is a modest attempt to fill the gap. It endeavors to point out and emphasize the technological importance of electrochemical processes, to stress their practical aspects, and to adopt the engineering viewpoint." This reviewer believes that the author has succeeded in his attempt. The volume is excellent from the engineering viewpoint.

The volume is divided into six sections: Theoretical Electrochemistry, Technical Electrochemistry, Electrolytics, Electrothermics, Electrochemistry of Gases, and Engineering. The first section is a brief introduction, evidently intended for the general reader and not for one actively interested in the subject. All the misprints in the volume found by this reviewer (four) were in this section. In the second section are very good accounts of corrosion, primary and storage cells, rectifiers, and electrochemical analysis. The third section comprises over half the book, giving an account of industrial applications of electrolysis. Electric furnaces and their products are treated in the fourth section. The electrochemical reactions in gases are given brief treatment in the next section, and the last section treats of materials of construction and the economics of power as applied to electrochemical processes.

The volume is profusely illustrated with photographs and diagrams, and contains numerous tables of operating data, as well as an appendix of electrochemical equivalents.

Obsolete processes are mentioned only occasionally, and are always definitely designated as such. Obsolete operating data, when given, are also properly labeled and are not likely to be misinterpreted.

The book should be valuable as a reference for practical data as well as a textbook for students. C. N. Richardson

* * *

COLLOID CHEMISTRY, THEORETICAL AND APPLIED. VOLUME III. TECHNOLOGICAL APPLICATIONS. Edited by *Jerome Alexander.* 655 pages, illustrated. The Chemical Catalog Company, Inc., New York, 1931. Price, $10.50.

This is the first of two volumes on Technological Applications in Alexander's four-volume series on Colloid Chemistry. The first volume, Theory and Methods, and the second volume, Biology and Medicine, appeared in 1926 and 1928, respectively. The fourth and final volume is promised in a few months. This book, to which forty-six people contributed, consists of forty-two papers on widely diversified topics. The editor collaborated with Professor McBain in the first paper, "Cohesion and Adhesion," and contributed two additional papers, "Chemical Warfare" and "The Colloidal State in Metals and Alloys."

Among the first eleven papers dealing primarily with general principles, such subjects are treated as the practical results of x-ray researches, wetting of solids by liquids, swelling, catalysis, adsorption, and grinding. The next six papers are concerned with mechanical processes, such as electrical precipitation of suspensoids, the use of colloid mills and the supercentrifuge, filtration, and flotation. The remaining twenty-five papers take up such subjects as the role of colloid chemistry in geology, mineralogy, ceramics, cements and mortar, metallography, corrosion of iron, petroleum, coal tar, asphalt, graphite, the soil, and wheat and wheat flour.

The editor has brought together, in so far as possible, the papers dealing with related topics; he has included numerous notes and cross references; and he has designated each paper as a chapter, in an attempt to give the work some semblance of continuity. In spite of this, however, this volume, like the preceding ones, is little more than a collection of articles each written without any knowledge of the contents of the others and without any special reference to the others. This is not ideal, but it is probably the best available way of bringing together in relatively few pages the first-hand information of specialists in so many widely diversified fields.

Six years or more ago the editor undertook this comprehensive compilation. No doubt he found it easy to persuade almost two hundred people the world over to write articles dealing with their special line of work. But to get the articles written and in form for publication is another matter! From the size of the volumes and the number of contributions it would appear that the editor has accomplished even more than he started out to do. Even though the price is about 1.5 cents per page, every scientific and technical library will find these books well worth the cost.

Harry B. Weiser

* * *

EXAMINATION OF WATER: CHEMICAL AND BACTERIOLOGICAL. *By William P. Mason.* 6th edition, revised by *Arthur M. Buswell.* 224 pages, 34 diagrams and photographs. John Wiley & Sons, Inc., New York, 1931. Price, $3.00.

The present edition of this work represents a revision and enlargement, both in size and number of pages, of a well-known little book that has served its modest purpose in the field of water analysis for many years. In the section dealing with chemical analysis, the reviser has adhered in general to the subject matter of previous editions, with expansion of topics to include such subjects as hydrogen-ion concentration and its determination, chemical composition of natural waters, determination of free chlorine, and methods of the American Railway Engineering Association for estimation of mineral constituents. Other new features having to do with chemical analysis are a chapter devoted to exercises in water-softening, coagulation, and chlorination, and, in the form of an appendix, a chapter on the preparation of permanent standards for use in analysis.

In the reviewer's opinion, the material in the latter chapter would better have been distributed under the various determinations it concerns, where one would expect to find the information. Also, in presenting the various tests, a more logical sequence might have been followed that would have brought together tests that deal with similar forms of matter. There is no apparent reason, for example, why hydrogen-ion concentration should be placed between the tests for temperature and color.

Only 17 pages are devoted in a rather sketchy way to the subjects of bacteriological and microscopical analysis. For students' use a broader discussion of the significance of these examinations would have been desirable.

There is a short appendix of "problems in interpretation of bacterial tests," one of rather questionable value containing forms for recording purification data, one on the conversion of certain metric units to English equivalents, one on temperature corrections for specific gravity of brines, and finally one which is a 36-page reprint from Public Health Reports and which deals with drinking-water standards promulgated for common carriers in interstate commerce.

There is failure in places to balance properly the amount of subject matter. Some 19 pages are given over to ammonia determinations and 6 pages to zinc, while only passing mention is given to the subject of carbon dioxide.

The book will be useful in supplementing Standard Methods of Water Analysis, which is a manual of procedures. As a complete text on the subject of water analysis, it leaves much to be desired. Melville C. Whipple

* * *

In the bibliography of the review of "Benzol (Benzene) Poisoning," by Carey P. McCord [Ind. Eng. Chem., 24, 253 (1932)], the publisher's address should be the Industrial Health Conservancy Laboratories, 34 W. Seventh Street, Cincinnati, Ohio.

POTENTIOMETRIC TITRATIONS. A THEORETICAL AND PRACTICAL TREATISE.

By I. M. Kolthoff and N. Howell Furman. 2nd edition, 482 + xiv pages, 73 figures. John Wiley & Sons, Inc., New York, 1931. Price, $6.00.

The general style and scope of the first edition of this work have been preserved in the new volume, although marked changes in content are evident. An idea of the difference may be gained from the fact that the new text contains approximately 40 per cent more material than its predecessor, although the amount of fundamental theory has been noticeably revised and abbreviated.

The first section, comprising about one-seventh of the text, is devoted to a discussion of the fundamental principles of potentiometric titrations, including related theory. These are concisely presented with the aid of exemplary tables and figures.

In the following section, generously illustrated, the same amount of space is devoted to apparatus and technic. Here a considerable amount of new and useful material has been added, notably on bimetallic systems, differential titrations, and electronic-tube applications. In the last-mentioned case, a new and quite complete, though noncritical, treatment has been added. If properly designed apparatus is used, the reviewer cannot agree to the necessity for observing some of the precautions mentioned at the end of the chapter. It should be noted, however, that here the authors quote other workers.

Most of the remainder of the book is devoted to practical applications and here again a great amount of new subject matter has been introduced. Metal electrodes and the glass electrode receive increased recognition as do many oxidation-reduction methods. Among the last are determinations based on the use of ceric, chromous, uranous, nitrite, and fluoride ions.

The work is concluded with an extensive bibliography and tables of useful constants.

To one interested in this field the text furnishes an enjoyable and practical source for reading and reference. The subject matter throughout is presented in a thorough and useful manner and should be appreciated by both the student and the practical chemist.

H. M. Partridge

DIE CHEMISCHE BETRIEBSKONTROLLE IN DER ZELLSTOFF- UND PAPIER-INDUSTRIE UND ANDERSEN ZELLSTOFF VERABERTENDEN INDUSTRIEN.

By Carl G. von Schwalbe and Rudolf Sieber. 3rd edition, 547 pages. Julius Springer, Berlin, 1931. Price, 33 marks.

This is the third edition of an important handbook of control methods intended for use in the pulp and paper industry. The first edition appeared in 1919 but was speedily exhausted by the winter of 1920. The second edition published in 1922 has been out of print for some time. All chemists interested in the technical control of the processes related to the manufacture of pulp and paper, and for cellulose required by the explosive, celluloid, and artificial-silk industries, will welcome the appearance of the third edition. The material and methods are complete through the first half of 1931.

The third edition contains much of the material to be found in the second, although the treatment of the sixth chapter of the second edition on methods for the investigation of pulps has been divided into two new sections: one deals with investigation of half stuffs, the other with investigation of bleached pulp. The fifth chapter of the second edition on bleaching has been inserted between these two new sections. These sections likewise have been further subdivided to differentiate between wood pulp on the one hand, and jute, hemp, linen, and cotton pulps (rags) on the other.

Among the sections which have been rather thoroughly revised are those by Sieber on operations in the boiler house, on pulp and paper manufacture, and on white water recovery; and by Schwalbe on raw-fiber half stuffs, bleaching, and bleached pulps.

The inclusion of so many analytical methods without sufficient criticism or direction leaves the reader rather bewildered as to which to select. The reviewer is of the opinion that new, untried, or unsatisfactory material should, at the most, receive relatively short notice in a book of this type, leaving for detailed discussion only those methods which are of proved worth. This is a minor criticism, however of an extremely valuable book.

The book is well printed and has been greatly improved over the earlier editions through the use of boldface titles for subject headings of the various methods. Both paper and binding are of high grade.

Harry F. Lewis

FLOTATION. ROTH'S SAMMLUNG CHEMIE UND TECHNIK DER GEGENWART, BAND XIII.

By Erwin W. Mayer and Hubert Schranz. 593 pages, 175 illustrations, 7 tables. S. Hirzel, Leipzig, 1931. Price, paper, 33 marks; bound, 35 marks.

This volume contains a tremendous collection of valuable information on the subject of flotation. It is supplemented by a large number of references to the original literature of forty-nine different industrial and scientific journals and technical papers. Moreover the references are up to date, even including publications of 1931.

A brief historical section introduces the subject. A portion of the volume is devoted to a description of the various machines used in connection with the practice of flotation. Then methods of procedure are taken up in detail, from the general consideration of the fundamentals of the physics and chemistry of interfaces, to the influence of various factors on the flotation of minerals. Some of the factors discussed are pulp density, fineness of grinding, temperature, pH of the solutions, and reagents used for collectors and frothers. Procedures for the treatment of the important sulfide ores are then given, and the practice in plants all over the world tabulated. It is unfortunate that the European policy of secrecy in such matters necessitates the omission of many data that should otherwise have been included in a work of this kind. The selective flotation of lead-zinc sulfides and of various complex sulfide ores is discussed from the theoretical as well as the practical standpoint. The possibilities of the floating of a considerable number of nonsulfide minerals, such as cerussite, malachite, azurite, rhodochrosite, siderite, hematite, phosphate, barite, fluorite, cryolite, talc, micas, calcite, pyrolusite, chromite, scheelite, kaolin, coal, and others, are discussed as to methods and commercial applications.

An appendix with a list of floatable minerals, a list of available literature on the subject, and an excellent subject and author index make this volume a veritable mine of valuable information for either the industrial worker or the theoretical investigator in the field of flotation.

A. E. Koenig

DER KALKSTICKSTOFF IN WISSENSCHAFT, TECHNIK UND WIRTSCHAFT.

By H. Heinrich Franck, W. Makkus, and F. Janke. xvi + 213 pages. Ferdinand Enke, Stuttgart, 1931. Price, paper, 19.20 marks.

This monograph is No. 6 of the new series of Ahrens' Sammlung chemischer und chemisch-technischer Vorträge. The two senior authors are the directors of the Central Laboratory, and of the Agricultural Division, respectively, of the Bayerische Stickstoff-Werke A. G., whose plants at Trostberg and Piesteritz produce about six-sevenths of Germany's "lime-nitrogen," and about one-third of the world's total. Nevertheless, the subject is treated in the main from a broad standpoint, and cyanamide in all its aspects—scientific, industrial, agricultural, and economic—is adequately summarized for the first time. The treatment is selective rather than exhaustive, but very numerous references to the literature are given, many as late as 1931.

The first section (Janke, 134 pages) deals briefly with the discovery and early development of cyanamide, and outlines the technical details of its production and transformation into other products; this is followed by an elaborate discussion of the large-scale development of the industry during and since the War, both in Germany and throughout the world. The procedures employed by every plant are outlined, as are the history, production, and financial status of all companies engaged in cyanamide manufacture. The numerous and up-to-date tables of German and world production of fixed nitrogen in its various forms should prove useful.

The second section (Franck, 38 pages), after a brief résumé of earlier knowledge of cyanamide chemistry, gives a good summary of the recent (in part unpublished) investigations conducted by the Bayer Company. Several newly patented procedures which may prove important in reducing costs are described, and valuable thermochemical and thermodynamic data are included.

The last section (Makkus, 36 pages) deals with the utilization of cyanamide in agriculture as fertilizer, pest-eradicator, and weed-killer. The value of this section for the American reader is greatly decreased by the almost complete avoidance of the problem of cyanamide in mixed fertilizers. In any case, Makkus' discussion is essentially an argument in favor of cyanamide, rather than an unbiased treatment of its behavior in the soil and the difficulties peculiar to its utilization. Arthur F. Benton

ELECTRICITY. WHAT IT IS AND HOW IT ACTS. VOLUME II. *By Andrew W. Kramer.* xiv + 290 pages, 13 × 19.5 cm. Technical Publishing Company, Chicago, 1931. Price, $2.00.

This little book evidently represents a tremendous amount of work on the part of the author. He tells (and tells well) in nonmathematical language the various ways in which electrons are supposed to act, both directly and indirectly. This causes him to touch on the subjects of visible light, x-rays, radio, radioactivity, cosmic rays, magnetism, crystal analysis, and wave mechanics. Abstruse mathematics is replaced by a series of analogies which are not taken too seriously by the author. It would be asking too much to expect such a treatment to completely satisfy a scientific specialist, but the book is evidently not written for him. Neither is it written for the casual reader who has never had any scientific training. It will be a very inspiring book for high-school teachers of physics, for electrical engineers who wish to get a taste of modern physics and physical chemistry, and for college seniors who have taken the customary sophomore and junior physics courses and now wish to see their subject in perspective. For such readers the author has done wonderfully well. They will forgive him a very occasional slip (for instance, ".... sodium chloride, lead sulfide and in fact most metals...."), which they can correct at once as they read, and will love him for his clarity of style and his knack of bringing out interrelationships between the topics which he treats. If a few of its readers gain the incentive to take up the grind of going to the bottom of the subject (mathematics, abstractions, and all) the book will have justified all the labor that has been spent on it. Wheeler P. Davey

HANDBUCH DER KÜNSTLICHEN PLASTISCHEN MASSEN. *By Oskar Kausch.* 353 pages. J. F. Lehmans Verlag, Munich, 1931. Price, 20 marks; bound, 22 marks.

In addition to the above title, the author states on the title page of this book that it is a Systematic Review of Patents on the Preparation and Properties of Plastic Masses and Their Industrial Application, and that is exactly what it is.

The book is divided into 14 chapters, each dealing with a different type of plastic material, both natural and synthetic. A short abstract of each patent is given, and, for the most part, they are arranged in chronological order so that the development of each plastic industry can be easily followed. Appended to the description of the patents is a list of the commercial names of the plastic masses, their composition, and the manufacturer, as well as a list of the patent numbers and the countries in which they were issued. In all, a little more than two thousand patents of various countries have been abstracted; these are divided as follows: Germany, 655; Austria, 106; Switzerland, 96; Great Britain, 351; France, 262; Belgium, 2; United States, 572. The book is fairly comprehensive, and for anyone wishing to find out the patent situation in any given country, it would be of great help. As a textbook on the chemistry of plastic masses, it is not of great value.

In general, it is a book which should interest all those engaged in research work on plastic materials, irrespective of their nature, since it points out practically everything that has been done in any given line, and should therefore show the way to future research. It is a book which will doubtless be of value and benefit to all workers in the plastic field. W. J. Kelly

DIE BIERBRAUEREI. II TEIL. DIE TECHNOLOGIE DER BIERBEREITUNG. *By Hans Leberle.* 2nd edition, 642 pages, illustrated. Ferdinand Enke, Stuttgart, 1931. Price, 35.50 marks.

The book is a revision of the earlier work published some six years ago. The author states that the revision was necessary because of the many new developments in the art of brewing, particularly in its chemical and biological aspects. Nearly all the chapters have been rewritten.

Leberle starts the book with 65 pages devoted to the raw materials of brewing, including malts, grains, water, hops, etc. The second and main portion, some 560 pages, deals with the manufacture of beer in all its aspects. There are 10 chapters in this division as follows: Grinding of Malt, Preparation of Wort, Separation of Wort, Boiling and Hopping, Yield, Cooling of Wort, Fermentation (theory, practice, and after-treatment), Racking and Clarifying, Shrinkage, Properties of Beer.

Every subject is treated fully and scientifically, and, taken as a whole, this is the most up-to-date and complete exposition of this interesting subject the reviewer has seen. Search failed to find reference to the manufacture of that peerless American brew, "Heimgemacht," but perhaps a resident of Germany feels no immediate need of that for himself; as for us, "coals to Newcastle." John R. Eoff

DIE ANALYSENMETHODEN DER DÜNGEMITTEL. EIN BUCH DER PRAXIS. *By Alfred Suchier.* 79 pages, 3 figures. Verlag Chemie, G. m. b. H., Corneliusstrasse 3, Berlin W. 10, Germany, 1931. Price, 6 marks.

This volume presents the analytical methods that have stood the test of years of practical application in the central laboratory of the Verein für chemische und metallurgische Produktion Aussig, Czechoslovakia's largest fertilizer-manufacturing concern. It is divided into five sections, captioned Phosphorus, Nitrogen, Potash, Mixed Fertilizers, and Lime Fertilizer Materials, respectively. The first three sections, however, are not restricted to the determinations indicated by their headings but include all the analytical methods that are applied to the various phosphatic, nitrogenous, and potassiferous fertilizer materials. Procedures are given, for example, for the determination of ferric oxide, alumina, magnesia, carbon dioxide, fluorine, silica, etc., in phosphate rock. It is in such methods that the American chemist will find most interest, since, for the determination of phosphoric acid, nitrogen, and potash, he confines himself customarily to the methods prescribed in "Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists." A valuable feature of the book is a final series of tables giving the averages of the results that have been found for various fertilizer materials. Albert R. Merz

CHEMIE UND CHEMISCHE TECHNOLOGIE TIERISCHER STOFFE. *By Georg Grasser.* 272 pages. Ferdinand Enke, Stuttgart, 1931. Price, 17 marks, 60 pfennigs.

This is the twentieth volume in Enke's Bibliothek für Chemie und Technik. It bears the subtitle "An Introduction into Applied Zoo Chemistry." This is an intriguing, but a too-ambitious undertaking to be accomplished in 272 pages, including an index. Many would wish that in a few hundred pages there could be condensed the chemistry of the meat-packing industry relating to tanning, gelatin and glue, fats, oils, oleomargarine, hormones, enzymes.

The result in the present volume is a very fragmentary treatment of the various subjects. In such fast-moving fields as the hormones and enzymes, many of the statements are incorrect or several years behind the date of the foreword (summer, 1931).

For the American reader, much of the information on products or processes is inapplicable, owing to the specialized control of the meat-packing industry by the Bureau of Animal Industry. David Klein

MARKET REPORT—FEBRUARY, 1932

THESE PRICES UNLESS OTHERWISE SPECIFIED ARE THOSE PREVAILING IN THE NEW YORK MARKET, FEBRUARY 15, FOR COMMERCIAL GRADES IN CARLOAD QUANTITIES

Newer Chemicals

Acetaldehyde, drums, lc-l., wks...lb.	.18½
Acetaldol, 50-gal. drums.........lb.	.27
Acetylene tetrachloride, *see* Tetrachloroethane	
Acid, abietic....................lb.	.12
Adipic........................lb.	.72
Linoleic......................lb.	.16
Ammonium linoleate, drums......lb.	.15
Amyl furoate, 1-lb. tins..........lb.	5.00
Aroclors........................lb.	.40
Butyl carbitol, *see* Diethylene glycol monobutyl ether	
Cellosolve, *see* Ethylene glycol monobutyl ether	
Furoate, tech., 50-gal. drums...lb.	1.00
Carbitol, *see* Diethylene glycol monoethyl ether	
Cellosolve, *see* Ethylene glycol monoethyl ether	
Acetate, *see* Ethylene glycol monoethyl ether acetate	
Crotonaldehyde, 50-gal. drums...lb.	.32
Dichloroethyl ether, 50-gal. drums.lb.	.06
Diethylene glycol, drums.........lb.	.14
Monobutyl ether, drums.......lb.	.24
Monoethyl ether, drums.......lb.	.15
Diethylene oxide, 50-gal. drums...lb.	.50
Dioxan, *see* Diethylene oxide	
Diphenyl........................lb.	.30
Ethyl acetoacetate, 50-gal. drums.lb.	.65
Carbonate, 90%, 50-gal. drums..gal.	1.85
Chlorocarbonate, carboys......lb.	.30
Ether, absolute, 50-gal. drums..lb.	.50
Furoate, 1-lb. tins.............lb.	5.00
Ethylene chlorhydrin, 40%, 10-gal. cbys....................lb.	.75
Dichloride, 50-gal. drums......lb.	.05
Glycol, 50-gal. drums..........lb.	.25
Monobutyl ether, drums, wks.lb.	.24
Monoethyl ether, drums, wks.lb.	.17
Monoethyl ether acetate, drums, wks...............lb.	.19½
Monomethyl ether, drums...lb.	.21
Oxide, cyl..................lb.	2.00
Furfuramide(tech.),100-lb. drums.lb.	.30
Furfuryl acetate, 1-lb. tins.......lb.	5.00
Alcohol, tech., 100-lb. drums....lb.	.50
Furoic acid (tech.), 100-lb. drums.lb.	.50
Glyceryl phthallate..............lb.	.26
Glycol stearate..................lb.	.18
Isopropyl ether, drums...........lb.	.10
Lead dithiofuroate, 100-lb. drums.lb.	1.00
Magnesium peroxide, 100-lb. cs...lb.	1.15
Methyl acetate, drums..........gal.	1.20
Cellosolve, *see* Ethylene glycol monomethyl ether	
Furoate, tech., 50-gal. drums...lb.	.50
Paraldehyde, 110-55 gal. drums..lb.	.20½
Phosphorus oxychloride, 175 cyl...lb.	.20
Propyl furoate, 1-lb. tins.........lb.	2.50
Strontium peroxide, 100-lb. drums.lb.	1.25
Sulfuryl chloride, 600-lb. drums, crude.......................lb.	.15
Distilled.......................lb.	.40
Tetrachloroethane, 50-gal. drums.lb.	.09
Trichloroethylene, 50-gal. drums..lb.	.10
Triethanolamine, 50-gal. drums...lb.	.40
Trihydroxyethylamine linoleate...lb.	.40
Trihydroxyethylamine stearate...lb.	.35
Vinyl chloride, 16-lb. cyl.........lb.	1.00
Zinc dithiofuroate, 100-lb. drums..lb.	1.00
Perborate, 100-lb. drums.......lb.	1.25
Peroxide, 100-lb. drums........lb.	1.25

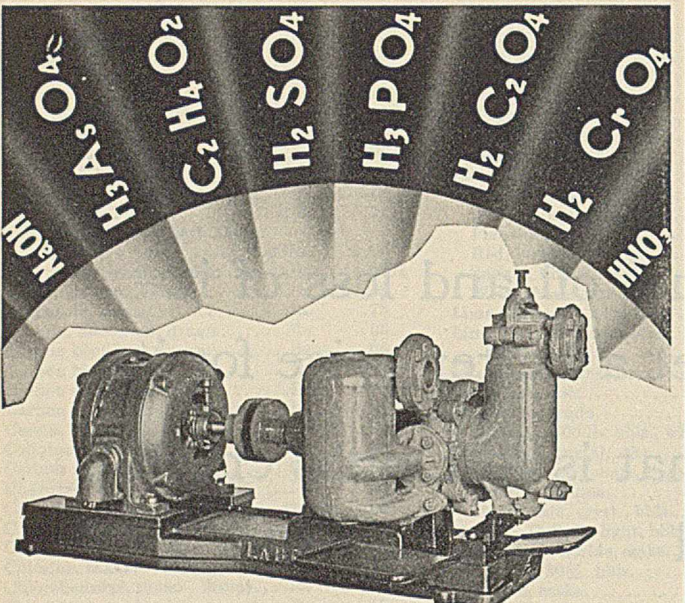
Chemicals Previously Quoted

Acetanilide, U. S. P., powd., bbls..lb.	.24
Acetic anhydride, 92-95%, cbys...lb.	.21
Acetone, drums, wks.............lb.	.10¼
Acetphenetidin, bbls.............lb.	1.25
Acid, acetic, 28%, c/l., bbls..100 lbs.*	2.40
56%, c/l., bbls.........100 lbs.	4.60
Glacial, c/l., bbls.......100 lbs.	8.10
Glacial, U. S. P., c/l., carboys ....100 lbs.	8.85
Acetylsalicylic, bbls...........lb.	.75
Anthranilic, 99-100%, drums..lb.	.85
Benzoic, tech., bbls...........lb.	.40
Boric, bbls....................lb.	.06⅓
Butyric, 100% basis, cbys......lb.	.80
Chloroacetic, mono-, bbls., wks..lb.	.18
Di-, cbys...................lb.	1.00
Tri-, bbls...................lb.	2.50
Chlorosulfonic, drums, wks.....lb.	.04½
Chromic, 99%, drums.........lb.	.13¼
Cinnamic, bottles.............lb.	3.25
Citric, U. S. P., cryst., bbls......lb.	.33½
Cresylic, pale, drums.........gal.	.49
Formic, 90%, cbys., N. Y......lb.	.10¼
Gallic, U. S. P., bbls..........lb.	.74
Glycerophosphoric, 25%, 1-lb. bot.........................lb.	1.40
H, bbls., wks..................lb.	.65
Hydriodic, 10%, U. S. P., 5-lb. bot.........................lb.	.67
Hydrobromic, 48%, cbys., wks..lb.	.45
Hydrochloric, 20°, tanks, wks. ....100 lbs.	1.35
Hydrofluoric, 30%, bbls., wks...lb.	.06
60%, bbls., wks.............lb.	.13
Hydrofluosilic, 35%, bbls., wks..lb.	.11
Hypophosphorus, 30%, U. S. P., 5-gal. demis................lb.	.85
Lactic, 22%, dark, bbls........lb.	.04
48%, light, bbls., wks........lb.	.11
Mixed, tanks, wks.........N unit	.07
S unit	.08
Molybdic, 85%, kegs..........lb.	1.25
Naphthionic, tech., bbls........lb.	nom.
Nitric, c. p., cbys.............lb.	.11
Nitric, 36°, c/l., cbys., wks. ....100 lbs.	5.00
Oxalic, bbls., wks..............lb.	.11
Phosphoric, 50%, U. S. P......lb.	.14
Picramic, bbls.................lb.	.65
Picric, bbls., c/l...............lb.	.30
Pyrogallic....................lb.	1.50
Salicylic, tech., bbls...........lb.	.33
Stearic, d. p., bbls., c/l.........lb.	.08
Sulfanilic, 250-lb. bbls.........lb.	.14½
Sulfuric, 66°, c/l., cbys., wks. ....100 lbs	1.60
66°, tanks, wks............ton	15.00
60°, tanks, wks............ton	10.50
Oleum, 20%, tanks, wks.....ton	18.50
40%, tanks, wks.........ton	42.00
Sulfurous, U. S. P., 6%, cbys....lb.	.05
Tannic, tech., bbls............lb.	.23
Tartaric, U. S. P., cryst., bbls...lb.	.24½
Tungstic, kegs................lb.	1.40
Valeric, c. p., 10-lb. bot........lb.	2.50
Alcohol, U. S. P., 190 proof, bbls..gal.	2.57
Amyl, from pentane, tanks.....lb.	.203
Amyl, Imp. drums...........gal.	1.75
Butyl, drums, c/l., wks........lb.	.148
Cologne spirit, bbls...........gal.	2.69
Denatured, No. 5, comp. denat., c/l., drums................gal.	.34½
Isoamyl, drums...............gal.	4.00
Isobutyl, ref., drums.........gal.	1.00
Isopropyl, ref., drums........gal.	.60
Propyl, ref., drums...........gal.	1.00
Wood, *see* Methanol	
Alpha-naphthol, bbls............lb.	.57
Alpha-naphthylamine, bbls.......lb.	.32
Alum, ammonia, lump, bbls., wks. ....100 lbs.	3.30
Chrome, casks, wks.......100 lbs.	5.00
Potash, lump, bbls., wks...100 lbs.	3.35
Soda, bbls., wks..........100 lbs.	3.45
Aluminum, metal, N. Y.....100 lbs.	22.90
Aluminum chloride, anhyd., commercial, wks., drums extra, c/l..lb.	.05
Aluminum stearate, 100-lb. bbl....lb.	.20
Aluminum sulfate, comm'l, bags, wks...................100 lbs.	1.25
Iron-free, bags, wks.......100 lbs.	1.90
Aminoazobenzene, 100-lb. kegs...lb.	1.15
Ammonia, anhydrous, cyl., wks...lb.	.15½
50,000-lb. tanks, wks..........lb.	.05625
Ammonia, aqua, 26°, tanks, wks., contained NH_3..............lb.	.05½
Ammonium acetate, kegs........lb.	.33
Bifluoride, bbls...............lb.	.21
Bromide, 50-lb. boxes.........lb.	.35
Carbonate, tech., casks........lb.	.08
Chloride, gray, bbls.......100 lbs.	5.25
Lump, casks...............lb.	.10½
Iodide, 25-lb. jars.............lb.	5.20
Nitrate, tech., cryst., bbls......lb.	.08½
Oxalate, kegs.................lb.	.22
Persulfate, cases..............lb.	.26
Phosphate, dibasic, tech., bbls..lb.	.10¾
Sulfate, bulk, wks........100 lbs.	1.10
Amyl acetate, tech., from pentane, tanks.......................lb.	.175
Aniline oil, drums...............lb.	.14½
Anthracene, 80-85%, casks, wks..lb.	.60
Anthraquinone, subl., bbls........lb.	.50
Antimony, metal................lb.	.06⅜
Antimony chloride, drums.......lb.	.13
Oxide, bbls...................lb.	.08½
Salt, dom., bbls...............lb.	.22
Sulfide, crimson, bbls..........lb.	.25
Golden, bbls................lb.	.16
Vermilion, bbls..............lb.	.38
Argols, red powder, bbls.........lb.	.07
Arsenic, metal, kegs.............lb.	.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	56.50
Chloride, bbls., wks...........lb.	.03¾
Dioxide, drs., wks.............lb.	.12
Hydroxide, bbls...............lb.	.05¼
Nitrate, casks.................lb.	.07¼
Barium thiocyanate, 400-lb. bbls..lb.	.27
Barytes, floated, 350-lb. bbls., wks. ....ton	23.00
Benzaldehyde, tech., drums......lb.	.60
F. F. C., cbys.................lb.	1.40
U. S. P., cbys.................lb.	1.15
Benzidine base, bbls.............lb.	.65
Benzol, tanks, wks.............gal.	.20
Benzoyl chloride, cbys...........lb.	1.00
Benzyl acetate, F. F. C., bottles...lb.	.75
Alcohol, 5-liter bot............lb.	1.20
Chloride, tech., drums.........lb.	.30
Beta-naphthol, bbls..............lb.	.22
Beta-naphthylamine, bbls........lb.	.58
Bismuth, metal, cases...........lb.	1.00
Bismuth, nitrate, 25-lb. jars......lb.	.95
Oxychloride, boxes...........lb.	2.95
Subnitrate, U. S. P., 25-lb. jars.lb.	1.20
Blanc fixe, dry, bbls............ton	70.00
Bleaching powder, drums, wks. ....100 lbs.	2.00
Bone ash, kegs..................lb.	.06
Bone black, bbls.................lb.	.08¼
Borax, bags.....................lb.	.02½
Bordeaux mixture, bbls..........lb.	.11½
Bromine, bot....................lb.	.36
Bromobenzene, drums...........lb.	.50
Bromoform, jars.................lb.	1.80
Butyl acetate, drums, c/l.........lb.	.159
Cadmium bromide, 50-lb. jars....lb.	1.40
Cadmium, metal, cases..........lb.	.55

---

* Contract price.

Cadmium sulfide, boxes	lb.	.60
Caffeine, U. S. P., 5-lb. cans	lb.	2.40
Calcium acetate, bags	100 lbs.	2.00
Arsenate, bbls	lb.	.05½
Carbide, drums	lb.	.05½
Chloride, drums, wks., flake	ton	21.00
Cyanide, 100-lb. drums	lb.	.30
Nitrate, bags	ton	35.00
Phosphate, monobas., bbls	lb.	.08
Tribas., bbls	lb.	.11
Calcium carbonate, tech., bags,	100 lbs.	1.00
U. S. P., precip., 175-lb. bbl	lb.	.06½
Camphor, Jap., cases	lb.	.49
Carbazole, bbls	lb.	.75
Carbon, activated, drums	lb.	.08
Carbon bisulfide, drums	lb.	.05
Carbon black, cases	lb.	.06
Carbon dioxide, liq. cyl	lb.	.06
Carbon tetrachloride, drums	lb.	.06¼
Casein, stand. gr., bbls	lb.	.07
Cellulose acetate, bbls	lb.	.80
Cerium oxalate, kegs	lb.	.33
Charcoal, willow, powd., bbls	lb.	.06
China clay, bulk	ton	8.00
Chloral hydrate, drums	lb.	.70
Chlorine, liq., c/l., cyl	lb.	.04
Chlorine, tanks	100 lbs.	1.75
Chlorobenzene, mono-, drums	lb.	.10
Chloroform, tech., drums	lb.	.15
Chromium acetate, 20° soln., bbls.	lb.	.05
Coal tar, bbls., wks	gal.	.10
Cobalt, metal, kegs	lb.	2.50
Cobalt oxide, bbls	lb.	1.35
Cod-liver oil, bbls	bbl.	30.00
Copperas, c/l., bulk	ton	14.50
Copper, metal, elec	100 lbs.	6.25
Copper carbonate, bbls., 52/54%	lb.	.16½
Chloride, bbls	lb.	.22
Cyanide, drums	lb.	.39
Oxide, red, bbls	lb.	.15½
Sulfate, c/l., bbls	100 lbs.	2.75
Cotton, soluble, bbls	lb.	.40
Cream tartar, bbls	lb.	.19¼
Cyanamide, bulk, N. Y.	Ammonia unit	.97½
Diaminophenol, kegs	lb.	3.80
Dianisidine, bbls	lb.	2.35
Dibutylphthalate, drums, wks	lb.	.22$^{1}/_{8}$
Diethylaniline, drums	lb.	.55
Diethylene glycol, drums	lb.	.14
Diethyl phthalate, drums	lb.	.23
Diethyl sulfate, tech., drums	lb.	.30
Dimethylaniline, drums	lb.	.26
Dimethylsulfate, drums	lb.	.45
Dinitrobenzene, drums	lb.	.15½
Dinitrochlorobenzene, bbls	lb.	.13
Dinitronaphthalene, bbls	lb.	.34
Dinitrophenol, bbls	lb.	.23
Diphenylamine, bbls	lb.	.34
Diphenylguanidine, bbls	lb.	.30
Epsom salt, tech., bbls., c/l., N. Y.	100 lbs.	1.70
Ether, nitrous, bot	lb.	.80
Ether, U. S. P., drums	lb.	.09
Ethyl acetate, tanks, c/l	lb.	.09
Bromide, drums	lb.	.50
Chloride, drums	lb.	.22
Methyl ketone, drums	lb.	.30
Ethylbenzylaniline, 300-lb. drums.	lb.	.88
Ethylene dichloride	lb.	.05
Chlorohydrin, anhyd., drums	lb.	.75
Glycol, c/l., wks	lb.	.25
Feldspar, bulk	ton	6.50
Ferric chloride, tech., bbls	lb.	.05
Ferrous chloride, cryst., bbls	lb.	.06
Ferrous sulfide, bbls	100 lbs.	2.50
Fluorspar, 98%, bags	ton	31.00
Formaldehyde, bbls	lb.	.06
Formaniline, drums	lb.	.37½
Fuller's earth, bags, c/l., mines	ton	15.00
Furfural drums, tech., contract, works	lb.	.10
Glauber's salt, bbls	100 lbs.	1.00
Glucose, 70°, bags, dry	100 lbs.	3.14
Glycerine, c. p., drums	lb.	.11¼
G salt, bbls	lb.	.42
Hexamethylenetetramine, tech., drums	lb.	.46
Hydrogen peroxide, 25 vol., bbls	lb.	.05½
Hydroquinone, kegs	lb.	1.20
Indigo, 20%, paste, bbls	lb.	.12
Iodine, crude, 200-lb. kgs	lb.	4.20
Iodine, resubl., jars	lb.	4.65
Iodoform, bot	lb.	6.00
Iridium, metal	oz.	160.00
Kieselguhr, bags	ton	50.00
Lead, metal, N. Y	100 lbs.	3.75
Lead acetate, bbls., white	lb.	.10½
Arsenate, bbls	lb.	.10
Oxide, litharge, bbls	lb.	.05¾
Peroxide, drums	lb.	.20
Red, bbls	lb.	.06¾
Sulfate, bbls	lb.	.06½
White, basic carb., bbls	lb.	.07¼
Lime, hydrated, bbls	100 lbs.	.85
Lime, live, chemical, bbls., wks.	100 lbs.	1.05
Limestone, ground, bags, wks	ton	4.50
Lithopone, bbls	lb.	.04½
Magnesite, crude	ton	32.00
Calcined, 500-lb. bbls., wks	ton	40.00
Magnesium, metal, wks	lb.	.30
Magnesium carbonate, bags	lb.	.06
Chloride, drums	ton	36.00
Fluosilicate, cryst., bbls	lb.	.10
Oxide, U. S. P., light, bbls	lb.	.42
Manganese chloride, casks	lb.	.07½
Dioxide, 80%, bbls	ton	80.00
Sulfate, casks	lb.	.07
Mercury bichloride, cryst., 50 lbs.	lb.	1.59
Mercury, flasks, 76 lbs	flask	65.00
Meta-nitroaniline, bbls	lb.	.67
Meta-phenylenediamine, bbls	lb.	.80
Meta-toluylenediamine, bbls	lb.	.67
Methanol, pure, synthetic, drums, wks	gal.	.37½
Tanks, wks	gal.	.35½
Methyl acetone, drums	gal.	.50
Salicylate, cases	lb.	.42
Methyl chloride, cylinders	lb.	.45
Michler's ketone, bbls	lb.	3.00
Naphtha, solvent, tanks	gal.	.26
Naphthalene, flake, bbls	lb.	.03¾
Nickel, metal	lb.	.35
Nickel salt, single, bbls	lb.	.10
Double, bbls	lb.	.10
Niter cake, bulk	ton	11.50
Nitrobenzene, drums	lb.	.08½
Oil, castor, No. 1	lb.	.10
China wood, bbls	lb.	.07½
Coconut, Ceylon, tanks	lb.	.04½
Cod, N. F., tanks	gal.	.25
Corn, crude, tanks, mills	lb.	.03⅜
Cottonseed, crude, tanks	lb.	.04
Lard, edible, bbls	lb.	.11¼
Linseed, bbls	lb.	.07
Menhaden, crude, tanks	gal.	.20
Neat's-foot, pure, bbls	lb.	.09½
Oleo, No. 1, bbls	lb.	.07⅛
Olive oil, denat., bbls	gal.	.75
Foots, bbls	lb.	.04¾
Palm, Lagos, casks	lb.	.04
Peanut, crude, bbls	lb.	.07
Perilla, bbls	lb.	.06½
Rapeseed, bbls., English	gal.	.39
Red, bbls	lb.	.06⅝
Soy bean, crude, bbls	lb.	.043
Sperm, 38°, bbls	gal.	.68
Whale, bbls., natural, winter	gal.	.56
Ortho-aminophenol, kegs	lb.	2.15
Ortho-dichlorobenzene, drums	lb.	.08
Ortho-nitrochlorobenzene, drums	lb.	.28
Ortho-nitrophenol, bbls	lb.	.85
Ortho-nitrotoluene, drums	lb.	.16
Ortho-toluidine, bbls	lb.	.20
Palladium, metal	oz.	19.00
Para-aminophenol, kegs	lb.	.78
Para-dichlorobenzene	lb.	.15½
Para-formaldehyde, cases	lb.	.38
Paraldehyde, tech., drums	lb.	.20½
Para-nitraniline, drums	lb.	.48
Para-nitrochlorobenzene, drums	lb.	.25
Para-nitrophenol, bbls	lb.	.45
Para-nitrosodimethylaniline, bbls	lb.	.92
Para-nitrotoluene, bbls	lb.	.29
Para-phenylenediamine, bbls	lb.	1.15
Para-toluidine, bbls	lb.	.40
Paris Green, 250-lb. kegs	lb.	.25
Phenol, drums	lb.	.14¼
Phenolphthalein, drums	lb.	.80
Phenylethyl alcohol, 1-lb. bot	lb.	7.00
Phosphorus, red, cases	lb.	.45
Phosphorus trichloride, cyl	lb.	.35
Phthalic anhydride, bbls	lb.	.15
Platinum, metal	oz.	37.00
Potash, caustic, drums	lb.	.06⅛
Potassium acetate, kegs	lb.	.28
Bicarbonate, casks	lb.	.09½
Bichromate, casks	lb.	.08
Binoxalate, bbls	lb.	.14
Bromate, cs	lb.	.35
Carbonate, 80–85%, calc., casks.	lb.	.04¾
Chlorate, kegs	lb.	.08
Chloride	ton	34.55
Cyanide, cases	lb.	.55
Meta-bisulfite, bbls	lb.	.11
Permanganate, drums	lb.	.16
Prussiate, red, casks	lb.	.37½
Yellow, casks	lb.	.18½
Titanium oxalate, bbls	lb.	.21
Pyridine, drums	gal.	1.50
Resorcinol, tech., kegs	lb.	.65
Rochelle salt, bbls., U. S. P	lb.	.16
R salt, bbls	lb.	.42
Saccharin, cans	lb.	1.70
Salt cake, bulk	ton	14.00
Saltpeter, gran., bbls	lb.	.06
Silica, ref., bags	ton	22.00
Silver nitrate, 16-oz. bot	oz.	.23¼
Soda ash, 58%, light, bags, contract, wks	100 lbs.	1.15
Soda, caustic, 76%, solid, drums, contract, wks	100 lbs.	2.50
Sodium acetate, bbls	lb.	.04½
Benzoate, bbls	lb.	.42
Bicarbonate, bbls	100 lbs.	1.85
Bichromate, casks	lb.	.05
Bisulfite, bbls	lb.	.04
Bromide, bbls., U. S. P	lb.	.31
Chlorate, kegs	lb.	.05¾
Chloride, bags	ton	12.00
Cyanide, cases	lb.	.16½
Fluoride, bbls	lb.	.07
Metallic, drums, 12¼-lb. bricks.	lb.	.19
Naphthionate, bbls	lb	.52
Nitrate, crude, 200-lb. bags, N. Y	100 lbs.	1.76½
Nitrite, bbls	lb.	.07
Perborate, bbls	lb.	.18
Peroxide, cases	lb.	.21
Phosphate, trisodium	100 lbs.	3.20
Picramate, kegs	lb.	.69
Prussiate, bbls	lb.	.11½
Silicate, drums, tanks, 40°	100 lbs.	.75
Silicofluoride, bbls	lb.	.05¼
Stannate, drums	lb.	.18
Sulfate, anhyd., bbls	lb.	.02
Sulfide, cryst., bbls	lb.	.02½
Solid, 60%	lb.	.03½
Sulfocyanide, bbls	lb.	.28
Thiosulfate, reg., cryst., bbls	lb.	.02½
Tungstate, kegs	lb.	.70
Strontium carbonate, tech., bbls	lb.	.07¼
Nitrate, bbls	lb.	.09
Sulfur, bulk, mines, wks	ton	18.00
Sulfur chloride, red, drums	lb.	.05
Yellow, drums	lb.	.03½
Sulfur dioxide, commercial, cyl	lb.	.07
Sulfuryl chloride, drums	lb.	.10
Thiocarbanilid, bbls	lb.	.26½
Tin	lb.	.22¼
Tin tetrachloride, anhydrous, drums, bbls	lb.	.16½
Oxide, bbls	lb.	.23½
Titanium dioxide, bbls., wks	lb.	.21
Toluene, tanks	gal.	.30
Tribromophenol, cases	lb.	1.10
Triphenylguanidine, drums	lb.	.58
Triphenyl phosphate, bbls	lb.	.60
Tungsten, powder	lb.	1.65
Urea, pure, cases	lb.	.11
Whiting, bags	100 lbs.	1.00
Xylene, 10°, tanks, wks	gal.	.26
Xylidine, drums	lb.	.36
Zinc, metal, E. St. Louis	100 lbs.	3.17
Zinc ammonium chloride, bbls	lb.	.05½
Chloride, granulated, drums	lb.	.05¾
Oxide, Amer., bbls	lb.	.06½
Stearate, bbls	lb.	.20
Zinc dust, bbls., c/l	lb.	.06


$NaOH$
H_3AsO_4
$C_2H_4O_2$
H_2SO_4
H_3PO_4
$H_2C_2O_4$
H_2CrO_4
HNO_3


VIBROX

THE KINETICS OF HOMOGENEOUS GAS REACTIONS

by LOUIS S. KASSEL Ph. D.

Associate Physical Chemist, U. S. Bureau of Mines
Experiment Station

A. C. S. MONOGRAPH NO. 57

330 Pages $6.50

HOMOGENEOUS GAS REACTIONS have attracted the attention of an increasing number of workers during the last few years, largely because they appear to be the most fertile field for the development of a really fundamental understanding of reaction kinetics.

Until now, however, there has been no book available devoted to a complete and critical discussion of this field. This monograph is designed to fill the need for such a book.

In the arrangement of material, the requirements of all classes of readers have been kept in mind. Theory and experiment are presented separately; in the experimental part, in particular, every effort has been made to provide in non-mathematical language a statement of all the essential features of the theoretical developments.

The recent work on chain reactions is treated in great detail. Reactions for which the chains start or stop at the walls, but are propagated in the gas phase, are included.

A considerable amount of photochemical work is discussed, since in many cases the combination of thermal and photochemical data permits much clearer interpretation than would otherwise be possible.

In the theoretical treatment there is included a rather detailed discussion of the applications which have been made of the new quantum mechanics; this treatment is designed to be understandable by chemists whose knowledge of the recent developments in physics is quite meager.

CHAPTER CONTENTS

INTRODUCTION

PART I.—Theory

1. **Elementary Reactions and Their Energy of Activation**
The types of elementary reactions. Order and mechanism. Statistical mechanical interpretation of temperature coefficients.

2. **Statistical Mechanical Interlude**
The Maxwell-Boltzmann distribution law. Distribution of velocities. Numbers of collisions. Applications to quantized systems. Microscopic reversibility. Distribution law for groups of harmonic oscillators.

3. **Bimolecular Reactions**
Bimolecular associations. Bimolecular metatheses involving free atoms; applications of quantum mechanics. Other bimolecular metatheses.

4. **Trimolecular Reactions**
The intermediate compound theory. The number of triple collisions in a perfect gas. Triple collisions in a real gas. Triple collisions vs. intermediate compounds.

5. **Unimolecular Reactions**
General form of the theory of collisional activation. Detailed development of a single form. Variant forms. Quantum mechanical interpretations: the radioactive analogy; the Auger effect analogy. The effect of inert gases.

6. **Complex Reactions**
Complex mechanisms that do not involve a chain. Non-branching chains. Branching chains.

PART II.—Experiment

7. **Experimental Methods of Reaction Rate Measurement**
General methods. Homogeneity. Order of a reaction. Temperature of coefficient. Methods of calculation and accuracy.

8. **Second Order Reactions**
Review of the theory. The occurrence of second order associations. Reactions of atomic hydrogen, oxygen, sodium, potassium, halogens. Decomposition of hydrogen iodide. Synthesis of hydrogen iodide. Decomposition of nitrogen dioxide. Decomposition of nitrosyl chloride. Formation of hydrogen sulfide. Formation and decomposition of nitric oxide. Homogeneous catalyses.

9. **Third Order Reactions**
The oxidation of nitric oxide. The reaction of nitric oxide with chlorine. The reaction of nitric oxide with bromine. The reduction of nitric oxide by hydrogen. The rate of recombination of atomic bromine; of atomic chlorine; of atomic hydrogen. The rate of formation of sodium dioxide.

10. **First Order Reactions**
Review of the theory. The decomposition of nitrogen pentoxide. The decomposition of azo compounds: azomethane, azoisopropane, methylisopropyl diimide, dimethyltriazene. The decompositions of dimethyl, methylethyl, methylpropyl, diethyl, diisopropyl and dipropyl ethers. The rearrangement of pinene. The decomposition of nitryl chloride. The decomposition of nitrous oxide. The decompositions of propionic aldehyde, acetone, saturated hydrocarbons and alkyl amines. The isomerization of dimethyl maleate. First order heterogeneous reactions.

11. **Complex Reactions—Part I**
The formation of hydrogen bromide. The decomposition of ozone, including the catalytic action of nitrogen pentoxide and of chlorine. The reactions between ozone and bromine. The reactions between hydrogen and chlorine, including the catalytic action of water vapor, and the negative catalysis by oxygen and other substances. The methods of highly dilute flames, and of diffusion flames, and applications. The decomposition of ethylene oxide. The oxidation of hydrocarbons and aldehydes. The oxidation of ethylene. Polymerization reactions. The decomposition of acetaldehyde.

12. **Complex Reactions—Part II—Branching Chains**
The oxidation of phosphorus vapor. The oxidation of phosphine. The reactions of hydrogen and oxygen, and the sensitization by nitrogen dioxide and by free atoms; the Alyea interpretation. The oxidation of carbon disulfide.

APPENDIXES—The Radiation Hypothesis Heats of Dissociation

THE CHEMICAL CATALOG COMPANY, Inc.
419 FOURTH AVENUE NEW YORK, U. S. A.

Weather-Ometer

IF YOUR products are subject to weather exposure they should have more thorough testing than is possible with variable outdoor tests.

Use the scientific WEATHER-OMETER instead—the accepted "yard-stick" for weather-testing. This device enables you to duplicate in the laboratory ordinary outdoor weather exposure. Gives accurate, dependable results in days where outdoor tests take years. Another thing: Any WEATHER-OMETER test can be exactly duplicated at any time or at any place.

Bulletin IC-3 contains many facts about the WEATHER-OMETER. Send for copy now!

Atlas manufactures the FADE-O-METER, LAUNDER-OMETER, and ARC LAMPS for irradiating food stuffs.

ATLAS ELECTRIC DEVICES CO.
361 W. SUPERIOR ST. CHICAGO, ILL.
NEW YORK BOSTON LONDON

SARCO STEAM TRAP

Sarco Thermostatic Steam Trap is about one-third the size and price of mechanical traps, yet it does the same work.

The Sarco saves in installation cost, too. It can be screwed right into the pipe line. Saves building a platform or digging a pit. Doesn't leak or waste steam. Cannot air bind.

Make every unit independent of every other by individual trapping. That insures just the right supply pressure for each unit, eliminates radiation loss and prevents holding up water.

Sent on 30 days' free trial. Write for booklet D-95.

SARCO CO., Inc.
183 MADISON AVE., NEW YORK, N. Y.
Branches in Principal Cities

NEWARK'S newest!

Removable, protected bottom strainer.

Chemists, engineers and operating men who have tried this new strainer are enthusiastic about it. They like the "quickly removable bottom"—a time saver. They can accomplish more per screen. The cloth is easily cleaned. One frame and a wide variety of cloths will take care of as many uses. The lower rim protects the wire cloth bottom.

Whatever your problems may be in the wire cloth line, put them up to us. We make wire cloth and wire cloth products for all industries, which, of course, includes the great chemical industry. Expert advice is cordially given on all separation, filtration and kindred problems.

We will be glad to have you check over the list at the right which includes our principal products used in chemical laboratories and plants. Mail to us and your request will be given prompt attention.

"NEWARK" Cloths are produced in every weave; every mesh; every length; every width; and of every malleable metal—monel, aluminum, brass, copper, bronze, phosphor bronze, nickel, plain steel, manganese steel, stainless steel, silver, gold, platinum, "Nichrome," tinned metals, special alloys, etc.

NEWARK WIRE CLOTH COMPANY
354-368 Verona Ave.,
Newark, N. J.

West Coast Representatives:
The Pacific Metals Co. Ltd., Los Angeles and San Francisco, Calif.

NEWARK

Newark Wire Cloth Co.
354-368 Verona Ave.
Newark, N. J.

I am particularly interested in the following:—

- ☐ Removable Protected Bottom Strainers;
- ☐ The "Newark" Cornerless Testing sieve—U. S.—A. S. T. M. standard;
- ☐ The finest wire cloth in the world—400 mesh—160,000 square openings per sq. in.;
- ☐ "Newark" Metallic Filter Cloth;
- ☐ Gasketed Metallic Filtered Cloth;
- ☐ Double Crimped Heavy Steel Wire Screen;
- ☐ Centrifugal Cloths;
- ☐ Steel Wire Cloth;
- ☐ Stainless Steel Cloth;
- ☐ Monel Metal Cloth;
- ☐ "Nichrome" Cloth;
- ☐ Bolting Cloth;
- ☐ Bran Duster Wire Cloth;
- ☐ Dutch Cloths;
- ☐ Tinned Milled Screen Cloth;
- ☐ Brass, Copper and Bronze Cloth;
- ☐ Coal and Sand Screens;
- ☐ Market Grade Brass and Copper Wire Cloth;
- ☐ Extra Fine Phosphor Bronze Wire Cloth;
- ☐ Foundry Riddles;
- ☐ Fruit Testing Sieves.

Name..
Firm..
Street..
City........................State........................

Every industrial chemist, chemical engineer, and metallurgist will find useful information in the following A. C. S. Monographs.

PROTECTIVE METALLIC COATINGS

By HENRY S. RAWDON

277 Pages **Illustrated** **Price $4.25**

An up-to-date survey of the field of corrosion prevention, or retardation, particularly of iron and steel, especially useful to the engineer, manufacturer, metallurgist and chemist. The various coating methods—hot-dipping, cementation, metal spraying, electroplating, alloying, chemical treatment, etc.—are described in detail, as are the coatings produced by these methods using zinc, tin, copper, nickel, chromium, and other metals. Methods of testing such coatings are given and an extensive bibliography is appended.

BEARING METALS AND BEARINGS

By W. M. CORSE

383 Pages **Illustrated** **Price $5.25**

A practical study of the fundamental principles and practices involved in the selection of bearings and bearing metals, together with a bibliography of reference literature from 1900–1928 inclusive.

TIN

ITS MINING, PRODUCTION TECHNOLOGY, AND APPLICATIONS

By C. L. MANTELL, Ph.D.

366 Pages **Illustrated** **Price $5.25**

A comprehensive survey of the various phases of the production of tin from its ores to its commercial application. The history, physical and chemical properties, and the production, distribution, and consumption of the metal have been presented and discussed from the viewpoint of the chemist, the metallurgist, and the chemical engineer rather than from the viewpoint of the mining engineer or the mechanical engineer. Secondary tin and detinning of tin plate scrap has been treated from the economic as well as from the metallurgical and chemical viewpoint.

THE CHEMICAL CATALOG COMPANY, Inc.
419 Fourth Avenue, New York, U. S. A.

Is Your Compressed Air System Sick?

Many compressors, vacuum pumps, Diesel engines and blowers that keep on running, ought to be on the "sick list." For they waste compressed air and oil and do not operate efficiently when carbon causes the valves to stick and when cylinders, pistons, etc. are worn and scored by the billions of sharp, gritty dust particles that get into machines with unfiltered air.

Feed your machines air that has been filtered through a Protectomotor and they will operate 3 to 5 times longer before overhauling is needed. Protectomotor Air Filters remove 999 of every 1,000 particles of dust and grit from the air. Consequently they reduce wear 75 to 85% and reduce carbon 60 to 70%.

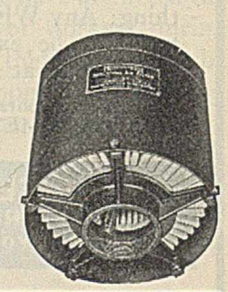
The Protectomotor is a dry filter. No cleaning solution or tanks are needed. Can be quickly cleaned with compressed air without removing the filtering unit. It operates from six months to one year before cleaning is necessary.

More than 350,000 Protectomotor Filters in use.

Write for catalog.

Staynew Filter Corp.
17 Leighton Ave.
Rochester, N. Y.

PROTECTOMOTOR
REG. U. S. PAT. OFF.
99 9/10 Per Cent EFFICIENT
AIR FILTERS



Your April advertising copy with cuts should be forwarded so that it will reach us by the 10th of March.

April Forms Close

March 15, for Press

Advertising Department

Industrial and Engineering Chemistry
419 Fourth Avenue New York