

shown to be no more than 0.8 per cent and is probably of the order of 0.1 per cent; this would be reduced even more in a plant where efficient washing devices could be used. Samples show no charring when placed in a flame and thus indicate a lack of kerosene on the caustic.

In producing fused caustic in the pots, some purification is undoubtedly affected by the sulfur treatment, but there are conflicting opinions as to whether the final product has more or less impurities than the original 50 per cent liquid. In any case, about 5 per cent of the batch in a caustic fusion pot contains a high percentage of iron and has a dark color. These caustic bottoms must be reworked or sold at a low price; with this crystalline caustic no such dregs are obtained.

PHYSICAL CHARACTERISTICS. Anhydrous caustic soda is marketed in the following forms—fused, flakes, pellet, powder, and in one case as cubes. The various special forms are for isolated uses and usually command a premium above the base price for fused. Fused caustic is difficult to handle and hard to dissolve and usually entails high handling costs. Flake dissolves more easily but commands a higher price. Pellets are used for laboratory and analytical purposes.

The caustic produced by this process is a fine free-flowing crystalline material. Its apparent density is approximately the same as flake caustic and consequently the packaging costs would be about the same. It could be shipped in a Dry-Flow tank car because of its fluidity, or in a standard tank car from which it could be dissolved at the buyer's plant. By virtue of its crystalline structure and fine state of division, this caustic dissolves rapidly, and consequently handling costs for the consumer will be lower. Other workers using this caustic report that it reacts more rapidly in alkali fusions,

saponifications, and other similar reactions, and that it has a higher melting point, which indicate possibly a different physical constitution. It would be ideal for use as a laboratory reagent.

Conclusions

Anhydrous caustic soda was prepared continuously from 50 per cent solution on a small pilot-plant scale utilizing the partial-pressure evaporation process of Kokatnur. Kerosene was used as a diluent in the evaporation; and that remaining on the solid particles was removed by centrifuging and washing with a solvent. This solvent was then purified by distillation for re-use. The total heat cost was calculated at about 350 pounds of coal per ton of caustic from 50 per cent solution (only about 150 pounds from 70 per cent solution) or one third the present cost in the usual caustic fusion. Because of the protective film action of the kerosene, practically no corrosion of equipment was noted and it appears that production equipment might be fabricated of steel. The material produced was of high purity; it was a fine powder which was of a crystalline nature, free flowing, and apparently of more rapid chemical reactivity because of its greater surface area.

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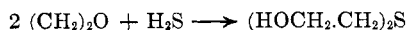
THIODIGLYCOL

Unit Process and Operations Involved in Its Synthesis from Ethylene Oxide and Hydrogen Sulfide

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THIODIGLYCOL was prepared first by Meyer (2) in 1885 by a somewhat expensive method, which has generally been used since in its manufacture as an intermediate in the production of mustard gas (2,2'-dichlorodiethyl sulfide). Cheaper methods of preparation might introduce new and more peaceful uses for this material which contains the potentially important carbon-sulfur-carbon linkage. Chichibabin (1) synthesized thiodiglycol from ethylene oxide and hydrogen sulfide by the sealed-tube method; Nenitzescu and Scarlatescu (3) combined these gases in molecular proportions to form the product continuously in yields of 90 per cent, but under what appear to have been conditions far below the optimum:



The reaction is thus a condensation of two cheap and readily available gases; it gives immediately, quantitatively, and irreversibly a pure liquid of high boiling point (168° C. at 14 mm.). Nenitzescu and Scarlatescu assumed that the reaction took place in two steps, that either activated carbon or a

previously prepared amount of thiodiglycol was necessary as a catalyst for the reaction, and that the reaction was essentially accomplished in the gas phase. Preliminary work indicated that all of these assumptions were wrong; it appeared that the reaction was conducted most readily in the liquid phase of previously produced thiodiglycol.

If the reaction occurs in the liquid phase, it is obvious that a first step must be the absorption of the two gases by the liquid, and this part of the mechanism might be understood by applying the methods of Whitman (6) and others. The chemical reaction in the liquid then might be studied as a second step by the application of well established kinetic methods involving the familiar equations for the reactions of different order, the equation of Arrhenius, etc. (see, for example, such standard works as Taylor and Hinshelwood, 5).

A simple method of studying the rate of reaction of two gases is the reading of the change of their total pressure in a closed reaction chamber. Since the volume is constant, the total amount of gases at any instant is directly measured by the pressure. This simple reading of pressure at various

Thiodiglycol is useful chiefly as a starting material for the manufacture of mustard gas, but the Meyer synthesis used during the war is expensive. Production from ethylene oxide and hydrogen sulfide was studied, and it was found that the reaction in the gas phase was extremely slow; but after being dissolved in liquid thiodiglycol, the gases reacted rapidly. The absorption or solution of the gases was the first hindrance to the production of thiodiglycol; and after means were devised for the analysis of the data to enable the separate study of the reaction rate itself, it appeared to be of the third order. Although the extremely simple apparatus used and the quantities involved were small, data applicable to manufacturing processes were obtained; the extreme simplicity of this method of manufacture was indicated; and thiodiglycol approaching the theoretical in amount was formed from a given amount of starting gases, which reacted much faster (owing to gas absorption considerations) when supplied in correct molecular amounts.

times during the reaction is not only a measure of the unreacted gas (and hence of the reacted gas and of the percentage of gas removed) but also of the concentration or the driving force which causes the reaction to proceed. Thus it is a measure both of an extensive and of an intensive quantity. If equilibrium between the gas and liquid phase is obtained, this pressure is also a direct measure of the concentration of gas in the liquid phase. These several aspects of the pressure determination are important in the design of the apparatus, in its use, and particularly in the evaluation of the data obtained.

Apparatus and Method

A simple apparatus making possible the study of pressure changes (and hence gas removal) in a closed chamber previously charged with the two gases was assembled. It was desirable to investigate the rate of gas removal as influenced by temperature, pressure, and gas-liquid contact area, as well as its mechanism which apparently must be a combination of gas absorption to the liquid phase and chemical reaction in the liquid phase to form more of the same liquid.

The apparatus finally developed for these experiments is shown in Figure 1; details of the reaction chamber are given in Figure 2:

Since the thiodiglycol undergoes discoloration and decomposition at about 60° C., the upper experimental temperature limit was chosen near this point. From room temperature to decomposition temperature, hot water was suitable for the maintenance of constant temperature, and for this purpose a water jacket enclosed the reaction chamber. Water was heated in a copper coil by Bunsen burners and circulated at substantially constant temperature through the jacket. Control of the amount and temperature of circulating water was thus possible.

For measurement of pressure, a tube was connected from the reaction chamber to a mercury-filled manometer capable of indicating a pressure differential of 2.5 atmospheres. The scale was graduated in millimeters. Since one end of the manometer was open to the atmosphere, readings were of gage pressure. An inlet for gas was provided which led from a Y-tube connected with the two gas cylinders. A third inlet at the top of the reaction chamber allowed for the permanent introduction of a thermometer.

At the bottom of the reaction chamber a larger inlet permitted packing to be easily introduced. The vacuum line was connected here and ran to a trap so that the product could be collected and examined and the pump protected from the product. The pump was a large Cenco Hi-Vac capable of evacuating the reaction chamber to an absolute pressure below 1 mm. of mercury.

The internal volume of the chamber was 250 cc. by actual measurement; and the internal area was calculated to be 410 sq. cm. For increasing the surface area, solid glass beads were used. The beads possessed a mean measured diameter of 3.6 mm. Five hundred beads gave a total glass and void volume of 30 cc., corresponding to 6 cc. per hundred beads. The void volume for 500 beads was 17.5 cc., corresponding to 3.5 cc. per hundred beads. The actual volume per hundred beads was 2.5 cc. The average diameter calculated from volume measurements was 3.62 mm. per bead, and the average surface area was 0.412 sq. cm. per bead. The beads were supported by a small tuft of glass wool placed over the vacuum inlet.

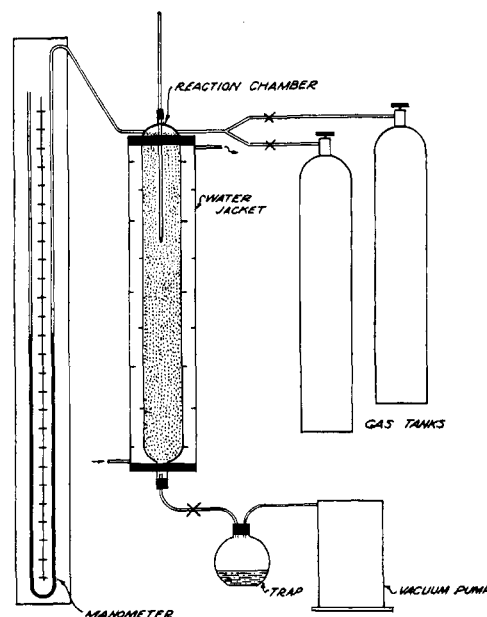


FIGURE 1. APPARATUS

The gases used in these experiments were obtained from The Matheson Company. The ethylene oxide and the hydrogen sulfide were both 99.9 per cent pure; the impurities in each case were atmospheric gases. The thiodiglycol used for priming the initial experiments was obtained in the reaction chamber with activated carbon; by high absorption of the gases, the molecular density of the gases adsorbed on the carbon approached that of a liquid.

Since the reaction was exothermic, certain difficulties arose in the maintenance of constant temperature. A balance had to be reached in each series of experiments between the temperature of the circulated water and the rate at which it was circulated, to prevent temperature rise during reaction. By reaching the balance temperature of the water which would just maintain the desired reaction temperature, control could be affected to within 0.5° C. The temperature in the water jacket could be set only against the internal thermometer reading while a run was in progress.

After careful evaluation of several possible methods of operation, one was devised for the investigation which combined a slight compromise between accuracy and simple manipulation. The gases at room temperature were admitted to the reaction chamber in amounts measured by the pressure on the manometer. The sum of the partial pressures of the two gases was measured

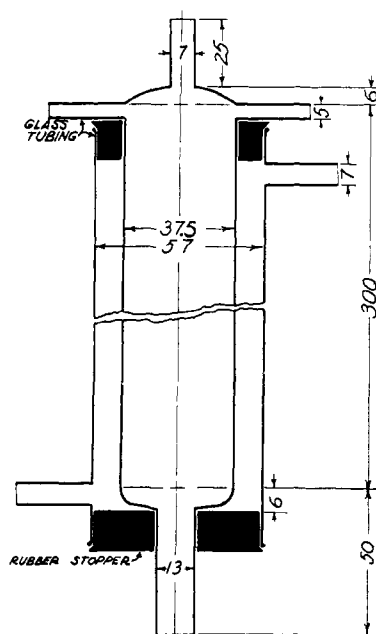


FIGURE 2. REACTION CHAMBER
(DIMENSIONS IN MILLIMETERS)

on the manometer; and as the reaction proceeded, the lowering of the pressure on the manometer indicated the amount of gases used up and hence the rate of gas removal, presumably first by solution, then by reaction.

At first the chamber was flushed with ethylene oxide until the pressure was 1 atmosphere, and then closed. Hydrogen sulfide was rapidly run in to build up the pressure to an absolute manometer reading of an additional 0.5 atmosphere. The flushing process produced bad results in timing which could later be attributed to the fact that the thiodiglycol on the walls was first saturated with ethylene oxide, with an additional 1 atmosphere of ethylene oxide included in the chamber. When compared with the 0.5 atmosphere of hydrogen sulfide next added, the ratio of the reactants actually corresponded to a ratio greater than 2 to 1.

This point led to the use of a vacuum pump. The chamber could not only be purged of gases rapidly, but any residual gas in solution in the thiodiglycol on the walls could be stripped by eliminating the partial pressure of the gases in contact with the solution. In this way each run started with a fresh thiodiglycol surface. Also, the sluggishness of the ethylene oxide to evaporate from the cylinder was overcome by the pressure differential between the cylinder and the evacuated chamber.

Preliminary experiments indicated that in 3 seconds the maximum absorption of the ethylene oxide by the liquid on the walls would be equivalent to a drop of 2 cm. in the total pressure of 76 cm. The gas could be run in easily in that time, with this allowance for the pressure drop due to solution. Therefore the highest pressure recorded was 74 cm. of ethylene oxide and the maximum error from this cause became some very small fraction of the total amount of ethylene oxide introduced.

The addition of hydrogen sulfide introduced other difficulties. Only half as much hydrogen sulfide had to be used. In addition to the initial solution or absorption by the liquid on the walls, there was also the problem that it was possible for the reaction to proceed during the time of introduction of the second reactant. The measurement of the hydrogen sulfide on the manometer would also include a reduction of pressure due to the continued solution of ethylene oxide.

Determination of the rate of solution of the sulfide in the thiodiglycol on the walls of the chamber showed it to be relatively

slow at a partial pressure of 0.5 atmosphere as against that of the oxide at a partial pressure of 1 atmosphere. Three seconds elapsed after the ethylene oxide was introduced before the hydrogen sulfide was admitted. Since the hydrogen sulfide was under high pressure, it could be introduced in another 3 seconds. By this time the pressure of the oxide had been reduced still further; but the reading on the manometer at the instant the sulfide introduction was started was observed, and the desired addition was based on this reading. A further correction of 2 cm. was allowed on the pressure gauge for decrease during the addition of the sulfide. This method of applying corrections in the initial amounts of gas added so as to obtain the desired 2 to 1 ratio was applied over the entire range of temperatures and surface areas investigated.

The criterion of the accuracy of this method lay entirely in the final residual pressure remaining in the reaction chamber after the reaction had been allowed to go to completion. After each series of runs at one temperature, the reaction was allowed to go to completion and the maximum residual absolute pressure was never more than 5 mm.; this corresponded to a low total error, particularly when the small impurities in the gases are considered. The objection that the reacting ratio may not have been 2 to 1 but possibly some small variation from this ratio masked by the correction factors, is not significant. Also, if the reaction proceeded faster at some very small variation from the molecular ratio, it would have shown up in the residual pressure.

To illustrate the control of the temperature and clarify the final procedure, the entire method of experimentation will be recapitulated: The hot water circulated about the reaction chamber until the desired temperature was nearly reached. The chamber was then completely evacuated and charged several times; each time a closer adjustment to the desired temperature within the chamber was possible. At the same time the internal surface was covered by the deposition of a new layer of thiodiglycol synthesized during the adjustment to replace that drained off since the last run. In general, about six or eight priming charges were necessary. After the second or third charge, the time was taken for a large drop in pressure equal to the working range of the experiment so that the amount of the corrections necessary to obtain the desired 2 to 1 mixture could be determined. As soon as these over-all trials showed constant time and temperature, the apparatus was considered ready for a run on which data would be taken. The chamber was evacuated to a pressure of 1 mm. and was closed at the bottom. The ethylene oxide was run in and then turned off. Hydrogen sulfide was introduced, and the stop watch was started; the time was noted for each successive decrease of 2 cm. in the pressure. The zero point of time could be taken at any pressure reading, but in the usual case where a total of 1.5 atmospheres (114 cm.) of gas was used, 96, 98, or 100 cm. was the starting point.

Only a small fraction of a cc. of product was formed for each run, and samples were examined for color. Aggregate samples were identified by conversion into mustard gas. Because of the danger involved in handling this material, the practice was frequently not followed and additional identification was omitted.

For those experiments in which the effect of increased surface was investigated, the packing was inserted through the bottom of the chamber and primed by adding a large quantity of thiodiglycol at the top of the packing; the beads were swirled about and allowed to drain overnight. For unpacked experiments, the wall of the chamber was coated and allowed to drain for the initial priming.

In all work in which both gases were present, 1 atmosphere of ethylene oxide and 0.5 atmosphere of hydrogen sulfide were added to give a molecular ratio of 2 to 1. It would have been desirable to observe the drop in partial pressure of each gas separately, but this could not conveniently be done. It was therefore necessary to assume that, for every drop in pressure, two thirds was due to the removal of ethylene oxide and one third to the removal of hydrogen sulfide. This assumption was largely justified by the fact that, when the run was allowed to go to completion, there was no residual gas (i. e., the pressure approached zero) and thus no excess of one or the other.

Data

Experiments were carried out with two basic objects. The first was the determination, under various conditions, of the over-all rate of gas absorption or solution and reaction combined—i. e., the rate of gas removal. From an industrial point of view this is most important; probably in any large-scale production of thiodiglycol it would be most advantageous to run the gases under pressure (or liquefied ethylene oxide)

into a reaction chamber and draw the product off at the bottom. The synthesis thus accomplished would be a single-stage operation requiring but a single unit at constant pressure. The second object was the determination of the physico-chemical effects of solution rate and reaction rate independently to gain an insight into the mechanics of the reaction.

Four runs were recorded for each temperature under any given conditions and represent four consecutive series of data which were in close agreement. Where four runs did not agree in succession, the work was repeated until agreement was obtained. A graph was drawn from the data of the quadruplicate runs tabulated for each set of conditions. Each curve thus represents the mean of four sets of readings.

When the data had thus been established for one temperature under the given conditions, the temperature was changed and the work repeated. In general it was desired to obtain data for temperatures of 25°, 35°, 45°, 55°, and 65° or 68° C.; but in the case of the greatest reaction velocity, the data for the top temperature could not be determined satisfactorily because of the high rate at which the gases were removed by reaction.

Each group of data obtained for the several temperatures, averaged for the four individual runs, constituted a series. Series *A* was obtained with the reaction chamber empty, series *B* with 1000 glass beads for packing as above mentioned, and series *C* with 3000 glass beads for packing.

Series *D* was run without packing. But the full 1 atmosphere of ethylene oxide was charged and absorbed in the thiodiglycol on the walls of the chamber until it came to substantial equilibrium; i. e., the pressure on the manometer (about 52 cm.) remained practically unchanged after a long period; then the 0.5 atmosphere of hydrogen sulfide was added, and the data taking was started immediately in the regular manner. The ethylene oxide removal prior to the addition of hydrogen sulfide was merely a gas absorption operation since there is no chemical reaction in the solution of the one gas in thiodiglycol; and the constancy of the final pressure merely indicated a saturation of the film of liquid with ethylene oxide. Similarly, in other experiments the absorption or solution of hydrogen sulfide in the thiodiglycol was observed by the addition of 0.5 atmosphere of hydrogen sulfide to the evacuated chamber; in this case, the final pressure after substantial equilibrium or saturation was about 26 cm. The rate of gas removal (pressure drop) in both of these two cases showed a negligible variation with different temperatures as compared to the variation in rate with different temperatures when both gases were present; thus there could be and was a chemical reaction.

Series *E* was run at a single constant temperature of 55° C. without packing. It consisted of three quadruplicate runs, one reproduced from series *A* with the stoichiometric ratio of 2 to 1 for the amount of ethylene oxide and hydrogen sulfide, one with an excess of ethylene oxide, and one with an excess of hydrogen sulfide compared to this molecular ratio. Although these excesses were intended to be about 10 per cent in each case, the molecular ratios were actually 2.1 to 1 and 1.82 to 1, respectively. As the deductions from this series are only qualitative, these actual ratios are not important.

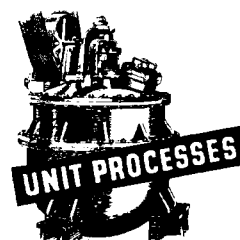
In addition to the quantitative data, qualitative experiments were performed which were not further investigated:

1. Attempts to perform a reaction between ethylene oxide and hydrogen sulfide without the use of thiodiglycol. In the clean chamber, thoroughly washed and dried, the pressure dropped from 115 to 75 cm. in 2 hours at 68° C. with small globules of thiodiglycol condensing out on the wall of the chamber. Presumably most of even this slow reaction was accomplished in the

first microscopic droplets which were formed.

2. Attempts to perform a reaction with aniline, in which the gases and product are soluble, in place of thiodiglycol as the liquid coating. The surface produced fairly rapid rates of gas removal at 68° C., and the aniline showed no effect of possible sulfide sensitivity.

3. Attempts to perform a reaction with kerosene in which the hydrogen sulfide and product are insoluble. Slow but definite rates of gas removal were produced.



Relative Value of Data

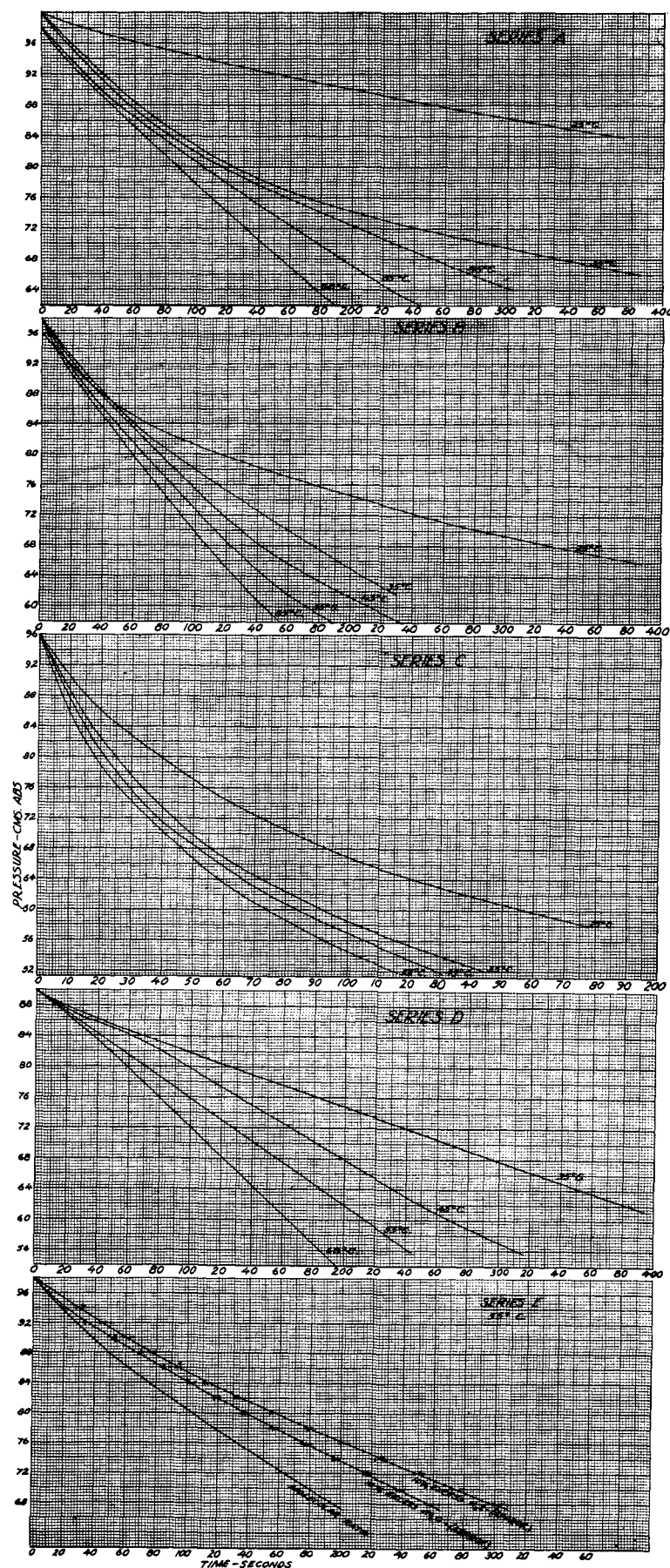
The data for series *A*, *B*, *C*, *D*, and *E* are summarized in Figure 3. All data were taken before an attempt was made to correlate the numerical values or understand their significance. In general, in series *A*, *B*, and *C* the curves representing runs at 25° C. fall considerably away from the curves for higher temperatures. No reason can be advanced except that within the proximity of this temperature to the boiling point of ethylene oxide the material may not act as a permanent gas with the regularity with which it acts at higher temperatures in regard to diffusion and other properties. It may be associated or have some other abnormality which makes its behavior at 25° C. erratic since the runs at this temperature are not consistent to the same degree as those at higher temperatures. Because of this discrepancy it is necessary to eliminate runs at 25° C. from further consideration without, however, the full understanding and justification that would be desirable.

General Mechanism and Methods of Study

If the previously mentioned evidence of the experiments with dry walls is accepted—namely, that the reaction in the gas phase is extremely minute in amount—substantially all of the mechanism of removal must then be accomplished in the liquid phase of thiodiglycol. Obviously, before a reaction can occur in the liquid phase, the gases must be absorbed into this liquid phase. Series *D* shows that the thiodiglycol absorbs either gas separately to produce what must be a typical solution of a gas in a liquid. The mechanics of such a gas absorption operation have been studied and well established by a long series of investigators; and the mathematical understanding of such absorption is also fairly well established from the work of Whitman and Keats (6) and a large number of later investigators.

The absorption of either gas in the liquid to form a typical solution can be accomplished only up to the solubility of the gas (or gases) in that liquid; and the solubility ranges were determined relatively by the preliminary work of series *D*. The addition, then, of the second gas would allow the absorption of that gas in the liquid up to the saturation point. Of much greater effect, as previously shown, is the fact that the two gases react with each other in this liquid phase to give condensation, the condensation product being thiodiglycol. Thus it appears that the two gases may be removed from the gas phase in infinite amounts (if they were so supplied) since they react in the liquid phase to form more of the same liquid.

The evaluation of these experiments by studying the dropping of pressure (or the amount of gas removal) and the rate at which this pressure drops necessitate a study of the absorption and of the kinetics of the chemical reaction itself. Unfortunately these two processes are proceeding simultaneously; it is therefore necessary to study the data in such



a manner that the effect of either the physical absorption or the chemical reaction may be separated one from the other to allow distinct quantitative reasoning. The condition for gas absorption in which chemical reaction takes place when a single gas is absorbed in a chemically reactive liquid, such as the absorption of carbon dioxide by caustic solutions, has been studied for many reactions by numerous investigators. In these cases, however, only a single gas enters the reaction, and the further complication of a second gas reacting either with the liquid itself or with the first gas has not been investigated. Nevertheless, to a certain extent the same methods of evaluating the data may be used.

It is usual to consider the conditions which in one stage or another of gas absorption present a so-called controlling condition regulating the operation in its entirety. Thus the first step will be the study of the present data to determine if there are sections of any runs in which either absorption or chemical reaction is by itself so effective that it controls the entire operation. "Controls" is used here in the sense usual in gas absorption studies. If parts of the experimental data are "controlled" by gas absorption, obviously they may be studied by the technique of that field; and if other parts are "controlled" by the chemical reaction, they may be studied by the methods used in kinetic studies of reaction rates.

Initial Parts of Curves, Controlled by Absorption

The graphs for series A, B, and C (Figure 3) show that there is a rapid drop in the pressure of each of the individual curves at the start of the experiment; this rate of pressure drop decreases considerably as time passes and as gas is removed from the gas phase. It also appears that this first part of each of these curves is reasonably well represented by a straight line. In order to substantiate this point, the differentials for series A are shown in Table I. These differentials represent the time for each pressure drop of 2 cm. of mercury. Thus they would correspond, if divided by the time, to $\Delta p/\Delta t$. For example, in series A a fairly constant differential is obtained of about 10 seconds for the early part of the data for each experiment (except, that for 25° C.) down to about 88 cm. of mercury. Thus, a substantially straight line results since the differentials with respect to the pressure are practically constant.

Of even greater interest is the fact that from 35° to 68° C. this differential is always about the same; thus, regardless of the temperature, the rate of dropping off of the pressure at the start of the run is approximately constant. Clearly this does not indicate the rate of removal of gas which would be expected in an operation where a chemical reaction exerts a

FIGURE 3. SUMMARY GRAPHS

controlling influence, because a chemical reaction would be expected to proceed at considerably different rates under these different temperatures. It might be expected, however, that if absorption is controlling, the rate of gas removal due to this absorption might be substantially constant even over such differences in temperature as 35° to 68° C.

The solubilities of these gases and their rates of absorption do not vary to any extent over this temperature range, as mentioned previously. Compare this portion of the curves for series *A*, *B*, and *C* with that of series *D* in which this effect has been substantially eliminated. Also, the absorption might be expected from the Whitman equation to be proportional to a difference in the pressure between the gas in the gaseous phase and the gas at the interface of the liquid phase; and at least at the start, this would be represented approximately by a straight line. These initial parts of the curves should be roughly parallel, which is actually the case in the graphs. This conclusion from the data is limited to that part of the curve above a pressure of 87 cm. for series *A* and corresponding pressures for the other series, and indicates that the part of the run above this pressure is controlled by absorption alone. Thus, some time is necessary initially to dissolve the gases before reaction can start.

TABLE I. DIFFERENTIATION OF SERIES A

Pressure Cm. Hg	Time Sec.	Δt Sec.	$\Delta p / \Delta t$ Cm./sec.	Pressure Cm. Hg	Time Sec.	Δt Sec.	$\Delta p / \Delta t$ Cm./sec.
35° C.				45° C.			
98	9	10	0.20	98	7	10	0.20
96	19	10	0.20	96	17	9	0.22
94	29	10	0.20	94	26	10	0.20
92	39	10.5	0.19	92	36	10	0.20
90	49.5	10.5	0.19	90	46	10.5	0.19
88	60.5			88	56.5		
55° C.				68° C.			
96	9	10	0.20	96	5	10	0.20
94	19	10	0.20	94	15	10	0.20
92	29	10	0.20	92	25	10	0.20
90	39	10	0.20	90	35	10	0.20
88	49			88	45		

Fortunately, the curves drop off at a slower rate following this initial part where absorption controls; this indicates that the additional effect of reaction is to slow down the rate of gas removal. In other words, an additional hindrance to the disappearance of gas from the gaseous phase shows up as the result of an increase in concentration of gas or even of saturation in the liquid phase; and the rate of gas disappearance decreases. The increase of concentration in the liquid phase must then be dissipated by the reaction itself; but this rate seems much lower than the gas absorption except at the higher temperatures.

Effect of Temperature in Final Parts of Curves

Inspection of the broad spread between the several runs in the lower part of a series shows that a difference in temperature becomes important there as compared to the upper part where absorption alone is controlling. This is the first indication of the importance of the chemical reaction itself as compared to that of the gas absorption.

The next step is to attempt to apply the Arrhenius equa-

tion in which a plot of the logarithm of the rates of gas removal (dp/dt) against the reciprocal of the absolute temperature will give a straight line for chemical reactions which are not composite.

Early workers suggested the possibility that the chemical reaction involved between these two gases was accomplished in two stages. In this event there would be a preliminary and then a secondary condensation; it is obvious that the secondary reaction would involve a heavier molecule. However, it is inconceivable that a reaction between the two molecules of low weight in the first stage (i. e., ethylene oxide and hydrogen sulfide) would have the same temperature coefficient as the reaction with the molecule of higher weight in the secondary stage (i. e., ethylene oxide with the condensation product of the first stage).

The data for series *D* are suitable for testing with the Arrhenius equation. Incidentally, it is obvious from the graph of this series that the preliminary part of the curve, in which absorption is normally controlling, is extremely small; this is what would be expected from the fact that the liquid phase was saturated with ethylene oxide before the run itself was started. Thus the initial gas absorption was small before reaction could start. The data for series *D* were differentiated (Table II), and the logarithms of these differentials are tabulated for each pressure measured in the range below about 72 cm. of mercury. This pressure of 72 cm. was taken because it represents a mean point below which the course of the reaction itself is expected to be controlling. This will be shown later.

The differentiation was performed on values for the three temperatures, 45°, 55°, and 68° C.; substantially constant values of dp/dt and of the logs dp/dt were obtained. For each measured pressure below 72 cm., a cross plot of these values of log dp/dt against the reciprocal of absolute temperature is plotted as shown in Figure 4; it is apparent that a single straight line represents the data for each different measured pressure in each of the three constant-temperature runs.

As a diverse case series *C* was selected in which the reaction chamber was fully packed; the large area facilitated the solution of the gases, although preliminary absorption was not allowed as in series *D*.

Here again three different temperatures, 35°, 45°, and 55° C., were taken and again the values of the differentials dp/dt at successive pressures were calculated as well as the logarithms of these differentials. The data are shown in Table II and are plotted for each of the measured pressures against the reciprocals of the three absolute temperatures (Figure 4). In this case the data do not fall on identical points, as in the case of series *D*, but form lines for each one of the measured pressures. The three plotted points did not give straight lines for each different pressure; but the amount by which these three points vary from straight lines represents an over-all error in measurement between the three temperatures of only 0.2 second. Since the data were usually recorded only to the nearest second from observations, the timing of the rapid reactions in series *C* was difficult, and there was a consistent lag in reading pressures. There is evidence that within the accuracy of the data and for the purpose of the following conclusions these three points may be regarded as showing the straight lines called for to justify the application of the Arrhenius equation. (Similarly, straight lines were obtained from runs *A* and *B* but are not included here.)



TABLE II. DIFFERENTIATION OF SERIES D AND C

Series D					Series C				
Pressure Cm. Hg	Time Sec.	Δt	dp/dt	Log dp/dt	Pressure Cm. Hg	Time Sec.	Δt	dp/dt	Log dp/dt
45° C.					35° C.				
72	164	17	0.1175	0.070	66	63	9	0.222	0.346
70	181	17	0.1175	0.070	64	72	10	0.200	0.302
68	198	17	0.1175	0.070	62	82	11	0.182	0.260
66	215	17	0.1175	0.070	60	93	11.5	0.167	0.223
64	232	17	0.1175	0.070	58	104.5	12.5	0.154	0.188
62	249	17	0.1175	0.070	56	116.5	13	0.148	0.156
					54	129.5	14.5	0.133	0.124
					52	144			
55° C.					45° C.				
72	128.5	14.5	0.138	0.141	66	59	7	0.286	0.456
70	143	14	0.143	0.155	64	66	8	0.250	0.398
68	157	14	0.143	0.155	62	74	9	0.222	0.346
66	171	14	0.143	0.155	60	83	10	0.200	0.302
64	185	14	0.143	0.155	58	93	11	0.182	0.260
62	199	15	0.134	0.128	56	104	12	0.167	0.223
60	214	14	0.143	0.155	54	116	13	0.154	0.188
58	228				52	129			
68° C.					55° C.				
72	101	10.5	0.190	0.280	66	52	6	0.333	0.522
70	111.5	10.5	0.190	0.280	64	58	7	0.286	0.456
68	122	10	0.200	0.302	62	65	8	0.250	0.398
66	132	11	0.182	0.261	60	73	9	0.222	0.346
64	143	11	0.182	0.261	58	82	10	0.200	0.302
62	154	10	0.190	0.280	56	92	11	0.182	0.260
60	164	10	0.190	0.280	54	103	12	0.177	0.223
58	174	11	0.182	0.262	52	115			
56	185								

The conclusion drawn from Table II and Figure 4 is that the behavior in the lower reaches of the curve is controlled by a chemical reaction rate and not by the absorption rate; i. e., the rate of absorption is so rapid by comparison with the rate of reaction that it produces an unappreciable hindrance to gas removal. This conclusion is justified since it is extremely improbable that any absorption phenomenon would fit the Arrhenius equation.

Since it would be inconceivable that the change of reaction rate with temperature for a reaction involving two stages of molecular association would be the same as for a reaction involving the single-stage association of lighter molecules, it becomes apparent that a single reaction describes the mechanism by which the entire association is accomplished. In other words, the simple association of one molecule of hydrogen sulfide with two of ethylene oxide takes place and controls the drop in pressure in the lower reaches of the curves. The mechanism of this reaction may be investigated by the mathematical methods long used for the study of homogeneous reactions. For as already demonstrated, the reaction does not take place in the gaseous phase with the formation of a nonvolatile liquid product but does take place only in the liquid phase; it is therefore homogeneous.

Determination of the Order of the Reaction

For homogeneous reactions there are criteria dependent upon the reaction rate which make possible the identification

of the order of the reaction when conducted isothermally. If $\log P$ plotted against time gives a straight line, the reaction will conform to the first order. If the reciprocal of the pressure plotted against time gives a straight line, the reaction will be of the second order; if the reciprocal of the pressure squared against time gives a straight line, the reaction will be of the third order. Although these rules are usually made in terms of the concentration, C , the statements are equally valid as made above in the terms of pressure P since in this case the concentrations and the pressures are measurable one by the other.

In the present case it can be shown that in the lower reaches of the curves reaction controls the removal of gas (since it is so much slower than the rate of absorption). It may be assumed, therefore, that the pressure on the surface of the film is the same as the pressure in the body of the gas, and thus that the sum of the two partial pressures in each case will be equivalent to the total pressure. In all of this work it has been necessary to assume that the pressure is always in the ratio of two parts of ethylene oxide to one part of hydrogen sulfide; and since this partial pressure in the gas phase is always in this ratio, it must be in equilibrium in the film of liquid in the same ratio of partial pressures. The reaction occurs in a liquid film of extremely small thickness; and it is reasonable to assume that the partial pressures throughout that film are the same as the partial pressures on the surface. Thus the pressures measured in those parts of the experiments controlled by reaction may be regarded as representing the sum of the respective partial pressures in the liquid phase and hence by some proportional factor as representing the sum of the concentrations of gases in this liquid phase; or since the ratio of either gas pressure or concentration to the total is always fixed, the measured pressure indicates directly the concentration of either gas in the liquid phase.

Figure 5 shows that the plot of \log pressure against time does not noticeably improve the curves—i. e., does not tend to straighten them; similarly, the plot of the reciprocal of pressure against time (Figure 6) does not tend to straighten the curves. But the plot of the reciprocal of the pressure squared against time (Figure 7) does straighten the curves, particularly in their lower reaches. The straightening of the lines by this method would follow if the reaction were known to be of the third order and if the effect of absorption were nonexistent; therefore it seems fair to conclude that the chemical reaction involved is of the third order and that, in the part of the curves where straight lines are obtained by this method of plotting, the reaction is controlling and the effect of absorption is negligible. The lines representing series C plotted in this way are almost continuously straight without any transition point (the 55° C. line is straight). Furthermore, the lines for identical temperatures of series A and D have slopes which, in the lower reaches where they are straight, are practically the same. Thus the lines are parallel for any given temperature above 35° C. As the higher temperatures are approached, the parallel condition becomes more marked.

In series A the rate of gas removal was naturally slower than in D because in the case of D the liquid had been previously saturated with one of the reactants; hence the time

necessary for the initial absorption before reaction could get well started has been greatly minimized. As we consider higher temperatures, it becomes noticeable that the parallelism is more exact because of the greater speed of the reaction at those higher temperatures. This shows that the reaction velocity seems to be dependent only upon the temperature in series *A* and *D* because the rates become identical (at different times) even though the experiments were different. We may further conclude that the reaction alone is the controlling factor in the lower parts of the curves. Of additional interest is the comparison of the curves of series *A* and *D* with those of series *C*. In series *C* the internal surface area introduced into the reaction chamber was almost sufficient to eliminate completely the transition between the distinct absorption and reaction mechanisms. However, despite the broadly different methods employed, only the absorption quality underwent appreciable alteration. The plot of series *B* was omitted since it produces curves, as would be expected, intermediate between series *A* and *C*.

In the curves for series *E* emphasis was laid upon the fact that an excess of either of the gases over the desired 2 to 1 molecular ratio reduced the rate of gas removal tremendously.

This is further indication of a third-order reaction involving the association of three molecules simultaneously. If the desired gas ratio will not always supply these three molecules (two of ethylene oxide, one of hydrogen sulfide), the reaction is slowed down considerably.

Both the initial and final parts of the individual curves have been discussed. It has been shown that absorption is dominating in the first part; i. e., before the reaction could take place the proper amount of gas had to be absorbed in the liquid film, at a considerable rate almost unaffected by the feeble amount of reaction initially. The latter part of each curve is controlled by the chemical reaction. Since the speed of absorption was so much greater than the speed of reaction, the gases were supplied in ample quantities by solution in the liquid which could thus be regarded as saturated with both gases. There was thus no appreciable hindrance to the reaction by an insufficiency of gas; i. e., in this case the reaction controlled because it was so much slower than absorption. The intermediary parts of the curves, where there is a transition between the two controlling factors, are unaccounted for; but since the rate of gas removal is evidently dependent on both in this range, the combination of the relatively complicated functions makes impossible any pertinent observations of this intermediate range.

Absorption and Reaction

It has been shown that both absorption and reaction control the removal of the gases in the reaction chamber, and that at the start absorption was controlling up to the point where the liquid was unable to absorb the two gases at the rapid initial rate. Then the reaction of the gases in the liquid phase to accomplish their chemical removal came into play, and its relatively slower rate reduced the rate of gas removal as shown by the pressure drop. At a later stage when the saturation of the gas in the liquid phase had probably become complete and was maintained complete by gas absorption under the conditions of pressure of the gas bounding the liquid, the subsequent removal of gas was controlled by the rate at which the gas could be used up within the liquid itself. This assumption of saturation then allows the assumption that the concentrations of the gases in the liquid phase are directly proportional to the measured pressure; i. e., gas absorption is by comparison infinitely fast and exerts no hindrance on the chemical reaction.

In the case of series *E*, the rate of absorption was slowed down because the gas was not supplied in the correct ratios required for the reaction. Othmer (4) showed in the case of steam-air mixtures in contact with heat transfer surfaces that the steam has to diffuse through a film of air in order to reach the heat transfer surface; at this surface it is removed by condensation and has its latent heat removed. The air, on the other hand, tends to congregate in a film through which diffusion takes place as a result of mass motion of the gas mixture toward the surface and of the separating tendency of the steam in condensing and leaving the air behind. Somewhat the same condition exists in the event that the two reacting gases involved were not in the proportion that would allow their chemical removal in the liquid phase. In other words, when there is an excess of ethylene oxide over the 2 to 1 ratio, that excess tends to build up a film of higher concentration of ethylene oxide adjacent to the surface than in the body of the gas phase because that excess is not removed chemically. Thus a film in the gas phase is formed through which the correct ratio of hydrogen sulfide must diffuse. In the case of the steam-air mixture it was shown that even as much as 0.5 per cent of air was extremely effective in preventing the steam from reaching the surface. Therefore, it would be expected and has been shown here that 5 or 10 per cent of the one gas in excess causes a considerable reduction in the rate of gas removal.

Patent protection on certain new aspects of this reaction is being secured.

Conclusions

Several contradictions arise concerning the work of Nenitzescu and Scarlatescu. Synthesis does not occur primarily in the gas phase, autocatalyzed by the product, nor is the function of activated carbon one of catalysis. The small reaction that does occur in the gas phase proceeds hundreds of times more slowly than in the liquid phase. The reaction is neither heterogeneous nor composite and may be accomplished with a yield of 99+ per cent instead of 90 per cent as reported by them.

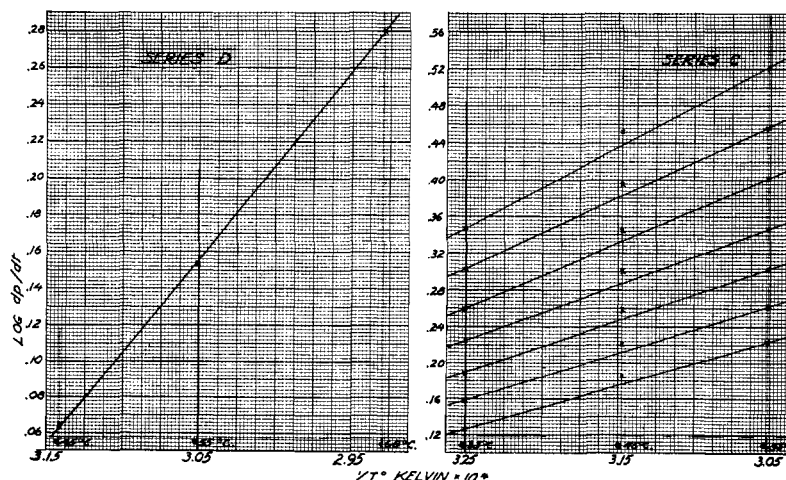
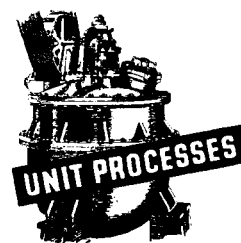
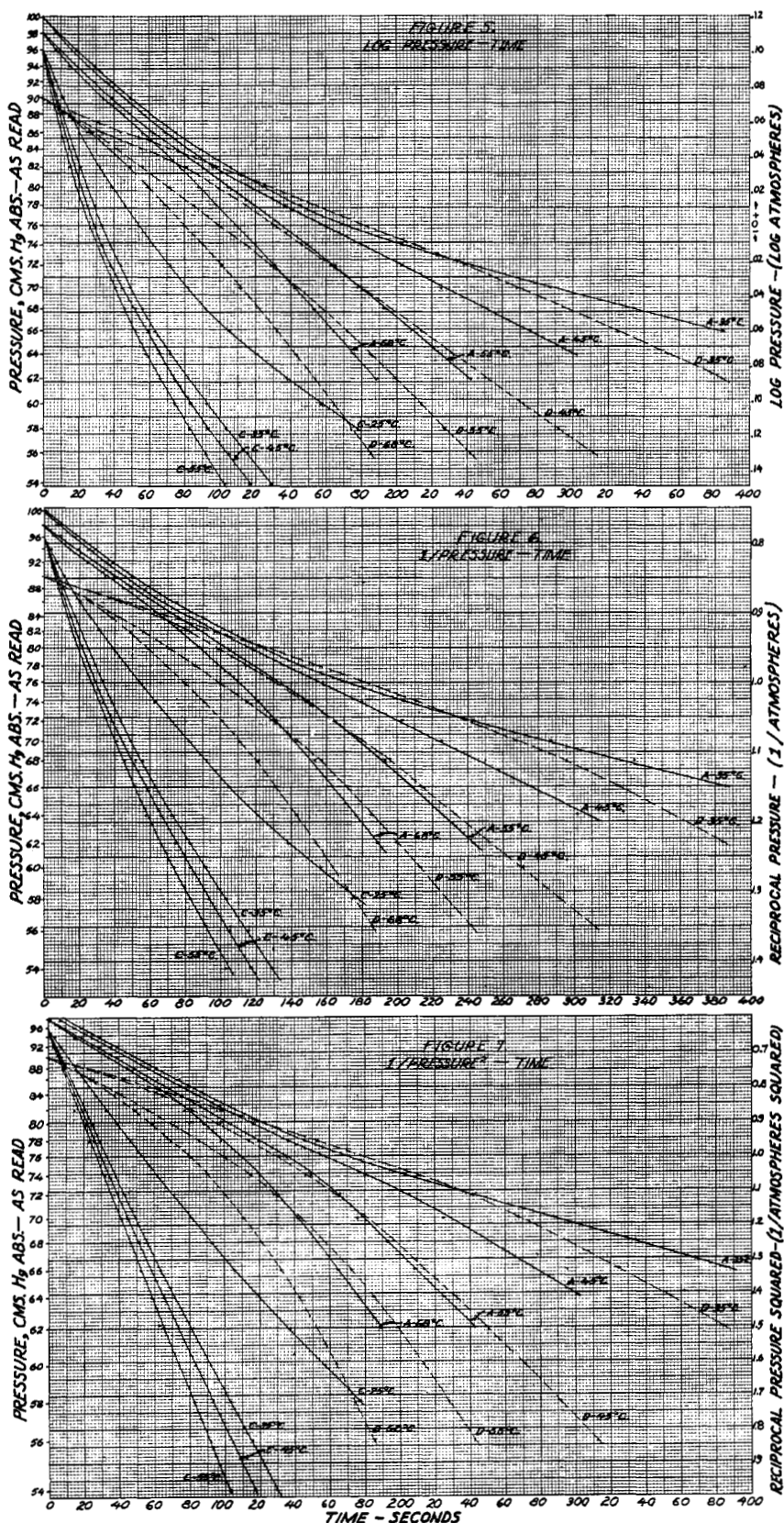


FIGURE 4. $\log dp/dt$ vs. $1/T^\circ \text{ K}$.



FIGURES 5, 6, AND 7

The association may be defined as the homogeneous reaction in thiodiglycol (or other liquid solvent) of solutions of the two gases to form the liquid product; and the formation of the solutions is described by the usual mathematics of absorption involving the differences in the pressures of the gases above the solution, the differences of concentration in solution, the temperatures of solution, and the area over which solution occurs.

The reaction conforms to the third order, the association involving the simultaneous union of two molecules of ethylene oxide and one molecule of hydrogen sulfide. The percentage of the reactants transformed per unit time under given pressure conditions may be calculated from the kinetic equations of the third order, and the variation of the rate of reaction with temperature may be calculated from the Arrhenius equation. The distinct factors of absorption alone (such as surface area, etc.) are not effective upon the rate of reaction.

Between the rates of absorption and reaction it may be stated that, unless the absorption area is reduced to absurdity, the rate of absorption is considerably greater than the rate of reaction; and that the absorption, say under conditions of constant-pressure operations, may be rendered "spontaneous" by the application of moderate pressure (4 or 5 atmospheres) and further by the application of internal surface.

The rate of reaction of the gases in a regenerative system such as this, where new solvent is always being formed, can be increased only for a given temperature by the elevation of the pressure, or for a given pressure by the elevation of the temperature, or by a combination of both devices. The capacity will be determined from the volume maintained at that pressure and the amount of product withdrawable from the calculation of the third-order equation for a specific temperature.

Through the use of moderate pressures and temperatures involving only simple routine devices, and in a small chamber devoid of moving mechanism, hydrogen sulfide and either gaseous or liquid ethylene oxide (depending upon whether the selected pressure and temperature will liquefy this material) may be continuously run into the chamber and the product continuously drawn off; the product so obtained will

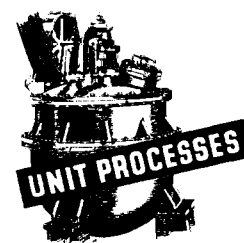
represent a yield in excess of 99 per cent and the product will be over 99 per cent pure.

Since thiodiglycol possesses both a military and potential synthetic significance, the object of this investigation has been to determine whether a distinct operation exists in this recently discovered reaction whereby thiodiglycol can be synthesized commercially. The Meyer method has been prohibitively expensive for the last fifty years, particularly by comparison with the method outlined here which operates at a small fraction of the former raw material, process, and equipment costs.

Acknowledgment

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for investigation. They are also appreciative of the assistance on kinetic theory given them by C. E. Waring of the Institute.]



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HYDROLYSIS OF PEANUT HULLS

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The action of water and dilutions of sulfuric acid on finely ground peanut hulls was studied at 20°, 50°, 80°, and 100° C. with liquid to solid ratios of 10 to 1 and 8 to 1.

For the series of concentrations of 0.2, 1.03, 2.15, 4.47, and 7.47 *N* at 20°, 50°, and 80° C., a modified reactor was used which consisted of a dryer to recirculate the saturated air and ceramic crocks to hold the masses. The highest yields of reducing sugars produced under the conditions investigated occurred at 80° C. with 8 hours of treatment and at 4.47 *N* concentration. Calculated as dextrose, this is a yield of 29.3 per cent of the weight of the dry hulls. Higher concentration of acid resulted in decomposition of the peanut hulls and hydrolysis products. Temperature showed a marked increase in hydrolysis.

For the 100° C. series, hydrolysis at 0.2, and 0.4 *N* was studied over a 48-hour period in a closed jacketed kettle. Results showed that the carbohydrate portions of the peanut hulls form into pentoses and some other reducing sugars. Over a long period of time even the 0.4 *N* concentration produced decomposition.

ACCORDING to Lloyd and Palmer (7), "the term hydrolysis is applied to reactions of both organic and inorganic chemistry wherein water affects a double decomposition with another compound, hydrogen going to one component, hydroxyl to the other".

Much of the work on the chemical transformation of pentosic-cellulosic-lignosic materials has been done with a view to producing either a cellulose pulp or pentose sugars and their derivatives. It has been shown that the pentosan and cellulose portions of these materials are hydrolyzed by the action of dilute acids to form pentose and hexose sugars and their further hydrolytic products.

Hydrolysis of Cellulose

According to Schorger (14), dilute acids at the boiling point, or when allowed to dry on the fibers of cellulose, produce chiefly hydrocellulose which may be converted into glucose by the action of dilute acids under pressure (15). Groggins (8), however, states that the glucose resulting from the hydrolysis is partly decomposed if left in contact with the acid at high temperature and pressure. He states that cellulose can also be hydrolyzed to cellobiose by its own specific enzyme, cellulase. Minor (12), in explaining the mechanism of hydrolysis of cellulose, reports that a mucilaginous, soluble dextrin is first formed which is adsorbed by the remaining cellulose to form a reactive insoluble mass known as hydrocellulose. Like Schorger, Minor concludes that the complete hydrolysis of cellulose leaves only soluble dextrans. Spurlin (16) states that structure of the fiber and degree of swelling have no detectable influence on the type of reaction when the degradation of cellulose is accomplished by the action of dilute acids. He also states that the rate of reaction is not dependent on the fiber structure or degree of swelling since the hydrolysis does not depend on the diffusion of any substance.

Hydrolysis of Pentosans

Pentosans constitute the major portion of that part of cellulosic material known as hemicellulose, a polysaccharide soluble in dilute alkalies and convertible into simple sugars by heating with dilute acids under pressure (13). According to Holleman (10), pentosans are polyoses of the pentose sugars such as xylose, arabinose, and mannose.

On heating with dilute acids, the pentose sugars are decomposed to form furfural. The quantitative determination of pentoses or pentosans is based on the quantitative conversion of pentoses to furfural by 12 per cent hydrochloric acid (3).