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STUDIES OF FAST REACTIONS WHICH EVOLVE GASES. THE REACTION OF SODIUM-POTASSIUM ALLOY WITH WATER IN THE PRESENCE AND ABSENCE OF OXYGEN

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Received November 22, 1952

The general experimental technique for the study of rapid reactions evolving gases has been described by McKinney and Kilpatrick.³ An improved apparatus has now been developed for following simultaneously the pressure and ignition of the reaction. Both the early technique and the improved method have been applied to the reaction of sodium-potassium alloy with water in the presence and absence of oxygen. It has been found that if oxygen is present we have an interesting example of ignition delay which explains the second pressure rise reported previously. When the excess of water relative to the alloy is reduced sufficiently, ignition takes place on contact, and only one maximum is recorded, corresponding to the second pressure rise reported previously. The improved apparatus permits the contacting of one milliliter of each of the reactants in two milliseconds. A possible limitation to the speed with which chemical reactions may be followed by measuring their pressure is discussed. The reaction of sodium-potassium alloy with ethanol, the hydrolysis of aluminum borohydride, and the hydrolysis of triethyldialane are reported.

Methods to determine the rate of very fast reactions in solution have been devised principally by Hartridge and Roughton¹ and by Chance.² These methods require that the two reactant solutions be mixed by passing them through a constriction of some kind. The mixed solution then flows rapidly down a tube, and concentration measurements at different points yield the extent of reaction at different times. The concentrations are usually measured by a physical method, such as light absorption. Flow methods such as these, however, do not seem suitable for the study of rapid reactions which evolve large amounts of gases.

Two constant-volume reactors for the purpose of studying reactions evolving gases have been designed and constructed. The reactors contact two solutions by forcing them together just as in the older methods, but as soon as all of the reactants are contacted the flow is cut off and the reaction is allowed to take place in a closed volume. The progress of the reaction is followed by a pres-

(1) H. Hartridge and F. J. W. Roughton, Proc. Roy. Soc. (London), 104A, 376 (1923), and subsequent papers.

(2) Britton Chance, J. Franklin Inst., 229, 455 (1940).

sure-recording system. The reactors will be referred to as reactor I and reactor II.

Instrumentation

Design of Reactor I.—Reactor I has been described by McKinney and Kilpatrick, ³ and the reader is referred to Fig. 1 of that paper. A pressure of 2000 p.s.i.g. from a nitrogen tank is applied to a pneumatic injector placed above the reactor. The injector is capable of suddenly applying the pressure to two floating pistons. The reactant solutions to be studied are contained in cylinders directly below the pistons. One cylinder contains 25 ml. of one reactant solution, the other contains 1 ml. of a second reactant solution. The pressure forces the floating pistons down, causing the solutions to flow through two opposing jets into the mixing chamber, and mixing is accomplished in this way. The mixed solution then flows out into the bomb cavity. This type of pneumatic injector was first used by Neas, Raymond and Ewing⁴ during a study of the catalytic decomposition of H₂O₂. They used only a single piston forcing the peroxide solution into a metal beaker containing the catalyst solution. A similar single-fluid injection method was recently reported by the Admiralty Research Laboratories.⁶ The mixing

(3) C. D. McKinney, Jr., and M. Kilpatrick, Rev. Sci. Instruments, 22, 590 (1951).

(4) C. C. Neas, M. W. Raymond and C. O. Ewing, M. I. T. Report No. 11, DIC 6351, November 1, 1946.

(5) Office of Naval Research, London, Technical Report ONRL-52-52, May 16, 1952. efficiency seems very uncertain, however, when one liquid is merely sprayed into a static pool of the other.

The pressure rise in the reactor is followed with the aid of a strain gage manufactured by the Statham Laboratories, Inc. The strain gage is in the form of a Wheatstone bridge, and is supplied by an A. C. signal whose frequency may be varied over a wide range. The bridge is balanced for minimum output at the beginning of a run. The output of the gage is amplified and applied to the vertical plates of a cathode ray tube. The horizontal plates are supplied by a single sweep time base so that the unbalance of the bridge is plotted as a function of time on the screen of the oscilloscope. The amplitude of the resulting trace at any time is thus proportional to the transient pressure in the bomb reactor. The trace is recorded by photographing the screen of the oscilloscope.

Reactor I was first used to study the reaction of lithium borohydride with aqueous acid solutions, which is relatively slow, having a half-time of the order of one second.⁶ It was next used to study the much faster reaction of liquid sodium-potassium alloy with excess water. Two typical pressure-time curves for this reaction are shown in Fig. 1. The calculated final pressure of hydrogen is given at the lower right.



Fig. 1.—Pressure rise in reaction of sodium-potassium alloy with excess water in the presence of air (reactor I): A, run no. 145; B, run no. 59.

Interpretation of Traces from Reactor I.—To interpret these curves it is necessary to know how rapidly the reagents are contacted and mixed. The small piston falls in 5 msec. and the large one in 9 msec. as determined by independent measurements. How rapidly the pistons fall when operating together was established by running the reaction of permanganate ion with an excess of acidified peroxide solution; this reaction is known to be very rapid.⁷ Oxygen evolution was found to be complete in about 9 msec. The completeness of mixing was verified by the absence of the permanganate color after the run.

The pressure-time curves given in Fig. 1 for the alloywater reaction show two very large maxima, which, however, were not entirely reproducible. In the run represented by the upper curve the second pressure maximum occurred 40 msec. after mixing began, while in the run represented by the lower curve the first pressure maximum was much lower and the second displaced much farther in time, occurring some 86 msec. after mixing began.

In all of these runs laboratory air was present initially in the reactor. The observed final pressure was much lower than the theoretical yield of hydrogen. It was considered likely that the second pressure maximum was due to the explosion between the hydrogen produced by the reaction and the oxygen present in the reactor atmosphere. This was verified by carrying out the reaction in a nitrogen atmosphere; no explosion occurred and the theoretical yield of hydrogen was obtained in 8 msec., *i.e.*, in the mixing time, with only a slight maximum.

The lack of reproducibility of the height of the first maximum and of the induction period of the explosion is believed

(6) M. Kilpatrick and C. D. McKinney, Jr., J. Am. Chem. Soc., 72, 5474 (1950).

(7) B. Chance, J. Franklin Inst., 229, 737 (1940).

due to the fact that the two pistons may not begin to fall at precisely the same time in every run. The large piston sometimes starts 1 or 2 msec. before the small one, which forces water into the jet of the cylinder containing the metal. This early reaction heats up the mixing area so that the reaction eventually takes place at a higher temperature, which is probably responsible for shortening the induction period of the explosion. A heightened first maximum is always associated with a shortened induction period. The first maximum is probably due to the heat of the reaction, the heat produced by reaction in the jet not being transferred to the metal walls of the reactor as efficiently as when the reaction takes place in the swiftly flowing stream.

That a delayed explosion really occurs was further demonstrated by photocell measurements. A window was installed in the bomb and a photocell circuit constructed to record light emission on the oscilloscope in a way similar to the recording of pressure. The presence of a delayed ignition was verified.

Design of Reactor II.—Another and more powerful reactor was built to avoid the difficulty due to the uneven starting of the two pistons and to provide an apparatus which would contact more nearly equal volumes of reactant solutions. This latter requirement is necessary because the apparatus is intended to serve in ignition delay studies on fuel-oxidant systems.

The apparatus without the pneumatic injector is shown in Fig. 2; the injector is fitted to the top of the reactor. The gas pressure is suddenly applied by the injector to the single large piston which then drives two smaller ones. The reactant solutions are contained in the cylinders below the two small pistons. The solutions are forced together in a mixing plate by head-on contact just as in reactor I, and the stream then collides with a baffle plate and is dispersed about the reaction bomb. It is apparent that the pistons must travel together since they are actuated by a single positive drive. Reactor II is considerably more powerful than reactor I because of the hydraulic advantage gained in having a piston with a large area drive smaller ones. The reactor may be immersed in either a hot or a cold bath so



Fig. 2.—Cross-sectional assembly drawing of bomb reactor II.

that the initial temperature may be varied. One observation arm of the reactor is closed with a plexiglass window and the other joins with the piping leading to the strain gage.

In order to determine the time required for the pistons to fall, a photoelectric timer was built. The timer, which is not shown in the figure, consisted of a small plastic rod that was fastened to the top of the small pistons so that it would fall with them; it was painted with black stripes one-eighth inch apart. A light source was placed to shine through a hole leading to the striped rod. The light transmitted by the rod was focused on a photocell or the other side of the When the rod fell with the pistons a rapidly alreactor. ternating light intensity was applied to the photocell, and the output was amplified and plotted against time on the oscilloscope. In this way the course of the piston fall could be determined.

Figure 3 is a plot of the simultaneous⁸ measurement of the piston fall and of the pressure produced by the reaction of 1 ml. of sodium-potassium alloy with 1 ml. of water. It is apparent that the pressure rise is delayed somewhat with respect to the displacement of the piston. This is due to the fact that the diaphragm of the strain gage is about 18 inches from the mixing area. The initial pressure wave would re-quire about 1.5 msc. to travel this distance through the bomb atmosphere. The operation of the photoelectric system should be essentially instantaneous. It is clear that the reactor discharged its contents in 2.3 msec. In several other runs values between 2.1 and 2.5 msec. were found.

Limitations of the Method.-Some difficulty was encountered in the interpretation of the traces obtained with reactor II because of the presence of noise. With both of the reactors it was found necessary to place a heavy rubber connection between the reaction bomb and the strain gage so that noise could not be transmitted through the metal parts of the apparatus. Figure 4 shows the nature of the noise present in the traces from reactor II. This type of noise was present in reactor II because the connecting arm between the reactor and the strain gage had to be shortened and its diameter increased to improve the time response of the recording system in a manner consistent with the im-proved injection rate of reactor II, which decreased the attenuation of the shock waves produced by the injection and reaction processes and they were recorded Numerous experiments were performed to show that the noise was not inherent in the pressure gage or due to a metallic vibration of some part of the reactor. Variations in the reactor gasketing had no effect on the noise. The noise could be damped out by placing kinks or orifices in the connecting arm. This latter fact indicates that the noise is not inherent in the strain gage.

It was found that in order to record faithfully a pressure rise of several atmospheres in 2 msec. a scattering of the wave heights of 10-20% must be tolerated for the first part of the trace. If the pressure rise is to be recorded in 4 msec. the connecting arm can be arranged to allow no more than about 5% scatter of the pressure data. It appears that the noise is a function of the injection and reaction processes and of the cavity in which they occur. In order to improve the recording speed it would seem to be necessary to analyze the structure of the shock waves and relate them in some way to the extent of reaction. This may set an upper limit to the speed with which chemical reactions may be followed by

measuring their pressure. Rice, Woods and Miller⁹ in a study of the reaction of alkali metals with water found a similar disturbance of audio frequency in their oscilloscope traces. They suggest that this might have been due to the oscillation of gas bubbles under the solution. They initiated the reaction by breaking vials of the metal under water.

Results

Reaction of Sodium-Potassium Alloy with Water. -This reaction using excess water has already been mentioned in connection with reactor I. The reaction yields the theoretical amount of hydrogen as fast as the reactants are mixed; the pressure

(8) Simultaneous measurements were made possible through the use of two oscilloscope and camera set-ups.

(9) T. K. Rice, F. J. Woods and R. R. Miller, Naval Research



Fig. 3.—Plot of simultaneous measurement of piston descent and pressure rise in NaK₂-water reaction (Reactor II).

passes through a slight thermal maximum and some time later the hydrogen-oxygen explosion occurs if oxygen is present. The composition of the alloy may be represented approximately by the formula NaK_2 so the reactions would be

$$NaK_{2} + 3H_{2}O \longrightarrow 1.5H_{2} + 2KOH + NaOH (1)$$
$$2H_{2} + O_{2} \longrightarrow 2H_{2}O (2)$$

The data obtained using reactor I are shown in Table I. The first group was obtained with air present in the bomb atmosphere. The runs are arranged in the order of the height of the thermal maximum. The overswing is the difference between the pressure of the thermal maximum and the pressure corresponding to the succeeding minimum; since this overswing is thought due to inefficient mixing, as discussed previously, the data near the top are probably more nearly correct. The second column of data is to be compared to 0.62

		TABLE I		
Read	TION OF NaK	² with Exces	S WATER (RI	sactof. I)
		Pressure (atm.)		Induction
Run	Overswing	Minimum	Explosion	msec.
		Air		
33	0.11	0.70	3.40	80
59	.25	.61	3.91	86
36	. 43	.65	3.57	44
155	. 44	.57	2.52	50
152	. 53	.79	2.96	47
154	.75	.79	3.40	54
145	1.44	.73	5.52	<u>-0</u>
		5-10% Oz		
52	0.10	0.61	3 . 32	37
	0.0	036 M Acetalo	lehyde	
61	0.07	0.65	3.18	-40

	5-10%	$O_2-0.036 M A$	cetaldehyde	
60	0.31	0.48		
		10 M KOI	Ι	
54	0.31	0.48	3.47	44
		10 M KOH-5	-10% O ₂	
		A 11	0.00	00



Fig. 4.—Oscilloscope trace of NaK₂-water reaction (reactor II), time base: 100 msec.

atm., the theoretical yield of hydrogen calculated from the stoichiometry of the reaction and the free volume of the bomb reactor. The third column gives the maximum explosion pressure and the fourth the induction period of the explosion.

The second group of data summarizes runs which were made to test the effect of additives and changes of atmosphere. When the atmosphere contained 5–10% O₂ instead of the usual 21%, the induction period decreased to 37 msec. even though the first maximum was very small. Using a solution 0.036 M in acetaldehyde instead of pure water, a similar shortening of the induction period occurred. Using both of these conditions, there was no explosion whatever.

In two experiments, 10 N KOH was substituted for the water. It was found that the rate of production of hydrogen was the rate of mixing, just as in the case of the reaction with pure water, although the induction periods were markedly shorter. In a further effort to slow the reaction a run was made using 11 M water in acetone solution: a relatively powerful explosion occurred with no induction period.

The reaction between sodium-potassium alloy and water was also studied in reactor II. Its use to determine the mixing rate and to study the noise problem has already been mentioned. Reactor II mixes equal volumes of reagent solutions and in the case of the alloy-water reaction this corresponds to a 2.3 to 1 stoichiometric excess of water. Although the ratio is fixed, the absolute amount of the two reactants may be varied from about 1.20 ml. down to zero. An example of the type of trace obtained is shown in Fig. 4. There is only one maximum, which occurs in 2-3 msec., i.e., the mixing time. This maximum is found to be associated with the hydrogen-oxygen explosion. Several photocell traces of the reaction showed that there was light emission beginning at the instant mixing began. The data obtained using reactor II are summarized in Table II, where they are

arranged in the order of the amount of reactants used. From the known amount of alloy the expected yield of hydrogen is calculated; this is compared to the observed maximum pressure and to the observed final pressure. The low maximum pressure in run 43 suggests that the explosion was inhibited in some way. With the exception of run 43 the difference in the calculated and observed final pressures indicates that the explosion consumes 30-50% of the hydrogen yield.

TABLE II Reaction of NaK2 with Water (Reactor II)

		Fressur	e (atm.)	
Run	Final (Calc.)	Maximum	Final (Obs.)	Final (Calc -obs.)
nun	(Cal(.)	A :	(003.)	(Calc008.)
		Air		
24	1.03	8.31		
43	0.89	3.71	0.61	0.28
47	. 82	6.02	.37	. 45
44	. 82	6.81	. 32	. 50
16	. 80	6.25	. 31	.49
27	.72	6.69	.25	.47
26	. 59	3.10	. 14	. 45
40	. 57	4.42	.23	.35
27	. 5 2	3.90	. 12	. 40
39	.43	2.81	.10	. 33
		Wet packing	5	
42	0.82	3.56	0.78	0.04
		$1-2\% O_2$		
21	0.95	5.81		
19	. 59	3.72	0.37	0.21
		0.0% Oz		
18	0.80	3.74	0.61	0.19
17	. 61	2.59	.37	.24

In one run, run 42, the lower part of the reaction bomb was filled with wet glass rods; here the data indicate that no explosion occurred. A run made using dry glass rods showed the usual behavior. With the oxygen removed from the bomb and replaced with nitrogen the maximum pressures are seen to be lower and the final pressures more nearly equal to those expected. The constant discrepancy in the final pressure, calculated minus observed, in the oxygen-free runs is probably due to unreacted alloy remaining in the mixing jets.

Reaction of Sodium-Potassium Alloy with Ethanol.—The reaction can be represented by the equation

$$\begin{array}{r} NaK_2 + 3C_2H_5OH \longrightarrow \\ 1.5H_2 + 2C_2H_5CK + C_2H_5ONa \quad (3) \end{array}$$

This reaction was studied in both of the reactors. The results obtained using reactor I with an excess of ethanol have already been reported.³ The reaction was shown to be first order with respect to the alloy; the half-time of the reaction was calculated to be 6.3 ± 0.8 msec. Since the reaction is heterogeneous between the two liquid phases, it is uncertain just what the first order relationship implies.

In reactor II, where equal volumes of reactants are mixed, the alloy is in a 1.42 to 1 stoichiometric excess over the alcohol. The pressure-time curve for the reaction carried out in the presence of air shows that the reaction is similar to the alloy-water case. There are two pressure maxima, the second beginning only 4 or 5 msec. after mixing. A powerful light flash was noted for these runs and hence the second maximum probably involves the hydrogen-oxygen explosion. Carbon deposits were found after the runs, suggesting the participation of alcohol in the explosion. It is interesting that the induction period for the explosion is about 4-5 msec. for a one-to-one volume ratio, whereas for an excess of alcohol there is no explosion.

The Hydrolysis of Aluminum Borohydride.—The reaction of aluminum borohydride with excess water was studied in reactor I. The data were not entirely reproducible because of the uneven starting of the pistons as discussed previously; this difficulty was particularly important in the study of this reaction because it was found that the borohydride attacked the neoprene gaskets and caused them to swell. Enough runs were made, however, to establish the general nature of the reaction. A typical pressure-time plot is shown in Fig. 5.

The data yield some information concerning the mechanism of the reaction. The following reactions are similar to the ones proposed by Kilpatrick and McKinney for the hydrolysis of lithium borohydride⁶

 $Al(BH_4)_3 + 3H_2O \longrightarrow$

$$Al(OH)_3 + 1.5B_2H_6 + 3H_2$$
 fast (4a)

 $1.5 B_2H_6 + 9H_2O \longrightarrow 3H_3BO_3 + 9H_2 \text{ slow (4b)}$ Al(BH₄)₃ + 12H₂O \longrightarrow

 $A(OH)_3 + 3H_3BO_3 + 12H_2$ over-all (4c)

In the case of lithium borohydride, it was shown that a partial hydrolysis occurred and that the slow hydrolysis of diborane completed the over-all reaction. The only reaction that took place in the bomb reactor, while the recording system was operative, was the hydrolysis to diborane. In the case of aluminum borohydride, the equation for partial hydrolysis (eq. 4a) predicts a final pressure of 1.58 atm., while if complete hy-



Fig. 5.—Pressure rise in aluminum borohydride hydrolysis (reactor I).

drolysis (eq. 4c) occurred, one would expect a final pressure of 4.20 atm. in the bomb reactor. The observed final pressures correspond more nearly to that expected for partial hydrolysis. It has been shown that the over-all hydrolysis is completed only slowly.⁹ Schlesinger, Sanderson and Burg¹⁰ have shown, however, that if the reaction is carried out very slowly, complete hydrolysis takes place quantitatively. It should be pointed out that any interference from the hydrogen-oxygen reaction would not seriously affect these data since a pressure drop of only 0.63 atm. could be realized even if all of the oxygen were consumed.

The Hydrolysis of Triethyldialane.—The reaction has been shown by Austin, *et al.*,¹¹ to proceed according to the equation

$$(C_2H_5)_3Al_2H_3 + 6H_2O \longrightarrow 2Al(OH)_3 + 3C_2H_{\theta} + 3H_2 \quad (5)$$

The reaction has been studied in reactor I using excess water. The reaction is completed within the mixing time of the reactor and the pressure passes through a slight thermal maximum. The final pressures were between 75 and 100% of that calculated from equation 5. Several runs were made using 2.5 N sulfuric acid instead of pure water and no difference was noted.

Materials. Sodium-Potassium Alloy.—The allow was in part purchased from the Mine Safety Appliances Co. The material was freed from oxide by filtration through a fine glass capillary in an all-glass vacuum system. The alloy analyzed 83.9% K. Several early runs were made with alloy which had been redistilled by the Naval Research Laboratory at Washington, D. C., and which was stated to contain 76.2% K by weight. The material was loaded into the reactors in such a way that it did not come into contact with the atmosphere.

Ethanol.—Gold Shield Alcohol was used without further purification.

Aluminum Borohydride.—The aluminum borohydride was supplied by the Naval Research Laboratory at Washington, D. C. It melted in the range -64 to -65° and the vapor pressure at 0° was 117 mm in good agreement with the values given by Schlesinger, Sanderson and Burg.¹⁰

the values given by Schlesinger, Sanderson and Burg.¹⁰ **Triethyldialane**.—An impure sample was received from the Aerojet Engineering Corporation. The material was purified by distillation in a high vacuum apparatus.

Acknowledgment.—The authors gratefully acknowledge the support of this research by the Office of Naval Research under Contracts N7onr-329, Task Order 3, and Nonr-630(00).

DISCUSSION

C. A. BOYD (Chemical Corps Biological Laboratories).----In the pressure-time traces shown in this paper, it is inter-

(10) H. I. Schlesinger, R. T. Sanderson and A. B. Burg, J. Am. Chem. Soc., 62, 3421 (1940).

(11) P. R. Austin, et al., Chemical Department, E. I. du Pont de Nemours and Company, O.S.R.D. Report 5922, October 1, 1945. esting to note the "hash" of fine structure which occurs under certain conditions. This is strongly suggestive of a similar type of phenomenon which is sometimes observed in powder driven rockets. The authors suggest that this evenly-spaced fine structure is due to a type of acoustic resonance occurring within the reaction chamber and have taken precautions to damp it out by suitable means. However, it would seem that if this is the explanation one would expect the resonance frequency to be pressure dependent and, to a first approximation, vary as the square root of the pressure. Since apparently this is not the case one might conclude that either the resonance is due to the excitation of some low frequency mode of the experimental equipment, or it is a real manifestation of the reaction.

N. DAVIDSON (California Institute of Technology).—Dr. R. Ogg of Stanford has suggested the possibility that the ignitions observed in this paper are initiated by hydrogen atoms formed in the initial step of the alkali metal, water reaction. I have no objection to this interesting possibility, but we should inquire whether there are other possible explanations. Is it certain that the observed explosions are not initiated thermally? For reactor I, with the large excess of water, the heat ot reaction, if uniformly distributed, cannot raise the temperature very much, but there might be local hot spots where the hydrogen-oxygen explosion is initiated. In reactor II, there is only a slight excess of water; the adiabatic reaction temperature might be quite high. In Table II, for the experiments with oxygen absent and no explosion, the maximum transient pressure increase is four and a half times the calculated pressure increase for an isothermal reaction. There was an additional initial pressure of one atmosphere of nitrogen. Depending on whether or not the stoichiometric excess of water vaporizes, this indicates an increase in absolute temperature by a factor of 1.2 or 2.5, *i.e.*, from 300 to 360° or 750°K. The latter temperature might be great enough to initiate explosion.

M. KILPATRICK.-In reply to Dr. Davidson, it is most

likely that the adiabatic reaction is high enough to thermally initiate the explosion in reactor II. In reactor I, however, it is doubtful that such temperatures are reached.

SIMON BAUER (Cornell University).—Professor Kilpatrick and co-workers should be commended for having done a careful and painstaking job in developing a rapid mixing device for the study of fast reactions between two liquid phases. The contacting time between reactants in such an apparatus is limited essentially by the inertia of the masses which have to be transported. It is presumed that the drag on the small pistons due to viscosity or friction, depending on whether a liquid film or a ring of solid material is used to seal the piston against the backflow of liquid, can be minimized. It scems to me that a contacting time of about 5 milliseconds is very near the limit attainable for useful masses of reactants, unless excessively large injection pressures are used.

Two points should be considered before conclusions based on data obtained with such a reactor are accepted unequivocally. (a) The time required for essentially complete mixing may be longer than the contacting time. In addition to this unknown time factor there is the matter of properly integrating over the extent of the reaction which occurs during the time of injection. (b) Whenever a fast reaction occurs involving also a change in phase, one must ascertain that the rate limiting step is the reaction studied, and not some nucleation process. Has this point been considered by the authors?

M. KILPATRICK.—In reply to Dr. Bauer's remarks, the authors are well aware that the time of mixing may be longer than the contacting time and that one must always consider other processes which may be rate limiting. In reference (3), McKinney and Kilpatrick discuss this problem in connection with the design of reactor I and prove that effective mixing can be obtained in 10 milliseconds. It was also demonstrated in the present paper that 1 ml. of each reactant may be effectively mixed in about 2 milliseconds in reactor II, see Fig. 3.

KINETICS OF THE THERMAL DECOMPOSITION OF NITRIC ACID VAPOR. II. MECHANISM

By HAROLD S. JOHNSTON, LOUISE FOERING AND R. J. THOMPSON

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The decomposition of nitric acid vapor has been followed in detail at 400° by optical analysis for both nitric acid and nitrogen dioxide. The effects on the rate of water vapor, oxygen, nitrogen dioxide, nitric oxide, hydrogen, carbon monoxide, methane, benzene and inert-gas pressure were tested. The reaction is more complex and the rate faster than was previously proposed. The fast initial rate is inhibited by nitrogen dioxide, unaffected by water and oxygen, and sustained by nitric oxide. In the presence of an excess of any of the reducing agents, the rate is first order in nitric acid, independent of reducing agent concentration, and the same order of magnitude as the initial rate of decomposition of nitric acid alone. Results

are in accord with the mechanism: $HNO_2 \xrightarrow{a} HO + NO_2$; $HO + HNO_3 \xrightarrow{C} H_2O + NO_3$. (NO₂ and NO₃ are equivalent

to nitrogen pentoxide, and they quickly give nitrogen dioxide and oxygen). Nitrogen dioxide reverses step a to inhibit the initial rate of reaction. Reducing agents remove HO to prevent step b thus sustaining the initial rate; however, further complexities also arise. By extrapolation to zero time the unimolecular rate constant a can be found, and its value definitely "falls-off" with inert gas pressures below one atmosphere.

Previous work¹ on the thermal decomposition of nitric acid vapor led to the conclusion that in small glass cells the reaction was heterogeneous below 300° , and in the presence of one atmosphere of nitrogen it was a fast homogeneous first-order reaction above 400° . A partial mechanism was proposed whereby nitric acid decomposes to hydroxyl radical and nitrogen dioxide. Meanwhile Fré-

der in the temperature range 260 to 450° and he emphasized the effect of nitric oxide. The present study was carried out in order to get information on the secondary reactions of the primary dissociation products. The decomposition of nitric acid was followed in detail from the initial time to completion, the effect of reaction products was studied, and a variety of reducing agents were added to get qual-

jacques² has reported the initial rate to be second or-

(1) H. S. Johnston, L. Foering, Y. S. Tao and G. H. Messerly, J. Am. Chem. Soc., 73, 2319 (1951).

(2) Claude Fréjacques, Compt. rend., 232, 2206 (1951).

itative information about the reactions of hydroxyl radicals in this system.

Experimental

These studies have been made in several different reaction systems. Figure 1 gives a schematic diagram of each reactor. The first three systems Fig. 1a, b, c were essentially flow systems. Nitrogen (or other carrier gas) passed through an all-glass saturator containing anhydrous nitric acid at 25° and this stream was diluted to the desired extent with another stream of nitrogen. The details of the flowmeters are omitted in Fig. 1.

Figure 1a.—This is the system used in the previous study. The mixture of nitrogen and nitric acid was brought from room temperature to about 400° by flowing through a hot glass coil into a reaction cell. In this apparatus the initial rate was missed, since it necessarily occurred in the heating coils. To follow a reaction the stopcock was closed isolating a sample of hot gases in the reaction cell and the concentration of nitrogen dioxide was followed in the usual manner³ by the photoelectric tube, oscilloscope and camera.



Fig. 1A —Apparatus No. 1 all Pyrex glass; reaction cell 2.5×10 cm.; another cell 0.6×10 cm.

Figure 1b. Flow and Quench Apparatus.—From a 0.5mm. capillary tube, a slow stream of nitrogen carrying nitric acid vapor was quickly heated from about 60° to about 400° by mixing with a large excess of preheated nitrogen. The nitrogen was preheated by flowing through a 2-meter coil cf 4-mm. Pyrex tubing imbedded between two cast aluminum blocks, each 2.0 cm. thick, 10 cm. wide and 40 cm. long. The hot mixed gases flowed through 40 cm. of 4 mm. i.d. glass tubing, and at the exit of the furnace it was quenched to lower temperature by mixing with a fast stream cf nitrogen at room temperature. Typical flow rates were: nitric acid stream, 10 to 30 ml./min.; preheat, 600 to 1200 ml./min.; quench same as preheat. This apparatus overcame some of the difficulties of flowthrough-furnace systems. The contact time was wellknown, since the initial time was sharply defined by mixing the reactant with preheated gas and the final time was likewise sharply defined as the hot stream was suddenly



Fig. 1B.—Apparatus No. 2 flow and quench; all Pyrex glass; reaction tube 0.6×40 cm.

(3) H. S. Johnston and D. M. Yost, J. Chem. Phys., 17, 386 (1949).

cooled by mixing with the cool stream. Knowledge of flow rates at room temperature, the temperature of the furnace and the volume of the reaction zone permitted calculation of the contact time at known temperature. Temperature was measured by a platinum-rhodium thermocouple inserted into the reaction tube, or inserted into the aluminum block.

As the quenched gases left the reaction zone they passed through a flexible glass bridge into a 10-cm. quartz cell in a Beckman spectrophotometer and out an exit tube. The leads were sufficiently flexible to permit the cell to be rushed over and a blank quartz cell put in the light beam. Thus at one temperature a steady state could be set up, and as the gases flowed, any wave length from 206 to 700 m μ could be used to analyze for remaining reactants and for reaction products. By turning a three-way stopcock the nitric acid vapor could be made to bypass the furnace, and thus its initial value was found by the spectrophotometer. Also the nitric acid stream could be frozen out with Dry Ice and analyzed chemically. Nitrogen dioxide was analyzed by light of $436 \text{ m}\mu$. Both nitrogen dioxide and nitric acid absorb radiation at 210 m μ , but the optical density at 210 m μ due to nitrogen dioxide was subtracted off to give the concentration of nitric acid. Nitrogen tetroxide absorbs extremely strongly at 210 m μ and to avoid this correction the quartz cells were maintained at 65°

quartz cens were maintained at 65. Figure 1c. High Temperature Optical Cell.—This apparatus used the good features of both preceding systems. Nitric acid was brought to 400° by mixing with excess preheated gas. The hot reactant was isolated in a reaction cell 1.0 cm. i.d. and 4.8 cm. long, which was imbedded in the same aluminum block as the preheat line. The cell had quartz windows and connected to Pyrex glass through graded seals. The exit slit of the Beckman spectrophotometer was focused by a quartz lens through the reaction tube to 1P28 electron multiplying photoelectric tube. The output of the phototube was sent either to an oscilloscope or an electronic voltmeter. This system was sensitive down to 200 m μ . Duplicate runs were made using radiation of 210 and 436 m μ , and in this way both the appearance of nitrogen dioxide and the disappearance of nitric acid cculd be followed. By quickly closing the six-way stopcock one simultaneously cut off the nitric acid line, preheat line and exit line, thus isolating the reactants at constant volume and constant temperature. Blank runs were made with bromine to see under what conditions diffusion from the cell would have to be considered.



Fig. 1C.—Apparatus No. 3: reaction cell had Pyrex body quartz windows, 1.0 cm. × 4.8 cm.

Figure 1d. Low Pressure Apparatus. In order to vary the total gas pressure some studies were carried out in a 22liter Pyrex reaction bulb below 100° and in a 2-liter Vycor bulb around 400°. Gas pipets of known volume were filled to known pressure as measured by a null-type bourdon gage and then they were emptied into the evacuated bulb. The reaction was followed by appearance of nitrogen dioxide.

Nitric acid vapor attacked and charred ordinary stopcock grease at room temperature and as it did so there was evolved a large amount of volatile material. All stopcocks in these

(4) H. S. Johnston and R. L. Perrine, J. Am. Chem. Soc., 73, 4782 (1951).



Fig. 1D.—Apparatus No. 4, low pressure system; bulb 22-liter Pyrex, another 2-liter Vycor.

systems were lubricated with a chlorotrifluorocarbon $^{\rm s}$ stopcock grease.

The most surprising discovery made in this study was that nitric acid vapor around 400° attacked stainless steel to produce a copious amount of a gaseous material containing chromium, presumably CrO₃. Thus several attempts to make a high-pressure reactor were unsuccessful.

Results

1. Decomposition of Nitric Acid Alone.-With the third apparatus there were obtained complete time curves of nitric acid concentration from essentially zero time. To avoid heterogeneity the temperature was set at a fairly high value, 397°. At this and at higher temperatures the decomposition of nitrogen dioxide was slow compared to the initial rate of decomposition of nitric acid. In Fig. 2 there are plotted four curves of log nitric acid against the time for different initial concentrations of nitric acid. If the reaction were simply first order,¹ all these curves should be straight lines with the same slope. If the reaction were simply second order,² these plots of log nitric acid vs. time should be curved lines of quite different, that is, non-parallel form. It is seen in Fig. 2 that the plots are nonlinear, but they are parallel throughout. When these data were plotted as log rate vs. log nitric acid, it was seen that as a function of time this reaction has no order at all. When these data were



(5) Halocarbon Products Corp., 2012-88th Street, North Bergen, New Jersey.

plotted as log initial rate vs. log initial nitric acid, it was found that the initial rate was first order in nitric acid. Thus there was a fast initial first-order rate followed by a slower rate, which implied inhibition by the reaction products. The fact that the curves in Fig. 2 are parallel throughout implies that the inhibition function is dimensionless, that is, it depends only on the ratio of nitric acid to some product or products and not on their absolute value.

$$-\frac{\mathrm{d}\left[\mathrm{HNO}_{3}\right]}{\mathrm{d}t} =$$

k [HNO₃] [dimensionless inhibition function] (1)

The molecular products of the decomposition of nitric acid are oxygen, water and nitrogen dioxide, and each of these was added to the preheating stream to see if it inhibited the initial rate. When oxygen was used as the carrier stream in place of nitrogen or with a 5-fold excess of water vapor over nitric acid, the entire curve was superimposable on one of those of Fig. 2, and thus these products were not responsible for the observed inhibition. When nitrogen dioxide was added to the preheat stream, it was found to have a strong inhibitory effect. Figure 3 shows four curves plotted as log [HNO₃] vs. time. The initial nitric acid concentration was



Fig. 3.—Effect of small amounts of added nitrogen dioxide on decomposition of nitric acid vapor at 397°. Initial $\rm HNO_3, 0.51 \times 10^4$ in each case; initial NO₂, respectively, in mole/l. $\times 10^4$, 1.93, 1.42, 0.62, 0.

 0.5×10^{-4} mole/l. in each case, and the initial nitrogen dioxide concentrations were 0, 0.62, 1.42 and 1.93×10^{-4} mole/l. Up to this point the data required the use of eq. (1) and required the appearance only of nitric acid and nitrogen dioxide in the dimensionless inhibition function. The following general rate expression was tested against the data.

$$-\frac{\mathrm{d} [\mathrm{HNO}_3]}{\mathrm{d}t} = \Lambda [\mathrm{HNO}_3] \frac{[\mathrm{HNO}_3] + B [\mathrm{NO}_2]}{[\mathrm{HNO}_3] + C [\mathrm{NO}_2]}$$
(2)

This expression fulfills eq. (1) and it would give inhibition by nitrogen dioxide if the constant C were larger than B. For the curves shown in Fig. 2 the following rate "constants" were obtained between each successive point

$$k = \Delta [\text{HNO}_3] / \Delta t [\text{HNO}_3]_{av}$$
(3)

where $[HNO_3]_{av}$ represents the average nitric acid concentration across the interval $\Delta[HNO_3]$. By taking eq. (2) to each of two extremes, the values of A, B and C could be found from the measured k's.



The first extreme condition is that of excess nitrogen dioxide such that $[HNO_3] << C[NO_2]$, and in this case

$$k = \frac{AB}{C} + \frac{A}{C} \frac{[\text{HNO}_3]}{[\text{NO}_2]}$$
(4)

Equation (4) is tested in Fig. 4. For large relative values of nitrogen dioxide, the curve goes through the origin, implying that B is zero. For large relative values of nitric acid, the points fall below the straight line, indicating that under these conditions the nitric acid term should not be dropped from the denominator of eq. (2). If B is zero, eq. (2) under all conditions has the form

$$\frac{1}{k} = \frac{1}{A} + \frac{C}{A} \frac{[\text{NO}_2]}{[\text{IINO}_3]}$$
(5)

Equation (5) is tested in Fig. 5 and it is seen to have the correct form, a straight line of intercept 1/A and slope C/A. At 397° in the presence of one atm. of nitrogen, the value of A is 0.32 sec.⁻¹ and C is 3.8.



Fig. 5.—Inhibition of rate of nitric acid decomposition by nitrogen dioxide during a given run, initial HNO₃ \times 10⁻⁴ mole/l.: Δ , 16; \bigcirc , 1.0; +, 0.22.

When the rate of decomposition of nitrogen dioxide is negligible so that the amount of nitric acid decomposed is equal to the amount of nitrogen dioxide present, eq. (5) can readily be integrated. Let $x = [HNO_3]$, and x_0 is the initial value of x. The integrated equation is

$$At = C\left(\frac{x_0}{x} - 1\right) - (C - 1)\ln\frac{x_0}{x}$$
(6)

A small number of runs was made at low total pressures. The partial pressure of nitric acid was varied from 1 to 20 mm. and also various amounts of nitrogen were added. At low total pressures, eq. (5) was obeyed, but the value of A and of C "falls off" with decreasing total pressure. Between 1 and 10 mm. Aand also C are very nearly proportional to the total pressure.⁶

2. Decomposition of Nitric Acid Vapor in the Presence of Nitric Oxide.—Smith⁷ stated that nitric oxide reacts very rapidly with nitric acid at room temperature, but the mechanism was uncertain, especially with respect to surface effects. Smith showed that the reaction was at least partially heterogeneous and

that it might or might not be partially homogeneous. A series of runs were made in the 22-liter bulb at 70° with nitric oxide and nitric acid and some runs were made with water and nitrogen dioxide also. All substances were present at about 0.5 to 1 mm. There was no detectable reaction in 10 minutes in any case; thus the fast low temperature reaction of nitric oxide and nitric acid is probably entirely heterogeneous.

In the apparatus shown in Fig. 1c, a series of runs at high temperature was made in which nitric oxide was introduced from the preheat line. In Fig. 6 there is plotted log $HNO_3 vs.$ time for nitric acid alone, for nitric acid plus nitrogen dioxide, and for nitric acid plus various amounts of nitric oxide. The curve drawn in for nitric acid alone is computed from the integrated equation, eq. (6). A



Fig. 6.—Effect of nitric oxide on rate of decomposition of nitric acid at 397°: initial HNO₃ 1.6 \times 10⁻⁴ mole/l.; quantities of NO₂ and of NO are units of 10⁻⁴ mole/l.

(6) These studies at low pressures are the first of a series supported by U. S. Naval Ordnance Test Station, Inyokern, Task order 2. N123s-80063.

(7) J. H. Smith, J. Am. Chem. Soc., 69, 1741 (1947).

small amount of nitric oxide increased slightly the initial rate, but inhibition by nitrogen dioxide still occurred. With the addition of 3-fold excess nitric oxide, the rate was first order in nitric acid almost to completion, but finally there was some inhibition. Going from a 3-fold excess of nitric oxide to 6-fold increased the initial rate only slightly and the curve was first order with respect to time for nitric acid somewhat further. Table I gives the initial (0 to 2.5 sec.) rates of reaction of nitric acid in the presence of nitric oxide for two series of runs.

TABLE I

EFFECT OF NITRIC OXIDE ON INITIAL RATE OF DECOMPOSI-TION OF NITRIC ACID VAPOR AT 397° IN PRESENCE OF 1 ATM. OF NITROGEN

Concn., m HNO3	nole/l × 104 NO	Initial (0 to 2.5 sec.) rate constant, sec. ⁻¹
0.98	0	0.16
. 98	0.86	. 21
. 98	3.10	.28
. 98	17.0	. 34
1.55	0	. 14
1.55	0.83	. 20
1.55	5.0	. 34
1.55	10.8	. 36

In the presence of a 19-fold excess of nitric oxide the first-order rate constant was 0.34 sec.^{-1} over virtually the entire run and it will be recalled that from Fig. 5 the rate of decomposition of nitric acid extrapolated to zero nitrogen dioxide was 0.32sec.⁻¹. Thus with excess nitric oxide, the rate of reaction is first order in nitric acid, independent of nitric oxide and the rate constant is the same as the initial rate of decomposition of pure nitric acid. Also, the ratio of final nitrogen dioxide to initial nitric acid is twice as great in the presence of a large excess of nitric oxide as in the case of nitric acid alone.

3. Decomposition of Nitric Acid Vapor in the Presence of Reducing Agents.—A small number of runs was made in apparatus Fig. 1c with carbon monoxide added to the preheat line. When log $[HNO_3]$ was plotted against time, it was seen that a straight-line relation applied throughout and thus the reaction is first order in nitric acid. Variation of carbon monoxide has shown the rate to be first order in nitric acid and independent of carbon monoxide if it is present in large excess.

Hydrogen, like carbon monoxide, was found to induce nitric acid to disappear by a first-order law throughout the run. Considerable variation of hydrogen pressure showed the rate to be first order in nitric acid and independent of hydrogen for small absolute amounts of nitric acid and large relative amounts of hydrogen. For large pressures of nitric acid, about 18 mm. and about 29 mm. of hydrogen, there appeared to be an explosive limit in the flow-and-quench apparatus just above 400°; however, considerably more work will be needed to substantiate this observation and to characterize the explosion limits if they exist. Aside from this behavior, the first-order rate constants were the same in the presence of carbon monoxide and hydrogen, and from 350 to 450° they were the same order of magnitude (though always somewhat larger) as the initial rate of decomposition of nitric acid alone.

Preliminary studies were made on the reaction of nitric acid vapor with benzene and with methane. No wave length could be found in the visible or ultraviolet region which would permit these reactions to be followed quantitatively. An arbitrary and empirical procedure was used to get order of magnitude estimates of these rates. A wave length was selected in the ultraviolet where the optical density D increased due to formation of unknown products. The runs were allowed to go to completion to give D_{∞} , the optical density at infinite time. The difference $D_{\infty} - D$ was some measure of how far the reaction had yet to go. A plot of log $(D_{\infty}$ -D) against time gave a straight line and thus a firstorder rate constant. These empirical rate constants were the same within a factor of two or three of that for the initial decomposition of nitric acid alone.

Discussion

1. Nitric Acid Alone.—It has been found that the initial decomposition of nitric acid vapor and the reaction of nitric acid with nitric oxide, carbon monoxide, hydrogen, methane and benzene all occurred with about the same rate and with about the same temperature dependence. In all cases the rate was first order in nitric acid and zero order with respect to reducing agent if it was present in excess. In no case was there any evidence of nitric acid vapor reacting bimolecularly with any of these reducing agents. Thus for all of these reactions there must be a common rate-determining first-order reaction of nitric acid.

In the previous study¹ it was proposed that nitric acid decomposes by way of

$$HNO_3 \xrightarrow{a} HO + NO_2$$
 (7)

Present work showed inhibition by nitrogen dioxide which would be due to reversal of step a to give

$$HO + NO_2 \xrightarrow{0} HNO_3$$
 (8)

The straight line and non-zero intercept of Fig. 5 implied that nitric acid competes with nitrogen dioxide for some radical, presumably HO and thus step c is proposed

$$HO + HNO_3 \xrightarrow{c} H_2O + NO_3$$
(9)

with instantaneous⁸ removal of NO₃ by

N

$$O_{3} + NO_{2} \longrightarrow NO_{2} + O_{2} + NO$$
(10)
$$NO_{3} + NO \longrightarrow 2NO_{2}$$
(11)

Since decomposing nitric acid gives nitrogen dioxide, not nitric oxide, as the molecular product, one may not write step c to give $H_2O + NO + O_2$. Using the mechanism a, b and c above and making the steady-state assumption for HO, one obtains the following rate expression

$$-\frac{d[HNO_3]}{dt} = 2a [HNO_3] \frac{1}{1 + (b/c) [NO_2] / [HNO_3]}$$
(12)

This is identically the form which fits the data as seen previously where the empirical A is 2a, and the

(8) For a review of this subject, H. S. Johnston, J. Am. Chem. Soc., **73**, 4542 (1951).

empirical C is the ratio b/c. When the rate is extrapolated to zero nitrogen dioxide, the rate expression is

$$-\frac{\mathrm{d}[\mathrm{HNO}_3]}{\mathrm{d}t} = 2a[\mathrm{HNO}_3] \tag{13}$$

or twice that of the elementary unimolecular reaction a (which is, of course, itself a composite term involving excitation, de-excitation, and reaction). The runs made at low total pressures showed that term a which is a first-order constant with respect to time during a single run was itself proportional to total pressure around 1 mm. The inert gas nitrogen, as well as reactant, was effective in increasing the value of a. Thus the term a showed exactly the behavior expected of an elementary unimolecular reaction and this behavior is very strong evidence in favor of this mechanism. According to the mechanism, term b is the rate constant for a bimolecular association and c is the rate constant for a regular bimolecular reaction. Thus the ratio b/c is also expected to decrease with a decrease in total pressure. This effect has also been observed, and around 1 mm. total pressure the value of b/chas fallen off to such an extent that inhibition is almost undetectable, in fact, plots of log HNO_3 vs. time are straight virtually to completion.

At this point it can readily be seen why early work¹ in this Laboratory disagreed so seriously with Frejacques.² The early work here was done at one atmosphere total pressure and thus the rates were first order with respect to varied initial partial pressure of nitric acid. Also the method used missed the initial portions of Fig. 2 and after about one half-life the plot of log [HNO₃] vs. time is more or less linear for a considerable range. Fréjacques did not use carrier gas, most of his work was at low enough temperatures to show the initial rate and the curving sections of Fig. 2 would fit a second-order time plot better than one of first order. Since there was no carrier gas, most of Frejacque's work was at such low pressures that he was in essentially the second-order region of the unimolecular reaction. Thus the present mechanism reconciles the divergent findings between the first two investigators of this reaction.1,2

2. Nitric Acid and Nitric Oxide.-In some kinetic systems, the addition of a small amount of nitric oxide changes completely the rate. This situation was not true here. A small amount of nitric oxide had only a small effect. The general form of the rate curves remained the same as with nitric acid alone; the more nitric oxide added, the longer was the initial rate first order. Even with a 20-fold excess of nitric oxide, the rate never exceeded the initial rate of decomposition of nitric acid alone. These facts indicate that nitric oxide somehow removed HO and prevented the occurrence of step b. The rate constant with excess nitric oxide was 2a, not just a as it would be if it removed all hydroxyl radicals but had no other effect. The following step is sufficient to explain these effects

$$HO + NO + HNO_3 \xrightarrow{d} H_2O + 2NO_2$$
 (14)

If step d is added to the mechanism above the differential rate expression is the same as eq. (12) except the ratio b/c is replaced by b/(c + d[NO]). Step d is proposed only tentatively and as a working hypothesis for the continuing studies.

3. Nitric Acid and the Reducing Agents.—Carbon monoxide and hydrogen sustain and slightly exceed the initial rate of decomposition of nitric acid alone. The sustaining of the initial rate could be due to the rapid reaction with the hydroxyl radicals

$$CO + OH = CO_2 + H$$
(15)
$$H_2 + OH = H_2O + H$$
(16)

The fact that the rate of disappearance of nitric acid exceeds step a by a factor of 3 to 5 indicates that the hydrogen atoms bring about a short chain reaction including nitric acid. Since some results indicated an explosive limit, some branching chain process should be expected, perhaps such as

$$H + HNO_3 = NO + 2HO$$
(17)

With hydrocarbons this work and a study of other work in the literature⁹ leads to a mechanism for gasphase nitration

$$HNO_3 = HO + NO_2$$

$$HO + RH = H_2O + R$$
 (18)

$$R + NO_2 = RNO_2$$

In gas-phase nitration there are many further complications such as decomposition of $\rm RNO_2$, reaction of R with oxygen, decomposition of R, etc., but this scheme is proposed as the underlying mechanism.

DISCUSSION

G. R. Cowan (University of Minnesota).—Will you please clarify your discussion of the effect of added NO? You assert that NO formed by reaction (10)

$$\mathrm{NO}_3 + \mathrm{NO}_2 \longrightarrow \mathrm{NO}_2 + \mathrm{O}_2 + \mathrm{NO}$$
 (10)

reacts again by (11)

$$NO_3 + NO \longrightarrow 2NO_2$$
 (11)

but that added NO reacts by (14)

$$HO + NO + HNO_3 \longrightarrow H_2O + 2NO_2$$
 (14)

Would not the added NO also react with the NO₃ formed in (9)

$$HO + HNO_3 \longrightarrow H_2O + NO_3 (9)$$
?

H. S. JOHNSTON.—In the absence of added nitric oxide, its steady-state concentration is too low to contribute to reaction (14). At room temperature we believe reaction (11) to be 10^6 faster than (10), and in the presence of added nitric oxide reaction (11) probably predominates in the removal of NO₃. So long as there remain considerable amounts of added nitric oxide, it reacts both by way of (11) and (14).

S. BENSON (University of Southern California).—There are frequently wall effects in the reactions of OH radicals. Was there any evidence for heterogeneous reactions in your studies?

H. S. JOHNSTON.—Concerning surface reactions, let us refer again to our first study on nitric acid kinetics, reference 1 of this article. We found the reaction to be primarily heterogeneous below 300° in small glass tubes and homogeneous above 400° . The present study was carried out under conditions previously shown to be homogeneous.

(9) H. B. Hass and L. G. Alexander, Ind. Eng. Chem., 41, 2266 (1949).

ON THE KINETICS OF ELEMENTARY REACTIONS IN FLAMES AND ITS RELATION TO THE ENERGY DISTRIBUTION OF ACTIVE SPECIES^{1,2}

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The elementary reactions which occur in stationary flames may give rise to non-equilibrium distributions of the products and intermediates among their internal degrees of freedom. Under the appropriate conditions, these non-equilibrium distributions persist to some extent in steady state flames and are thus amenable to experimental observation. Some of these elementary reactions and the experimental observations relating to the subsequent non-equilibrium distributions are discussed here briefly. A theoretical analysis of the non-equilibrium steady states in flames, where the flame is considered schematically as a homocontinuous open reaction system, can give valuable information regarding the kinetics of the elementary flame reactions. A simple example of this type of analysis is presented here for the case of an adiabatic electronic excitation with subsequent equilibrizing collisions and radiational depopulation.

I. Introduction

It is the purpose of this paper to discuss some of the aspects relating to the kinetic study of the elementary reactions occurring in steady state flames such as the premixed oxyhydrogen or oxyhydrocarbon flames. These elementary free radical reactions, whose mechanism has been discussed in some detail previously,³ take place at very high temperatures (between 1500-3500°K.) in the flame reaction zone and this factor in conjunction with the generally low activation energy of these reactions makes for very fast reaction rates which are exceedingly difficult to measure directly. One approach toward overcoming this difficulty has been the development of rapid scanning spectrometers for the infrared⁴ whose time constants, it is hoped, will be sufficiently short to resolve these elementary flame reactions in The results obtained so far by this scanning time. method look very promising.

Another approach to this problem of studying the kinetics of very fast flame reactions, and the one with which this paper is primarily concerned, is the study and analysis of the steady state set up in these stationary flames. For such an approach to be successful it is necessary that the steady state set up in a flame be a "non-equilibrium steady state," i.e., a steady state with a non-thermal distribution of the reaction products and/or intermediates among their various energy states. Such a nonequilibrium steady state of an open reaction system⁵ has a kinetic information content which is equivalent to that of a temporally variant closed reaction system and it is thus possible to obtain some kinetic data from its analysis. This method is equivalent to the "steady state" treatment used in the study of the kinetics of free radical reactions in closed systems in that it involves the comparison of experimental data with expressions derived from various assumed reaction mechanisms. In the case of open reaction system flames this comparison

(1) Supported by the Bureau of Ordnance, U. S. Navy, under Contract NOrd 7386.

(2) Presented at the Symposium on Kinetics of Very Fast Reactions of the Division of Physical and Inorganic Chemistry, American Chemical Society Meeting at Atlantic City, September 18, 1952.

(3) See. e.g., K. J. Laidler and K. E. Shuler, Chem. Revs., 48, 153 (1951).

(4) (a) B. W. Bullock and S. Silverman, J. Optical Soc. Am., 40, 608
 (1950); (b) P. J. Wheatley, E. R. Vincent, D. L. Rotenberg and G. R. Cowan, *ibid.*, 41, 665 (1951).

(5) For a definition and a discussion of open reaction systems, see K. G. Denbigh, M. Hicks and F. M. Page, *Trans. Faraday Soc.*, 44, 479 (1948).

is to be made, however, not between the rate expressions, but between the experimentally observed and the theoretically derived non-equilibrium distributions in the steady state.

To evaluate the applicability of this approach, the production and persistence of these non-equilibrium distributions and the experimental evidence relating thereto will be considered briefly. This will then be followed by a discussion of the method by which the form and the pressure (collision) dependence of these non-equilibrium distributions are to be obtained from the assumed reaction mechanisms.

II. The Origin of Non-Equilibrium Distributions in Flames

The finding of a non-equilibrium or a non-equipartition distribution among the various levels of the intermediates and products in flame reactions is in agreement with some of the theoretically predicted properties of reaction systems. It has been pointed out⁶ that in a chemical reaction involving a transfer of energy among the various degrees of freedom there will be a different reaction rate for each energy level of the final state. The distribution of products (and intermediates) among the energy levels, which is to be obtained by summing the rates for each level, will then in general not be an equilibrium one. Some explicit calculations of Golden and Peiser⁷ along these lines appear to confirm these predictions. The equilibrium distribution (Boltzmann distribution) of products is then re-established through equilibrizing inelastic collisions after the reaction has taken place.

There are several reasons why these non-equilibrium distributions would be expected to appear very prominently in steady state flames. The free radical reactions which give rise to a flame are usually very exothermic and the large amount of energy liberated, if it should go preferentially into some particular degree of freedom, could readily lead to a noticeable abnormal excitation of reaction intermediates and products. Owing to a possible lack of complete collisional equilibrization of the newly produced species in these stationary flames, this abnormal excitation may persist to some extent in a steady state. And finally, the spectroscopic technique by means of which the energy distribu-

(6) H. Eyring, J. Walter and G. E. Kimball, "Quantum Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1944, Ch. XVI
(7) S. Golden and A. M. Peiser, J. Chem. Phys., 17, 630 (1949).

tions are investigated in flames lends itself particularly well to the detection of any non-thermal energy distribution that may obtain.

Some of the specific processes in flames which may give rise to reaction products and intermediates in non-equilibrium distributions will now be discussed briefly. The list to follow cannot be considered as complete but includes some of the more important processes.

A. Electronic Non-equilibrium Distributions. (1).—If an adiabatic chemical reaction gives rise to products in an electronically excited state rather than in the ground state, there will result an electronic non-equilibrium distribution in which [A*]/ $[A]_{exp} >> [A^*]/[A]_{equil.^8}$ A well known example of this appears in the carbon monoxide-oxygen flame where the CO_2 is produced directly in the electronically excited CO₂⁽³II) state by

$$O(^{3}P) + CO(^{1}\Sigma^{+}) + M \longrightarrow CO_{2}^{*}(^{3}II) + M$$
 (1)
The reaction

 $O(^{3}P) + CO(^{1}\Sigma^{+}) + M \longrightarrow CO_{2}(^{1}\Sigma_{g}^{+}) + M$ (2)

leading to ground state CO_2 is "forbidden" by the Wigner spin conservation principle and will take place at a much lower rate than reaction (1).⁹ It is thus to be expected that there will be an excess of CO_2^* over that predicted from thermal considerations and this is borne out by experimental measurements of the light yield of carbon monoxide flames.¹⁰ This particular type of electronic excitation and its effects on the energy distribution of the reaction system will be discussed in more detail in Sec. III.

(2).—Electronic excitation of atoms, radicals or molecules can also be brought about by the transfer of vibrational to electronic energy in inelastic collisions. It has been pointed out¹¹ that in the physical quenching of electronically excited species the quenching molecule is often left in a vibrationally excited state. By the principle of detailed balancing, the inverse process, *i.e.*, electronic excitation by collision with vibrationally excited species will also take place at an appreciable rate. If the vibrationally excited species have energy in excess of thermal energy, this excess vibrational energy may be transferred during the collisions and thus produce a non-equilibrium electronic distribution in the collision partner. A classic example of this type of electronic excitation is the excitation of sodium by vibrationally excited¹² sodium chloride

$$\operatorname{NaCl}' + \operatorname{Na}(^{2}S) \longrightarrow \operatorname{NaCl} + \operatorname{Na}^{*}(^{2}P)$$
 (3)

first studied by Polanyi¹³ and discussed in more detail later by Magee.¹⁴ This process has also been proposed by Gaydon and Wolfhard¹⁵ to account for the

(10) E. Kondratjewa and V. Kondratjew, Acta Physicochim. U.R.S.S., 4, 547 (1936); 6, 625, 748 (1937).

(11) K. J. Laidler, J. Chem. Phys., 10, 34 (1942).

(12) The superscript prime here, as in subsequent expressions, will denote the vibrationally excited species.

(13) M. Polanyi, "Atomic Reactions," Williams and Norgate, London. 1932.

(14) J. L. Magee, J. Chem. Phys., 8, 687 (1940).

(15) A. G. Gaydon and H. G. Wolfhard, Proc. Roy. Soc. (London), 201A, 561 (1950).

apparently non-thermal excitation of C_2 to the C_2^* (A³II_g) state.

(3).—A non-thermal electronic excitation may also be brought about by the direct transfer to a third body of the energy liberated in an association (recombination) reaction. Since the energy liberated in such an elementary reaction may be much larger than the exothermicity of the over-all process, the concentration of the electronically excited species produced in a reaction of the type

$$A + B + C \longrightarrow AB + C^*$$
 (4)

may be much higher than that calculated thermally on the basis of the energy liberated in the over-all process.

The non-thermal electronic excitation of metals¹⁶ such as Fe, Pb and Tl, which were added to premixed oxyhydrocarbon flames for the purpose of measuring line reversal temperatures, has been attributed to the above process.¹⁷ The necessary energy of excitation, which for some of the observed Fe lines must have been at least 170 kcal./mole was postulated to be supplied by the very exothermic association reactions $C_2 + O_2 \rightarrow 2CO$ or 2C +

 $O_2 \rightarrow 2CO.$ B. Vibrational Non-equilibrium Distributions. (1).—Electronically excited species which may have been produced in excess of their equilibrium concentrations by one of the processes described above may transfer their electronic energy as vibrational energy to other molecules in inelastic collisions. This process of physical quenching with vibrational excitation of the quencher, which is the inverse of A2, can be quite efficient under the proper conditions 3,11,18 and will lead to an initial vibrational non-equilibrium distribution of the quenching molecules. The redistribution of the initial excess vibrational energy of the quencher during subsequent collisions may then lead to a type of equilibrium, non-equipartition distribution¹⁹ between the vibrational and rotational degrees of freedom which would manifest itself as vibrational "temperature" considerably in excess of both the rotational and the adiabatic flame "temperature." A possible example of this type of behavior may be furnished by the $OH(^{2}\Sigma^{+})$ radicals in the interconal zone of the oxyacetylene flame which appear to have a vibrational "temperature" of about 3750°K. compared to rotational and adiabatic flame "temperatures" of about 3000°K.²⁰

(2).—It appears quite probable from theoretical considerations⁶ that the intermediates and products of chemical reactions are formed *initially* in vibrational non-equilibrium distributions. Owing to the formidable difficulties involved in studying this problem,²¹ there has been as yet no explicit quantitative treatment which would permit a more detailed discussion. An extension of the work of Golden and Peiser⁷ to include the effect of chemical reactions on the distribution of products among the vibrational energy levels would be of great value.

- (17) N. Thomas, J. Chem. Phys., 20, 899 (1952).
 (18) H. S. W. Massey and E. H. S. Burhop, "Electronic and Ionic Impact Phenomena," Oxford University Press, London, 1952, Ch. VII.
- (19) K. E. Shuler, J. Chem. Phys., 18, 1466 (1950).
- (20) K. E. Shuler, ibid., 18, 1221 (1950).
- (21) G. Castellan and H. M. Hurlburt, ibid., 18, 312 (1950).

⁽⁸⁾ The superscript star here, as in subsequent expressions, will denote the electronically excited species.

⁽⁹⁾ For a more detailed discussion, see: V. F. Griffing and K. J. Laidler, "Third Symposium on Combustion, Flame and Explosion Phenomena," Williams and Wilkins Corp., Baltimore, Md., 1949, p. 432 or ref. 3.

⁽¹⁶⁾ A. G. Gaydon and H. G. Wolfhard, *ibid.*, 205A, 118 (1951).

(3).—Predissociations, radiationless transitions and perturbations in general may affect the distribution of chemical species among their vibrational (and rotational) energy levels. These processes, however, do not bring about any non-equilibrium distributions; they only serve as a very sensitive *test* for the presence of non-equilibrium conditions in flames. If equilibrium obtains in the flame, then each process will, by the principle of detailed balancing, be exactly balanced by the inverse process. It is only when non-equilibrium conditions already obtain in a flame, independent of any possible predissociations and perturbations, that these processes will be effective by revealing the departures from equilibrium in the form of abnormal vibrational (or rotational) energy distributions of the affected species. This is well demonstrated by the work of Durie²² who showed that the effects of the predissociation in the ${}^{2}\Sigma^{-} - {}^{2}\Pi$ system of CH are suppressed as the conditions in the flame approach thermal equilibrium.

As a possible example of the effects of predissociation for a flame in which complete equilibrium apparently does not obtain, one may cite the abnormal excitation of $OH(2\Sigma^+)$ to the v' = 2 level in oxyhydrogen and oxyacetylene flames.²³ This abnormal excitation, which is particularly pronounced in low pressure flames, has been attributed²⁴ to the inverse predissociation

$$O(^{3}P) + H(^{2}S) \longrightarrow OH(^{2}\Sigma^{-}) \longrightarrow OH(^{2}\Sigma^{+})$$
 (5)

involving H and/or O atoms in excess of their equilibrium concentrations. Subsequent work has shown²⁵ that this predissociation of $OH(^{2}\Sigma^{+})$ and $OH(^{2}\Sigma^{-})$ in conjunction with the excess concentration of H and/or O atoms manifests itself as a vibrational non-equilibrium distribution of OH- $(^{2}\Sigma^{+})$ in the inner cones of both oxyhydrogen and oxyacetylene flames.

C. Rotational Non-equilibrium Distributions. (1).—It appears reasonable from the consideration put forth previously⁶ that the products of elementary chemical reactions may be produced directly in a rotational non-equilibrium distribution. This is analogous to the case B2 discussed above. The work of Golden and Peiser⁷ would seem to bear out this expectation and the "pseudo-canonical" distribution derived by them for the H₂ + Br reaction is quite similar to that actually observed for OH and C₂ in some flames.^{15, 25b}

(2).—The physical quenching of electronically excited species may well lead to a non-thermal rotational excitation of the quenching molecule. While this case has not yet been treated explicitly, it would appear to be readily susceptible to a quantitative treatment by an extension of Laidler's work on physical quenching¹¹ using *effective* potential curves which include the rotational energy of the molecules. The intersection of the potential surfaces then would give information as to both the vibrational and rotational states of the quenching

(24) A. G. Gaydon and H. G. Wolfhard, Proc. Roy. Soc. (London), 208A, 63 (1951).

(25) (a) H. P. Broida and K. E. Shuler, J. Chem. Phys., 20, 168 (1952);
 (b) K. E. Shuler and H. P. Broida, *ibid.*, 20, 1383 (1952).

molecule immediately after the act of quenching. It appears quite evident that the molecules would leave these quenching encounters grouped about a rather narrow range of rotational energy states which will be adjusted to a Boltzmann distribution only by subsequent inelastic collisions.

(3).—The breakup of polyatomic molecules under the impact of highly energetic atoms or molecules (or electrons) is believed to produce fragments with non-thermal rotational excitation and distribution.²⁶ In order for this non-equilibrium rotational distribution of the dissociation product to show up in ultraviolet emission spectra, it will of course be necessary that the breakup of the polyatomic molecule be accompanied by the simultaneous electronic excitation of the particular fragment. Except for the case where the impinging particle is an electron,²⁷ there has been no quantitative treatment of this process of rotational excitation. It is, however, quite often invoked as a possible mechanism for abnormal rotational excitation in flames^{17,25b} where it ties in well with other observations on the behavior and properties of the various radicals under study.28

D. The Effects of Energy Loss by Radiation.— Since most flames are quite transparent there is little re-absorption of the radiated energy and the energy lost by radiation is not balanced by the inverse process of absorption.²⁹ It is evident that this loss of energy, which can only be partially compensated by collisional excitation, may lead to non-equilibrium distributions as the upper energy states (electronic, vibrational and rotational) are irreversibly depopulated by radiation. Since the spontaneous emission of radiation is a unimolecular process whereas the partially compensating excitational collisions are bimolecular processes, this radiationally produced non-equilibrium distribution will be markedly pressure-dependent and will show up prominently only at low pressures.³⁰ Some simple calculations have been made by Gaydon and Wolfhard³¹ who found, in agreement with the discussion given above, that the effects of radiative depopulation on the energy distribution of Na atoms

(26) O. Oldenberg, Phys. Rev., 46, 210 (1934).

(27) K. Niira, J. Phys. Soc. Japan, 7, 193 (1952).

(28) This section should really be completed by adding a discussion of the translational non-equilibrium distributions which may be produced in flames. Owing to the experimental difficulties encountered in determining the translational distribution of chemical species in flames (see e.g., A. G. Gaydon and H. G. Wollhard, *Proc. Roy. Soc.* (London), **199A**, 89 (1949)) there are, however, hardly any data at hand which could be utilized to check the theoretically obtained results. (I. Prigogine and E. Xhrouet, *Physica*, **15**, 913 (1949); I. Prigogine and M. Mahieu, *ibid.*, **16**, 51 (1950); K. Takayanagi, *Progr. Theor. Phys.* (Japan), **VI**, 486 (1951)).

(29) For a more detailed discussion see e.g., J. L. Magee, "The Effect of Radiation in Flames," University of Wisconsin, Naval Research Laboratory, CM627, August 25, 1950.

(30) It must be borne in mind that the depopulation of the upper energy levels takes place also by bimolecular quenching collisions. The u. v. radiative lifetime of most species is of the order of 10^{-8} sec. so that the rate of radiation is about 10^8 [E] where [E] is the concentration of excited species. The rate of the bimolecular collisional depopulation (in moles per liter per second) is of the order of 10^{12} [M][E] where [M] is the concentration of the quencher. It is thus readily evident that only at very low pressures does the radiational depopulation become more important than the collisional one in bringing about a departure from equilibrium conditions.

(31) A. G. Gaydon and H. G. Wolfhard, Proc. Phys. Soc. (London), 654, 19 (1952).

⁽²²⁾ R. A. Durie, Proc. Phys. Soc. (London), 65A, 125 (1952).

⁽²³⁾ A. G. Gaydon, Rev. inst. franc. pétrole et Ann. combustibles liquides, IV, 405 (1949).

added to flames are significant only at low pressures of the order of $^{1}/_{100}$ atm. The effects of this irreversible radiational depopulation of excited energy levels on the distribution of the reacting species among these levels will be considered explicitly in the calculations presented in Sec. III.

E. The Persistence of Non-equilibrium Conditions in Flames.-The experimental results discussed above indicate that non-equilibrium conditions do persist to some degree in steady state flames despite the equilibrizing effects of inelastic collisions subsequent to the chemical reaction. The extent of this persistence depends on: (1) The extent and type of departure from equilibrium distribution brought about by the chemical reactions and subsequent specific energy transfer processes. (2) The number and the effectiveness of the equilibrizing collisions suffered by the excited species prior to and during its period of transit through the spectroscopic field of view. (3) The interplay of these two factors, and others not explicitly considered here which gives rise to the observed steady state flames.

As regards factor (1) there is as yet hardly any quantitative information on hand which would permit a more detailed discussion. Some of the available data bearing on factor (2) have been reviewed by Oldenberg and Frost³² and Massey and Burhop.¹⁸ Some additional data on the effect of pressure (collisions) on the persistence of nonequilibrium distributions are furnished by the work of Gaydon and Wolfhard on low pressure flames.³³ Figure 1, which is based partly on their data and partly on data obtained by the author and Broida,^{25b} shows the rotational "temperature" of $OH(^{2}\Sigma^{+})$ in the oxyacetylene flame as a function of pressure between 1.5 and 760 mm. It well illustrates the equilibrizing effects of the increased number of collisions at higher pressure on the initial non-equilibrium distribution. The work of Broida³⁴ on the effects of various inert diluents on the "temperature" and rotational distribution of $OH(^{2}\Sigma^{+})$ in different flames is also in line with the above result.

As regards factor 3, it is extremely difficult to take a rigorous quantitative account of the interplay between all the various factors which go to make a steady state flame and which ultimately determine the possible persistence of non-equilibrium conditions in flames. A detailed treatment of the persistence of non-equilibrium distribution in flames would have to follow along the lines of Hirschfelder's and Curtiss' work³⁵ and take into account all the many variables that enter into the formation, the structure, and the propagation of steady state flames. In analyzing the steady state with special reference to the chemical kinetics of the elementary flame reactions it may, however, not be necessary to follow such an absolute route and it will be assumed in the treatment below that it is

(32) O. Oldenberg and A. A. Frost, Chem. Revs., 20, 99 (1937).

(33) A. G. Gaydon and H. G. Wolfhard, Proc. Roy. Soc. (London), 194A, 169 (1948).

(34) H. P. Broida, J. Chem. Phys., to be published.

permissible to isolate to some extent the chemical kinetics from the other factors which are involved in the formation and propagation of these steady state flames.





III. Kinetic Analysis of the Steady State Distributions in Stationary Flames

The Steady State Equations.—This analysis is based principally on Denbigh's work on the kinetics of open reaction systems.^{5, 36} Stationary flames of the type with which this paper is concerned are open reaction systems in that there is a continuous flow of matter across the boundaries of the system. Like most other open reaction systems, stationary flames will reach a steady state where there are no more macroscopic changes in the system with respect to time. In the case of chemical systems such as flames it is possible to obtain a special type of steady state which for want of a better name may be called a "non-equilibrium steady state." This is a steady state whose displacement from static equilibrium is not due solely to the continuous flow of matter (or energy) through the system but which, in addition, is displaced from static equilibrium by the partial "freezing in" of the non-equilibrium distributions which were brought about by the chemical reaction within the system. It is the thesis of this paper that the analysis of such "non-equilibrium steady states" can give some information as to the kinetics of the elementary reactions which produced it.

A premixed stationary flame corresponds most closely to what Denbigh³⁶ calls a *heterocontinuous* system in that it is invariant with respect to time but changes in composition along (and across) the direction of flow. In the treatment to follow a *homocontinuous* model³⁶ will, however, be used. This model, which assumes both invariance of composition with respect to time and with respect to the spatial coördinates can be treated more easily. Its use for flames can be justified on the basis that the reaction zone (or parts thereof), which are the only regions with which we will be concerned here,

(36) K. G. Denbigh, Trans. Faraday Soc., 43, 648 (1947).

⁽³⁵⁾ J. O. Hirschfelder and C. F. Curtiss, *ibid.*, **17**, 1076 (1949); THIS JOURNAL, **55**, 744 (1951); see also "Third Symposium on Combustion, Flame and Explosion Phenomena," Williams and Wilkins Co., Baltimore, Md., 1949, p. 121,

are of such small extensions that they may as a first approximation be considered of uniform composition.³⁷ The small extension of this volume under study also justifies the use of a uniform flame temperature for this homocontinuous model. The uniformity of composition for the reactants which enter the reaction zone is provided for premixed flames by the mixing of fuel and oxidant in the torch butt. The complete homocontinuous reaction system is shown schematically in Fig. 2.



Fig. 2.—A schematic picture of a flame as a homocontinuous open reaction system.

The great mathematical advantage of studying the steady state is that the time no longer enters as an independent variable. The choice of the homocontinuous model obviates the use of spatial coördinates. The equations which describe the steady state of a homocontinuous open reaction system are thus simple algebraic ones rather than partial differential equations and integration, which may often be extremely difficult, is replaced by the much simpler process of finding the real and positive roots of algebraic equations.

The treatment of the steady state of open reaction systems differs somewhat from the "steady state" analysis used for chain reactions in closed systems. In the latter case one makes the assumption that the lifetimes of the *free radicals and atoms* are very short compared to the duration of the reaction so that $\langle d[R]/dt \rangle_{av}$. = 0 where [R] is the "steady state" concentration of these short-lived species. In the case of open reaction systems, the steady state is truly time invariant for *all* species and the analysis proceeds by setting up simple mass balance equations for *all* the species which enter into the reaction.

The reaction to be studied here as an example of the general method is of the type Al of Sec. II, *i.e.*, an adiabatic chemical reaction leading predominantly to the production of electronically excited species. For added simplicity only the electronic excitation will be considered explicitly and it will furthermore be assumed that only the first excited state is populated to any extent. This assumption is a very reasonable one for electronic excitation. These reactions can then be considered as purely atomic ones or as molecular reactions with a Boltzmann distribution in the rotational and vibrational degrees of freedom. The reaction scheme to be analyzed is

$$\mathbf{X} + \mathbf{Y} \xrightarrow[k_{-1}]{k_{1}} \mathbf{A}^{*} + \mathbf{Z} \tag{I}$$

$$X + Y \xrightarrow[k_{-5}]{k_5} A^{\circ} + Z \qquad (V)$$

$$\mathbf{M} + \mathbf{A} \underbrace{\stackrel{k_2}{\longleftarrow}}_{k_{-2}} \mathbf{M} + \mathbf{A}^* \tag{II}$$

$$A^{\circ} + A^{\circ} \xrightarrow{k_{3}} A^{\circ} + A^{*}$$
 (III)

$$\mathbf{A}^* \xrightarrow{k_4} \mathbf{A}^\circ + h\boldsymbol{\nu} \tag{IV}$$

where [M] = [X] + [Y] + [Z] and A° is the ground electronic state of species A.

Reaction (I) represents the adiabatic chemiproduction and the chemical quenching of electronically excited A^{*}; reaction (V) refers to the non-adiabatic production of ground state A[°]. These two reactions are equivalent to reactions (1) and (2) of Sec. IIA. Reactions (II) and (III) are collisions of the 1st and 2nd kind where k_2 and k_{-2} are averaged rate constants for [M] = [X] + [Y] + [Z]. Reaction IV is the "irreversible" emission of radiation discussed in IID. It is desired to obtain an expression for $A^*/A = A^*/(A^* + A^\circ)$ as a function of the pressure in order to investigate the type and the persistence of the non-equilibrium distribution in the steady state as a function of the number of equilibrizing collisions and of the radiational depopulation of the excited state.

The mass balance for the steady state is obtained by equating the amount of any species which enters the reaction volume plus the amount formed internally by chemical reactions or collisions with the amount transformed internally and the amount which leaves the reaction volume. In writing these equations, brackets will be used to denote the steady state concentrations and parentheses for the initial concentration of the species which enter the reaction volume from outside the reaction system (see Fig. 2).

These mass balance equations are

for A*:
$$V_{8}\{k_{1}[X][Y] + k_{2}[M][A^{\circ}] + k_{3}[A^{\circ}]^{2}\} = V_{8}\{k_{-1}[Z][A^{*}] + k_{-2}[M][A^{*}] + k_{-3}[A^{*}][A^{\circ}] + k_{4}[A^{*}] + u[A^{*}]$$
 (6)

where $V_{\rm S}$ is the volume of the flame which is being observed in the spectroscopic field of view³⁸ and uis the volume rate of flow of the gases. Dividing by $V_{\rm S}$ one obtains

$$k_{1}[\mathbf{X}][\mathbf{Y}] + k_{2}[\mathbf{M}][\mathbf{A}^{\circ}] + k_{3}[\mathbf{A}^{\circ}]^{2} = k_{-1}[\mathbf{Z}][\mathbf{A}^{*}] + k_{-2}[\mathbf{M}][\mathbf{A}^{*}] + k_{-3}[\mathbf{A}^{*}][\mathbf{A}^{\circ}] + k_{4}[\mathbf{A}^{*}] + t^{-1}[\mathbf{A}^{*}] \quad (7)$$

where $t = V_{\rm S}/u$ in the average residence time of A^{*} in the volume $V_{\rm S}$. Proceeding in an analogous manner for the other species gives

for A°:
$$k_{5}[X][Y] + k_{-2}[M][A^{*}] + k_{-3}[A^{*}][A^{\circ}] + k_{4}[A^{*}] = k_{-5}[Z][A^{\circ}] + k_{2}[M][\Lambda^{\circ}] + k_{3}[A^{\circ}]^{2} + t^{-1}[\Lambda^{\circ}]$$
 (8)
for X: $t^{-1}(X_{0}) + k_{-1}[Z][A^{*}] + k_{-5}[Z][\Lambda^{\circ}] = t^{-1}X + k_{1}[X][Y] + k_{5}[X][Y]$ (9)

(38) This is an important point. The results of the calculations are to be correlated with the experimental spectroscopic observations and the important quantity is thus the volume which is observed spectroscopically and *not* the total volume of the reaction zone.

⁽³⁷⁾ A similar approximation is made with good success in the application of open reaction system kinetics to biological systems where a living cell is obviously not of uniform composition but where a small element of the cell may be taken as uniform in composition for the purpose of calculations.

for Y:
$$t^{-1}(Y_0) + k_{-1}[Z][A^*] + k_{-5}[Z][A^\circ] = .$$

 $t^{-1}[Y] + k_1[X][Y] + k_5[X][Y]$ (10)
for Z: $k_1[X][Y] + k_5[X][Y] =$

$$k_{-1}[\mathbf{Z}][\mathbf{A}^*] + k_{-5}[\mathbf{Z}][\mathbf{A}^\circ] + t^{-1}[\mathbf{Z}] \quad (11)$$

where (X_6) and (Y_0) are the concentration of species X and Y as they enter the volume $V_{\rm S}$.³⁹

If one introduces the variable $[R] = [A^*]/[A^\circ]$ and solves eqs. (7-11) for it, one obtains a fourthorder equation in [R]

$$a[R]^{4} + b[R]^{3} + c[R]^{2} + d[R] + e = 0$$
 (12)

where the coefficients $a, b, c \ldots$ are complicated combinations of the various rate constants and the quantities (X_0) and (Y_0) . This exact eq. (12) would have to be solved numerically for [R] by assigning appropriate values to the k's and (X_0) and (Y_0) . For the special case of interest here, namely, the adiabatic formation of the electronically excited species A^{*} one has $k_1 >> k_5$ and for this condition, and with the additional simplification $k_2 = k_3$ and and $k_{-2} = k_{-3}$,⁴⁰ eq. (12) reduces to

$$\frac{[\Lambda^*]}{[\Lambda^\circ]} = \frac{k_2\{(X_0) + (Y_0)\} + t^{-1}}{k_{-2}\{(X_0) + (Y_0)\} + t^{-1} + k_4}$$
(13)

It will be shown later on by a representative numerical calculation that for a reasonably high energy of excitation $A^{\circ} \rightarrow A^{*}$ of the order of several ev., one has $[A^{*}] << [A^{\circ}]$ at all pressures so that [A] = $[A^{\circ}] + [A^{*}] \approx [A^{\circ}]$. One can thus rewrite (13) in its final form as

$$\frac{[\mathbf{A}^*]}{[\mathbf{A}]} = \frac{k_2 p + t^{-1}}{k_{-2} p + t^{-1} + \tau^{-1}}$$
(14)

where $p = (\mathbf{X}_6) + (\mathbf{Y}_6)$ is the pressure of the reaction system and $\tau = 1/k_4$ is the radiative lifetime of $\mathbf{A}^{*,41}$

The Dependence of $[A^*]/[A]$ on Pressure.—Before the distribution $[A^*]/[A]$ can be studied as a function of pressure, *i.e.*, as a function of the number of equilibrizing collisions, it will be necessary to consider the pressure dependence of the various quantities in eq. (14). The radiative lifetime τ , being a molecular constant, is not a function of the pressure. Since the adiabatic temperature of a flame varies with the pressure, the rate constants k_2 and k_{-2} will be pressure dependent. This indirect dependence of k on p is, however, small compared to the linear factor p in kp and may thus be neglected to a first approximation.

The pressure dependence of the average residence time $t = V_{\rm S}/u$ is intimately connected with the

(39) In writing the mass balance equations in the form of eqs. (7-11), one makes the tacit assumption that the net rate of diffusion out of the volume Va is the same for all the species. One can then include the diffusion terms in the flow rate u and assume $t_{A^*}^{-1} = t_A^{-1} = t_X^{-1} \dots$ etc., as will be done below. If the molecular weight of the various species is not too different, this approximation is not too bad. In more exact treatments, particularly if the reaction involves H atoms which have a high rate of diffusion, these diffusion terms which are of the form $k_{\text{Diff}}^A[A] = (A_0)$ should be introduced explicitly.

(40) This assumes that A has the same efficiency for energy transfer as M in collisions of the 1st and 2nc kind.

(41) It would appear from eq. (14) that $[A^*]/[A]$ depends only upon the rate constants k_2 and k_2 . This is, however, not the case since the principle of detailed balancing at equilibrium furnishes the additional relation $k_1k_{-2}k_{-5} = k_{-1}k_2k_5$ between the rate constants. Equation (14) could thus be written as

$$\frac{[\mathbf{A}^*]}{[\mathbf{A}]} = \frac{\{(k_1k_2k_5)/(k_1k_5)\} \ p + t^{-1}}{\{(k_1k_2k_5)/(k_1k_5)\} \ p + t^{-1} + \tau^{-1}}$$

burning conditions and the structure of the flame. The "spectroscopic volume" $V_{\rm S}$ is pressure dependent for fixed spectroscopic slit dimensions only in as far as the thickness of the flame is affected by changes in pressure. It has been found⁴² that the maintenance of stable premixed flames requires larger burner diameters at lower pressures so that the total depth of the flame will increase with decreasing pressure. The thickness of the reaction zone is inversely proportional to the pressure⁴² and thus also increases with decreasing pressure. For any given pressure it is, however, possible to vary the volume rate of flow u over a rather wide region and still maintain a stable flame. It is evident, therefore, that there is no unique and specific relationship between $t = V_{\rm S}/u$ and p and that the dependence of t on p is governed primarily by the burning conditions.⁴³ For any specific set of experimental conditions the particular pressure dependence of t can readily be introduced into eq. (14).

For the sake of simplicity it will be assumed here that the burning conditions are such that t is independent of p over a wide range of pressure. Equation (14) can thus be used as it stands to evaluate the pressure dependence of the distribution of A among the energy states A^* and A° .

At a sufficiently high pressure, t^{-1} and τ^{-1} can be neglected compared to k_2p and $k_{-2}p$ and eq. (14) becomes

$$\frac{[\mathbf{A}^*]}{[\mathbf{A}]} = \frac{k_2}{k_{-2}} = \frac{[\mathbf{A}^*]}{[\mathbf{A}]} \text{ equilibrium}$$
(15)

so that the distribution tends, as is to be expected, to the equilibrium one as the number of collisions is increased. At very low pressures, k_2p and $k_{-2}p$ can be neglected compared to t^{-1} and τ^{-1} and eq. (14) becomes

$$\frac{[A^*]}{[A]} \sim \frac{1}{1 + (\tau/t)^{-1}} \sim \frac{\tau}{t}$$
(16)

so that the distribution appears to be governed principally by the rate of radiation and the residence time of the various species in the volume $V_{\rm S}$.⁴⁴ The energy loss by radiation, which enters into eq. (14) as the inverse of the radiative lifetime, tends to decrease $[A^*]/[A]$ below its equilibrium value at all pressures as is to be expected from the discussion in IID. It is readily seen, however, that the departure from equilibrium due to this factor will be most pronounced at low pressures when τ^{-1} is of comparable magnitude or larger than $k_{-2}p$.³⁰

It is instructive to make a simple calculation of the effect of pressure on the distribution $[A^*]/[A]$ as given by eq. (14) and on the electronic "temperature" obtained therefrom. To calculate the average residence time t of the species in volume V_s , we use the data of Broida and Shuler.^{25a} For a slit width of 1×10^{-2} mm., a slit height of 1 mm., a spectroscopic aperture of f 10 and a flame thickness of about 1 cm. (at atmospheric pressure) one ob-

(44) This is, however, a quite meaningless result since stable flames probably cannot be maintained at arbitrarily low pressure.

⁽⁴²⁾ H. G. Wolfhard, Z. tech. Physik, 24, 206 (1943); A. G. Gaydon and H. G. Wolfhard, Fuel, 29, 15 (1950).

⁽⁴³⁾ This points up the necessity of specifying the exact burning conditions such as flow rates and burner dimensions in reporting experimental data on flames over a range of pressures so that the above analysis can be carried out.

tains a "spectroscopic volume" $V_{\rm S}$ of about 10^{-2} cm.³ when the flame is focused on the slit by means of a condensing lens of aperture f 10.⁴⁵ For a flow rate of about 200 cm.³/sec. one has $t = V_{\rm S}/u \sim 5 \times 10^{-5}$ sec. This is a quite reasonable value for the average residence time of the molecules in the rather small spectroscopic field of view. If one takes for the energy of excitation for $A^{\circ} \rightarrow A^*$ a value of 5 ev. and then assumes this to be the activation energy for process (II), one obtains $k_2 \sim 1 \times 10^{-2}$ sec.⁻¹ mm.⁻¹, $k_{-2} \sim 4 \times 10^6$ sec.⁻¹ mm.⁻¹ for a steric factor of unity and for an equilibrium flame temperature of 3000°K. The radiative lifetime τ was taken as 10^{-8} sec. When these values are substituted in eq. (14), one obtains the results shown in Table I. The electronic "temperatures" were calculated by assuming the ratios $[A^*]/[A]$ of Table I to be Boltzmann distributions.

TABLE I

THE DISTRIBUTION [A*]/[A] AND THE ELECTRONIC "TEM-PERATURE" DERIVED THEREFROM AS FUNCTIONS OF THE PRESSURE

[A*]/[A	Δ] _{equil} = 2 × 10 ⁻⁴	; T _{equilibrium} =	= 3000°K.
P (mm.)	Z (collision/sec.)	[A*]/[A]	Telectronic (°K.)
1	4×10^{6}	2×10^{-4}	6800
20	$8 imes 10^7$	1×10^{-4}	6200
100	$4 imes 10^8$	4×10^{-5}	5700
760	3×10^9	$7 imes 10^{-6}$	4900

It will be noted that equilibrium has not been reestablished in this example even at atmospheric pressure. The ratio $[A^*]_{760 \text{ mm}}$./ $[A^*]_{equil}$. ~ 10³ is of a reasonable order of magnitude for the excess concentration of electronically excited species for a non-equilibrium distribution at atmospheric pressure.⁴⁶ The calculated electronic "temperatures" are also of the right order of magnitude and agree fairly well with some experimentally determined non-equilibrium electronic "temperatures".¹⁶

In order to obtain a more comprehensive insight into the relation between the kinetics of the elementary reactions and the observed non-equilibrium distribution in flames it will be necessary to apply the method presented above to many additional elementary processes and reaction schemes of the type discussed in Sec. II. Complementary to this program is the extension and refinement of this type of steady state treatment to take a more explicit account of such factors as the structure of the flame, the detailed temperature and pressure dependence of the several variables, and the specific diffusion rates of the various species. A further, and major, extension would be the inclusion of the rotational and vibrational degrees of freedom into this steady state analysis. It is hoped to consider some of these points in more detail in a later communication.

Acknowledgments.—It is a pleasure to thank Dr. K. G. Denbigh, Department of Chemical Engineering, Cambridge University, England, for some very helpful correspondence in regard to the properties and behavior of open reaction systems.

DISCUSSION

S. SILVERMAN (Applied Physics Laboratory).—There are several comments that I wish to offer on the general topic of deviations from thermal equilibrium in flames.

1. In $CO-O_2$ flames, CO is not in rotational equilibrium but is in apparent vibrational equilibrium with the flame (thermodynamic) temperature. This holds true as far as 0.01 sec. beyond the reaction zone. A possible explanation is that the reaction

$$CO_2^* + O \longrightarrow CO + O_2 - 8.7$$
 kcal.

occurs with sufficient probability to maintain an abnormally excited rotational distribution for CO. 2. The $H_2 + Br_2 \rightleftharpoons 2HBr$ flame on the other hand

2. The $H_2 + Br_2 \rightleftharpoons 2HBr$ flame on the other hand shows vibration-rotation equilibrium with flame temperatures in good agreement with calculated values.

3. In the $\rm CO-O_2$ explosions in a spherical bomb there is apparently vibrational non-equilibrium in $\rm CO_2$. The radiation at 2.8 μ lags behind the pressure wave during primary burning by approximately 5×10^{-3} sec. which agrees qualitatively with the radiative life-time involved. There is a periodic fluctuation in the brightness temperature whose amplitude is as much as 150° K. following the arrival of the combustion wave at the wall of the bomb. This occurs with a frequency of ~ 10 c.p.s., and is unaccompanied by any pressure change at the wall. It is tentatively suggested that this after-burning is a localized phenomenon, perhaps complicated by turbulence, since it is observed only at frequencies where the emissivity of the hot gases is nearly unity.

N. DAVIDSON (California Institute of Technology).—In connection with the question of rate of attainment of rotational equilibrium, it is of interest to recall that ultrasonic dispersion data show that it takes several hundred collisions for rotational energy to equilibrate with translational energy in molecular hydrogen. Probably, the slowest rates of rotational equilibration will occur for molecules that are roughly spherical in shape, and that have hydrogen atoms on their peripheries.

S. BAUER (Cornell University).—If one considers dissociation reactions which result in fragments with anomalously high rotational energies, it appears that when the process is bimolecular there are no essential limitations imposed on the extent of rotational excitation except the net available energy. However, unimolecular processes are not as likely to produce this type of disequilibrium, firstly, because the translational and rotational energies available to the fragments in an adiabatic dissociation are generally small, and secondly, because some limitations are imposed by the requirement that angular momentum be conserved.



Consider a molecule which has sufficient total vibrational energy for dissociation. Its over-all rotational modes are in thermal equilibrium, and hence we must assume that these are at most, weakly coupled to the extensive excitation present in all the modes of vibration. Similarly, we must assume that rotation around the X—Y bond (ω) is not overly excited, for were that so, there would be very free rotation around that bond, and this mode is certainly strongly coupled to the over-all rotations. In the process of dissociation, the stretching mode ν_{a} goes over to a translational degree of freedom, while each of of the two bending modes, $\nu_{b,a}$ and $\nu_{b,a}$ —each doubly degenerate—goes over to a rotational and a translational degree of freedom. Due to anharmonicity, there must be equipartition among all the vibrational modes in the excited molecule prior to dissociation, but the process of dissociation requires that the amplitude of the stretching mode exceed a critical value, and this occurs at the expense of draining energy from other modes of vibration. It is true that the molecules most likely to dissociate before suffering a deactivating collision are the ones which have a total energy

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⁽⁴⁵⁾ I am indebted to Dr. H. P. Broida for this calculation.

⁽⁴⁶⁾ K. J. Laidler and K. E. Shuler, Ind. Eng. Chem., 43, 2758 (1951).

which is more than the minimum required, but the probability is low that whatever energy remains after dissociation be disproportionally distributed. Of course, a dissociation resulting from a non-adiabatic process, involving a transition from a metastable excited electronic state to a lower repulsive state is not so limited in energy.

Now consider the restrictions imposed by conservation of

momentum. It is clear that to yield products which show excessive rotational temperatures, the bond X-Y must break when the molecule is in a highly excited symmetric bending mode $\nu_{b,s}$. Furthermore, the J values for the two fragments must be roughly the same. This implies, unless their moments of inertia are comparable, that the available energy is distributed with considerable disparity.

THE THEORY OF FLAME PROPAGATION. IV

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The equations and boundary conditions which describe the one dimensional steady state propagation of flames have been derived and discussed previously. In this paper three examples are discussed: (1) the unimolecular decomposition of hydrazine; (2) the bimolecular reversible decomposition of nitric oxide; and (3) the two step chain mechanism describing the decomposition of ozone. The experimental flame velocity for the ozone decomposition is 55 cm./sec. as compared to our calculated value of 47 cm./sec.; for hydrazine decomposition although an experimental value will soon be forthcoming there is at present no data with which to compare our calculations. One purpose of these calculations is to learn the relative importance of the detailed chemical kinetics, heat conductivity and diffusion, insofar as they affect flame propagation. Another purpose is to learn more about the detailed structure of the flame zone. For example, from the calculations for the ozone decomposition it becomes apparent that for most chain reacting flame systems there is an enormous concentration of free radicals in the vicinity of the hot boundary thousands of times greater than would be expected on the basis of thermal equilibrium. The difficulties of treating specific flame systems are of two sorts. First, there is only a limited number of flames for which the complete system of chemical kinetics including the reaction rate constants are known. Secondly, in those cases where the chemical and physical constants are known there are still the mathematical problems of integrating the differential equations. Some of these systems of equations can be integrated easily while others require new types of mathematical methods and cannot be integrated numerically by the old methods even if super-high speed calculating machines are available.

In this paper the theory of flames is applied to three examples: (1) the unimolecular decomposition of hydrazine; (2) the bimolecular reversible decomposition of nitric oxide; and (3) the two step chain mechanism describing the decomposition of ozone.

A. The Equations Describing the Propagation of a Steady State, One-dimensional Flame

The following relations apply to the propagation of steady state one-dimensional flames²⁻⁵ in which the velocity of flow of the hot gases is small compared to the velocity of sound.

(1). Equations of Continuity

$$M dG_i/dx = m_i K_i(y_i, T) \quad i = 1, 2, ...$$
 (1)

Here M is the mass rate of flow of the gases, $M = \rho v$, where ρ is the gas density and v is the mass average velocity of flow; x is the distance from the flame-holder; G_i is the fraction of the mass rate of flow which is contributed by the i-th chemical species; m_i is the molecular weight of molecules of the i-th kind; y_i is the mole fraction of molecules of the i-th kind; and $K_i(y_i, T)$ is the net number of moles of the i-th species which are formed per cm.³ per

(2) (a) J. O. Hirschfelder and C. F. Curtiss, J. Chem. Phys., 17, 1076 (1949);
(b) "Third Symposium on Combustion, Flames and Explosion Phenomena." Williams and Wilkins, Baltimore, Md., 1949.
(3) J. O. Hirschfelder and C. F. Curtiss, THIS JOURNAL, 55, 774 (1951).

(4) J. O. Hirschfelder, C. F. Curtiss and D. E. Campbell, ref. 1.
(5) J. O. Hirschfelder, C. F. Curtiss. R. B. Bird and E. L. Spotz, "The Molecular Theory of Gases and Liquids," John Wiley and Sons,

Inc., New York, N. Y., 1953.

second as a result of chemical reactions. The mass rate of flow, M, is a constant determined by the boundary conditions.

(2). Equations of Diffusion

$$\frac{\mathrm{d}y_{\mathrm{i}}}{\mathrm{d}x} = \frac{M}{n} \sum_{\mathrm{i}} \frac{1}{\mathcal{D}_{\mathrm{i}j}} \left(y_{\mathrm{i}} \frac{G_{\mathrm{i}}}{m_{\mathrm{i}}} - y_{\mathrm{i}} \frac{G_{\mathrm{i}}}{m_{\mathrm{i}}} \right)$$
(2)

Here *n* is the total number of moles of gas per cm.³ and the \mathfrak{D}_{ij} are the coefficients of ordinary diffusion in a binary mixture of substances i and j. Equation (2) is a generalization of Fick's law to multi-component systems.

(3). Equation of Energy Balance

$$\frac{\lambda}{M}\frac{\mathrm{d}T}{\mathrm{d}x} = \sum_{\mathrm{i}}\hat{H}_{\mathrm{i}}G_{\mathrm{i}} - \left(\sum_{\mathrm{i}}\hat{H}_{\mathrm{i}}G_{\mathrm{i}}\right)_{\infty} \tag{3}$$

Here λ is the coefficient of thermal conductivity; \hat{H}_i is the enthalpy per gram of the i-th component; the subscript " ∞ " indicates the conditions at the hot boundary. Usually the \hat{H}_i are approximated by the form

$$\hat{H}_{i}(T) = \hat{H}_{i}(0) + \hat{C}_{i}T$$

where the \hat{C}_i and the $\hat{H}_i(0)$ are constants.

(4). The Equation of State

$$p = nRT$$
 (4)

Here p is the pressure and R is the gas constant. This perfect gas equation of state applies to flames at pressures below 50 to 100 atmospheres. At higher pressures, corrections for gas imperfections may be important.

The boundary conditions which the solutions to the flame equations must satisfy are the following:

Hot Boundary (designated by subscript " ∞ "), $x = \infty$.—At the hot boundary we assume com-

⁽¹⁾ This work was carried out under Contract NOrd 9938. Navy Bureau of Ordnance. Paper III, J. O. Hirschfelder, C. F. Curtiss and D. E. Campbell, "Fourth Symposium on Flames, Combustion and Detonations," Cambridge, Mass., 1952, Williams and Wilkins, Baltimore, Md.

plete chemical and thermal equilibrium. The y_i at this temperature are determined by the condition that the $K_i(y_i, T) = 0$. The $(G_i) \propto = m_i(y_i) \propto / \sum m_i(y_i) \propto$. The first derivatives of T, y_i and G_i with respect to x are then zero. The derivatives of y_i and G_i with respect to T however are not (us-

ually) zero at the hot boundary. Cold Boundary ((designated by the subscript "0"), x = 0.—At the cold boundary, the G_i are specified. They are simply related to the composition of the fuel gas mixture in the mixing chamber

$$(G_{i})_{0} = \binom{m_{i}(y_{i})}{j} m_{i}y_{j} \min \text{ chamber}$$
(5)

The values of the $(y_i)_0$ are not known a priori because of back diffusion up to the flame-holder. The temperature at the cold boundary is determined from eq. (3) by the requirement that $(dT/dx)_0$ have a specified value corresponding to a specified heat transfer to the flame-holder.

B. The Decomposition of Hydrazine

Flames resulting from the decomposition of hydrazine have been observed and studied by Murray and Hall.⁶ We consider here a theoretical study of these flames.

In the theoretical study of flame propagation the first question which arises is the nature of the kinetics of the decomposition. Murray and Hall found that in the decomposition of hydrazine the over-all reaction is

$$2N_2H_4 \longrightarrow 2NH_3 + N_2 + H_2 \tag{6}$$

However, Szwarc⁷ found that the first step in the decomposition is the unimolecular reaction

$$N_2H_4 \longrightarrow 2NH_2$$
 (7)

with the rate constant

$$k = 4 \times 10^{12} \exp\left(-60,000/RT\right) \tag{8}$$

The actual mechanism of the hydrazine decomposition is clearly a complicated chain reaction in which eq. (7) is the first step. The chain reaction aspects of the combustion of hydrazine have been discussed recently by Adams and Stocks.⁸

The present treatment of the hydrazine flame is based on an idealization of the decomposition mechanism. The initial unimolecular decomposition step, eq. (7), is considered and the remainder of the reactions are neglected. Thus we consider only two molecular species, N_2H_4 and NH_2 , which we designate by the subscripts "1" and "2," respectively. This idealization forms a simple example of the flame theory, although it only remotely resembles the hydrazine decomposition.

Now let us consider the values of the numerical constants entering into the equations describing the hydrazine flame. From the thermochemical considerations using eq. (6) for the over-all reaction, and from actual experimental measurements, Murray and Hall found that if the ambient temperature of the hydrazine is $T_0 = 423^{\circ}$ K., the flame tem-

(6) R. C. Murray and A. R. Hall, Trans. Faraday Soc., 47, 743 (1951)

(7) M. Szwarc, J. Chem. Phys., 17, 505 (1949).

(8) G. K. Adams and G. W. Stocks, "Fourth Symposium on Flames, Combustion and Detonations." Cambridge, Mass. 1952, Williams and Wilkins, Baltimore, Md. perature is $T_{\infty} = 1933^{\circ}$ K. Murray and Hall estimate that the enthalpy released by the decomposition of the hydrazine is 1000 cal./g. Thus the average specific heat is

$$\hat{C}_{p} = \frac{H_{1} - H_{2}}{T_{\infty} - T_{0}} = \frac{1000}{1510} = 0.6623 \text{ cal./g. deg.}$$
 (9)

Murray and Hall further estimated that at the flame temperature the thermal conductivity is $\lambda \infty = 0.0067$ cal./cm. deg. sec.

The reduced diffusion coefficient is defined as

$$\delta = \frac{2\bar{C}_p n \mathfrak{D}_{12} m_1 m_2}{\lambda(m_1 + m_2)} \tag{10}$$

where $m_1 = 32$ and $m_2 = 16$ are the molecular weights. The best estimate of the value of the diffusion constant consists of taking $\delta = 0.75$ and independent of temperature.

The equations describing the propagation of the hydrazine flame are: (a) The Equation of Energy Balance

$$dT/dx = sg \tag{11}$$

$$g = (T - T_{\infty}) + (T_{\infty} - T_{0})G_{1}$$
(12)

$$s = \frac{C_p}{\lambda} M = 99 M \text{ cm.}^{-1}$$
 (13)

(b) The Equation of Continuity

$$\frac{\mathrm{d}G_1}{\mathrm{d}x} = -s \frac{a}{M^2} y_1 e^{-60,000/RT}$$
(14)

where

where

$$R = 1.987 \text{ cal./mole deg.}$$
 (15)

 $a = 4 \times 10^{12} m_1 n \lambda / C_p = 8.164 \times 10^6 (g.^2/cm.^4 sec.^2)$ (16)

(c) The Diffusion Equation

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$$\frac{\mathrm{d}y_1}{\mathrm{d}x} = \frac{2s}{\delta} \left[\frac{2}{3} y_1 - \frac{1}{3} G_1 - \frac{1}{3} y_1 G_1 \right] \tag{17}$$

It is easy to show that in the neighborhood of the hot boundary the solutions of the flame equations are of asymptotic form

$$T = T_{\infty} + te^{\alpha x} \tag{18}$$

$$y_1 = ute \ \infty \tag{19}$$

$$G_1 = w t e^{\alpha x} \tag{20}$$

Direct substitution of these asymptotic forms into the flame equations leads to the values of the constants

$$\alpha = -\frac{\frac{a}{M^2} \exp\left(-60,000/RT_{\infty}\right)}{1 + \left[1 + \frac{3}{2} \delta \frac{a}{M^2} \exp\left(-60,000/RT_{\infty}\right)\right]^{1/2}}$$
(21)

$$w = (1 - \alpha)/1510$$
 (22)

$$= \frac{-aw}{M^2} \exp(-60,000/RT_{\infty})$$
(23)

From the values of dy_1/dT and dG_1/dT at T_{∞} , the values of y_1 and G_1 were estimated at T = 1926.75, 1920.5 and 1914.25°K. using a two term Taylor's series. These values then served as the starting point for the integration of the flame equations in the direction of the cold boundary, by the Milne method.⁹

(9) C. F. Curtiss, J. O. Hirschfelder and D. E. Campbell, University of Wisconsin Naval Research Laboratory Report, CM-690, 1952, p. 80. The best value of a/M^2 is 6×10^3 . This leads to a flame velocity of 127 cm./sec. This value is to be compared with the experimental value of 200 cm./sec. Table I gives the values of y_1 and G_1 as functions of the temperature. These variables are also shown in Fig. 1.

If the diffusion constant is taken twice as large as our best estimate, *i.e.*, if $\delta = 1.50$, the value of a/M^2 is 1.12×10^9 corresponding to a flame velocity of 93 cm./sec. The theoretical flame velocity is therefore not sensitive to the value of the diffusion constant.

TABLE I

$\delta = 0.75, a/M^2$	$= 6 \times 10^8 \text{ or } v_{\rm f} =$	127 cm./sec.
T, °K.	y	G
1933	0	0
1926.75	0.0034011488	0.039381898
1920.5	0068162803	.076817917
1914.25	.010236142	.11347764
1908	.013669619	. 14809440
1901.75	.017105082	. 18 253855
1895.50	.020554407	.21493759
1883	.027467170	.27783102
1870.5	.034417076	.33605424
1858	.041391349	.39097478
1833	.055438247	.48914128
1808	.069602911	.57396829
1783	.083882930	. 64669707
1733	.11276692	.76141900
1683	.14206143	.84257391
1633	.17172037	. 89844074
1583	. 20171599	. 93544294
1533	. 23200266	.95921552
1483	.26255953	.97369150
1433	. 29334936	.98227145
1383	.32436540	.98694231
1333	.35558293	.98949854
1233	.41861974	. 99134480
1133	.48253543	.99166222
1033	.54740370	.99173885
933	.61344376	.99171407
833	68086564	.99174342
733	.75012036	. 99171431
633	.82187158	.99174342
533	. 89782375	.99171431
433	.91683201	.99174342

C. The Nitric Oxide Flame

The theoretical possibility of producing a flame by the decomposition of nitric oxide has been investigated by Henkel, Hummel, Spaulding, Knaplund, Vandervort and Weeks.¹⁰⁻¹² The present discussion summarizes their work. According to the theoretical results, if nitric oxide is heated prior to combustion to a temperature above about 800°K. a steady state decomposition flame should be possible. At lower ambient temperature, a flame is theoretically possible but its flame velocity would

(10) M. J. Henkel, H. Hummel and W. P. Spaulding, "Third Symposium on Combustion, Flames, and Explosion Phenomena," Williams and Wilkins, Baltimore, Md., 1949, p. 139.

(11) M. J. Henkel, W. P. Spaulding, P. W. Knaplund and G. Vandervort. University of Wisconsin Naval Research Laboratory Report CM-564, January 1950.

(12) Unpublished calculations made by I. F. Weeks and the University of Wisconsin Naval Research Laboratory computing group.



Fig. 1.—The variables y and G as a function of the temperature T in a hydrazine flame. (The curve of G for a poor guess of the parameter a/M^2 is also indicated.)

be so small and its thickness so great it would be difficult to realize experimentally. Olsen and Loshaek tried unsuccessfully to produce such a flame. However, recently Wolfhard and Gaydon¹³ have succeeded. As a result, interest has been revived in the applications of our flame theory to this problem. A comparison between our calculations and the Wolfhard and Gaydon observations should help to determine the actual kinetic mechanism by which nitric oxide decomposes.

At the present time it is believed that nitric oxide decomposes into nitrogen and oxygen by a single step bimolecular reaction

$$2NO \xrightarrow{k}_{k'} N_2 + O_2$$
 (24)

The reaction rate constant in the forward direction at two temperatures and the thermochemical properties of NO, N_2 and O_2 are given in the International Critical Tables. From these it follows¹⁴ that the rate constants are

Forward rate,
$$k = 4.582 \times 10^{10} T^{-2} \exp (-65,300/RT) \text{ cm.}^3 \text{ mole}^{-1} \text{ sec.}^{-1}$$
 (25)

Reverse rate,
$$k' = 7.907 \times 10^{11} T^{-2} \exp^{-10^{11} T}$$

(-107,600/RT) cm.³ mole⁻¹ sec.⁻¹ (26)

The coefficients of binary diffusion were calculated accurately at each temperature assuming that the molecules attract each other at large separations with an energy varying as the inverse sixth power and repel each other at close separations with an en-

(13) H. G. Wolfhard, private communication, September, 1952.

(14) O. A. Hougen and K. M. Watson, "Chemical Process Principles," John Wiley and Sons, New York, N. Y., 1947, p. 813.

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TABLE II

FRACTION OF MASS RATE OF FLOW, CHEMICAL COMPOSITION AND DISTANCE IN A NITRIC OXIDE DECOMPOSITION FLAME AS A FUNCTION OF TEMPERATURE

 $(M = 0.0046 \text{ or } v_{\rm f} = 9.9 \text{ cm./sec.})$

T.		$(M \rightarrow 0.007)$	$v_{\rm f} = 3.3$ cm.	/ 500. /	
°K.	$G_{\rm NO}$	VNO	VN 2	2 O2	$x - x_{1900}$ ° (cm.)
3000	0.056419	0.0564228	0 471789	0 471780	+ m
2975	107516	0634884	468228	468281	0, 220007
2010	15500.1	0705313	464679	461701	177660
2005	902700	.0705313	404078	404791	. 177009
2920	. 2007 50	.0773790	.401120	.401290	. 100900
2900	. 200392	.0840233	.407074	.457803	.141248
2875	. 295306	.0916561	.454029	.454315	. 130061
2850	.338127	.0986757	. 450489	. 450835	. 121144
2825	.380030	. 105698	. 446949	. 447353	. 113552
2800	.419392	. 112700	. 443419	. 443881	. 107025
2775	. 458324	. 119716	. 439881	. 440403	. 101175
2750	. 494211	, 126702	. 436358	. 436940	.0959496
2725	.530046	. 133714	. 432822	.433464*	.0911376
2700	.562518	. 140687	. 429305	.430008	.0867280
2675	.595221	.147696	425771	426533	0825948
2650	624376	154659	422258	423083	0787374
2625	653973	161666	418794	.119610	0750760
2600	670024	168623	415914	416162	0716199
2000	706400	175629	411601	419601	.0710128
2010	.700499	. 173020	.411081	.412091	0051015
2000	. 7 29360	. 182383	, 408173	.409244	.0651215
2525	. 753054	.189590	. 404638	. 405772	.0620571
2500	.773021	. 196544	. 401130	. 402326	. 0591053
2475	.793940	.203558	. 397592	. 398850	.0562347
2450	.311173	.210515	. 394082	. 395403	.0534514
2425	.829511	. 217539	. 390539	. 391922	.0507297
2400	.844203	. 224503	. 387025	.388472	.0480762
2375	.860146	.231539	. 383475	. 384986	. 0454690
2350	.872501	.238513	. 379957	.381530	.0429153
2325	. 886250	.245566	. 376398	. 378036	. 0403957
23 00	.896480	.252555	. 372872	.374573	.0379180
2275	.908243	.259637	. 369302	.371061	0354644
2250	.916561	.266654	.365766	367580	0330431
2225	.926548	.273772	362182	364046	0306375
2200	933171	280822	358634	360544	0282564
2175	941591	287980	355033	356987	0258830
2150	946728	295069	351471	353460	. 0200000
2125	953783	302272	247859	240975	.0233291
2.20		.002212	. 511052	. 049070	.0211707
2100	.957636	. 309405	.344272	. 346323	.0188362
2073	. 903018	.010001	. 340029	.342710	.0164925
2000	. 900270	. 323848	. 337023	. 339129	.0141556
2025	.9/110/	.331174	.333345	.335481	.0118106
2000	.973006	. 338426	. 329705	.331869	.00946786
1975	.977075	. 345829	. 325989	.328182	.00711233
1950	.978159	.353155	. 322310	. 324535	. 00475490
1925	.981556	. 360643	.318551	. 320806	.00238030
1900	. 982027	. 368050	.314830	.317120	0
1875	. 984884	.375631	.311024	. 313345	00241100
1850	. 984869	. 383128	.307258	. 309614	00484769
1825	. 987302	.390813	. 303398	. 305789	00729712
1800	.986912	. 398409	.299583	. 302008	00977655
1775	. 989022	. 406208	. 295665	.298127	0122721
1750	. 988343	.413915	. 291794	.294291	- 0148023
1725	. 990210	.421841	.287812	290347	- 0173521
1700	.989322	. 429669	.283879	286452	- 0100113
1675	. 991011	.437735	279827	282138	- 0995540
1650	. 989970	445696	275827	278477	- 0959115
1625	.991533	453920	271695	97/225	- 0202110 - 0970064
1600	990387	462029	267691		0278904
1575	991863	470490	962400	. 470000	0306322
1010		. 110143	. 200400	. 200171	0334003

T

G_{NO}	¥NO	YN 2	¥02	$x - x_{1900}^{\circ}$ (cm.)
0.990645	0.478678	0.259269	0.262053	-0.0362262
. 992064	. 487200	255024	.257776	0390898
.990801	.495714	.250721	. 253565	0420196
.992182	.504479	.246343	.249178	0449936
. 990891	.513208	.241930	.244862	0480441
. 992248	.522222	.237428	.240350	0511467
. 990939	.531192	.232895	.235913	0543385
.992284	.540490	.228248	.231256	0575925
.990966	.549743	.223576	.226681	0609517
. 992302	.559385	.218760	.221855	0643861
.990978	.568954	.213928	.217118	0679466
. 9 923 11	.578993	.208914	.212093	0715997
.990984	.588945	. 203891	.207164	0754067
. 992314	. 599459	.198640	.201901	0793300
.990987	.609871	.193386	.196743	0834459
.992317	.620968	.187846	.191186	0877116
.990987	.631946	.182310	.185744	0922256
	.643784	.176406	.179796	— .0969393
	.655497	.170512	.173991	101986
	.668306	.164135	.167559	107311
	.680984	.157771	.161245	113106
	.695105	.150752	.154143	119315
	.709141	.143719	.147140	126241
	.725184	.135751	.139065	133841
	.741262	.127708	.131030	142670
	.760359	.118232	.121409	152779
	.779924	.108464	.111612	165489
	.804860	.0961060	.0990340	181481
	.832437	.0823846	.0851784	206467
	.874888	.0613980	.0637140	2401
	.845380	.0758007	.0788193	1924
	G_{NO} 0.990645 .992064 .992064 .992182 .990891 .992248 .990939 .992284 .990966 .992302 .990978 .992311 .990984 .992314 .990987 .992317 .990987	$\begin{array}{c c} G_{\rm NO} & \nu_{\rm NO} \\ \hline 0.990645 & 0.478678 \\ .992064 & .487200 \\ .990801 & .495714 \\ .992182 & .504473 \\ .990891 & .513208 \\ .992248 & .522222 \\ .990939 & .531192 \\ .992284 & .540490 \\ .990966 & .549743 \\ .992302 & .559385 \\ .990978 & .568954 \\ .992311 & .578993 \\ .990984 & .588945 \\ .992314 & .599459 \\ .990987 & .609871 \\ .992317 & .620968 \\ .990987 & .631946 \\ .643784 \\ .655497 \\ .668306 \\ .680984 \\ .695105 \\ .709141 \\ .725184 \\ .741262 \\ .760359 \\ .779924 \\ .804860 \\ .832437 \\ .874888 \\ .845380 \\ \end{array}$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $

TABLE II (continued)

ergy varying as the inverse twelfth power of their separations (Lennard-Jones (6-12) potential). The force constants for pure N_2 , O_2 and NO are well known.⁵ For collisions between unlike molecules we assume that the collision diameters are the arithmetic mean and the maximum energy of interaction is the geometric mean of those characteristic of the pure colliding molecules.

At high temperatures (around 3000° K.) most of the NO is decomposed and the mixture consists of equal parts of N₂ and O₂ whereas at low temperatures (around 800°K.) the mixture consists mainly of NO. Estimating the thermal conductivity under these two conditions and interpolating linearly between, we obtained as an approximate expression for the conductivity

$$\lambda = 7.5 \times 10^{-8} T \text{ cal. cm.}^{-1} \text{ deg.}^{-1} \text{ sec.}^{-1}$$
 (27)

In the temperature range under consideration (800 to 3000°K.), the enthalpies of the reacting species can be approximated by the relations

$$\tilde{H}_{NO} = 21,150 + 9T$$
 cal. mole⁻¹ (28)

$$\tilde{H}_{02} = \tilde{H}_{N2} = 9T$$
 cal. mole⁻¹ (29)

There is considerable computational advantage in assuming that the specific heats of the three reacting species are the same.

Either the temperature at the hot boundary or the temperature at the cold boundary may be specified. The other value is then determined by the equations. For convenience the value of T_{∞} is taken to be 3000°K. The values of the $(y_{.})_{\infty}$ and the $(G_i)_{\infty}$ are then determined by the condition that at the hot boundary the reaction rates are zero, that is $K_i(y_i, T) = 0$, and that the diffusion processes are zero. It is found that $(G_{NO})_{\infty} = (y_{NO})_{\infty} =$ 0.0564228 and $(y_{N_1})_{\infty} = (y_{O_2})_{\infty} = 0.471789$. It is then found from the energy equation that the temperature at the cold boundary if there is no heat sink is $T_0' = 782.6^{\circ}$ K. The presence of a heat sink necessary to stabilize the flame would increase the temperature of the cold boundary by a small amount.

In the equations representing the nitric oxide decompositions there is only one linearly independent G since

$$K_{N_2} = K_{O_2} = -1/2K_{NO}$$
(30)

The equations relating the G_i are

$$\frac{2G_{\rm NO}}{m_{\rm NO}} + \frac{G_{\rm N2}}{m_{\rm N2}} + \frac{G_{\rm O2}}{m_{\rm O2}} = \left[\frac{2G_{\rm NO}}{m_{\rm NO}} + \frac{G_{\rm N2}}{m_{\rm N2}} + \frac{G_{\rm O2}}{m_{\rm O2}}\right]_{\rm g} \quad (31)$$

and

$$G_{\rm NO} + G_{\rm N_2} + G_{\rm O_2} = 1 \tag{32}$$

There are two linearly independent mole-fractions, y_i , the only relation among the y_i being that the sum is unity.

Since all of the chemical reactions involved in this example are bimolecular it is easy to show from the form of the flame equations that the mass rate of flow, M, is proportional to the pressure; the flame velocity, $v_f = M/\rho_0$, is independent of pressure; and all of the distances in the flame zone vary inversely with the pressure. The numerical results which we quote are for a pressure of one atmosphere.

The flame equations are then eq. (1), (2), (3) and (4) in which the above constants are used. The asymptotic solutions in the neighborhood of the hot boundary are determined by a method discussed previously.³ This asymptotic solution was used to determine the conditions at the four temperatures: 3000, 2993.75, 2987.50 and 2981.25°K. The values at these four points then furnished the starting conditions for integrating the flame equations by the Milne method from the hot toward the cold temperature regions. Temperature rather than distance was taken to be the independent variable. Temperature intervals of 6.25° were taken down to 2975°K.; 12.5° intervals from there to 2925°K.; and 25° intervals thereafter. Figure 2 shows the function, $G_{\rm NO}$, for different values of the mass rate of flow, M. Since the gas in the mixing chamber is assumed to be pure nitric oxide, G_{NO} should be unity at the cold boundary or flameholder, T_0 approximately 783°K. Thus it is found that for nitric oxide preheated to around 783°K., the mass rate of flow is M = 0.0046 which corresponds to a flame speed of $v_{\rm f} = M/\rho_0 = 9.9 \, {\rm cm./sec.}$



Fig. 2.—The determination of the mass rate of flow for the nitric oxide decomposition flame.

Figure 3 shows the composition as a function of temperature. Note the small difference between the mole fractions of N_2 and the O_2 . Figure 4 shows y_{NO} , G_{NO} and T as a function of distance for various values of M. The temperature changes from 900 to 2900°K. in 0.40 cm. The distance from the flame to the flame-holder depends critically on the heat transfer from the flame to the flame to the flame holder. The values of G_{NO} , the chemical composition, and the distance from the point at which the temperature is 1900°K. are given in Table II.

It is interesting to consider the effect of variations in the parameters and the treatment on the calculated flame velocity. If the values of the coefficients of diffusion are reduced by a factor of 0.6 the flame velocity is increased from 9.9 cm./sec. to 13.1 cm./sec. Another calculation which was carried out consisted of idealizing the nitric oxide re-



Fig. 3.—Mole-fractions NO, O_2 and N_2 in a nitric oxide decomposition flame as a function of temperature for the correct value of M, M = 0.0046.



Fig. 4.—The chemical composition; fraction of mass rate of flow, $G_{\rm NO}$; and temperature as a function of distance in a nitric oxide decomposition flame. Here the zero of distance is taken to be the place where the temperature is 1900°K. The figures in parentheses are the assumed values of the mass rate of flow, M. The correct value of M is 0.0046.

action to the form $2A \rightleftharpoons 2B$ where B is a "pseudoproduct" corresponding to a mixture of O_2 and N_2 . In this case, the calculated flame velocity was 13.1 cm./sec. with the best diffusion constants and 18.6 cm./sec. when the diffusion constants were reduced by a factor of 0.6.

The nitric oxide decomposition flame has been considered in considerable detail from the standpoint of the Adams approximation procedure.^{11,15} Using this method, the flame velocity is given by a simple formula. However, the flame velocity calculated by the Adams method for the case of T =3000°K. is 6.4 times as large as that calculated by the rigorous solution of the flame equations. If we assume that for other flame temperatures the flame velocities calculated by the Adams method are in error by the same factor, we obtain the following estimates for the flame velocity for different flame or ambient temperatures:

(15) M. J. Henkel, W. P. Spaulding and J. O. Hirschfelder, "Third Symposium on Combustion, Flames, and Explosion Phenomena," Williams and Wilkins, Baltimore, Md., 1949, p. 127.

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™ °K.	°K.	(cm./sec.)
2800	568	4.5
3000	783	9.9
3200	1046	19
3400	1292	34
3600	1543	56
3800	1798	88
4000	2056	134

D. Decomposition of Ozone

The decomposition of ozone was first studied by Lewis and von Elbe.^{16,17} It is interesting to compare the applications of their theory of flame propagation and that discussed hereto for this case. For the purposes of comparison we have used the same numerical constants as the Lewis and von Elbe values except where otherwise noted. The present calculations were started by Gerstein and Linnett in the summer of 1950. Unfortunately at that time our mathematical methods of solution were not sufficiently far advanced to permit them to obtain an explicit solution.

The chemical reactions involved are

$$O + O_2 + X \xrightarrow[k_1']{k_1} O_3 + X \tag{33}$$

$$O + O_3 \xrightarrow[k_2']{k_2} 2O_2 \tag{34}$$

$$O_2 + X \xrightarrow{k_3} 2O + X \tag{35}$$

Here X represents a molecule of O_1 , O_2 or O_3 .

Lewis and von Elbe considered only reactions (1) and (2). They took as their rate constants

$$k_1 = 0.230 n y_1 y_2 b \quad k'_1 = 10.56 y_3 b \exp(-24,140/RT) (36)$$

$$k_2 = 7.15 \ y_1 y_3 b \exp(-6000/RT)$$

$$k_2' = 2.93 \ y_2^2 b \exp(-99,210/RT) (37)$$

Here y_1 , y_2 and y_3 are the mole fractions of O, O₂ and

 O_3 , respectively; *n* is the number of moles of gas per cm.³; and the constant *b* is

$$b = n^2 T^{1/2} 10^{12} \tag{38}$$

The rate constants for the reaction (3) are obtained by assuming that the reverse reaction occurs without activation energy; that the energy required for the forward reaction is 117,350 cal./mole; and that the forward reaction occurs every time that an oxygen molecule collides with any other molecule, provided that the relative kinetic energy of the colliding molecules is greater than the 117,350 cal./mole; the collision diameters of the molecules are taken to be those used by Lewis and von Elbe. These assumptions lead to the values

$$k_3 = 8.92 y_2 b \exp(-117,350/RT)$$
 $k_3' = 0.482ny_1^2 b$ (39)

To simplify the calculations, the n in k_1 and k_3' are set equal to n_{∞} .

The molal enthalpies of the three components are taken to be

$$m_1\hat{H}_1 = (1/2)C_2T + 58,675$$
 cal./mole (40)

$$m_2 \hat{H}_2 = C_2 T \qquad \text{cal./mole} \qquad (41)$$

$$m_3 \hat{H}_3 = (3/2)C_2T + 34,535$$
 cal./mole (42)

Here the 58,675 and the 34,535 are the heats of formation of oxygen atoms and ozone at the flame temperature, $T_{\infty} = 1250^{\circ}$ K. The assumption that the specific heats for the three species remain constant and are in the ratio of 1:2:3 is made for calculational simplicity. The value of C_2 is chosen so as to make the flame temperature equal to $T_{\infty} = 1250^{\circ}$ K. when the initial temperature is $T_0' = 300^{\circ}$ K.

$$C_2 = 8.078363 \text{ cal./mole}$$
 (43)

The thermal conductivity, λ , for the mixture of oxygen atoms, oxygen molecules and ozone is taken to be the same as that of pure O₂. At 1250°K. the thermal conductivity of O₂ gas is calculated¹⁸ to be $\lambda = 1.860 \times 10^{-4}$ cal./cm.-sec. The thermal conductivity at other temperatures is then taken to be

 $\lambda = 1.860 \times 10^{-4} (T/1250)^{1/2} \text{ cal./cm. sec.}$ (44)

In order to estimate the coefficients of diffusion let us define the quantity δ_{ij} , the reduced diffusion coefficient for the interdiffusion of molecules i and j

$$\delta_{ij} = \frac{2\hat{C}_p n \mathfrak{D}_{ij} m_i m_j}{\lambda(m_i + m_j)}$$
(45)

For the interdiffusion of oxygen molecules and oxygen molecules at 293°K., $pD_{22} = 0.20 \text{ cm.}^2 \text{ atm.}/\text{sec.}$, $\hat{C}_p = 7.017/32 \text{ cal./g. deg.}$, $\lambda = 6.22 \times 10^{-5} \text{ cal./cm. sec. deg.}$, $n = p/24044 \text{ moles/cm.}^3$. These values lead to

$$\delta_{22} = 0.94 \tag{46}$$

for oxygen-oxygen diffusion at 293°K. In order to obtain the values of the remaining δ_{ii} we assume that the values of the coefficients of diffusion of the binary pairs of O, O₂ and O₃ are such that the values of

$$\frac{2\mathfrak{D}_{j}m_{i}m_{j}}{(m_{i}+m_{j})} \tag{47}$$

are all the same, and hence lead to the same value of δ . For rigid spheres

$$\mathfrak{D}_{ij} = \frac{0.002628}{p\sigma_{ij}^2} \sqrt{\frac{(m_i + m_j)T^3}{2m_i m_j}}$$
(48)

Hence this assumption corresponds to assuming that σ_{ij} for these binary pairs varies as $[m_i m_i / (m_i + m_j)]^{1/4}$. We further assume that the value of δ is independent of temperature. This is equivalent to our previous assumption that \hat{C}_{ρ} is constant, and that the coefficients of diffusion and thermal conductivity vary with temperature in a manner characteristic of rigid spheres.

Now, let us consider an ozone flame under conditions corresponding to the experimental data which exist: The initial temperature is taken to be $T_0 = 300^{\circ}$ K., the ambient pressure is taken to be 0.821 atm. (624 mm.) and the mixture of cold gases in the mixing chamber is taken to be made up of 75% oxygen molecules and 25% ozone. The values of the G_i at the cold boundary are then

$$(G_1)_0 = 0, (G_2)_0 = 2/3, \text{ and } (G_3)_0 = 1/3$$

⁽¹⁶⁾ B. Lewis and G. von Elbe, J. Chem. Phys., 2, 283 (1934).

⁽¹⁷⁾ B. Lewis and G. von Elbe, Chem. Revs., 21, 347 (1937)

⁽¹⁸⁾ Here the calculation is carried out using the method discussed in Section 8.4d of "The Molecular Theory of Gases and Liquids," by J. O. Hirschfelder, C. F. Curtiss, R. B. Bird and E. L. Spotz, John Wiley and Sons, Inc., New York, N. Y., 1953. The constants used in the Lennard-Jones (6-12) intermolecular potential are $\sigma = 3.541$ Å., $\epsilon/k = 88.0^{\circ}$ K. The specific heat at 1250°K. is taken to be $C_V = 3.3112$ R.

Here the subscripts 1, 2 and 3 designate the O, O_2 and O_3 , respectively, and will be used in this sense throughout this section. Using the constants discussed above the flame temperature is $T_{\infty} =$ 1250°K.

The equations describing the ozone flame can then be written in the form: (1) The Energy Balance Equation

$$\mathrm{d}T/\mathrm{d}Z = g \tag{49}$$

where

$$z = \int_0^x \frac{M\hat{C}_2}{\lambda} \,\mathrm{d}x \tag{50}$$

and

 $g = T - 1250 + 2850 G_3 + 14526 46 G_1 \quad (51)$

(2) The Equations of Continuity

$$\frac{\mathrm{d}G_1}{\mathrm{d}T} = \left(\frac{a}{M^2}\right)\frac{K_1}{bgT} \tag{52}$$

and

$$\frac{\mathrm{d}G_3}{\mathrm{d}T} = \left(\frac{a}{M^2}\right)\frac{3K_3}{bgT} \tag{53}$$

Here

)

$$K_1 = -k_1 + k_1' - k_2 + k_2' + 2k_3 - 2k_3' \quad (54)$$

and

$$C_3 = k_1 - k_1' - k_2 + k_2'$$
 (55)

In these equations, the n in k_1/b and in k_3'/b is taken to be n = for computational convenience. The constant a in these equations is

$$a = \frac{m_1 b\lambda T}{\hat{C}_2} = 4.952 \times 10^4 p^2 \tag{56}$$

or for p = 0.821 atm.

$$a = 3.338 \times 10^4 \tag{57}$$

(3) The Equations of Diffusion

$$\frac{\mathrm{d}y_1}{\mathrm{d}T} = \frac{2}{g\delta} \left[\frac{1}{3} y_1 G_2 + \frac{1}{4} y_1 G_3 - \frac{2}{3} y_2 G_1 - \frac{3}{4} y_3 G_1 \right]$$
(58)

$$\frac{\mathrm{d}y_3}{\mathrm{d}T} = \frac{2}{g\delta} \left[\frac{3}{4} y_3 G_1 + \frac{3}{5} y_3 G_2 - \frac{1}{4} y_1 G_3 - \frac{2}{5} y_2 G_3 \right]$$
(59)

The real difficulty of treating the ozone decomposition arises from the very sharp rise in the oxygen atom concentration when the temperature decreases by a small fraction of a degree below the flame temperature. Actually the oxygen atom concentration increases a thousand-fold in a temperature interval of a fraction of a degree. This makes it difficult to start the integration from the hot toward the cold boundary. The other difficulty arises from the "stiffness" of some of the variables.¹⁹

At the hot boundary, the asymptotic solutions to the flame equations are of the form

$$T = T_{\infty} + t_1 e^{\alpha_1 x} + t_2 e^{\alpha_2 x} + t_3 e^{\alpha_2 x}$$
(60)

$$y_1 = (y_1)_{\infty} + u_{11}t_1e^{\alpha_1x} + u_{12}t_2e^{\alpha_2x} + u_{13}t_3e^{\alpha_3x} \qquad (61)$$

$$y_3 = (y_3)_{\infty} + u_{31}t_1e^{\alpha_1x} + u_{32}t_2e^{\alpha_2x} + u_{33}t_3e^{\alpha_3x} \quad (62)$$

$$G_1 = (G_1)_{\infty} + w_{11}t_1e^{\alpha_1x} + w_{12}t_2e^{\alpha_2x} + w_{13}t_3e^{\alpha_3x} \quad (63)$$

$$G_3 = (G_3)_{\infty} + w_{31}t_1e^{\alpha_1 x} + w_{32}t_2e^{\alpha_2 x} + w_{33}t_3e^{\alpha_3 x} \quad (64)$$

There are two negative roots α_1 and α_2 and one positive root, α_3 . The value of $||\alpha_1||$ is much smaller than the value of $||\alpha_2||$. Because the temperature approaches a finite value when x becomes large

(19) C. F. Curtiss and J. O. Hirschfelder, Proc. Natl. Acad. Sci., 38, 235 (1952).

positively, t_3 is taken to be zero. The possibility of solutions in which both t_1 and t_2 are non-vanishing allows the possibility of adjusting the values of G_1 as well as G_3 at the cold boundary. In actual practice, however, G_1 at the cold boundary is very close to zero and is not physically specified. In the following solutions we take t_2 to be zero. This leads to solutions of the flame equations for which G_1 is not quite mathematically zero at the cold boundary. However, we believe that the properties of the flame solutions are not sensitive to the value of $(G_1)_0$.

In order to obtain some qualitative information about the solutions of the flame equations, we first considered an hypothetical example in which no diffusion takes place, that is, $\delta = 0$. The information obtained proved quite valuable in the integration of the actual problem.

a. No Diffusion, $\delta = 0$.—The integration from the flame temperature, $T = 1250^{\circ}$ K. down to T =1230°K. proved very difficult. The solution was finally achieved by taking as an approximation $K_1 = 0$, as an algebraic equation in place of one of the equations of continuity. Subsequently it was shown that $K_1 = 0$ is a good approximation in this temperature range. The initial derivatives with respect to temperature turned out to be practically independent of the assumed value of a/M^2 . Not only was the first derivative of y_3 with respect to temperature calculated at T = but also the value of $(d^2y_3/dT^2) =$. From the three terms in a Taylor's series about T_{∞} , the value of y_3 was calculated at $T = 1248^{\circ}$ K. The value of y_3 was then calculated at 2° intervals from 1248° to 1230°K. using tangent integration.

The rest of the integration, T = 1230 to 300° K., was carried out by Milne integration of the equation for dG_3/dT for treating dG_1/dT as a "stiff equation" (rather than setting $K_1 = 0$). The temperature intervals were taken to be 6.25°. It was found that there was no substantial difference in the results obtained by setting $K_1 = 0$ (which corresponds to setting $dG_1/dT = 0$) or the results obtained by integrating dG_1/dT as a "stiff equation."

The best value of a/M^2 was 3.2×10^6 , corresponding to a flame velocity of $v_t = 85$ cm./sec. (the experimental value is 55 cm./sec.). The values of y_1 and y_3 as functions of temperature are given in Table III. Figure 5 shows y_2 and G_3 as functions of temperature. Since there is no diffusion, $G_i = m_i y_i / \sum_j m_j y_j$. Figure 6 shows y_1 as a function of temperature. The very sharp rise in y_1 is very surprising.

When the temperature has dropped 8° below the flame temperature y_1 is larger by a factor of 12,600 than the thermal equilibrium concentration of oxygen atoms at the flame temperature.

It is to be expected that in many flames, the concentration of free radicals near the hot boundary is greatly in excess of thermal equilibrium. The reason for this is that the free radicals, in this case oxygen atoms, are essentially in equilibrium with the fuel molecules in the region of the hot boundary. This is the significance of setting $K_1 = 0$. At the hot boundary where thermal equilibrium is established,

	No Diffusion ($\delta = 0$), $a/M^2 = 3.2 \times 10^6$ or $v_f = 85$ cm./sec.					
Т, °К.	y_1	¥3	G_1	G_{2}		
1250						
249	0.0002745	0.0000010193802	0.00013725	0.000001529		
1248	.000460465	.0000031079081	00023023	.000004662		
1246	.000809947	.000017727740	. 00040497	.00002659		
244	.000932571	.00011903054	.00046629	.000178546		
242	.000946754	.0013118997	.00047338	.001967850		
240	.000936274	.0051687425	.00046814	.007736741		
238	.000929287	.0088608649	00046464	.013238795		
236	.000915312	.012612677	.00045766	.018809007		
234	.000904905	.016433106	. 00045245	.024459751		
232	. 000894140	.020337254	.00044707	.030212172		
1230	.000883458	.024334775	.00044173	.036079111		
1225			000417052	.043428931		
218.75			.000403510	.057368012		
212.5			.000383597	.070948456		
200			.000352785	.095953195		
150			.000246051	.17887519		
100			.000167895	.23702922		
1050			.000111436	.27594656		
000			.0000714082	.30118259		
950			.000043862	.31636076		
900			.000025590	.32536026		
850			.000014039	. 32999322		
800			.000007151	.33253723		
750			.000003331	.33347679		
700			.0000013916	.33407269		

TABLE III

OZONE DECOMPOSITION

there is very little concentration of fuel molecules, O_3 . However, the concentration of fuel molecules increases linearly with T = -T. In this case, the value of y_3 eight degrees below the flame temperature is 5,000,000 times larger than at the flame temperature. Because of the large energy of formation of the free radicals, their concentration is very small at low temperatures. Thus the concentration of free radicals, y_1 , passes through a maximum a few degrees below the flame temperature.

b. Considering Diffusion, $\delta = 0.94$.—The solution to the equations describing the ozone decomposition flames is considerably more difficult to obtain when diffusion is taken into account. First, let us define $(y_1)_{eq}$ as the solution of the equation, $K_1/b = 0$, and $(G_1)_{eq}$ is the solution to the equation obtained by setting the left side of eq. (58) equal to zero. Then in place of y_1 and G_1 it is convenient to use the variables

$$\xi = [y_1/(y_1)_{eq.}] - 1$$
 (65)

$$\eta = [G_1/(G_1)_{eq}] - 1$$
 (66)

The equations for y_1 and G_1 are "stiff," and the equations are very difficult to integrate because of the rapid variation in y_1 and G_1 . The variables ξ and η vary much less than y_1 and G_1 . It was found that good solutions to the flame equation are obtained by using as algebraic equations the equations $f_1 = 0$ and $f_2 = 0$ instead of the differential equations $d\xi/dT = f$, and $d\xi/dT = f_2$. This corresponds to a first approximation in con-

sidering the ξ and η equations as "stiff." It has the great advantage that it permits us to use small temperature intervals which otherwise would not be possible. As in the case of no-diffusion, the values



Fig. 5.—The values of y_3 and G_3 as functions of temperature T in an ozone flame, without diffusion, $\delta = 0$.

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of y_3 and G_3 at $T = 1248^{\circ}$ K. were first obtained by evaluating the first and second derivatives at the flame temperature and using a three-term Taylor's series. The equations were then integrated by tangent integration with 2° intervals. However the solutions oscillated violently. This oscillation was traced to the value of $|dy_3/dT|$ at $T = 1248^{\circ}$ K., as determined from the Taylor's series y_3 and G_3 at $T = 1248^{\circ}$ K., being much too small. Finally it was discovered that these oscillations could be eliminated and a reasonable solution obtained if y_3 and G_3 at $T = 1248^{\circ}$ K. were adjusted so as to give the maximum value of $|dy_3/dT|$ at this temperature. The tangent integrations by 2° intervals down to $T = 1230^{\circ}$ K. provided the starting point for Milne integration by 6.25° intervals from 1230° K. down to T_0 .



Fig. 6.—The values of y_1 as a function of temperature T in an ozone flame, without diffusion, $\delta = 0$. Note the very sharp peak near the flame temperature.

The best value of a/M^2 was found to be 1.04 $\times 10^6$, corresponding to a flame velocity $v_{\rm f} = 47.2$ cm./sec. This is in excellent agreement with the experimental value of 55 cm./sec. The values of the y_3 , G_3 , η and ξ are given as functions of the temperature in Table IV. Figure 7 shows the variation of y_3 and G_3 with temperature and Figs. 8, 9 and 10 illustrate the variation of ξ , η and y_1 with temperature is similar to that which was found for the no-diffusion case. This variation may be explained by the following arguments. First,



Fig. 7.—The variation of y_3 and G_3 as functions of temperature in an ozone flame with diffusion, $\delta = 0.94$.

 y_3 varies linearly with temperature in the neighborhood of the hot boundary

 $y_3 = 2.6546 \times 10^{-10} + 0.89 \times 10^{-4} (T_{\infty} - T)$ (67)

Also, the value of ξ is approximately unity, that is y_1 is essentially $(y_1)_{eq}$ or the solution to the equation $K_1 = 0$. Substituting the linear relation for y_3 into the relation for $(y_1)_{eq}$, we find that

$$y_{1} \doteq (y_{1})_{eq} = \frac{7.5187 \times 10^{-8} + 0.0252076 (T_{\infty} - T)}{1 + 25.3345 (T_{\infty} - T)}$$
(68)

From eq. (68) it follows that at a temperature of 0.01° below the flame temperature, y_1 is already 2700 times larger than would be expected on the basis of thermal equilibrium.

If the reduced diffusion constant is taken to be $\delta = 0.75$ instead of $\delta = 0.94$, the best value of a/M^2 is 8.9×10^6 , corresponding to a flame velocity $v_t = 51$ cm./sec. Thus the flame velocity is not sensitive to the value of the diffusion constants which are selected.

In Table V, the various flame velocities are compared. It is hoped that the excellent agreement obtained by our calculations is not fortuitous.

The spatial relations in the ozone decomposition flame are obtained in the following manner. The energy balance equation, eq. (49) can be rewritten in the form

$$dx = \frac{m_2}{MC_2} \left(\frac{\lambda}{T^{1/2}}\right) \left(\frac{T^{1/2}}{g}\right) dT = 3.68 \times 10^{-4} \left(\frac{T^{1/2}}{g}\right) dT \text{ (cm.)} \quad (69)$$

The distance from the flame-holder to any reference point in the flame, say the place at which $T = 950^{\circ}$ K., depends strongly on the amount of heat transfer from the flame to the flame-holder. On

TABLE IV

Ozone Decomposition $\delta = 0.94, a/M^2 = 1.02 \times 10^7$ or $v_f = 47$ cm./sec.

°K.	y 1	$oldsymbol{y}_{2}$	¥3	G_1	G_2	G_{z}	$\xi + 1 = y_1/(Y_1)_{eq.}$	$\eta - 1 = G_1/(G_1)_{eq.}$
1250	7.518675×10 ⁻⁸	0.99999992	2.6546×10^{-10}	3.7593375×10-*	0.99999992	3.9819×10-10	1.00000000	1.00000000
1248	.000982322	.99883968	.000178	0.00051516225	. 99828484	0.0012	1.0187716	1.0683842
1246	.000957857	, 9 98 685 8 5	.000356296	.00046868564	. 99711733	. 00241398	0.9948401	0.97372607
1244	.000947902	. 9983656 7	.000686425	.00043501130	.99495272	.00461227	. 9916976	. 91091351
1242	.000938982	.99792170	.001139317	.00040385273	.99196992	.00762623	.9932566	. 85574138
1240	000929083	.99741763	.001653284	.00036500612	.98861328	.01102:72	. 9923195	. 78164948
1238	.000918970	.99688317	.002197857	.00031948748	.98509036	.01459015	. 9888986	68998344
1236	.000909221	. 99633070	.002760084	.00029290323	.98146351	01824359	.9933450	. 6 42867 11
1234	.000899229	. 99577174	.003329035	.00025926094	.97783045	.02191029	.9945903	57664779
1232	.000889237	.99520728	. 003903485	. 00022488540	. 97419432	.02558080	.9952644	. 50665999
1230	.000879282	.99463886	.004481861	.00019118065	.97056434	.02924448	. 9959350	43633005
1225	.000854629	.99320206	.005943312	00011081142	96163185	.03825734	. 9975888	. 26127558
1218.75	. 000824397	.99140309	.007772510	.00015661686	.95039816	.04944522	. 9996455	. 38478898
1212.50	.000794840	.98958886	.009616304	— .00007098511	. 93982812	.06024287	1.0016561	18179270
1206.25	.0C0766020	.98777967	.011454309	00015160291	.9292 78 92	.07087268	1.0036781	40486623
1200	.000737888	, 9 8 595956	.013302551	- .00022414158	.91914048	.08108367	1.0056429	62439931
1150	. 000538183	,97142628	.028035542	- 00059553013	. 84772977	.1528658	1.0208491	-2.3566411
1100	.000380359	. 95693988	.042679758	00068990577	.79298227	.2077076	1.0349136	- 3.9803396
1050	.000259433	.94252803	.057212535	00062841742	.75242852	. 2481999	1.0479681	- 5.4508381
1000	. 000169947	. 92820494	.071625115	00049844076	.72353714	. 2769613	1.0602688	-6.7413082
950	.000106301	.91398388	.085909816	00035617478	.70386583	. 2964903	1.0722411	- 7.8435277
900	.000063043	. 89938073	.10005623	00023218258	.69119115	. 3090410	1.0845036	- 8.7651205
850	.000035147	. 88591382	. 11405103	- 00013848362	,68352902	. 3166095	1.0979957	- 9.5298958
800	.000018226	. 87210491	.12787686	00007531698	.67925335	. 3208220	1.1140546	-10.170160
750	.000008676	. 85847827	. 14151305	00003703817	.67707174	,3229€53	1.1347272	-10.726089
700	. 000003728	.84506118	.15493509	— .00001623443	. 67608496	.3239313	1.1631379	-11.236546
650	. 000001416	.83188421	.16811437	00000621104	. 67568763	.3243186	1.2045303	-11.742852
600	. 000000462	. 81898341	.18101613	00000201223	.67555856	. 3244435	1.2679733	-12.282029
550	.000000125	. 80640434	. 19359553	- 00000052894	.67551796	. 3244826	1.3703965	-12.893859
500	. 000000027	.79420962	. 2057 9035	0000001056	. 67551370	. 3244864	1.5416849	-13.558420
450	. 000000004	.78249541	. 21750459	0000001412	. 67550860	. 3244914	1.8084635	-13.807852
400	$3.4878290 \times 10^{-10}$.77143470	. 22856530	$-8.6490961 imes 10^{-10}$.67551224	.3244878	1,9280899	-10.704073
350	8.3334979 × 10 ⁻¹²	.76152327	. 23847673	$-6.8442040 \times 10^{-12}$.67550845	. 3244916	1.2045175	- 2.2173702

the other hand the relative separations of two temperature points within the flame are very nearly independent of the heat transfer from the flame to the flame-holder. Therefore it is both easier and more significant to integrate eq. (69) relative to some reference point within the flame. If the values of g(T) are known for a set of equally spaced temperature intervals: T - h, T, T + h, and T





Fig. 8.—The variation of ξ with temperature in an ozone flame with diffusion, $\delta = 0.94$.

Fig. 9.—The variation of η with temperature in an ozone flame with diffusion, $\delta = 0.94$.

55

85



Fig. 10.—The variation of y_1 with temperature in an ozone flame with diffusion, $\delta = 0.94$. Note the very sharp peak near the flame temperature. Most of this rise takes place within one degree, as shown in the inset.

TABLE V

Comparison between Experiment and Theory for the Flame Velocity of an Ozone Decomposition

Exptl. flame velocity, cm./sec.

Value calcd. using best diffusion constants ($\delta = 0.94$), cm./sec. 47

Value calcd. using 20% smaller diffusion constants $(\delta = 0.75)$, cm./sec. 51

Value calcd. neglecting diffusion ($\delta = 0$), cm./sec.

- Value previously calcd. by Lewis and von Elbe^a neglecting diffusion and setting $y_1 = (y_1)_{eq}$, etc., cm./sec. 255
- $^{\rm a}$ B. Lewis and G. von Elbe, J. Chem. Phys., 2, 537 (1934).

+ 2h, then the increment in x is given approximately by the simple numerical integration formula

$$x_{T+h} - x_{T} = \frac{3.68 \times 10^{-4}}{24} h \left[-\left(\frac{T^{1/2}}{g}\right)_{T-h} + 13 \left(\frac{T^{1/2}}{g}\right)_{T} + 13 \left(\frac{T^{1/2}}{g}\right)_{T+h} - \left(\frac{T^{1/2}}{g}\right)_{T+2h} \right]$$
(70)

Figure 11 shows the results of these calculations. It is seen that the temperature changes from $T'_o + \frac{1}{4}(T_{\infty} - T_o) = 538^{\circ}$ K. to $T'_o + \frac{3}{4}(T_{\infty} - T'_o) = 1013^{\circ}$ K. in a distance of 0.012 cm. Such spatial relationships might be used in comparison

between experiment and theory if the data were available.



Fig. 11.—Temperature versus distance in an ozone decomposition flame (considering diffusion).

Acknowledgments.—A large number of calculations have gone into the developments discussed in this paper. Because of the complexity of the flame problems it has been necessary to develop special numerical methods to cope with specific difficulties as they arise. Also for each problem, calculations must be carried out for a number of values of the mass rate of flow before the correct value is found. On these accounts only a very small fraction of the work which was actually performed is discussed here. The authors are greatly indebted to the following people who carried out portions of the calculations: M. J. Henkel, P. W. Knaplund, W. P. Spaulding, G. Vandervort, I. F. Weeks, Lavon Hall, Marjorie Mason, Gloria Andekian, Ruth Straus, Dorothy Smith, Elaine Petersen, Alice Epstein, Catherine Denton, Yinglan Wang, Lois Brittenham, Clarice Wruck and Olga Skinner.

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DISCUSSION

H. REISS (Bell Telephone Laboratories).—In your consideration of the various transport processes, Dr. Hirschfelder, you regarded each process to be driven by its own potential; for example, the diffusion rate depended only on the concentration gradient, the heat flow, only on the temperature gradient and so on. How important is the coupling between these processes, that is, how much of the diffusion is thermal diffusion and so on? In other words, how justified is the neglect of the off-diagonal elements in the coupling matrix?

J. O. HIRSCHFELDER.—Direct calculations show that thermal diffusion and other off diagonal elements in the case of ordinary flames are completely negligible by orders of magnitude. However the neglect of radiation from flames is not always negligible and should be included in the detailed calculations. The equations for treating this have been derived by John Magee (The Effects of Radiation in Flames, UWNRL—CM 627 (1950)). See also Chapter 11, "Molecular Theory of Gases and Liquids," J. O. Hirschfelder, C. F. Curtiss, R. B. Bird and E. L. Spotz, to be published by John Wiley and Sons, Inc., 1953.

THE ABSORPTION SPECTRA OF FREE NH AND NH₂ RADICALS PRODUCED BY THE FLASH PHOTOLYSIS OF HYDRAZINE¹

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The flash photolysis of hydrazine has been investigated and a critical limit for the energy of the photolysis flash has been found above which 80% of the initial hydrazine may be decomposed in a single flash but below which no appreciable decomposition occurs. This limit corresponds to a thermal explosion limit for the hydrazine. The absorption spectra of free NH and NH₂ radicals have been observed in the explosion reaction. The rotational temperature of the NH radicals in the explosion was found to be $\sim 1400^{\circ}$ K. NH₂ absorption bands were also observed in the non-explosive reaction but no NH bands were obtained. Possible interpretations of these results are discussed.

I. Introduction

Numerous free radical mechanisms² have been postulated in recent years to explain the kinetics of many thermal and photochemical reactions. Evidence for the existence of the radicals in many of these reactions is still largely chemical though some free radicals, e.g., CH₂, CH₃, C₂H₅, have been detected by mass spectrometry,³⁻⁵ while others, e.g., OH, CH, C₂, NH₂, have been detected by absorption spectroscopy.⁶⁻⁸ The latter techniques afford methods for the measurement of the concentrations of the free radicals and can yield information concerning the ionization potentials and precise geometries of the radicals.

The conditions which are favorable for the detection of free radicals by absorption spectroscopy are (i) long optical path, (ii) high concentration of radicals, (iii) high absorption coefficient, (iv) freedom from overlapping molecular absorption and (v) adequate resolving power. The maximum length of absorption tube in which it is experimentally convenient to generate free radicals is limited to a few meters. The length of the optical path may be increased further by a factor of 10-100, depending on the spectral region, by the use of a multiple reflection mirror system.^{9,10} In chemical systems where the lifetimes of radicals are generally very short, e.g., 10⁻²-10⁻⁶ sec., high concentrations of radicals can only be generated transiently by pulse techniques in which molecules are dissociated by intense short pulses of energy of duration comparable with the lifetimes of the radical. Photochemically this may be achieved by the flash photolysis technique first described by Norrish and Porter.¹¹ The most intense absorption spectra produced by the free radicals will in general be the electronic spectra lying in the photographic region below 10,000 Å. One or more absorption

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bands will usually lie in the readily accessible region between 2000 and 10,000 Å. and will probably be free from overlapping absorption by the parent molecule. Still stronger absorption bands should be found in the vacuum ultraviolet region¹² between 1000 and 2000 Å. but more difficulty may be encountered with the absorption bands of the parent molecule. For the detection of absorption spectra in the photographic region, it is important to use a spectrometer with a resolution comparable with the width of the absorption lines.⁶ Thus, while a prism spectrograph of low resolving power may be adequate for the observation of diffuse spectra or band heads, a grating spectrograph of high resolving power provides a more sensitive means for detecting fine line spectra.¹³

In the present paper some preliminary results on the flash photolysis of hydrazine are reported. A critical flash intensity has been found above which thermal explosion of the hydrazine occurs. The absorption spectra of free NH and $\rm NH_2$ radicals have been observed in the explosion reaction.

II. Experimental

The flash photolysis apparatus, which has been described elsewhere,¹⁴ consisted of a 1-meter quartz absorption tube and a 1-meter quartz flash tube surrounded by a cylindrical magnesium oxide screen. Anhydrous hydrazine at 8 mm. pressure was introduced into the absorption tube and subjected to flash photolysis by discharging a 500 μ F. bank of condensers charged to 4000 v. through the flash tube. The pressure in the system after photolysis was approximately doubled. An infrared absorption spectrum of the products in the region 2–15 μ showed weak hydrazine bands and indicated that 80% of the initial hydrazine had decomposed. All the other infrared absorption bands could be attributed to ammonia. The ammonia and hydrazine were condensed with liquid air and the residual gas was shown by mass spectrometer analysis to consist of H₂ and N₂ in the ratio H₂/N₂ ~ 1.5.

Absorption spectra of the photodissociation products in the region 2200–9000 Å. were taken within 1 millisecond of the photolysis flash by means of a second flash tube which was mounted on the axis of the absorption tube and emitted a continuum. The spectra were observed in various orders of a 21 ft. concave grating spectrograph using Eastman Kodak 103a0, 103aF and hypersensitised I N plates.

The $\rm NH_2$ bands in the region 4500–7500 Å, were observed and were photographed in the second order. The bands appeared with approximately the same intensity as the

(12) In this region, absorption spectra may often be obtained with pressures as low as $0.001~\rm mm.$ using an optical path length of 1 meter.

(13) In the case of the NH₂ absorption spectrum (ref. 8) a few thousand fine absorption lines were observed using the 2nd order of a 21ft grating spectrograph, but no absorption could be detected with a Hilger EI prism spectrograph.

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R(15)	R([0)	R(5)	Q(Q,O)	QU.1) P(5)	P((0)	P(15)
				2.11月秋日第		
3300 Å					3400	Å

Fig. 1.—Absorption spectrum of free NH radicals produced by the flash photolysis of hydrazine.

bands⁸ obtained by the flash photolysis of 1 mm. of NH₃. In addition the ${}^{3}\Pi_{i-}{}^{3}\Sigma^{-}$ bands¹⁵ of NH near 3360 Å. were also found and were photographed in the third order, lines up to K = 21 being visible in the P and R branches (Fig. 1). These bands were not observed in the flash photolysis of ammonia. Experiments on the lifetimes of the radicals showed that 2 milliseconds after the photolysis flash the absorption spectra of both radicals had almost completely disappeared.

Experiments with Added Helium —It was found that if an excess of helium (100 mm.) were added to the hydrazine (8 mm.) and the mixture subjected to flash photolysis, no over-all pressure change was observed after photolysis and no NH and NH_2 absorption spectra were obtained immediately following the photolysis flash. Furthermore the infrared absorption spectrum between 2 and 15 μ of the reaction mixture after photolysis revealed that no appreciable decomposition of the hydrazine had taken place.

A series of experiments was therefore carried out starting with hydrazine and adding progressively increasing pressures of helium. It was found that as the pressure of helium was increased the over-all pressure change in the reaction decreased (Fig. 2) and the intensities of the NH and NH₂ bands also decreased. Similar effects were observed when argon was substituted for helium.





Variation of the Light Intensity.—It was found that when hydrazine at 8 mm. pressure was subjected to flash photolysis with the magnesium oxide screen removed, no over-all pressure change accompanied the photolysis, no NH and NH₂ absorption spectra were observed immediately following the photolysis flash and virtually no hydrazine was decomposed by the flash. These results are in marked contrast with the results obtained using the screen. Since it did not appear that the screen could be increasing the effective light intensity in the region of 2200 Å. by a factor of more than 5–10, it was decided to carry out a series of experiments with the screen, varying the intensity of the light flash. It was found that there was a certain critical flash intensity above which considerable decomposition of the hydrazine could be brought about by a single flash but below which no appreciable decomposition occurred. Thus with a photolysis flash produced by discharging a 180 μ F. bank of condensers charged to 4000 v. through the photolysis flash tube, approximately 80% of the hydrazine could be decomposed in a single flash. When the experiment was repeated with a 160 μ F. bank of condensers charged to 4000 v. no appreciable decomposition of the hydrazine was observed. The critical flash limit presumably corresponds to a thermal explosion limit first observed for hydrazine by Bamford.¹⁶

Absorption spectra of the photolysis products for the nonexplosive reaction were taken immediately after the photolysis flash. Weak NH_2 absorption bands were observed but no NH absorption bands were obtained.

III. Discussion

The ultraviolet absorption bands of hydrazine below 2200 Å. appear $diffuse^{17}$ even under the high resolution of a grating spectrograph, presumably indicating a predissociation of the mclecule. It is uncertain however whether the primary act is

$$N_2H_4 + h\nu \longrightarrow NH_2 + NH_2$$
, or (1)

$$N_2H_4 + h\nu \longrightarrow N_2H_3 + H$$
 (2)

Several investigators¹⁸⁻²¹ have carred out photochemical experiments with hydrazine but have been unable to obtain conclusive evidence concerning the nature of the primary act. In the flash photolysis experiments carried out in the non-explosive region, the observation of the absorption spectrum of NH₂ radicals in the immediate photolysis products and the absence of the NH absorption bands and any other absorption bands which could be attributed to N_2H_3 radicals, suggests that the primary photochemical act is (1). It should be noted, however, that approximately 1 millisecond elapses between the beginning of the photolysis flash and the source flash and during this time some of the radicals could undergo 10^3-10^4 collisions. The absorption spectrum recorded therefore will not necessarily correspond to the primary photochemical products.

The existence of a critical flash limit necessitates a branching radical chain or a thermal chain mechanism for the explosion reaction. One possible mechanism which would produce chain branching and explain the formation of NH radicals in the explosion reaction is

$$N_2H_4 + h\nu \longrightarrow NH_2 + NH_2 \tag{1}$$

$$\mathrm{NH}_2 + \mathrm{N}_2\mathrm{H}_4 \longrightarrow \mathrm{NH}_3 + \mathrm{N}_2\mathrm{H}_3 \tag{2}$$

$$N_2H_3 \longrightarrow NH_2 + NH$$
 (3)

It is assumed that at low temperatures most of the NH_2 radicals recombine, but at higher temperatures reactions (2) and (3) predominate. The decrease in the over-all reaction and the reduction in the intensity of the NH and NH_2 absorption spectra

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⁽¹⁵⁾ G. W. Funke, Z. Physik, 96, 787 (1935).

by the addition of small amounts of helium may be due to stabilization of the N_2H_3 radicals by collision.

The over-all mechanism may be represented approximately by the equation

$$3N_2H_4 = 2NH_3 + 2N_2 + 3H_2 + 90.18$$
 kcal.

assuming values of +22.7 and -11.04 kcal./mole for the heats of formation of gaseous hydrazine²² and ammonia²³ at 25°, respectively. The heat generated by the reaction is sufficient to raise the temperature of the products adiabatically to $\sim 2000^{\circ}$ K. assuming reasonable values for the specific heats. At these temperatures it is possible that the NH radicals are produced by thermal cracking of the ammonia²⁴ or hydrazine. Experimental confirmation of the high temperature attained in the reaction is afforded by the observation of the (1,1) band of NH in absorption with moderate intensity. No estimate of the vibrational temperature of the NH radicals has been made but the rotational temperature estimated from the relative intensities of the rotational lines of the (0,0) band was $\sim 1400^{\circ}$ K.

If the efficiency of the photolysis flash lamp in the region below 2200 Å. were known a calculation of the quantum yield of the reaction would be possible. Furthermore an estimate of the critical explosion temperature could be made from the critical flash limit. No direct measurements of lamp efficiencies in this region, however, have been carried out. If the efficiency is assumed to be ϵ , then the energy absorbed by the hydrazine at the critical flash limit = $1/2\epsilon CV^2$ = 1360 ϵ joules = 325 ϵ cal. This will produce an adiabatic temperature rise ΔT such that $mC_v \Delta T = 325\epsilon$ where m = mass ofhydrazine = ~0.001 g. mcle and $C_v = \text{molar}$ specific heat = ~25 cal./g. mole. The quantum yield Φ may be determined by first calculating the energy which would be required to decompose 80%of the initial hydrazine assuming each hydrazine molecule decomposed absorbed one quantum of 2200 Å. radiation. This energy would be 0.8 \times 0.001 \times 130,000 cal. = 104 cal. Since the energy actually absorbed by the hydrazine at the

(22) L. F. Audrieth and R. A. Ogg, "The Chemistry of Hydrazine," John Wiley and Sons, Inc., New York, N: Y., 1951.

(23) "Selected Values of Thermodynamic Properties," National Bureau of Standards, Washington, D. C., 1949.

(24) H. H. Franck and H. Reichardt, Naturwissenshaften, 24, 171 (1936).

critical explosion limit is 325ϵ cal., the quantum efficiency $\Phi = 104/325\epsilon$. If ϵ is assumed to be 0.1–1.0%, then $\Delta T = 13$ –130° which is consistent with the range of values for the critical explosion temperature published in the literature.^{16,22} The quantum yield Φ then lies in the range 32–320 confirming a chain mechanism for the reaction.

IV. Concluding Remarks

The absorption spectra of several free radicals have now been observed by the method of flash photolysis and kinetic studies of certain reactions^{7,25} carried out. Experiments are being attempted with very fast flashes and low pressures of reactants so that radicals may be produced and their reactions studied in time intervals comparable with the mean collision time in the system. Such experiments should yield more detailed information concerning the reaction mechanisms, and should yield valuable data concerning the rates of energy transfer between the different degrees of freedom of molecules. Further attempts are also being made to observe the absorption spectra of free radicals in photochemical systems using continuous irradiation. The experiments are being carried out with long absorption paths using a multiple reflection mirror system in an attempt to compensate for the lower light intensity and lower radical concentrations.

The author wishes to thank Dr. G. Herzberg for his interest in this work and for many helpful discussions. The author is indebted to Dr. F. P. Lossing for the mass spectrometer analyses.

DISCUSSION

(1) H. E. GUNNING (Illinois Institute of Technology).— Our investigations of the chemistry of hydrazine indicate that the hydrazyl radical, N_2H_3 , is quite stable at 25°. The reaction $N_2H_3 \rightarrow NH_2 + NH$ probably occurs only at elevated temperatures, as in the experimental conditions used by Dr. Ramsay.

(2) S. W. BENSON (University of Southern California).— The NH bonds in NH_3 are very strong. Is there any evidence for the reaction

$$NH_2 + NH_2 \longrightarrow NH_3 + NH?$$

D. A. RAMSAY.—The absence of NH and the presence of NH_2 after the flash photolysis of ammonia suggests that this reaction is not important.

(25) N. Davidson, R. Marshall, A. E. Larsh, Jr., and T. Carrington, J. Chem. Phys., 19, 1311 (1951).

SHOCK WAVES IN CHEMICAL KINETICS: THE RATE OF DISSOCIATION

OF $N_2O_4^{1,2}$

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A shock wave may be used to increase the translational and rotational temperature of a gas by a definite amount in a time of the order of a few collision times. Depending on the gas, the vibrational adjustment time may be somewhat longer. Subsequent chemical reactions which are caused by the change in temperature and which are accompanied by a change in light absorption can be followed photoelectrically. Reactions with half times as short as 5 μ -sec. can be followed by this method. The plane uniform shock waves that are required are produced in a shock tube, *i.e.*, by bursting a diaphragm between two regions of gas at different pressures. By this method the rate of dissociation of N₂O₄ in the presence of a large excess of nitrogen or carbon dioxide has been studied from -20 to 28°, at total pressures of 0.5 to 7 atm. Near 1 atm. the rate law is $-d(N_2O_4)/dt = k(N_2O_4)(N_2)$; $k = 2.0 \times 10^{14} \exp(-11,000/RT)$ liter mole⁻¹ sec.⁻¹. At higher total pressures, the rates are less than the values predicted by the above equation, and it is estimated that the limiting first-order rate constant for the dissociation of N₂O₄ is $k = 10^{16} \exp(-13,000/RT) \sec^{-1}$. Within experimental error, carbon dioxide gives the same results as ntrogen.

Introduction

For the direct observation of the rate of a reaction, the system must be prepared in a nonequilibrium state, and means found for following its subsequent approach to equilibrium. Fast reactions accompanied by a change in light absorption in a convenient spectral region can be followed by a phototube-oscilloscope combination. If two reactants can be mixed in a time short compared with their reaction time, the non-equilibrium state



Fig. 1.—a, principal features of the apparatus: A, driving gas (compression chamber); B, N₂O₄-inert gas (expansion chamber); D, diaphragm; W, quartz window; S, mercury arc light source; S', schlieren light source; K, knife edge; F, spectrograph; P,P', photomultipliers. b, initial pressure configuration in the shock tube. c, after bursting of the diaphragm. Dotted line shows boundary between expanding and compressed gases.

(1) Research supported by the O.N.R., contract Nonr-222(01).

(2) Presented at the Symposium on "Kinetics of Very Fast Reactions," A.C.S. Meeting, Atlantic City, September 18, 1952. may be produced in this way. Johnston and Yost³ have mixed gases in 0.01 sec: in their kinetic studies and mixing times of 0.001 sec. or less are possible with solutions. Another method is to disturb a resting system by a pulse of excitation or energy and then to make fast observations on it. For example, a gas may be very rapidly heated and compressed by means of a shock wave.

In applying shock waves to problems in chemical kinetics, it was thought best to start with a reaction that is fairly simple kinetically and experimentally. The dissociation of N_2O_4 to NO_2 meets these requirements and has been of interest to chemists for many years. It represents the simplest possible type of unimolecular chemical reaction. Its kinetic behavior is known with moderate accuracy from sound dispersion measurements,⁴ but the considerable experimental and theoretical difficulties in this method make it desirable to study the reaction by more direct means.

Outline of the Method.—A shock tube is suitable for producing plane shock waves of constant temperature and density. The essential features of the method are indicated in Fig. 1. A typical shock wave, formed after bursting of the diaphragm separating nitrogen at 2 atm. from nitrogen plus 1% N₂O₄ at 1 atm., travels through the low pressure gas at a Mach number of 1.12 relative to the unshocked gas. The shock pressure is 1.4 atm. and the temperature rise is about 25°. The shock wave is of uniform strength as long as it is driven by gas expanding from the compression chamber. As gas passes into the shock front, the translational and rotational energy adjust to the new temperature within the time of a few collisions. At the temperatures involved, nitrogen has no significant vibrational heat capacity. In a molecule such as N₂O₄, with several low frequency vibrations, the vibrational energy should adjust within a few microseconds, leaving only dissociation to take place farther behind the shock front. The beam of light from the source S passes through the shock tube parallel to the plane of the shock front, through the shock tube parallel to the plane of the photomultiplier P. As soon as the shock front has passed through this beam, the photomultiplier and oscilloscope record the changing light transmission of the gas heated by the shock as it approaches equilibrium at the new tempera-ture and pressure. The reaction rate cannot be observed until the shock front has passed through the light beam. In the apparatus to be described below, a shock wave going slightly faster than the speed of sound traverses a 1-mm. light beam in about 3 μ sec. This fixes a lower limit to the reaction times that can be observed. Decreasing the width

⁽³⁾ H. S. Johnston and D. M. Yost, J. Chem. Phys., 17, 386 (1949).
(4) W. T. Richards and J. A. Reid, *ibid.*, 1, 114 (1933).
of the light beam would shorten this time, but by decreasing the light intensity on the photomultiplier, it would increase the noise level (shot noise at the primary photocathode) and hence decrease the sensitivity of the apparatus for detecting concentration changes.

For a perfect gas with constant heat capacity, the temperature and density behind the shock front are constant, and can be calculated from the shock velocity and the initial conditions. Shock waves in nitrogen containing about 1% N₂O₄, the present situation, show approximately this ideal behavior. The corrections required by the endothermic dissociation of the N₂O₄ are discussed in the Appendix. The velocity of the shock wave is determined by measuring its time of flight between the light beam S' of the schlieren optical system, and that of the observing system farther downstream.

Experimental

Linde pure dry nitrogen was used as the driving gas and as the diluent for the N_2O_4 . The N_2O_4 was taken from a Matheson cylinder, passed through P₂O₅, and the liquefied as treated with dry oxygen until its original green color disappeared and the solid obtained on freezing was white. A small high pressure cylinder was filled to 0.5 atm. with the gas thus purified. This was then diluted to about 1%with dry nitroger. Usually a full day was allowed for the gases to mix by diffusion in the cylinder. From here the mixture was withdrawn as needed for filling the shock tube. The composition of the mixture was determined with a Beckman Model DU spectrophotometer, using the equilibrium data of Verhoek and Daniels⁶ and the absorption coefficient for NO₂ of 113 liter mole⁻¹ cm.⁻¹ at 4375 Å. (10 Å. band width, tungsten source); this absorption coefficient was determined with the same instrument on a sample of gas in a 10-cm. cell, concentrations being measured by titration. Since mercury arcs were used for observations behind the shock wave, identical absorption coefficients of 150 liter mole⁻¹ cm.⁻¹ for the lines 4047 and 4358 Å. were determined by using the arc as light source in the spectrophotometer. Dixon' finds that Beer's law is valid for NO_2 , using a tungsten lamp and 40 Å. band width, and that there is no effect of temperature up to 85°

The shock tube is of the type frequently used in hydrodynamic studies.^{8,9} The steel tube, 5 cm. square in cross section, has quartz windows sealed with O-rings and fitted so that all surfaces inside the tube are flush. The diaphragm separating the gases at high and low pressure was usually the laminated cellophane (red zip tape) of the Dobeckmun Company. This will withstand a 1-atm. pressure difference and yet burst catastrophically when pricked by a needle moving on the end of a shaft sealed through the side of the tube with an O-ring. The gases are admitted to the shock tube through copper tubing, on which the dry N_2O -nitrogen mixture has little effect.

The dissociation of N_2O_4 at temperatures above 30° is too fast to measure conveniently in the present apparatus. In order to study the reaction over a range of temperature, the shock tube must be cooled. Alcohol, or trichloroethylene, cooled with Dry Ice, can be circulated through coils soldered to the tube, thus cooling it to temperatures as low as -35° .

In the observation system, a light beam from a Hanovia d.c. No. S352 mercury arc is defined by 1-mm. slits and, after passing through the shock tube, passes through a small spectrograph which isolates wave lengths between 4047 and 4358 for the photomultiplier. A 50-volt per stage collecting voltage gives 100 μ amp. of photocurrent through a 10 K load resistor. In some experiments there was used in place of the d.c. arc two G.E. AH4 a.c. mercury arcs, running 90° out of phase between two terminals of the three-phase power line and ground. Their light was combined with a half reflecting mirror. The resulting beam had about 15% 120-cycle modulation.

The oscilloscope was a Tektronix Type 512, in which the vertical amplifier has a response time of less than 1 μ sec. The total input capacitance was 60–100 $\mu\mu$ f., so that the response time, t_r , of the photomultiplier–oscilloscope combination was of the order of 1 μ sec. The signal to r.m.s. noise ratio for a photomultiplier is approximately $(it_r/ge)^{1/2} i =$ output photocurrent, e = electronic charge, g = gain of photomultiplier (about 10⁴ in the present instance). It is worthy of emphasis that in light modulation experiments with photomultipliers, optimum sensitivity is achieved with high light intensity and low multiplier gain. The calculated signal to r.m.s. noise ratio is 250. Practically, the limiting fractional change in photocurrent that could be observed was 0.02. This corresponds to a change in NO₂ concentration during reaction was $1 - 2 \times 10^{-4}$ mole liter⁻¹.

The density gradient in the shock front refracts the light beam from S' (Fig. 1) so that it clears the obstructing knife edge K and reaches the photomultiplier. The resulting signal, after amplification, triggers a thyratron, and this event is taken as the time at which the shock front passed the first window. Experiments indicate that there is a delay of from 0.5 to 1.5 μ sec. in the firing of the thyratron. In the runs with nitrogen as buffer gas, the following operat-ing procedure is used. The signal from the thyratron is fed into the magnified sweep circuit of the oscilloscope and also triggers a cathode-coupled Schmidt-type univibrator delay circuit.¹⁰ Shortly before the shock gets to the second window, the magnified sweep starts, and the external delay circuit puts a mark on it which comes at a known time after the shock passed the first window. From this and the position on the trace of the shock wave as seen by the photomultiplier at the second window, the shock velocity is found. This is known to the accuracy to which the univibrator can be calibrated, which is about 2 μ sec. for calibration of a 300-µsec. delay against the sweep of the oscilloscope, which is itself calibrated against a 100-kc. quartz crystal oscillator. The photographs shown in Figs. 2 and 3 were obtained us-ing the procedure outlined above. Measurement of these gives photocurrent, and hence concentration changes, as a function of time. The expected decrease in the concentration of N_2O_4 behind the shock front was directly observed using wave length 2537 Å, absorbed principally by N_2O_4 . No quantitative measurements were made in this way.

In order to increase the accuracy of the timing, a different procedure was developed in the later experiments, with carbon dioxide as inert gas. The thyratron signal from the schlieren circuit triggers the univibrator, the "flip" of which immediately starts one sweep, which is somewhat deflected below the horizontal zero line. The delayed "flop" starts a second sweep shortly before the shock reaches the observation window. The approximate value of the delay between the two sweeps, together with the phase difference between 10-µsec. time marks on them serves to fix the time difference between events on the two sweeps to within 0.2 µsec. Uncertainty due to the fact that the sweep is quite non-linear for the first 10 µsec. is eliminated by reflecting the thyratron trigger signal in a commercial delay cable, and applying the reflected signal to the vertical deflection system, 11 µsec. after the start. This is an absolute time mark on the linear part of the sweep.

Results

The results of this study of the rate of dissociation of N_2O_4 in the presence of a large excess of an inert gas are presented in Figs. 4 and 5. The results for the dependence of the first-order rate constant on total concentration, given in Fig. 4, indicate that for nitrogen the rate is approximately second order (first order with respect to nitrogen as well as with respect to N_2O_4) below concentrations of about 0.05 mole liter⁻¹, where the slope is nearly unity. At higher total concentrations, the dependence of the nitrogen concentration decreases, as is to be expected for a unimolecular reaction. From Fig. 4 it is estimated that the

(10) D. G. Marlow and C. R. Niesewanger, "Development of the Spark Shadowgraph," Navord Report No. 980, 1947, pp. 13-16.

⁽⁵⁾ For further details, see the Ph.D. thesis of T. Carrington, California Institute of Technology, 1952.

⁽⁶⁾ F. H. Verhoek and F. Daniels, J. Am. Chem. Soc., 53, 1250 (1931).

⁽⁷⁾ J. K. Dixon, J. Chem. Phys., 8, 157 (1940).

⁽⁸⁾ W. Payman and W. C. F. Shepperd, Proc. Roy. Soc. (London), A186, 293 (1949).

⁽⁹⁾ W. Bleakney, D. K. Weimer and C. H. Fletcher, Rev. Sci. Instruments, 20, 807 (1949).



Fig. 2.—Oscilloscope record of photocurrent for shock wave in pure nitiogen. The small positive "pips" are time marks 10 μ sec. μ part. On the lower trace, moving from left to right, the first small negative signal is a time mark from the external delay circuit. The sharp positive and negative spikes are schlieren effects as the shock wave passes through the light beam. The upper trace is for purposes of calibration. Increasing photocurrent corresponds to a downward (negative) deflection.

limiting low concentration rate constant with nitrogen as inert gas is 1.6×10^6 liter mole⁻¹ sec.⁻¹ at 25°, corresponding to a first-order constant of 6.4×10^{-4} sec.⁻¹ at 0.04 mole liter⁻¹. Using the observed activation energy (see below), this is 2.0

 $\times 10^{-14} \exp (-11,000/RT)$ liter mole⁻¹ sec.⁻¹. Johnston¹¹ has developed a method for evaluating a lower limit to the high concentration rate constant from data taken near the low concentration limit. In the present case, this gives $1\,\times\,10^{6}\,\,{\rm sec.}^{-1}$ as the lower limit to the high concentration rate constant at 25° , when applied to the nitrogen data. In the decomposition of N_2O_5 and N_2O , this minimum is exceeded by a factor of 11 and 3, respectively. Assuming a factor of 3 in the present case, and using as the activation energy in this limit the energy of dissociation, one has for the high concentration limit $k = 1 \times 10^{16}$ $\exp(-13,100/RT)$ sec.⁻¹. A firmer lower limit to this constant can be obtained directly from the experimental data. If it is assumed that at the highest total concentrations tion limit is fully attained (which is clearly not the case), the runs with nitrogen and with carbon dioxide give pre-exponen-

tial factors of 1×10^{15} and 2×10^{15} sec.⁻¹.

The line in Fig. 5 is drawn through points taken in the range 0.055 to 0.061 mole liter⁻¹, only the nitrogen values being used. These constants were calculated to 0.055 mole liter⁻¹ assuming the proportionality of the rate to the nitrogen concentration in this range. The resulting activation

(11) II. S. Johnston, J. Chem. Phys., 20, 1103 (1952).



Fig. 3.—Oscilloscope record of photocurrent, Mach number 1.117. Initial conditions and equilibrium conditions behind the shock wave were: nitrogen pressure, 749, 1000 nm.; temperature, -27.0° , -8.5° ; NO₂ concentration, 0.84, 2.3 (mole liter⁻¹ × 10⁴); N₂O₄ concentration, 1.9, 1.7 (mole liter⁻¹ × 10⁴); density ratio 1.24. After the shock front passes through the light beam (after the sharp positive spike), the photocurrent falls as dissociation proceeds, and levels off as the new equilibrium is reached. The smooth horizontal sweeps are voltage calibration. Increasing photocurrent corresponds to a downward (negative) deflection.

energy is 11.0 ± 0.6 kcal. mole⁻¹ over a 48° temperature range. The sound dispersion value⁵ is 13.9 ± 0.9 kcal. mole⁻¹. The energy of dissociation¹² at 25° is 13.1 kcal. mole⁻¹. At 25° and a total concentration of 0.055 mole liter⁻¹ (1% N₂O₄)



at the highest total concentrations investigated the high concentration limit is fully attained (which is clearly not the energy it here with the many with the activation energy 11 kcal. Fig. 4.—Dependence of first-order rate constants on total concentration: \bigcirc , inert gas N₂; \bigcirc , interpolated from Fig. 5 (N₂); \bigcirc , inert gas CO₂; \bullet , two concident CO₂ points. Nitrogen rate constants were calculated to 25° and CO₂ constants to -3° with the activation energy 11 kcal.

in nitrogen), the rate constant interpolated from Fig. 5 is $(8.3 \pm 1.3) \times 10^4 \text{ sec.}^{-1}$. The result from the sound dispersion measurements is⁴ (6.6 \pm 0.7) $\times 10^4 \text{ sec.}^{-1}$ at 25° and 0.036 mole liter⁻¹ (no inert gas), with a smaller effect of total concentration than has been found here. Comparison is difficult because of the presumably different efficiencies of nitrogen and NO₂-N₂O₄ in energizing

(12) W. F. Giauque and J. D. Kemp, ibid., 6, 40 (1938).

 N_2O_4 . The difference in activation energy and pressure dependence are in the right direction to be explained in this way. Within experimental error, carbon dioxide gives the same results as nitrogen.

The mean deviation of the points in Fig. 5 from the line is 15%. This could be accounted for by an error of 2 μ sec. in the timing, but the fact that the runs with carbon dioxide, where a more accurate timing method was used, were no better than those with nitrogen indicates that this is not the principal difficulty. The delay of the firing of the thyratron in the schlieren system should have been approximately constant for the runs plotted in Fig. 5. There were inevitably small air leaks, and it is possible that the nitrogen- N_2O_4 mixture in the shock tube may have contained as much as 1% of air. This could have no significant effect on the ratio of specific heats or on the mean molecular weight of the gas, and it seems unlikely that a reaction which goes as fast as the N_2O_4 dissociation would be greatly accelerated by a small amount of another inert gas in addition to the large excess of nitrogen. In calculating the initial conditions, the equilibrium constant of Verhoek and Daniels⁵ was extrapolated to low temperatures. Calculation shows that an error of as much as 30% in the equilibrium constant would not significantly affect the results. It seems likely that a principal source of error is the measurement of the photocurrent as a function of time on the oscilloscope trace.

Discussion

At the high concentration limit, the activation energy should be at least the critical energy, 12.8 kcal. mole⁻¹ (the energy of dissociation at 0° K.¹²). According to the classical coupled oscillator model of unimolecular reactions,¹³ the secondorder rate constant in the low concentration limit is given approximately by

$$k = Z(E_0/RT)^{s-1} ((s-1)!)^{-1} \exp(-E_0/RT)$$
(1)

in which Z is the kinetic theory collision number, E_0 is the critical energy, and s is the effective number of oscillators in the molecule. Equation 1 gives an activation energy less than the critical energy by (s - 3/2)RT. The experimental activation energy of 11 kcal. mole⁻¹ corresponds to 5 oscillators. The fact that the activation energy is less than the dissociation energy (13 kcal. mole⁻¹) means that the activation energy for the association of two NO₂ molecules is negative under these conditions. This is due to the fact that only relatively "cold" NO₂ molecules can stick together long enough for the resulting energized molecule to be stabilized to N₂O₄ by a collision with an inert gas molecule.

The second-order rate constant calculated from equation (1) using s = 5, $E_0 = 12.9$ kcal. mole⁻¹, and collision diameters 3.8 and 5.3 Å. for nitrogen and N₂O₄ can be approximately represented, in a small temperature interval around 280°K., by the equation $k = 7.6 \times 10^{13} \text{ exp } (-10,900/RT)$ liter mole⁻¹ sec.⁻¹, in good agreement with the

(13) L. S. Kassel, "The Kinetics of Homogeneous Gas Reactions," The Chemical Catalog Company Inc., New York, N. Y., 1932, Chap. 5.



Fig. 5.—First-order rate constants at a total concentration of 0.055 mole liter⁻¹: \bigcirc , data taken near 0.055 mole liter⁻¹ (N₂); \bigoplus , data taken near 0.03 mole liter⁻¹ (N₂); +, data taken near 0.064 mole liter⁻¹ (CO₂); ×, 3 coincident CO₂ points.

experimental relation, 2.0 \times 10¹⁴ exp (-11,000/*RT*).

The pre-exponential factor 10¹⁶ in the high concentration rate constant is 1000 times the "normal" value. This may be explained in terms of the Eyring transition state theory and some reasonable guesses as follows. If it is assumed that rotation about the N-N bond in the activated molecule is free, while in the normal molecule the contribution of the corresponding torsional vibration to the rotation function is two,¹⁴ the ratio of the classical rotation partition functions for the two molecules is 17. In this calculation the N-N distance in the activated molecule was taken to be that (3.1 Å.) for which the Morse function for the vibration which separates the NO_2 groups comes within kT of dissociation. If the contribution to the partition function of the four N-N bending vibrations in the normal molecule is neglected, (most of these have frequencies fairly large com-

(14) According to ref. 12, there is no free rotation in the normal molecule. J. S. Broadley and J. M. Robertson (*Nature*, **164**, 915 (1949)) find that crystalline N_4O_4 is planar, with a N-N distance of 1.64 Å. The value for the partition function is chosen by analogy with the results for ethane given by Herzberg, "Molecular Spectra and Molecular Structure II," D. Van Nostrand Co., Inc., New York, N. Y., 1945, p. 511.

pared with kT) and if frequencies of about 75 cm.⁻¹ are assigned to them in the activated molecule, the total partition function ratio will be brought up to 1000^{14a}. Contributions from vibrations other than N-N torsion and bending have been neglected, since they will be small and will tend to cancel. An even higher value of the ratio can be obtained by assuming, as has sometimes been done for the recombination of methyl radicals, that the NO₂ groups are free to rotate about three axes in the activated molecule.

The region of the transition between first- and second-order behavior in the dependence of the rate constant on total concentration may be estimated as occurring at the concentration at which the rate of collisional deactivation is comparable to the rate at which those energized molecules which contribute most to the over-all observed rate are decomposing. The rate of decomposition of the molecules which contribute most to the rate at the high concentration limit has been evaluated according to the classical theory by Benson,¹⁵ by maximizing with respect to energy the product of rate constant and distribution for energized molecules. This gives the energy, and hence the rate constant, for the most important molecules. Equating this rate to ZM gives for N₂O₄, the transition concentration, M, of the inert gas nitrogen, of 0.025 mole liter⁻¹ (s = 5) or 0.08 or (s = 4). In this calculation, the rate constant, $k_{\rm E}$, for the dissociation of molecules with excess energy $E - E_0$ is taken from the classical coupled oscillator theory as $k_{\rm E} = 10^{13} ((E - E_0)/E)^{s} - \frac{1}{1} \sec^{-1}$. One uses $10^{13} \sec^{-1}$ here as a "normal" frecuency factor, rather than the observed 1016, because, as already argued, a factor of 10³ is probably contributed by entropy effects. A more accurate treatment, using a (non-equilibrium) distribution function appropriate below the high concentration limit would give lower values. However, it is in general not true that the concentration determined by equating ZM to the most probable rate of decomposition of energizing molecules will lie in the middle of the transition range.

From the first-order rate constant for the dissociation of N₂O₄, and the equilibrium constant, the rate constant for the bimolecular association of two NO₂ molecules is 5.2×10^8 liters mole⁻¹ sec.⁻¹ at 25°. This corresponds to a steric factor of 5 $\times 10^{-3}$, using 4.6 Å. as the collision diameter of NO₂, and assuming no activation energy. A negative activation energy occurs only when the association is at least partly dependent on a third body.

The few experiments with carbon dioxide, included in Figs. 4 and 5, show it to be no more effective than nitrogen in energizing N_2O_4 molecules. The results of Johnston¹⁶ on the dissociation

(14a) NOTE ADDED IN PROOF.—From the height of the barrier hindering internal rotation, calculated from entropy considerations by Bernstein and Burns (Nature, 166, 1039 (1950)), one may calculate from the tables of Pitzer and Gwinn (J. Chem. Phys., 10, 428 (1942)) that the partition function for the torsional vibration is 3.1. With this value, N-N bending frequencies of 68 cm.⁻¹ are required to bring the partition function ratio up to 1000. of N_2O_5 show that carbon dioxide is about 1.7 times as effective as nitrogen in this case. According to their relative masses and diameters (N_2 , 3.7 Å.; CO_2 , 4.6 Å.), nitrogen should make 5% more collisions with N_2O_4 than does carbon dioxide. The vibrational relaxation time of pure carbon dioxide is 7 μ sec.¹⁷ at 1 atm. This would be 5 μ sec. at the lowest pressure (1.4 atm.) used in this work. Data earlier than this were not used in calculating the rate constant. The carbon dioxide was dried by passage through Drierite, but it is probable that, due to impurities and to the NO_2 - N_2O_4 mixed with it, its relaxation time was somewhat shorter than that for the pure gas.

Appendix

The differential equation for the isothermal rate of change of the NO_2 concentration following an arbitrary displacement from equilibrium will now be derived and integrated, taking into account the variation in density due to the departure from ideal behavior of a shock wave in a dissociating gas.

Subscripts have the following meaning: 1 refers to NO₂, 2 refers to N₂O₄, and 0 denotes formal quantities, calculated as though all the N₂O₄ were present as NO₂. Subscript *l* refers to the low pressure (undisturbed) region, f refers to values just behind the shock front before any reaction has taken place, and ∞ refers to final equilibrium values. Quantities without superscripts are evaluated at an arbitrary distance behind the shock front. Define the degree of dissociation *a* by

$$C_1 = \alpha C_0 / V, \qquad C_0 = C_0^l \tag{2}$$

where C is concentration, $V = \rho^l / \rho$, and ρ is density. Differentiation gives

$$\frac{\mathrm{d}C_1}{\mathrm{d}t} = \frac{C_0}{V}\frac{\mathrm{d}\alpha}{\mathrm{d}t} + \alpha C_0 \frac{\mathrm{d}(1/V)}{\mathrm{d}t} \tag{3}$$

the first term on the right is the algebraic sum of the rate of formation of NO₂ by dissociation of N₂O₄, and its rate of removal by association to form N_2O_4 .

$$N_2O_4 \xrightarrow{k_2} 2NO_2, K = k_2/k_1$$
(4)

 $(C_0/V)d\alpha/dt = (\partial C_1/\partial t)_v = 2k_2C_2 - 2k_1C_1^2$ which defines the rate constants k_1 and k_2 . The second term

which defines the rate constants k_1 and k_2 . The second term on the right of (3) gives

$$\alpha C_0 \mathrm{d}(1/V)/\mathrm{d}t = (\partial C_1/\partial t)_\alpha = -(C_1 V/V^2) \mathrm{d}V/\mathrm{d}t = C_1 (1+\nu) \mathrm{d}\nu/\mathrm{d}t \quad (5)$$

with the definition $1 - \nu = V/V_f$. In the next section, a relation between ν and $\Delta g_2 = g_2^t - g_2$ (where g is weight fraction) will be derived. For the purposes of the present calculation this can be approximated by $\nu = a\Delta g_2$ where a is about 10 in the cases of interest here. Using this, the relation between concentration, density and weight fraction gives

$$= \frac{W_1 V_1 C_1 / \rho^l - g_1^l}{g_1^l + 1/a} \equiv A C_1 + B$$
(6)

which is valid as long as ν is not much more than 0.05, as in the present case. W is molecular weight. Equation (6) may be used to eliminate $d\nu/dt$ in (5). Combining this result with (4) in which C_2 has been expressed in terms of C_1 , C_0 , and V, gives

$$dC_1/dt = (bC_1^2 + eC_1 + j)/[1 - (1 + \nu)(\nu - B)]$$
(7)

where $b = -2k_1$, $e = k_2(AC_0/V_f - 1)$, and $j = k_2C_0(1 + B)/V_f$. The terms ν^2 and νB in the denominator may be neglected, since ν^2 and -B are typically not greater than 0.05. In order to integrate (7), an average value of ν will be introduced as a constant. With any reasonable average value, $(1 + B - \nu)$ can only be in error by 2 or 3%. The smallness of ν and the resulting simplification in the treat-

ν

⁽¹⁵⁾ S. W. Benson, J. Chem. Phys., 20, 1064 (1952).

⁽¹⁶⁾ H. S. Johnston, private communication.

⁽¹⁷⁾ W. Griffith, J. Applied Phys., 21, 1319 (1950).

ment is due to the fact that the large excess of nitrogen is fairly effective in overbalancing the "chemical" heat capacity of N_2O_4 . Equation (7) may now be integrated.

$$\frac{1+B-\bar{\nu}}{\mathfrak{D}-k_2r}\ln\left|\frac{\Delta}{\Delta+k_2r/b}\right| = t + \text{const.}$$
(8)

$$k_2r = (e^2 - 4bj)^{1/2}$$
 and $\Delta = C_1^{\infty} - C_1$

The logarithm may be expanded to get a form useful when Δ is small:

$$\frac{1+B-\nu}{k_2r}\left[\ln\frac{Kr}{2\Delta}-\frac{2\Delta}{Kr}-\frac{1}{2}\left(\frac{2\Delta}{Kr}\right)^2\cdots\right]=l+\text{const}$$
(9)

The rate constant k_2 is determined from the slope of the quantity in brackets against time. A typical plot is shown in Fig. 6.

The time that appears above is of course the length of time that the gas being observed has been behind the shock front, which will be called the proper time, l_p . This is not equal to the time l_s measured by an observer in the laboratory, between the arrival at the observation window of the shock wave and of the segment of gas being observed. This "relativistic" effect is due to the fact that when the shock wave reaches the observing window, the gas that will appear there at time t_s later is already behind the shock front and has begun to dissociate. If the mass flow velocity u were constant behind the shock front, one would have

$$t_{\rm p} = t_{\rm s} u^l / u = t_{\rm s} \rho / \rho^l = t_{\rm s} / V \tag{10}$$

since u^{t_s} is the distance of the segment of gas behind the shock front and u is its velocity relative to the shock. The second equality above follows from the conservation of mass, equation (11) below. Equation (10) was used with a V averaged between V_t and the final equilibrium V, which were never very different.

It is now necessary to deduce the temperature to which the rate constant calculated above corresponds. A method will be developed for calculating the "frozen in" values of the temperature and density just behind the shock front, and also the final, equilibrium values attained farther back. From these two conditions, one obtains average values for temperature and density which may be considered constant during the part of the dissociation that is observed.

The development is motivated by the treatment of Bethe and Teller.¹⁸ It is based on relations expressing the fact that the flux of mass, momentum, and energy across any surface perpendicular to the one dimensional steady state flow is constant

$$\rho u = n$$
 l, density; u, flow velocity; n, mass flux (11)

$$P + nu = \text{const.}$$
 P , pressure (12)

$$En + \frac{1}{2}nu^2 + Pu = \text{const.}$$
 E, internal energy per gram (13)

These equations are written in a coördinate system moving with the shock wave. The situation may be pictured as a discontinuity, stationary in space, with low pressure gas flowing into it with supersonic velocity and gas at higher density and temperature flowing away from it with subsonic velocity. Applying these equations across a shock wave gives for the change in specific enthalpy

$$H - H^{l} = 1/2 \ u^{l_{2}} (1 - V)^{2} \tag{14}$$

This may be equated to the "chemical" expression for the enthalpy change

$$H - H^{l} = \beta R (T - T^{l})/W - L[(g - g_{2}^{l})/W_{2}]$$
(15)

in which W is mean molecular weight, and L is the enthalpy of dissociation of N₂O₄ per mole. βR is a mean "physical" heat capacity, a mole fraction average of the heat capacities of the component gases, considered as independent; $\gamma = \beta/(\beta - 1)$. The temperature may be eliminated from (15) by the relation

$$T'/T^{l} = V[1 + \gamma M^{2}(1 - V)]$$
(16)

obtained from (11) and (12) using the perfect gas law. M is a mean physical Mach number

$$M = (W u^{l_2} / \gamma RT)^{1/2}$$



Fig. 6.—Plot of experimental concentration data against time.

Combining the result with (14) and solving for V

$$V = \frac{1}{2\beta - 1} \left[\beta \left(1 + \frac{1}{\gamma M^2} \right) - \left(\left[1 - \beta \left(1 - \frac{1}{\gamma M^2} \right) \right]^2 + \frac{2 \left(2\beta - 1 \right) \Delta h}{u^{l_2}} \right)^{1/2} \right]$$
(17)
where $\Delta h = (g_2^l - g_2) L/W$. Setting $\Delta h = 0$ gives

$$V_t = \frac{1}{2\beta - 1} \left(1 + \frac{2\beta}{\gamma M^2} \right) \tag{18}$$

 V_t and T_t may be calculated from equation (18) and (16). From these, with a little experience, it is easy to make a good guess of V_{∞} and T_{∞} . These are then used with the equilibrium constant to calculate final concentrations, Δh , and hence a second approximation to V_{∞} and T_{∞} . It was seldom necessary to repeat this process. The agreement of the Δ at t = 0 calculated in this way with the observed was 10-15%. Typically $T_{\infty} - T_t$ was 1 or 1.5° and V/V_t was 0.95 or greater ($\nu = 0.05$ or less). With such small changes from the frozen-in to the equilibrium condition, it was not hard to decide on average values. V was arbitrarily taken as ${}^{2}{}_{4}$ of its final value, and T was taken as $T_t + {}^{3}{}_{4}(T_{\infty} - T_t)$ since the first part of the reaction was not observed. It is interesting to note that the temperature of the gas actually increases as a result of the endothermic process taking place in it. As the dissociation proceeds within the shock wave, energy is supplied to the flowing gas by a slowing down of the flow, with consequent increase in density, rather than by a decrease in temperature.

in density, rather than by a decrease in temperature. If the changes in V and T behind the shock front are too large to permit the use of average values, these quantities may be calculated at any point behind the shock front by using the observed values of Δ , and guessing a value of V, to find Δh , and hence V and T. This may be repeated if the first guess was too far off.

Acknowledgments.—We wish to thank Dr. W. M. Cady and Professor John G. Kirkwood for

⁽¹⁸⁾ H. Bethe and E. Teller, "Deviations from Thermal Equilibrium in Shock Waves," Aberdeen Proving Ground Report X117, 1940.

helpful discussions. The work has been supported by the Office of Naval Research. One of us (T.C.) is grateful for an Atomic Energy Commission Predoctoral Fellcwship. We are indebted to the Synchrotron staff for intellectual and material assistance with the electronic instrumentation, and to the Dobeckmun Company for the zip tape.

DISCUSSION

(1) R. M. NOYES (Columbia University).—Since the energy of activation is less than the energy needed to dissociate the molecule of N_2O_4 , the mode of motion leading to reaction "borrows" energy from other vibrational modes. This means that on the average these modes have less energy in the transition state than they do in the normal state of an undissociated molecule at the same temperature. In its present form, absolute reaction rate theory assumes a normal distribution of energies in all modes of motion except the one leading to reaction and is unable to handle situations like this.

These results indicate that the second-order rate constant for recombination of NO₂ radicals is proportional to total pressure even above two atmospheres. Gomer and Kistiakowsky (R. Gomer and G. B. Kistiakowsky, J. Chem. Phys., 19, 85 (1951)) found that the rate constant for recombination of CH₃ radicals is independent of pressure even down to 5 mm. Apparently energy is shuffled between different vibrational modes much more rapidly in an excited N₂O₄ molecule than it is in an excited C₂H₆. An alternative explanation could be based on the fact that the excited C₂H₆ has more total vibrational energy and must localize a larger fraction of this energy in one bond in order to dissociate.

(2) S. BENSON (University of Southern California).— I should like to comment on the usage of the phrase "lowpressure" limit of a unimolecular reaction.

In any detailed theory of a unimolecular reaction at pressures below the so-called high pressure limit, the form of the rate constant is given by¹⁹

$$k_{\text{obsd}} = P \int_{E^*}^{\infty} \frac{k_d(E)K(E)k(E)}{P \cdot k_d(E) + k(E)} \text{ or}$$

$$\sum_{E_i = E^*}^{\infty} \frac{P \cdot K(E_i) \cdot k(E_i) \cdot k_d(E)}{P \cdot k_d(E_i) + k(E_i)} \quad (1)$$

Where P is pressure, $k_d(E)$ is frequency of deactivating collisions, k(E) is the probability of spontaneous decomposition per unit time for an energized molecule of energy $E \ge E^*$ (the critical energy) and K(E) is the fraction of reactant molecules at equilibrium with energies in the range E, E + dE.

Some authors have assumed that there are pressures so low that the product $P \cdot k_d(E) \leq k(E)$ for all values of E and on the basis of such an assumption have proceeded to expand the denominator of equation (1) in a power series of the ratio $k(E)/P \cdot k_d(E)$.

The result of such an expansion is to give

$$k_{obs}(P \to 0) = P \int_{E^*}^{\infty} K(E) \cdot k_d(E) \left[1 - \frac{Pk_d(E)}{k(E)} - \left(\frac{P \cdot k_d(E)}{k(E)}\right)^2 - \dots \right] dE \quad (2)$$

$$\approx P \int_{E^*}^{\infty} K(E) \cdot k_{\rm d}(E) dE = P \int_{E^*}^{\infty} k_{\rm a}(E) dE \quad (3)$$

Where $k_{a}(E) = K(E) \cdot k_{d}(E)$ = specific rate of production of energized molecules. And it is then assumed that a plot k_{obsd} against P at low pressure gives a limiting slope equal to the last integral in equation 3.

Such an assumption cannot be justified in any theoretical terms since k(E) in any theory approaches zero as $E \to E^*$. Thus for any values of the product $P \cdot k_d(E)$ there will always be values of E for which k(E) is smaller than this value, and

(19) S. W. Benson, J. Chem. Phys., 20, 1064 (1952); L. Kassel, "Kinetics of Homogeneous Reactions," Reinhold Publ. Corp., New York, N. Y., 1932, Chap. V. we can see from equation 2 that the higher terms in the series become ∞ at E.

This is true for either a classical or quantum mechanical treatment of the system since in the former case k(E) is a continuous function of E while in the latter case, the closeness of the energy levels of the system near dissociation and the interaction of rotations with vibrations elso cause K(E) to become continuous in this region.

The fact that the experimental results lend themselves to a linear extrapolation is interesting but not a justification for the mathematical expansion and subsequent identification of experimental values with theoretical terms.

(3) H. S. JOHNSTON (Stanford University).—The assertion is that k(E) is a continuous, rather than quantized, function of energy above the critical energy. I feel that this assertion claims a knowledge about the nature of very highly excited molecules which we do not possess. We do not know how rotations combined with vibrations affect rate constants, nor do we really know the distribution of energy levels just above the critical energy. In a debate about whether a molecular function is quantized or continuous, I think the burden of proof lies on the one who contends it to be continuous. Fortunately, for this case we do not have to pursue the theoretical debate, for experimental data alone are capable of giving an unambiguous answer to the question.

For the sake of this discussion let us use Dr. Benson's nomenclature and his eq. 1. At some fixed very low pressure, let us break the integral into two parts: class 1 includes all terms for which $k(E) >> k_D(E)P$, and class 2 includes all other terms, that is, ones for which k(E) is only slightly greater, equal to, or less than $k_D(E)P$.

$$\frac{k_{\text{obsd}}}{P} = \int k_{\text{a}}(E) dE + \int k_{\text{a}}(E) \left[\frac{k(E)}{k_{\text{D}}(E)P + k(E)}\right] dE$$
Class 1 Class 2

The first integral is independent of P, but the second term depends on P. If we measure k_{obsd} as a function of P below our previously fixed pressure and if we find k_{obsd}/P to be independent of P (best seen from a plot of log k/P vs. log P), then we discover experimentally that the entire integral over class 2 is so small that it cannot be detected. It is easily seen that at all higher pressures, the relative effect of class 2 is equally small or smaller, and thus expansion of class 1 terms as in Benson's eq. 2 and in our articles²⁰ is completely valid. Thus good experimental data demonstrating second-order kinetics justify the phrase "low-pressure limit," justify the expansion in powers of the pressure, and justify the interpretations given to the expansion parameters. Furthermore, such data show that terms of class 2 are non-observables, and thus one may say they don't exist so far as kinetics is concerned.

We have extensive data on nitrogen pentoxide (in the presence of nitric oxide)²⁰ where various tests for second order have been made: plots of k_{obsd} vs. P, plots of k_{obsd}/P vs. P, and plots of log k/P vs. log P. In some cases we have more experimental error than in others, but in all cases and with many different foreign gases we get second-order kinetics at very low pressures. Fluorine monoxide, which may or may not decompose as an elementary unimolecular reaction, shows second-order kinetics with several different foreign gases.²¹ If one accepts our correction for heterogeneity in the thermal decomposition of nitrous oxide,²⁰ it also gives second-order kinetics at low pressures, here also the mechanism is not unambiguous. Nitric acid vapor promises to provide a good additional test of this question.

(4) S. BAUER (Cornell University).—Drs. Carrington and Davidson presented an ingenious and useful technique to chemical kinetics for use in the study of very fast gas reactions. With this chemical application of weak shock waves they have been able to make considerable headway with a problem which has challenged chemists for about 40 years. We have been developing another but related technique for the study of fast reactions, during the past two years; also, we have obtained preliminary data with our apparatus on

 ⁽²⁰⁾ H. S. Johnston, J. Chem. Phys., 19, 663 (1951); 20, 1103 (1952);
 J. Am. Chem. Soc., to be published; H. S. Johnston and R. L. Perrine, *ibid.*, 73, 4782 (1951).

⁽²¹⁾ W. Koblitz and H. J. Schumacher, Z. physik. Chem., **B25**, 283 (1934).





the N_2O_4 - NO_2 reaction. Our procedure is based on a flow method devised by Prof. Kantrowitz, who spoke to you on the physical phenomena in intense shock waves. Since our experiment and point of view differ from those of Davidson and Carrington, I shall briefly present the underlying principles and preliminary conclusion.

In contrast to the shock method which may be characterized by a step input of enthalpy, our experiment is characterized by a smooth imput of enthalpy, but with a controllable steepness for the rate of imput. Hydrody-namically it is described by a condition of adiabatic and isentropic flow in which a stagnation region is set up; the dimensions of this region determine the rate of enthalpy input, so that in the limiting case, as its dimensions approach zero, a shock condition is reached. Both experiments are essentially relaxation methods, wherein a system at equilibrium is displaced from that state by a relatively rapid injection of enthalpy, and it is then allowed to relax back to equilibrium. In both cases there is an effective heat ca-pacity lag. We have considered that both the heat capacity of the system due to vibrational degrees of freedom, and that due to the heat of reaction $[\Delta H_0(d\alpha/dT)_p]$ could lag behind the pressure and the heat capacity due to translation and rotation. Here then is an essential difference in our points of view. We were led to these experiments because we wish to study energy transfer processes in molecular collisions, and were only mildly excited about the possibility of measur-ing very fast reaction rates. Thus we started with the postulate that whereas translational and rotational degrees of freedom (except in the unique case of H_2) interact directly with the mass motion of the gas, and thus immediately reach equipartition, the vibrational degrees of freedom, and more so, dissociations such as occur in N_2O_4 , require numerous collisions for the establishment of equipartition and hence introduce a heat capacity lag.

The principle of the method is illustrated in Fig. A. The gas at equilibrium at (p_0, T_0, α_0) is allowed to expand adiabatically and isentropically through a properly shaped nozzle. For a slow enough expansion equilibrium is main-

tained at all times so that the gas at the exit of the orifice, now at a lower pressure and temperature and lower degree of dissociation (p_1, T_1, α_1) , may be regarded as the "pre-pared" sample. The enthalpy of the gas in a coördinate system moving with it at its mass velocity (u_1) , is less than that in the reservoir by $[Mu_1^2/2]$ per mole. Downstream, uniform streamline flow occurs until the gas gets to within about one diameter from the end of the "impact tube"— a source-shaped stationary obstruction which introduces a stagnation region in the vicinity of the central stream line. The velocity of the gas flowing along this stream line is thus brought back to zero, and enthalpy equal to $[Mu_1^2/2]$ is injected into the gas during a time which it takes to traverse a distance about half the diameter of the impact tube. Refer to this stage as No. 2. Inspection of Fig. B will prove instructive at this point. Clearly, were all degrees of freedom in the gas instantaneously to equilibrate with the enthalpy imput, the pressure and temperature after this adiabatic and isentropic compression would be equal to those in the reservoir $(p_2 = p_0; T_2 = T_0; \alpha_2 = \alpha_0)$. However, since the compression and hence the injection of enthalpy is rapid compared to the relaxation times of the lagging degrees of freedom, the gas at stage 2 is not at ther-modynamic equilibrium. The transition $1 \rightarrow 2$ is adiabatic modynamic equilibrium. The transition $1 \rightarrow 2$ is adiabatic but not isentropic. It will then revert relatively slowly to equilibrium, again, adiabatically but with a total gain in entropy. This occurs at the mouth of the impact tube into which the stationary gas is diffusing. The final equilib-rium condition, specified by subscript 3, is such that $p_2 = p_2 < p_0$; $T_3 < T_0$; $u_3 = 0$; $\alpha_3 < \alpha_0$. The net gair in en-tropy manifests itself as a lower equilibrium pressure, so that the experiment essentially consists of measuring accurately the small pressure difference $(p_0 - p_2)$ for various (p_0/p_1) ratios, which determine u_1 . $(p_0 - p_2)$ is a measure of the dissociation rate integrated over time, weighted essentially by $(\Delta F/T)$ along the path: $\int_{t_0}^{\infty} \Delta F\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right) \frac{\mathrm{d}t}{T}$. The relative velocity along the central stream line (u/u_1) is



plotted as a function of the reduced time $(t' = u_1 t/d)$ in Fig. B, for a source-shaped impact tube. Since most of the compression occurs over the reduced time interval 1.5 < t' < 2.5, the actual compression time is $\Delta t = d/u_1$; obviously the significant parameter is $[(d/u_1)/\tau]$, where τ is the relaxation time for the lagging reactions. In our ex-periments the minimum Δt is about 2 µsec.; the limitation arising both from the numerator (the diameter of the smallest impact tube we have been successful in preparing), and denominator (the maximum useful value of u_1 is the velocity of sound in the gas). However, useful data may be obtained from cases in which the significant parameter is of the order of 200. In the limiting case, for which [(d/ $(u_1)/\tau \rightarrow 0$, the enthalpy increment is injected over an infinitesimal interval compared to the characteristic time of the sample, and -hus becomes identical in operation with the shock technic. This is best illustrated by the following the shock define. I has a best must accur by the totsmag three diagrams (Fig. C) in which histograms are schemati-cally indicated for the enthalpy (and pressure), (translational + rotational) temperature, and degree of dissociation increments, for various reduced times (t/τ) . For a given impact tube diameter and (p_0/p_1) ratio, the magnitude of (d/u_1) is fixed. A family of curves is then obtained (as one proceeds from left to right) for successively increasing relaxation times. The limiting case of a long relaxation time corresponds to an effective step input of enthalpy, and thus to a shock wave. In Fig. Cb, the curve on the ex-treme left shows complete equilibrium, while the one on the extreme left shows complete equilibrium. extreme right illustrates the departure from equipartition when the vibrational modes lag behind the pressure change. Figure 3Cc is particularly interesting, because it shows that for the case of instantaneous compression, there must be a very brief period in which $(d\alpha/dt) < 0$, the gas associating faster than it is dissociating. This will occur for any mechanism which shows an increase in the total number of moles. The simplest example is

$$N_{2}O_{4} \xrightarrow{k_{a}} 2NO_{2}$$

$$p_{N_{2}O_{4}} = (1 - \alpha/1 + \alpha)p; \ p_{NO_{2}} = (2\alpha/1 + \alpha)p$$

$$\frac{1}{1 + \alpha} \left(\frac{d\alpha}{dt}\right) = k_{a} \left[\frac{1}{K_{eq}} \left(\frac{1 - \alpha}{1 + \alpha}\right) - \frac{p}{RT} \left(\frac{2a}{1 + \alpha}\right)^{2}\right]$$

Obviously, the factor (p/RT) increases sharply immediately after the step-input, whereas all the other terms in the bracket lag. (This includes K_{eq} , whose effective temperature is closer to that characteristic of the vibrational partition.) The data which Dr. Carrington presented did not show this effect; hence I suspect that it occurs in a



Fig. C.—Histograms for (d/μ_1) specified; α lagging. The difference between T_3 and T_0 is less than 1° and thus is negligible for most cases. They are related by means of the equation, $(\alpha_3 - \alpha_0)\Delta H^\circ = C_P(T_0 - T_3)$.

period less than the resolving time of their electronics, and is masked by the "spikes" he referred to.

The formal solution for the ratio of initial to final pressures is particularly simple when one assumes that the degree of dissociation is the only lagging degree of freedom. Then, for instantaneous compression

$$(1 + \alpha_0) R \ln p_0/p_2^{\infty} = (\alpha_0 - \alpha_1) \frac{\Delta H^{\circ}}{T_0} + (\alpha_1 D + E) \ln T_0/T_2 + \text{fnc} (\alpha_0, \alpha_1, \alpha_3)$$

where

$$D = 2 \tilde{C}_{\rm p}({\rm NO}_2) - \tilde{C}_{\rm p}({\rm N}_2{\rm O}_4); \ E = \tilde{C}_{\rm p}({\rm N}_2{\rm O}_4)$$

 T_{2} , maximum instantaneous temperature, immediately after step input of enthalpy.

fnc $(\alpha_0, \alpha_1, \alpha_3)$ introduces a small correction arising from the definition of standard states for ΔS° (1 atm., T_0)

This pressure defect is independent of the kinetic behavior, and is the maximum observable for $(d/u_1) << \tau$. However, when the relaxation time of the reaction becomes comparable to the characteristic time of the apparatus, the observed pressure defect will be less. Then

$$(1 + \alpha) R \ln p_0/p_2 = (\alpha_0 - \alpha_3) \frac{\Delta H^\circ}{T_0} + \operatorname{fnc}(\alpha_0, \alpha_3) + \int_{t_0}^{\infty} \left\{ D \ln T/T_0 - \frac{\Delta F}{T} \right\} \left(\frac{\mathrm{d}\alpha}{\mathrm{d}t} \right) \mathrm{d}t$$

where t_0 corresponds to the onset of the compression, and is generally taken to be the time at which $u = 0.99 u_1$; $\Delta F(t)$ is the instantaneous free energy of the flowing gas during this non-equilibrium period. One must then set up kinetic assumptions regarding ΔF , T, and $(d\alpha/dT)$ in terms of parameters, and integrate. The measured values of $(p_0 - p_2)$ under various conditions permit evaluation of these parameters. Our kinetic variable is the relaxation time, which, incidentally, may be defined only for systems which do not depart too much from equilibrium; it should not be confused with the half-time of the reaction.

Our experimental arrangement is illustrated in Fig. D. The pressure sensing device is a metal bellows, the extension of which is measured by the position of a core within the differential transformer. This manometer has a small internal volume, so that a steady state condition is rapidly attained. Our recorder traces show a sensitivity of 0.01 mm. with a precision of about 0.03 mm.; the time constant is two seconds, which is that of the recorder.

Our preliminary data show a relaxation time for the nitrogen tetroxide dissociation of $1.2 \ \mu \text{sec.}$, at $p_0 = 0.5 \ \text{atm.}$; $p_0/p_1 = 1.5$; $T_0 = 298^{\circ}\text{K}$. This is between the relaxation times computed from the rate constants quoted in the abstract (D and C) for the unimolecular mechanism ($\tau = 0.20 \ \mu \text{sec.}$) and the bimolecular mechanism ($\tau = 4.2 \ \mu \text{sec.}$). However, our value depends on the assumption made regarding other degrees of freedom which may be lagging. I believe that a combination of data from these two experiments will permit the unscrambling of the vibrational and dissociation relaxation effects.

I shall not take the time to make an extensive comparison between these two techniques. It is worth indicating that whereas we need large quantities of gas to push through the nozzle, in contrast to the small amounts used by Davidson and Carrington, we are not limited to a system in which the components have a characteristic strong absorption in the visible or ultraviolet regions.

I wish to acknowledge the careful experimental work of Mr. M. R. Gustavson, who constructed the apparatus and



obtained the data; also, the generous support of the Office of Naval Research.

N. DAVIDSON.—The brief period of time during which $(d\alpha/dt) < 0$ to which Dr. Bauer refers is, as Dr. Bauer points out, of the order of the vibrational relaxation time of N₂O₄, and, in our system, this is certainly less than the 3- μ -second resolving time of the experiment. Dr. Bauer's preliminary result that the rate of dissociation of N₂O₄ at 298° in the presence of ca. 0.5 atm. of N₂O₄–NO₂ gas is about three times faster than the rate measured by us, in the presence of the same pressure of nitrogen, is consistent with the idea that N₂O₄ is more effective than nitrogen in energizing N₂O₄

THE EXTENT OF HYDRATION OF SOME CRYSTALLINE PHASES OF SODIUM 1-ALKANESULFONATES¹

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An apparatus has been constructed in which the water of hydration of hydrated crystalline materials is determined by measurement of the volume of water vapor evolved at constant pressure from a small (1-30 mg.) sample with increasing temperature. Provision is also made for removal of samples for identification by X-ray diffraction powder patterns. Data are presented showing the extent of hydration and the stepwise nature of the dehydration of the $\alpha(RSO_3Na^{-1}/_8H_2O)$, $\epsilon(RSO_3Na^{-1}/_8H_2O)$, $\epsilon(RSO_3$

For some time work has been in progress in this Laboratory to differentiate and elucidate the structures of the hydrates of some sodium 1-alkanesulfonates.³⁻⁶ In order to investigate the very small available samples of some of these phases, we have constructed an apparatus in which the water is removed by gradual heating at constant water vapor pressure, while the amount of water is continuously measured by the volume of the vapor in a gas buret. The apparatus is similar in principle to others described earlier.^{7,8}

Description and Operation of Apparatus

A sample of appropriate size (1-30 mg. depending upon the material being studied) is weighed into a sample tube and introduced into a small glass bulb which is surrounded by a small oven. The bulb is connected with a gas buret (mercury-filled) either directly or through a Toepler pump by means of stopcccks. A small amount of water (enough to give an initial water vapor pressure of the desired magnitude) is added, the bulb is sealed off, cooled with solid CO_2 and evacuated to $\sim 10^{-3}$ mm. pressure. The solid CO_2 is then removed and the pressure adjusted to the desired value (15 mm. in the experiments reported below). The temperature of the oven is then increased in steps and the pressure and volume of the water vapor are read at each temperature by means of a cathetometer reading to 0.02 mm.

In some runs, a series of auxiliary bulbs containing small amounts of the material in thin-wall glass capillary tubes were connected to the main sample bulb. These could be sealed off at appropriate points during the experiment and the material used for X-ray diffraction powder patterns, thus identifying the product of each transition observed.

In the experiments on the sodium 1-alkanesulfonates reported below, the temperature was held constant after each step for at least 5 hours if no change in volume of water vapor was observed, and for at least 12 hours after no further change was observed in those cases where a transition was encountered. The temperature intervals were usually $\sim 5^{\circ}$.

Experimental Results

The α -, β - and ϵ -phases of sodium 1-hexadecaneand 1-dodecanesulfonates (C₁₆, C₁₂), the β -phase of sodium 1-tetradecanesulfonate (C₁₄), the α -phase of sodium 1-decanesulfonate (C₁₀) and the γ -phase

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(2) (a) Department of Anatomy, School of Medicine, University of Washington, Seattle 5, Wash. (b) Pulp Mills Research Project, University of Washington.

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of sodium 1-octanesulfonate (C_8) have been investigated, all at 15 mm. water vapor pressure.

All samples consisted of masses of single crystals which had been grown under suitable conditions and could be checked for phase identity and purity by microscopic examination.

The dehydration of the C₁₆- β -phase (Fig. 1) proceeded by three steps. At ~55°, ¹/₄ mole H₂O was lost, at ~74° an additional ¹/₈ mole of H₂O was lost and at ~102° a final ¹/₈ mole of H₂O was lost. No further appreciable loss of water was observed by heating to 180° and removing water from the sample tubes by means of the Toepler pump. X-Ray diffraction powder patterns taken on samples from separate runs establish the phases found under these conditions in the temperature range 55–74° as ϵ -phase and in the temperature range 74–102° as α -phase. The total amount of water lost by the β -phase in this run is 0.52 mole of H₂O. This value is to be compared with values of 0.502 and 0.53 on two macro weight loss determinations of the degree of hydration of this phase.

A sample of C_{16} - ϵ showed a loss of $^{1}/_{8}$ mole of $H_{2}O$ at $\sim 75^{\circ}$ and another corresponding loss at $\sim 108^{\circ}$. These transition temperatures are probably not accurate due to poor heat distribution in the oven during this run.

A sample of C_{16} - α showed a loss of $1/\epsilon$ mole H₂O at ~96°.

The dehydration of C_{12} - β -phase proceeded by two steps. At ~45°, ${}^{3}/_{8}$ mole of H₂O is lost. This is a β - α -phase transition, the ϵ -phase apparently having no stable temperature range where it is in equilibrium with water vapor at 15 mm. pressure. At ~98°, an additional ${}^{1}/_{8}$ mole of H₂O was lost. The total water of hydration lost in this run was 0.49 mole of H₂O.

The C₁₂- ϵ -phase did not show (Fig. 2) a definite ϵ - α -phase transition, but a marked loss of water with increasing temperature in the region of the β - α -phase transition of the C₁₂- β . At ~100°, a final 1/8 mole of H₂O was lost. For each of the first 5 points in the experiment more than 12 hours was allowed after no further change could be observed.

The C₁₂- α -phase showed only a $^{1}/_{8}$ mole of H₂O loss at $\sim 102^{\circ}$.

The C₁₄- β -phase is similar to the C₁₂- β , giving $^{3}/_{8}$ mole of H₂O at $\sim 50^{\circ}$ and $^{1}/_{8}$ mole of H₂O at $\sim 80^{\circ}$.

As an additional check on the hydration value of the α -phase, a sample of C₁₀- α was run. At $\sim 75^{\circ}$,



Fig. 1.—Dehydration isobar for β -phase of C₁₆H₃₃SO₃Na.

 $^{1}/_{8}$ mole of H₂O was lost. An X-ray diffraction powder pattern of the final product showed a $d_{001} =$ 29.1 Å. which compares well with $d_{001} =$ 28.9 Å. for single crystals of C₁₀- ζ -phase which grows from absolute methanol under anhydrous conditions. The hydration value of this run is to be compared with that of a macro weight loss determination on C₁₀- α^{5} which gave a value of 0.248 or $^{1}/_{4}$. In that run an attempt was made to differentiate surface water from structural water by X-ray diffraction powder patterns. The lack of a continuous measure of structural changes due to dehydration led to the erroneous value of $^{1}/_{4}$ hydrate of the α -phase which now seems definitely established as a $^{1}/_{8}$ hydrate.

The C_s- γ -phase is probably a monohydrate, although it apparently began to lose water already at 25°, making the first transition (to the α -phase) somewhat uncertain. At \sim 75°, the α -phase lost $^{1}/_{8}$ mole of H₂O.

Discussion of Results

The accuracy of the results is probably no better than 10%. The apparatus was not housed in a specially thermostated room. Temperature variations will introduce errors which become progressively worse at temperatures below 30°, since water vapor was assumed to be a perfect gas for the calculations. No correction was made for the progressive rise in temperature of the sample holder during the run. This would cause only a small error in most runs in the over-all H₂O loss, and a negligible error in the H₂O loss at a transition.



Fig. 2.—Dehydration isobar for ϵ -phase of $C_{12}H_{25}SO_3Na$.

No correction on pressure or volume was made for the meniscus height.

These phases have all been studied by singlecrystal X-ray crystallographic techniques^{3-6,9} and have been shown to have well-defined crystalline structures. The data presented here indicate clearly that these phases are definite, stoichiometric hydrates. This is corroborated by a few runs in which the water has been taken up again in a stepwise manner upon lowering the temperature, although some hysteresis has been observed which is being investigated further. The data for the C_{12} - ϵ -phase, considered alone, might have been interpreted as indication of an indefinite or variable hydration, but when they are considered in the light of the C_{16} - ϵ and C_{12} - β data, they are undoubtedly due to the metastability of C_{12} - ϵ under the conditions of the experiment.

Studies similar in intent but differing somewhat in technique from that presented here have been reported by Gardiner, Buerger and Smith⁸ and by Milligan, Bushey and Draper¹⁰ on the sodium salts of the fatty acids. Gardiner, *et al.*, worked at an unstated pressure of water vapor, probably of the order of 20 mm., while Milligan, *et al.*, used a pressure of $\sim 10^{-5}$ mm. Our data are similar to those of Gardiner, *et al.*, in indicating definite, stoichiometric hydrates.

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ELECTROKINETIC RELATIONS IN THE QUARTZ-ACETONE SYSTEM¹

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A pressure-decline technique previously developed for measurement of permeability has been extended to measurements of streaming potential, streaming current and electroösmotic pressure. These quantities, together with electrical resistance, were measured on acetone in quartz capillaries of the order of 1 micron diameter. The results were used to test the phenomenological equations of streaming and electroösmotic effects. The coefficients of the equations were not influenced by driving pressure, at least up to 20 cm. of acetone, nor by applied potential up to 1.2 v. The voltage range was probably limited by irreversible processes at the electrodes. For the first time with a non-aqueous liquid, Saxén's law was verified, within the 8% experimental uncertainty. Also for the first time, the electroviscous and electroösmotic conductance effects were measured directly. They amounted to 0.9%, in fair agreement with theory. Electrokinetic effects in non-aqueous liquids are probably caused by foreign ions from the solid.

In a previous paper,² general electrokinetic relations were derived from the equations

$$I = C_{11}E + C_{12}P V = C_{21}E + C_{22}P$$
(1)

where I and V are electric current and volume flow rate through a system of capillaries, and E and Pare differences of electric potential and pressure across the system.

Mazur and Overbeek³ independently proposed the same equations as a part of the theory of the thermodynamics of irreversible processes.⁴ According to this theory, the equations are correct provided the variables bear the proper relation to the production of entropy by electrokinetic processes, and if the current and flow are not too great. In addition, the theory states that $C_{12} = C_{21}$, a relation that also follows from Saxén's experimental law⁵ of the equality of streaming potential and electroösmosis.

The present paper describes an experimental test of these equations. The first question investigated was whether the individual terms were valid for the system under study, that is, whether current and flow were linear in the potential with constant pressure and linear in the pressure with constant potential. This question has been investigated extensively^{2,6} and can be answered affirmatively only in certain ranges for certain systems. The next question was whether the terms in P could be simply added to those in E, or whether there was a mutual interference between electrical and hydrodynamic effects. This question has received scant attention.^{2,7} A third question was to test the relation $C_{12} = C_{21}$ for the system under study. This has been verified in the form of Saxén's law, only with water and aqueous salt solutions.^{5,8,9} A final question was whether the electroviscous and elec-

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troösmotic conductance effects, as predicted from the equations,² could be observed experimentally. This has never been tested accurately by direct experiments on any system.

For the present study, the quartz-acetone system was selected as one which exhibits electrokinetic effects large enough to be easily measurable, and which makes possible a test of Saxén's law with a non-aqueous liquid. The measurements were more comprehensive in scope than any previously reported for a single system.

Electrokinetic quantities were measured by an extension of a pressure-decline technique previously reported from this Laboratory¹⁰ for measuring permeability, K = V/P, which is approximately¹¹ equal to C_{22} . A pressure-decline method was also used by Manegold and Solf¹² for measuring electroosmotic pressure, but a constant pressure head has always been used previously for streaming potential or streaming current.

The quantities measured are related to the coefficients of equations 1 as

streaming potential, $S = (E/P)_{I=0} = -C_{I2}/C_{I1}$ (2) streaming current, $i = (I/P)_{E=0} = C_{I2}$ (3)

electroösmotic pressure, $P_{\rm E} = (P/E)_{\rm V=0}E = -(C_{21}/C_{22})E$ (4)

Electrical resistance, R = E/I

$$= 1/C_{11}$$
 when $P = 0$

Experimental

Materials.—The quartz powder was size fraction "E-1," described elsewhere.¹³ It was cleaned with warm chromic acid, washed with deionized water and then with reagent acetone, and dried at 110° just before use.

Baker's reagent acetone was used without further purification, except for filtration through medium-grade fritted Pyrex on being transferred to the cell. Its specific conductivity was $2-5 \times 10^{-7}$ mho/em. The conductivity was not detectably altered after the acetone had flowed through the plug.

Apparatus.—The apparatus of Dodd, Davis and Pidgeon¹⁰ was modified, as shown in Fig. 1, for electrical measurements and to allow for the properties of acetone. The supporting membrane (medium grade fritted Pyrex) was cemented with water glass directly into precision-bore tubing. The entire plug then had a uniform cross section (5.06 cm.²). This also permitted the use of electrodes with the same diameter as the plug, so that the electric field was uniform. The lower electrode was pressed against the supporting disk

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Fig. 1.—Pressure-decline cell for electrokinetic measurements.

by a spring-shaped lead. The upper electrode had a flexible lead to allow close contact with the top surface of the plug, and a glass spacer to keep it perpendicular to the axis of the tube. The two electrodes in position were planar and parallel within 0.04 cm. They were made of perforated sheet platinum, lightly platinized just before use. Their presence was found to make no difference in the measured permeability.

Since no acetone-resistant lubricant could be found, stopcocks and joints were unlubricated, except for stopcock A which was separated from the acetone by a short column of air in the capillary lead tube. Leakage was avoided by eliminating all other stopcocks from the high-pressure part of the system and sealing the ball joint with a 5-cm. head of mercury.

Very low driving pressures were necessary for the electroosmotic measurements, so acetone itself was used as the manometric liquid, and the fluid head was allowed to decline to a few millimeters. At such low pressures, meniscus corrections would be appreciable, so they were avoided by attaching a precision-bore manometer tube on the lowpressure side with the same diameter (0.952 cm.) as that on the high-pressure side. Evaporation losses were prevented by guarding the openings with baths of acetone vapor. **Plugs**.—Plugs were formed by a vibrational method de-

Plugs.—Plugs were formed by a vibrational method described previously,¹³ which is believed to give a uniform packing. The fractional porosity was 0.40 ± 0.01 , and the "mean hydraulic radius"¹⁴ of the pores was 1.4 microns. The sized powder was used in an attempt to keep the capillary spaces within a limited size range.

Electrical Measurements: Resistance.—The electrical circuit is shown in Fig. 2. The precision components were: \mathbb{R}° , a wire-wound resistor, 0.750 megohm \pm 0.1%; G, a Leeds & Northrup galvanometer, 0.3-microampere full scale, accurate to 1%; and V, a Weston milliammeter, accurate to 0.5%, used to measure voltage because of its low



internal resistance (~ 1 ohm). The latter two components, with their damping and multiplying resistances, were calibrated in the circuit, using a potentiometer and standard resistors.

The resistance of the plugs was in the megohm range and could be measured with direct current. It was compared directly with R° by observing the galvanometer deflections when potential was applied for a few seconds, first to the plug and then to R° . As a check, readings were taken after reversing the potential and galvanometer in turn. The potential could be varied between 0.2 and 30 v. It has been customary to make such measurements with potertials of the order of 100 v.¹⁵ to reduce the error from any polarization at the electrodes. Here it was found that consistent results were obtained in the range up to about 3 v., by taking readings promptly after closing the circuit. At higher voltages the change due to polarization was too rapid. There were slow drifts in the resistance of some plugs, which made the effective value during a single pressure-decline run uncertain by about 2%.

Streaming Potential.-The electrodes were connected to the potentiometric circuit by throwing switch B (Fig. 2) to the right. Equation 3 shows that it is necessary in measuring streaming potential to measure the potential difference and the pressure while the net current through the plug is zero. In pressure-decline experiments the pressure and the potential are both decreasing; consequently the potentiometer was set at a fixed potential slightly lower than that necessary for balance and allowed to drift toward balance. The time was recorded when the galvanometer reached the null point, and the pressure was evaluated by interpolating on the straight-line permeability plot relating $\log P$ to time. Several readings were taken during each pressure-decline run. Figure 2 shows a typical plot of potential against pressure. The slope gives the quantity S (the downstream electrode was always positive). The points generally fell within 2.5 millivolts of a straight line, but the point at zero pressure was frequently farthest off the line, as in Fig. 3. This point was obtained by balancing a fixed potential with the potentiometer, as is done in the constant pressure technique. In practice, the greater accuracy of determining the time at which the galvanometer drifted past null was an advantage of the pressure-decline technique. Another advantage was that a composite value from observations at several pressures was obtained rapidly. As a corollary, it was easier to notice the interference of electrode effects, since they produced non-linear plots. Such plots were observed if

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Fig. 3.-Streaming effects by pressure-decline measurements.

streaming potential was measured just after a relatively large potential had been applied to the electrodes for more than a few seconds. This was evidently a polarization effect, which required several hours to decay. Streaming potential values could be reproduced within a few per cent. when polarization effects were avoided.

Streaming Current.-According to equation 4, streaming current must be measured when there is no potential difference across the capillaries. Consequently it was measured by switching the electrodes momentarily over to a short circuit through the galvanometer and reading the deflection. The time was used to evaluate pressure as with streaming potential. Figure 3 shows a plot of streaming current against pressure measured during the same run as the streaming potential. The current was more convenient to measure than the potential. However, the measurements were less reliable, since the current was of the order of tenths of microamperes, and it was influenced by strays. It can be seen in the figure that the points deviate erratically from the straight line. In many cases the slope of the line, which is the value defined as i, was uncertain by several per cent.

Some streaming current measurements were made by leaving the electrodes short-circuited through the galvanometer continuously, instead of for a few seconds at a time. This method gave plots curving upward in the region above 0.1 microampere, evidently due to some sort of polarization effect. When continuous currents were less than 0.06 microampere, the points generally fell on a straight line.

When current was linear in pressure, it may be assumed that the condition E = 0 was satisfied. Another indication of the correctness of the measurements is that they were consistent with resistance measurements made during the same run, according to the equation

$$S/i = R \tag{5}$$

Several comparisons of S/i and R gave an average discrepancy of 3.1% which is less than the experimental errors.

Electroösmotic Pressure.—If C_{22} is considered as the ratio of flow to pressure, it should be measured with zero potential difference. However, it can be measured as a differential coefficient in the presence of any constant potential

$$(\partial V/\partial P)_{\rm E} = C_{22}$$

Under this condition, the relation between flow and pressure is

$$V = C_{22}(P - P_{\rm E}) \tag{6}$$

The integration constant $P_{\rm E}$ is the pressure when V = 0, and is a function of E. Obviously, this is electroösmotic pressure as defined in equation 4.

When permeability measurements were made with an applied potential and the integration constant was omitted, the logarithmic plots were curved. By trial and error, it was possible to determine within 0.03 cm. of acetone the quantity that must be added to give the straightest line; this was the electroösmotic pressure. The slope could be determined within the 0.8% plotting uncertainty. Constant potential was applied to the electrodes through the potentiometric circuit.

Results

As in the experience of previous workers,^{16,17} electrokinetic quantities were not easily reproducible, having different values for different plugs and varying in time with the same plug. Table I summarizes the results obtained with the techniques described. (S/R)L is proportional to the "zeta potential." The values given for R are exclusive of the resistance of the supporting disk; RA/L is the specific resistance of the powder plug. The specific conductivity of acetone within the pores was about twice that in the bulk phase.

In contrast with the variability of electrical quantities, the permeability, K, of a given plug was substantially constant over periods up to several weeks. The starred values in the table are corrected for the effect of the supporting disk. For comparison with these, values were calculated from the observed porosity and the known surface area.¹³

The object of the present investigation was only to obtain relations between the quantities. For this purpose the quantitative results reported, except where stated otherwise, are short-range comparisons on plug No. 10, with which the most comprehensive series of measurements was made.

The first two of the four questions raised earlier are answered most easily by examining the results to see whether the coefficients of equations 1 (C_{11} , C_{12} , C_{21} and C_{22}) are constants independent of changes in P and E.

Influence of Pressure.—The various quantities were measured over the following ranges of pressure (centimeters of acetone): K, 0.5 to 30; R, 0 to 20; S, 7 to 29; i, 7 to 29; $P_{\rm E}$, 1 to 3. There were no variations outside the experimental errors previously stated. Consequently the coefficients C_{22} , C_{12} and $C_{11} = 1/R = i/S$ are constant over relatively wide pressure ranges. Influence of Potential.—Departures from the

Influence of Potential.—Departures from the linearity expressed in equations 1 became evident after E passed a certain value. Probably this

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	A	verage deviation	ns are giver	n; number	of determination	ons in paren	tneses	
Plug No.	Av. S, volt/barye \times 10 ⁶	Av. R. ohm \times 10 ⁻⁶	L, cm.	RA/L, ohm cm. \times 10 ⁻⁶	Av. (S/R) , amp. $\times 10^{12}$	(S/R)L, amp. cm. $\times 10^{12}$	Av. K meas., cm. ³ /sec./barye \times 10 ⁷	$K_{,}$ calc.
4	38.5 ± 2.9	2.26 ± 0.17	3.43	3.3	15.7 ± 1.2	54	6.31 ± 0.04	
	(6)	(6)			(6)		(6)	
5	41.6 ± 0.6	3.36 ± 0.03	3.72	4.6	11.9 ± 0.2	44	$7.01^* \pm 0.09$	7.80
	(3)	(3)			(3)		(5)	
6	38.9 ± 2.2	2.72 ± 0.10	4.02	3.4	13.1 ± 0.3	53	$6.89* \pm 0.03$	5.77
	(4)	(4)			(4)		(13)	
7	26.4	2.95	4.13	3.6	8.4	35	3.21 ± 0.05	
	(1)	(1)			(1)		(4)	
8	32.7 ± 1.7	2.55 ± 0.05	2.64	4.9	11.8 ± 0.5	31	6.09 ± 0.05	
	(4)	(4)			(4)		(4)	
9	42.1 ± 1.4	1.33 ± 0.02	1.43	4.7	27.6 ± 0.4	39	19.25 ± 0.17	
	(2)	(2)			(2)		(4)	
10	38.5 ± 6.0	3.83 ± 0.89	6.08	3.0	9.7 ± 0.7	59	$5.48^*\pm0.08$	5.18
	(58)	(36)			(43)		(85)	

uncertainty.

TABLE I
SUMMARY OF EXPERIMENTAL RESULTS
Average deviations are given: number of determinations in parenthe

departure was not strictly an electrokinetic effect, but occurred at the electrodes. However, electrodes are a necessary part of the irreversible system and their influence was not studied separately.

Resistance was constant within 0.6% up to about ± 3 v., and permeability, measured as the slope of a plot of equation 6, was constant within 1.3% up to ± 1.2 v. Both quantities showed larger deviations at larger voltages.

The value of C_{21} was obtained as a slope by plotting $C_{22}P_{\rm E}$ against E. Potentials as high as 8.5 v. were applied (with plug 5) and in all cases the plot was a straight line within the plotting uncertainty of about 5%. Figure 4 shows the plot for plug 10. In drawing the lines, it was not assumed that they passed through the origin; in general they did not, but behaved as if there had been a polarization potential, E_0 , that affected all readings equally. It may be concluded that C_{21} is independent of voltage in the range studied. However, it apparently has a different value when the potential is reversed. There was some indication that the sign of the discrepancy depends on the sign of E_0 . If this is an electrode effect which acts in opposite directions in the positive and negative ranges, it should cancel by averaging. Such averaging has been customary in electroösmotic experiments.^{17,18}

Saxén's Law.—A comparison of C_{12} and C_{21} is given in Table II. The variations in the C_{21} column represent maximum plotting uncertainty, and those in the C_{12} column are average deviations. The prevailing value of C_{12} changed with the sign of the applied potential, in the opposite direction from C_{21} . Comparing averages, we see that

TABLE II

TEST OF SAXEN'S LAW (units are c.g.s.-e.s.u \times 10³/3^a)

C ...

	011	012
E(+)	10.3 ± 0.5	9.3 ± 0.7
E(-)	8.1 ± 0.6	10.5 ± 0.5
Av.	9.2	9.8 ± 0.8

 a In practical electrical units the table gives $C_{21} \times 10^5$ and $C_{12} \times 10^{12}.$

(18) F. Fairbrother and M. Balkin, J. Chem. Soc., 389 (1931).

Saxen's law is verified within the experimental

Fig. 4.—Electroösmotic pressure: the upstream electrode defines the sign of the voltage.

Electroviscous Effect.—In porous solids the electroviscous effect is the decrease of liquid flow due to the streaming potential. It can be evaluated by measuring the permeability, K_s , with electrodes short-circuited to destroy the streaming potential, and comparing with the ordinary value, K. This comparison is shown in Table III. The difference between the two permeabilities is not

TABLE III

ELECTROVISCOUS AND ELECTROÖSMOTIC CONDUCTANCE Effects

	DICHOL	0		
	$K_s \times 10^7$	$K \times 10^{7}$	$\Delta R_v/R$	$\Delta R/R$
No. of measurements, n	19	32	32	42
Mean value	5.566	5.515	0.0097	0.0005
Av. deviation	0.027	0.030	0.0057	0.0064
Probable error, %	0.095	0.089	0.084	0.084
% difference between				
means	0.	92	0.	92
Odds against random				
occurrence	2 imes	106	2 imes	107
Av. $(S^2/KR) \times 10^9$				
(± av. δ)	0.76 =	± 0.07	0.66 =	± 0.10

much larger than the average deviation of the measurements. However, it is likely that the variations are largely due to random errors and can be treated statistically. The probable error of each mean (0.6745 $\sqrt{\Sigma\delta^2/[n(n-1)]}$, where $\delta = \text{devia$ $tions}$) is shown and it is seen that the chance of obtaining the 0.92% difference between the means by random errors is very small. Theoretically² this effect in per cent. should be equal to the average value of $(S^2/KR) \times 10^9$ prevailing during the experiments. The table shows that the agreement is fair. Since the electroviscous effect is virtually negligible for the system studied here,¹⁹ it seems unlikely that it ever attains the large values of 10 to 60% sometimes claimed from indirect measurements.²⁰

Electroösmotic Conductance Effect.-There is also a difference between electrical resistance measured at constant pressure, $R = (\partial E / \partial I)_{\rm P}$, when the electric field produces electroösmotic flow, and that measured when flow is prevented by closing the stopcock, $R_{\rm V} = (E/I)_{\rm V} = \iota$. In per cent. this difference is also theoretically equal to (S^2/KR) \times 10⁹. In Table III, $\Delta R_{\rm v}$ is the change in resistance on closing the stopcock, and ΔR is the change in resistance between successive measurements without closing the stopcock. Again it can be seen that a statistically reliable difference was measured which agrees passably well with the theoretical value. This effect is related to part of the "surface conductance,"² but it has never before been considered independently.

Origin of Electrokinetic Effects on Non-aqueous Liquids.—It is generally recognized that electrokinetic effects arise when an electric double layer is formed at the interface between liquid and solid. The origin and general character of this layer are understood for solutions of electrolytes, and for pure liquids like water and the lower alcohols which are capable of appreciable ionization. The nature of the phenomena in other liquids has not been clear. Coehn's rule²¹ would imply an electrostatic charge, but this rule has been largely dis-

(20) G. H. Bishop, F. Urban and H. L. White, THIS JOURNAL, 35, 137 (1931); H. L. White, B. Monaghan and F. Urban, J. Gen. Physiol. 18, 515 (1935); L. J. Klinkenberg, "Drilling and Production Practice 1941." American Petroleum Institute, New York, N. Y., 1942, p. 200; B. F. Ruth, Ind. Eng. Chem., 38, 564 (1946).

(21) Reference 4, p. 401.

credited by later work.^{18,22} Strickler and Mathews²³ suggested "oriented adsorption" of molecules, and Fairbrother and Balkin¹⁸ found some correlation between dipole moments and " ζ -potentials." However, molecular adsorption cannot account for continuous electroösmosis. Gortner²⁴ concluded that actual ionization of the molecules of the liquid must occur and that the data indicated that ionization must be a specific reaction between the solid and the liquid.

Actually it seems more reasonable to assume that foreign ions from the solid are responsible for the surface charge, and the property of the liquid which is most important is its solvent power for electrolytes, either in bulk or in surface layers. Kraus and his co-workers²⁵ have found in conductance studies that electrolytic contamination must be minimized by using cells with the lowest possible ratio of surface to volume. This ratio is enormous in electrokinetic studies with porous solids. The examples in Table IV illustrate how, even in the most careful work of this sort, the liquids used have contained relatively large amounts of foreign ions.

TAI	DIF	IV
1 A I	BLL	1 1

SPECIFIC (Conductivities	OF "PURE" I	AQUIDS
	Water	Acetone	Nitrobenzene
Kraus ²⁶	$0.05 imes10^{-6}$	$0.5 imes10^{-9}$	1×10^{-10}
Fairbrother ¹⁸	$1.7 imes10^{-6}$	$2.0 imes10^{-7}$	1.4×10^{-8}
Gortner ²⁷	$4.8 imes 10^{-6}$		2×10^{-8}
Wijga ⁹	$0.39 imes10^{-6}$		

Evidently the absolute significance of electrokinetic measurements is limited even after elaborate purification procedures. Consequently these were considered unnecessary in the present study of phenomenological relations between electrokinetic quantities.

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(23) A. Strickler and J. H. Mathews, J. Am. Chem. Soc., 44, 647

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(25) N. L. Cox, C. A. Kraus and R. M. Fuoss, Trans. Faraday Soc.,

[15] A. D. OG, O. A. Riada and C. M. Fullos, Full Soc., 71, 31, 749 (1935); V. F. Hnizda and C. A. Kraus, J. Am. Chem. Soc., 71, 1565 (1949).

(26) C. A. Kraus and W. B. Dexter, *ibid.*, **44**, 2468 (1922); M. B. Reynolds and C. A. Kraus, *ibid.*, **70**, 1709 (1948); R. E. Van Dyke and C. A. Kraus, *ibid.*, **71**, 2694 (1949).

(27) W. McK. Martin and R. A. Gortner, THIS JOURNAL, 34, 1509 (1930); R. A. Gortner and H. B. Bull, Proc. Natl. Acad. Sci. U. S., 23, 256 (1937).

⁽¹⁹⁾ Cf. J. C. Henniker, J. Colloid Sci., 7, 443 (1952).

THERMAL ANALYSIS OF THE SYSTEMS HYDRAZINE-METHANOL AND HYDRAZINE-ETHANOL

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Data based on thermal analysis of the systems hydrazine-methanol and hydrazine-ethanol arc reported. Three addition compounds are formed in the system hydrazine-methanol. The compound N_2H_4 -CH₃OH exhibits an incongruent melting point at -47.3°. The compounds N_1H_4 -2CH₃OH and N_2H_4 -4CH₃OH melt at -57.8 and -69.5°, respectively. One addition compound, N_2H_4 -2C₂H₃OH, melting at -31.2° is formed between hydrazine and ethanol. Phase diagrams of both of these systems are presented.

Introduction

Derivatives of hydrazine have been known for a long time and salts of hydrazine have been known at least since Curtius² isolated several of these compounds in 1887. Since that time, the chemistry of hydrazine has received considerable attention; the physical properties of the pure material have been established with a high degree of certainty and its structure elucidated. However, relatively few investigations have been reported on studies of hydrazine as a solvent. Although those familiar with nitrogen chemistry have recognized hydrazine as an homolog of ammonia with considerably better solvent properties for polar compounds than ammonia, data on a relatively small number of hydrazine systems are reported. Friedrichs³ reported an extensive study of the system hydrazine-ammonia. Semishin⁴ and Mohr and Audrieth⁵ studied the system hydrazine-water. Other binary systems of hydrazine reported include thymol,⁶ phenol,⁶ acetamide,⁶ urea,⁷ diphenylamine⁶ and hydrazine azide.⁸

Because methanol and ethanol are strongly polar compounds, the hydrazine-ethanol and hydrazinemethanol systems may be expected to show behavior similar to the hydrazine-water system. These systems were studied by thermal analysis techniques and phase diagrams were constructed from the data obtained.

Experimental

Materials.—Anhydrous hydrazine was prepared by dehydration of Fairmount commercial hydrazine (94.7% N_2 - H_4). Three parts by weight of hydrazine were added to two parts of freshly fused potassium hydroxide which had been pulverized in a desiccator box, and the mixture allowed to stand for two hours. The hydrazine was then distilled in an all-glass apparatus under a nitrogen atmosphere at a pressure of 60-80 mm. In order to minimize danger of explosion the apparatus was thoroughly flushed with nitrogen before heating the distillation flask. After distillation was complete the flow of nitrogen was allowed to continue until the apparatus had cooled. The entire assembly was surrounded by a safety shield during the operation. Approximately 75% of the hydrazine was distilled. Sevently to one hundred grams was prepared at a time and more was distilled as required. The product was analyzed by the direct iodate method⁹ and redistilled from freshly fused

(1) U. S. Naval Powder Factory, Indian Head, Maryland.

(2) T. Curtius, Ber., 20, 1632 (1887).

- (3) F. Friedrichs, Z. anorg. allgem. Chem., 187, 221 (1923).
- (4) V. I. Semishin, J. Gen. Chem. (U.S.S.R.), 8, 654 (1938).
- (5) P. H. Mohr and L. F. Audrieth, THIS JOURNAL, 53, 901 (1949).
- (6) V. I. Semishin, J. Gen. Chem. (U.S.S.R.), 13, 625 (1943).
- (7) V. I. Semishin, ibid., 9, 83 (1939).

(8) A. L. Dresser, A. W. Browne and C. M. Mason, J. Am. Chem. Soc., 55, 1963 (1933).

(9) R. A. Penneman and L. F. Audrieth, Anal. Chem., 20, 1058 (1948).

potassium hydroxide if analysis did not indicate substantially complete dehydration. The hydrazine prepared in this manner analyzed 99.9% and had a freezing point of 1.52°, which is in good agreement with the value of 1.53° reported by Scott, Oliver, Gross, Hubbard and Huffman.¹⁰ U. S. I. absolute ethyl alcohol was distilled at atmospheric pressure from freshly calcined calcium oxide. Suitable precautions were taken to exclude moisture. A. C. S. reagent grade, acetone-free, methanol was distilled at atmospheric pressure from magnesium.

After purification was completed all subsequent operations with the purified materials were carried out in a desiccator box in an atmosphere of dry nitrogen.

Apparatus.—Freezing and melting points were determined in a cell which was designed so that the contents were completely protected from contact with the atmosphere. Stirring was accomplished with a spiral glass stirrer actuated by a solenoid acting on an iron bar sealed into the upper end of the stirrer. The entire cell was surrounded with a clear glass dewar flask which provided uniform changes in temperature when the assembly was immersed in cooling or warming baths. The temperature in the cell was measured with a copper-constantan thermocouple inserted into a thermocouple well which contained n-propyl alcohol as a thermal conducting medium. Temperatures on the system hydrazinc-ethanol were obtained from the thermocouple potential measured with a Leeds and Northrup Portable Precision Potentiometer. For the system hydrazine-methanol, warmspeedomax recorder. A Leeds and Northrup Type G Speedomax recorder. A Leeds and Northrup low-level am-plifier was employed which made it possible to vary the scale on the Speedomax from 50 to 2000 microvolts. In most of the work the 200 microvolt cools was used making most of the work the 200 microvolt scale was used, making it possible to read the thermocouple potential to one microvolt.

During the course of the investigation of the hydrazinemethanol system it became necessary to isolate and analyze a solid phase. For this purpose a modification of the standard cell was made. The new cell was larger and the thermocouple well was inserted through a $^{19}/_{38}$ standard taper joint. A filter stick was also fitted with a $^{19}/_{38}$ standard taper joint and when the mixture was cooled to the desired temperature the stirrer was stopped and the thermocouple well assembly was removed and replaced with the filter stick. The filter stick was connected to a trap and when suction was applied the liquid phase was drawn off. After the crystals had been allowed to melt, a sample was removed and analyzed.

The copper-constant thermocouple was calibrated in place in the cell by measuring the freezing points of purified materials. Freezing points of benzene, water, carbon tetrachloride, mercury, chloroform and toluene were determined and a correction curve plotted. From this curve a correction was applied to the freezing points of the mixtures being studied.

Procedure for Melting and Freezing Points.—The solutions of ethanol and methanol with hydrazine were prepared by direct weighing. One of the components was first added to the cell in the desiccator box under a nitrog en atmosphere. The cell was then removed and weighed. The same procedure was followed for the second component. After the cell was filled it was placed in the dewar and the apparatus was immersed in a cooling bath. Cooling was accomplished

(10) D. W. Scott, G. D. Oliver, M. E. Gross, W. N. Hubbard and H. M. Huffman, J. Am. Chem. Soc., 71, 2293 (1949). with Dry Ice-acetone baths or liquid nitrogen according to the temperature required. The system hydrazine-ethanol was studied by determining cooling curves in which time was plotted against temperature. In all cases supercooling was observed and the equilibrium line of freezing was extrapolated back to the cooling curve of the liquid to determine the freezing point. In the study of the hydrazinemethanol system such excessive supercooling was encountered that it was impossible to obtain reproducible freezing points from cooling curves. Melting points were therefore determined from warming curves in the following manner. The approximate freezing point of a given mixture was obtained from a cooling curve. After the mixture was frozen the apparatus was immersed in a bath having a temperature $5-10^{\circ}$ higher than the approximate freezing point. As the mixture warmed up it was stirred and the temperature recorded. Sharp and reproducible breaks occurred in the curves at the melting point.

Results and Discussion

Freezing point-composition data for the system hydrazine-ethanol are presented in Table I and shown graphically in Fig. 1. The phase diagram indicates the existence of one addition compound, N_2H_4 ·2C₂H₆OH, which has a melting point of -31.2°. The eutectic between hydrazine and this compound contains 55 mole per cent. ethanol and freezes at -33.7°. The eutectic between ethanol and the compound, which contains approximately 98 mole per cent. ethanol, freezes at -117.3°. Mixtures containing more than 90 mole per cent. ethanol exhibited such excessive supercooling that data in this region of the phase diagram were obtained only with great difficulty from cooling curves. The usual methods, such as producing cold spots on the freezing point cell, were unsuccessful in inducing rapid crystallization.



Fig. 1.—Freezing point-composition diagram for the system $N_2H_4-C_2H_6OH$.

In the work on the hydrazine-methanol system, supercooling of the mixtures was so great that determination of freezing points from cooling curves

TABLE I FREEZING POINTS OF THE SYSTEM HYDRAZINE-ETHANOL

Eth a nol, mol e %	F.p., °C.	Eutectic	Ethanol, mole %	F.р., °С.	Eutectic
0.0	+1.52		58.9	- 32.7	
6.3	-1.2		62.3	- 31.8	
7.6	- 1.6	-34.2	64.9	- 31.5	
16.9	- 4.4		67.6	- 31.8	
20.3	- 5.9	-33.9	70.5	-32.1	
23.5	- 6.7	-33.9	73.4	- 32.8	
27.6	- 8.5	-33.8	76.0	-33.2	
31.5	-10.2	-33.9	79.6	- 36.4	-116.7
34.9	-12.3	-33.5	79.9	-36.7	
37.9	-15.5	-33.9	82.1	- 37.7	
40.5	-15.5	-33.7	85.9	- 42 4	
45.0	-20.3	-33.7	88.5	- 46.0	
46.8	-23.1	-33.5	91.7	- 51.0	
48.4	-25.4	-33.4	94.8	- 62 .6	-117.4
51.0	-29.3	-33.5	98.2	-115.0	
54.2	-33.5		100.0	-114.0	
56.3	-33.5	-33.7			

was discontinued. The phase diagram was therefore plotted from melting points obtained from warming curves determined in the manner described in the previous section. Melting pointcomposition data for this system are summarized in Table II and the phase diagram given in Fig. 2. Three addition compounds, N_2H_4 ·CH₃OH, N_2H_4 · 2CH₃OH and N_2H_4 ·4CH₃OH, are formed. Melting points of these compounds are -47.3, -57.8 and -69.5°, respectively. Eutectics are found which melt at -60.0 and -100°.

TABLE II

MELTING]	Points	OF THE	SYSTEM	HYDRAZINE	-Methanol
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		15 01 1113	~ · · · ·			
Meth- anol, mole %	M.p., °C.	Eutectic	Meth- anol, mole %	М.р., °С.	Meth- anol, mole %	М.р., °С.
0.0	+1.52		57.1	-47.9	67.1	-57.9
5.1	- 1.2		57.6	-53.3	68.1	-58.0
10.0	- 3.5		58.0	-55.3	69.6	-58.4
15.1	- 6.3	-62.3	59.0	-58.3	71.4	-60.4
20.1	- 8.1	-61.8	59.1	-48.9	74.5	-61.5
25.1	-12.3	-61.8	59.5	-50.0	75.2	-64.1
31.5	-16.4	-61.8	60.0	-49.0	75.7	-63.0
37.2	-21.2	-60.3	60.3	-49.7	77.0	-64.8
37.5	a	-60.8	60.5	-49.0	78.0	-66.3
39.9	-24.3	-60.0	61.0	-49.6	78 .9	-68.5
42.3	-26.9		62.0	-50.5	79.8	-69.4
45.1	-31.2	-59.7	62.2	-51.0	83.9	-69.9
45.4	a		62 .6	-50.9	87.9	-72.9
50.5	-38.2		62.9	-50.9	90.2	-76.0
52.9	-42.8	-60.1	63.0	-51.6	9 2 .5	-79.8
53.8	-45.1		63.2	-58.5	93.5	-82.1°
55.0	-47.0		63.9	-51.9	94.9	-85.4
55.9	-49.6	-60.7	64.0	-53.3	97.7	-95.9
	-47.0		64.9	-58.1	98.6	-99.0
57.0	-52.7		66.2	-57.8	100.0	-98.0
-						

^a Incongruent m.p. -47.3. ^b Eutectic -100.0.

The compound N_2H_4 ·CH₃OH exhibits an incongruent melting point and its existence was established by isolation and analysis of the solid phase separating from a cooled mixture containing 59.4% methanol. Separation of the liquid from the solid phase was accomplished in the special freezing point cell described in the previous section. The possibility of compound formation was indicated by the nature of the phase diagram in the region 55-59 mole per cent. methanol. Two curves were obtained over this range of compositions. Points on the lower curve were found when the mixtures were melted immediately after freezing. When the frozen mixtures were allowed to stand for three or more hours, points were found on the upper liquidus line. Because a phase diagram of this type could also represent a transformation in the solid state, analysis was made of the solid phase in order to establish definitely the existence of the compound. The upper liquidus line therefore represents a stable equilibrium between liquid and solid phases while the lower curve indicates a metastable equilibrium. Above a temperature of -47.3° the compound N₂H₄·CH₃OH decomposes into solid hydrazine and methanol. Because of the slow formation of this compound, equilibrium was not always reached on cooling, and points on a metastable eutectic line between hydrazine and N_2H_4 ·2CH₃OH were found in some cases.

In both systems a drifting of the eutectic lines toward lower temperatures was observed as the mixtures became richer in hydrazine. This behavior is probably due to the use of cooling curves for determining the eutectic temperature and to the supercooling which was always observed. As the mixtures approached pure hydrazine, very little of the eutectic mixture was left when final solidifica-



Fig. 2.—Melting point-composition diagram for the system N_2H_4 -CH₃OH.

tion took place and the small thermal effect was insufficient to compensate for the supercooling. No reliable data could be obtained for the eutectic line between the compounds N_2H_4 ·2CH₃OH and N_2H_4 ·4CH₃OH.

PHOTOTHERMAL DECOMPOSITION OF MIXED SILVER AND MERCUROUS OXALATES

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Coprecipitated mixtures of silver and mercurous oxalates containing 50-60 mole per cent. of the latter exhibit very much higher rates of photothermal decomposition than do the separate components. X-Ray diffraction studies show no evidence of new compound or solid solution formation. A catalytic mechanism consistent with all experimental evidence is postulated to explain the apparent anomaly. The rate increase is proposed to be due to local catalytic thermal decomposition of silver oxalate on mercury centers formed photothermally, in addition to the characteristic photothermal decomposition occurring in each oxalate. The presence of potassium oxalate increases the rate of photolysis of silver and mercurous oxalates and of their mixtures. Nitrogen oxides apparently inhibit their photothermal decomposition.

Introduction.—Considerable work involving the study of the thermal decomposition of silver oxalate has been reported.¹⁻¹⁰ Sheppard and Vanselow¹¹

(1) J. Y. MacDonald and C. N. Hinshelwood, J. Chem. Soc., 127, 2764 (1925).

- (2) S. E. Sheppard and W. Vanselow, J. Am. Chem. Soc., 52, 3468 (1930).
 - (3) J. Y. MacDonald, Nature, 137, 152 (1936).
 - (4) J. Y. MacDonald, J. Chem. Soc., 832 (1936).
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- (6) J. Y. MacDonald and R. Sandison, Trans. Faraday Soc., 34, 589 (1938).
- (7) T. H. James, J. Chem. Phys., 10, 744 (1942).
- (8) R. L. Griffith, ibid., 14, 408 (1946).
- (9) P. I. Bel'kevich and A. A. Volkova, J. Phys. Chem. (U.S.S.R.), 20, 1103 (1946).
- (10) F. C. Tompkins, Trans. Faraday Soc., 44, 206 (1948).
- (11) S. E. Sheppard and W. Vanselow, U. S. Patent No. 1,976,302 (Oct. 9, 1934).

found that the rate of thermal decomposition of silver, mercurous and mercuric oxalates was increased by prior exposure to ultraviolet light, and made use of these materials as the basis for what they called photothermography. Benton and Cunningham¹² also noted the effect of light exposure upon the thermal decomposition of silver oxalate. The work to be reported herein is a study of the photothermal decomposition of mixed silver and mercurous oxalates.

Experimental Method.—The materials to be tested were precipitated and then suspended in gelatin, following which their relative rates of photothermal decomposition were determined by photographic sensitometric methods. This is valid because the extent of darkening of the emulsion is de-

⁽¹²⁾ A. F. Benton and G. L. Cunningham, J. Am. Chem. Soc., 57, 2227 (1935).

pendent upon the amount of metal formed in the decomposition. Mixtures over the entire range of composition were prepared and tested.

The inclusion of 6 millimoles of combined metal in 60 ml. of emulsion just prior to coating was adopted as standard. All operations were carried out in a dark-room under a yellow Wratten Series O safelight. Distilled water was em-ployed exclusively. Taking the case of a coprecipitated mixture of equimolar quantities of silver and mercurous oxalates as an example, the intimate mixture of oxalates was prepared by rapid addition of a mixture of 10 ml. of 0.3 N AgNO₃ and 10 ml. of 0.3 N HgNO₃ (the latter con-taining 7% by weight concd. HNO₃) to 20 ml. of a solution of 0.36 N K₂C₂O₄ (excess). The composition of the mixture was thus predetermined in preparation since the precipita-tions are quantitative. The precipitate was separated in a filtering crucible, washed with water, and removed before caking by making a slurry in the crucible with 20 ml. of a sol containing 3 g. of Kodak #1099 ash-free gelatin at 40° . The mixture was stirred for 15 minutes at 40° at a rate sufficient to accomplish dispersion but not so high as to pro-duce froth. The emulsion thus formed was then passed twice through a warmed hand homogenizer, and 25% excess potassium oxalate was added as 4.2 ml. of 0.36 N K₂C₂O₄ solution. The emulsion was adjusted to a volume of 60 ml. and stirred once more for 10 minutes at 40°. While still stirring, 0.8 ml. of emulsion was removed with a medicine dropper and applied to the surface of a clean glass slide $1'' \times 2.25''$. Drying was accomplished on a level aluminum block at 80°. The emulsion thus heated was found to be more sensitive than one dried at room temperature, but approximately the same as if it were dried at room temperature and then heated at 80° for about 2 minutes.

Determination of the sensitivity of the coated emulsion (and thus the relative rate of photothermal decomposition) was made by exposing the plates for varying lengths of time to the full radiat on from a Hanovia mercury vapor lamp, type 16200, 125 watts. The exposures were made at a distance of one yard through a Compur leaf-type shutter with aperture $1^{1}/_{8}$ " in diameter. The shutter was mounted two inches from the light source. The plates were placed behind a perforated mask to provide both exposed and unexposed areas for measurement of photographic density. Thermal development was carried out by placing the plate emulsion-side up for one minute in a nichrome-wound aluminum block oven at 120°. The density over background au-value (Δd) for each plate was determined with an Ansco-Sweet densitometer, Model 11, and the characteristic curve of the emulsion was obtained by plotting Δd against log relative exposure (log exposure time). From this curve it is possible to determine relative speed similar to that used for X-ray film. Such a relative speed is k/E. In this case, k was taken as 100 and E the exposure in seconds required to produce a Δd value of 0.4. This relative speed has been of photothermal decomposition of the mixtures studied.



Fig. 1.—Photothermal decomposition: curve 1, $Ag_2C_2O_4$; curve 2, coprecipitated $Hg_2C_2O_4 + Ag_2C_2O_4$ in 3:2 ratio; curve 3, coprecipitated $Hg_2C_2O_4 + Ag_2C_2O_4$ in 1:1 ratio; curve 4, $Hg_2C_2O_4$; curve 5, physical mixture of $Hg_2C_2O_4 + Ag_4C_4O_4$ in 1:1 ratio.

Results. (1).—Coprecipitated mixtures of silver and mercurous oxalates containing 50–60 mole per cent. of the latter exhibit very much higher rates of photothermal decomposition than do the separate components, but the photolysis rates of such mixtures are only intermediate between those of the components. The characteristic curves resulting from photothermal decomposition of the key emulsions are given in Fig. 1. Table I makes evident the strong dependence of relative speed of photothermal decomposition. In Fig.

TABLE I

RELATIVE SPEEDS	of Coprecipitated	MIXTURES	OF SILVER
A	ND MERCUROUS OXAL	LATES	

Mole % Hg2C2O4	Relative speed
0	<0.01
10	<0.01
20	1.7
30	0 . 02
40	. 6
50	14.7
60	18.0
70	2 . 9
80	2.5
90	1.8
100	1.9

2, there are plotted the characteristic curves obtained upon photolysis of the emulsions (as determined by "print-out" at a distance of ten inches from the standard light source).



Fig. 2.—Photodecomposition: curve 1, $H_{g_2}C_2O_4$; curve 2, coprecipitated $H_{g_2}C_2O_4 + Ag_2C_2O_4$ in 1:1 ratio; curve 3, $Ag_2C_2O_4$.

(2).—Physical mixtures of the silver and mercurous oxalates, as opposed to coprecipitated mixtures, exhibit rates of photothermal decomposition intermediate between those of the individual oxalates.

(3).—X-Ray diffraction powder patterns indicate that the coprecipitated mixtures contain only the two individual compounds, and no compound or solid solution of the type silver mercurous oxalate.

(4).—It has been found that the products of coprecipitation of silver and mercurous oxalates have a yellow cast, whereas either oxalate alone or a physical mixture of the two is perfectly white. However, all indications are that there is no relation between yellowing and spectral sensitivity. The absorption characteristics of silver oxalate, mercurous oxalate, and 1:1 physical and coprecipitated mixtures of the two were obtained with a Beckman DU spectrophotometer by the diffuse reflectance method. The results, illustrated in Fig. 3, confirm the observations made visually that the coprecipitated mixtures absorb in the blue. However, a determination of the spectral response of emulsions over the entire range of composition by exposure to the spectrum of an iron arc in a Bausch and Lomb Quartz Spectrograph indicates rather uniform spectral sensitivity, with response confined to the ultraviolet (2255-3090 Å.). The intensity of the yellow cast apparently has no relation to photothermal decomposition rate, for coprecipitated mixtures in the range 0.5-5 mole per cent. mercurous oxalate were found to be the most deeply colored.

(5).—MacDonald⁴ has reported that metallic mercury has a strong catalytic effect upon the thermal decomposition of silver oxalate. This was confirmed in the present work by determination of the darkening obtained upon heating a coated silver oxalate emulsion which had been stirred with metallic mercury.

(6).—The rate of photothermal decomposition of silver and mercuric oxalates coprecipitated in a 1:1 atomic ratio of Ag and Hg was found to be considerably higher than that of either component, although the mixture was white in color. The rate is, however, lower than that of similar mixtures containing the mercurous compound, since the inherent sensitivity of mercurous oxalate is much greater than that of mercuric oxalate.

(7).—As was stated in the section headed Experimental Method, large quantities of excess oxalate (as the potassium compound) were added to the emulsions. Van der Meulen, et al.,13 at Rutgers University have found that the addition of 25 % or more excess potassium oxalate very greatly increases the photothermal decomposition rate of mercurous oxalate. Similar effects have been noted in the present work for silver oxalate and for mixtures of the two heavy metal oxalates. The increase in the rate of thermal decomposition of silver oxalate resulting from the presence of a small excess of potassium oxalate during precipitation has been reported by MacDonald.³ In the present work, 25% excess oxalate has also been found to increase the rate of photodecomposition of silver oxalate, mercurous oxalate, and mixtures of the two.

(8).—Nitrogen oxides have been observed to have an inhibiting effect upon the photothermal decomposition of the metal oxalates studied. This has also been noted independently by Van der Meulen¹³ for mercurous oxalate.

Discussion.—The results obtained may be explained on the basis of a catalytic step in the photo-

(13) P. A. Van der Meulen, *et al.*, Progress Reports on Signal Corps Contract No. DA36-039-sc-54.



Fig. 3.—Reflection characteristics: curve 1, $Ag_2C_2O_4$; curve 2, $Hg_2C_2O_4$; curve 3, physical mixture of $Hg_2C_2O_4 + Ag_2C_2O_4$ in 1:1 ratio; curve 4, coprecipitated $Hg_2C_2O_4 + Ag_2C_2O_4$ in 1:1 ratio.

thermal decomposition of coprecipitated silver and mercurous oxalates. Photolysis experiments have shown that the abnormal increase in photothermal decomposition rate does not result from the light phase of the process. If Hg nuclei are first formed from the sensitive $Hg_2C_2O_4$ by photolysis and early in the thermal process, these nuclei could act as catalytic centers for decomposition of the silver oxalate. In addition, of course, each oxalate would concurrently undergo its characteristic photothermal decomposition. The fact that an emulsion containing a physical mixture is only intermediate in sensitivity between those of either oxalate alone indicates that a very intimate mixture of the oxalates is required to provide conditions under which the Hg nuclei will be in sufficiently close contact with the silver oxalate to have an effect upon its thermal decomposition rate. Since such close intimacy is required, decomposition does not spread to unexposed areas.

The catalytic mechanism proposed is supported by the parallel effect observed in the silver oxalatemercuric oxalate system.

All indications are that the yellow cast of the coprecipitated mixtures is due only to exceedingly small quantities of mercurous ion actually having entered the silver oxalate lattice; *i.e.*, an impurity effect brought about by coprecipitation.

In reference to the inhibition effect observed with nitrogen oxides, it has also been reported in the literature^{1,12} that oxygen inhibits the thermal decomposition of silver oxalate. Since the electronic structures of O_2 and NO are very similar, both having unpaired electrons (as does NO₂ as well), it is interesting to speculate whether the mechanisms of their inhibiting effects may be related.

Acknowledgment.—The authors wish to express their appreciation to Dr. P. A. Van der Meulen and his co-workers at Rutgers University and to Mr. Steven Levinos for the many discussions on this subject, and to Mr. Andrew Drukalsky for preparation of most of the X-ray diffraction powder patterns to which reference has been made.

THE INTERACTION OF URANYL IONS WITH UX₁(Th²³⁴) IN ACID SOLUTION

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Studies were continued of the rate of adsorption of UX_1 (thorium) from acid uranyl nitrate solutions by means of a carboncoated dipping Geiger-Müller tube. The appearance of a maximum in the curve was investigated. The effects of different acids, thickness of absorbent coating and variation of temperature were examined. The maximum was shown to be due to the opposing processes of adsorption and desorption by uranyl salts. The effects of varying the uranyl concentration were studied. The appearance of a maximum was attributed to two irreversible consecutive reactions in a non-equilibrium process. The maximum amount of UX_1 adsorbed by a fixed thickness of adsorbent from an acid solution at a fixed uranyl to UX_1 ratio was shown to be approximately constant over an eightfold variation of uranyl salt concentration.

A previous paper in this series¹ described a technique for the study of radiocolloids, in which a dipping Geiger-Müller counter tube was used simultaneously as an accumulator and a detector. The surface of the tube was coated with colloidal graphite, which served as an adsorbent. When adsorption occurred on the surface, more of the absorbing species diffused into the counting volume of the tube, and a marked increase in the counting rate was observed as time elapsed. This method was used to study several systems which previously had been shown by other investigators to be radiocolloidal under certain conditions. They were $UX_1(Th^{234})$ associated with uranyl nitrate, and RaE(Bi²¹²) which was carrier-free. In general, where other techniques demonstrated radiocolloidal behavior the suggested method did the same; and this was also true for the failure to exhibit colloidal properties.

In the course of this research, the adsorptiontime behavior of $UX_1(Th^{234})$ was studied in strongly acid uranyl nitrate solutions. In a 3 N nitric acid solution, the curve was observed to go through a maximum in a few hours. This behavior, which preliminary investigation did not clarify, appeared to be the result of competing processes of a complicated character. It is the subject of inquiry in this report.

Investigation of Reproducibility.—The reproducibility of the accumulation rate was investigated as a function of the number of applied graphite coatings. Unlike the earlier results in more dilute uranyl nitrate solutions,¹ it was found that in solutions containing 10 g. of uranyl nitrate per liter, the greater the number of applied coatings, the more rapid the adsorption of activity with time. This occurred in 1 N HCl as well as in the uranyl nitrate solution at its natural pH (about 3). Two conclusions can be drawn from these experiments. The first is that the surface appears to be involved in the phenomenon. The second conclusion is that reproducibility will be difficult to achieve in more concentrated uranyl nitrate solutions, because of the problem of attaining a reproducible thickness of coating; and hence only gross effects can be investigated under such conditions.

Effect of Temperature.—Studies were conducted on a solution containing 10 g. of uranyl nitrate per liter of 2 N nitric acid and 2 N hydrochloric acid, respectively, at temperatures of 23.0 and 34.0 (\pm 0.1°). A metal G-M counter tube was inserted into Lusteroid shells which were given two applications of a dilute Aquadag slurry. The effect of temperature on the accumulation rate appoared to be of the same order as the uncertainty observed in duplicate runs with the same number of applied coatings, *i.e.*, about 10%. Further experiments were conducted at room temperature without temperature control.

Tubes.-One difficulty which was encountered in this

work was the occasional failure of dipping tubes after a short period of operation. Since different counter tubes showed quite different counting efficiencies, wall thicknesses and sensitive surfaces, any related series of experiments were performed with the same tube. Several of the tubes were metallic and were inserted into Lusteroid shells whose carbon-coated exteriors served as the adsorbing surfaces. In other situations, glass tubes were coated and used directly in the solution. In most of the work reported in this paper, the tubes which were used were much less sensitive than those employed earlier, when the phenomenon of a maximum was first observed and hence do not show the maximum clearly. By way of example, a large glass counter directly immersed in an active solution showed an adsorbed accumulated activity of 1500 counts per minute at the maximum, and a decrease to approximately 1,000 counts per minute some hours later. A metal tube inserted into a Lusteroid shell showed, for the same solution, a maximum accumulation of about 480 counts per minute, decreasing to 400 counts per minute some hours later.

Effect of Acid on the Adsorption Rate of $UX_i(Th^{231})$.— In this series of experiments a metal tube was inserted into a coated Lusteroid shell. Figure 1 shows the result of variation in nitric acid concentration on a solution of 1 g. of uranyl nitrate per liter of acid. In more strongly acid solutions a maximum is observed after several hours. With decreasing acidity, the extent of adsorption increases, until for 0.1 N nitric acid and the acid-free uranyl nitrate solution continued accumulation is observed even after 120 hours.

Comparable experiments performed with hydrochloric acid solutions and with acetic acid solutions gave results which closely paralleled those obtained in nitric acid.

which closely paralleled those obtained in nitric acid. Figure 2 demonstrates the adsorption rates observed in sulfuric acid systems. It can be seen that sulfuric acid markedly represses the adsorption of UX_1 , even in 0.1 N solution. The effect is even more sharply apparent in Fig. 3, in which a direct comparison is made of the effects of 0.1 N solutions of hydrochloric, nitric and sulfuric acids on UX_1 adsorption. It is clear that there is much less adsorption in the sulfuric acid solution. This is consistent with the known chemistry of thorium, since Sidgwick² reports extremely soluble thorium sulfates, and Ephraim³ states that soluble sulfate complexes of thorium are known.

A marked contrast was observed between the adsorption of UX_1 from 0.1 N hydrochloric acid and that from 0.1 N hydrofluoric acid. The latter is remarkably effective in suppressing the adsorption of UX_1 . This suppression would seem to indicate soluble complex formation in the presence of a large excess of fluoride. However, the known analytical chemistry of thorium does not indicate a fluoride coordination beyond four.

The general conclusions which can be drawn from the series of adsorption experiments described in the preceding section are somewhat limited. Both the type of acid employed and the concentration have an effect on the time required to reach a maximum, as well as on the level of adsorbed activity. Acids which complex thorium seem to suppress adsorption. The results are not incensistent with the view that some sort of aggregate is the species adsorbed,

(2) N. V. Sidgwick, "The Chemical Elements and Their Compounds," Oxford, Clarendon Press, 1950.

(3) F. Ephraim, "Inorganic Chemistry," Nordernan Publishing Co., New York, 1943.

⁽¹⁾ I. Adler and J. Steigman, THIS JOURNAL, 56, 493 (1952).



Fig. 1.—Adsorption of UX₁ as the concentration of the HNO₃ is varied. The concentration of the uranyl nitrate is 1 gram per liter of solution: A, 0.1 N; B, no added acid; C, 0.5 N; D, 1 N; E, 3 N.



Fig. 2.—Adsorption of UX₁ as the concentration of sulfuric acid is varied: A, $0.1 N H_2SO_4$; B, $0.25 N H_2SO_4$; C, $1 N H_2SO_4$; D, $3 N H_2SO_4$.



Fig. 3.—Comparison of the effects of 0.1 N solutions of hydrochloric, nitric and sulfuric acid on the adsorption of UX_1 : A, 0.1 N HNO₃; B, 0.1 N HCl; C, 0.1 N H₂SO₄.

since the extent of adsorption is markedly decreased as the acid concentration is increased. It is improbable that the thorium ion is the adsorbed species, since practically no displacement from carbon by high concentrations of neutral electrolytes is observed at the natural pH of uranyl nitrate (pH 3).^{4,5} In addition, prior aging of the uranyl nitrate-

(4) J. Schubert, A.E.C.D. 1910.

(5) I. Adler, Ph.D. Thesis, Polytechnic Institute of Brooklyn, 1952, now at the Geochemistry and Petrology Section, Bureau of Geological Survey, Department of the Interior, Washington, D. C. UX₁ system in concentrated nitric acid, followed by dilution to 3 N, results in markedly less adsorption than that observed with a freshly prepared solution in 3 N nitric acid.¹ A reasonable interpretation of this effect is that a colloidal oxide aggregate has been broken down by the action of the concentrated acid. It is difficult to see how such an aging treatment would affect a process involving either ionic or molecular species. While this hypothesis is at variance with the known chemistry of thorium compounds in strong acid solutions, other workers have observed that at the level of concentration employed in these experiments zirconium, yttrium and thorium itself exhibit colloidal properties which markedly decrease or disappear as the concentration of the metal is increased to say $10^{-6} M.^{6-8}$ It is, of course, probable that the fraction of thorium present as colloid in strong acid solutions may be quite small; but its presence is certainly not excluded.

These conclusions, however, do little to clarify the forces operating to produce a maximum. For this reason several experiments were undertaken in which adsorbed UX_1 was desorbed.

The first experiments on desorption were designed to discover whether hydrochloric acid was the desorbing agent effective in producing the maximum. A graphite-coated glass G-M tube was introduced into a uranyl nitrate solution (1 g. per liter of 1 N hydrochloric acid). The count was observed to increase from an initial rate of 600 min.⁻¹ to a maximum of 1,000 min.⁻¹. The same tube was then stripped, recoated with aquadag, and permitted te accumulate UX₁ from a uranyl nitrate solution ($pH \sim 3$), for a period of 24 hours. The counting rate had increased to approximately 18,000 min.⁻¹. It was removed, thoroughly rinsed with distilled water and introduced into a 1 N hydrochloric acid solution. The count decreased quite rapidly at first, but then reached a steady value of 12,000 min.⁻¹, which was much greater than that observed in the adsorption study (1,000 counts/minute). The results are shown in curves A and B of Fig. 4. Curve A represents the initial adsorption from a 1 N HCl solution of uranyl nitrate; curve B describes the desorption in 1 N HCl solution. It is clear that rather concentrated solutions of hydrochloric acid are capable of removing only a minor fraction of the



Fig. 4.—Curve A, adsorption of UX_1 from 1 N HCl: curve B, desorption of previously adsorbed UX_1 in 1 N HCl; curve C, desorption of previously adsorbed UX_1 in 1 N HCl containing 2 grams of urany! nitrate/liter.

(6) J. D. Kurbatov and M. H. Kurbatov, THIS JOURNAL, 46, 441 (1942).

(7) J. D. Kurbatov and M. H. Kurbatov, J. Chem. Phys., 13, 208 (1945).

(8) M. H. Kurbatov, B. H. Webster and J. D. Kurbatov, THIS JOURNAL, 54, 1239 (1950).



Fig. 5.—A, no uranyl nitrate; B, 1 gram uranyl nitrate per liter: C, 2 grams uranyl nitrate per liter; D, 4 grams uranyl nitrate per liter; E, 8 grams uranyl nitrate per liter.

adsorbed UX_1 activity, and hence are not the major factor in causing the onset of the maximum. Since uranyl nitrate is a constituent of these solutions (as a ready source of UX_1), it was decided to test its effect on UX desorption

from Aquadag. Curve C of Fig. 4 shows the desorption of accumulated (adsorbed) UX_1 in a 1 N hydrochloric acid solution containing 2 g. per liter of uranyl nitrate. It can be concluded that the uranyl ion is more effective than strong acids in desorbing UX_1 , and hence is involved in an interaction with UX_1 .

A series of experiments were performed in which the ratio of uranyl on to UX₁ was varied, and adsorption rates were studied. The UX₁ was prepared free of uranyl salts by ether extraction and a uranyl nitrate solution was freed of UX₁ by repeated filtration through activated charcoal. All solutions had approximately the same initial activity, but the concentration of uranyl nitrate was varied. The solutions from which adsorption took place were prepared in 0.5 N hydrochloric acid. It appears that the higher the ratio of uranyl to UX₁, the less the extent of adsorption, and the more quickly the maximum is reached. This is shown in Fig. 5.

Several experiments were designed to test the effect of addition of one or another component to a system which had reached a steady state. In one, for example, UX, was adsorbed trom a

one, for example, UX_1 was adsorbed from a uranyl nitrate solution which contained 4 g./liter, in 1 N hydrochloric acid. The count rose from 600 min.⁻¹ to about 800 min.⁻¹ in one hour, and then decreased to 700 min.⁻¹ at the end of 4 hours. At this point an equal quantity of uranyl nitrate equilibrated with UX₁ was added, increasing the observed activity to 1150 min.⁻¹. There was practically no further adsorption of activity. It thus appears that a balance has been reached between the adsorption of UX₁ and its removal by uranyl salts. In contrast, Fig. 6 shows the effect of adding UX₁ (free from uranyl salts) to the system at a time when no net adsorption is noticeable. Part A shows the initial adsorption of UX₁ from uranyl nitrate solution in 1 N hydrochloric acid. At point B more UX₁ is added. It can be seen from part C of the graph that marked adsorption again occurs. The converse is also true; Fig. 7 shows that uranyl nitrate free of UX₁ causes a marked



Fig. 6.—The effect of adding UX_1 free of uranyl nitrate at the point where adsorption of the UX_1 had stopped.

desorption when it is added to a solution from which adsorption had reached a steady value.

Discussion

It must be concluded that the uranyl ion in acid solution is causing desorption of UX_1 from the graphite and that it is this process which is opposing the continuing adsorption of UX_1 on the carbon surface. The interaction of these opposing processes is reflected in the adsorption curve, which results in a maximum in acid solution. A similar effect has been reported by Kurbatov, Webster



Fig. 7.—A, initial adsorption; B, the addition of uranyl nitrate free of UX_1 ; C, resulting desorption of the adsorbed UX_1 .

and Kurbatov.⁶ Using retention by filter paper as an experimental criterion of radiocolloid formation, they found that the fraction of UX_1 retained by the paper (presumably as flocculated gel or adsorbed colloid) is markedly reduced in acid solution if uranyl salts are present.

The appearance of a maximum in the timeadsorption curve, rather than an asymptotic approach to a steady state indicates that nonequilibrium opposing processes are involved. The curve is similar to that which would be obtained if two irreversible consecutive reactions of differing but comparable rates were occurring as in the case of radioactive transient equilibrium.⁹ The first reaction is the adsorption of UX_1 on the surface of the carbon. This is, for a given solution, a diffusion-controlled process. The second step is the removal of UX_1 by the uranyl salt in the acid solution, a process whose rate would depend upon the prior accumulation of thoria, some power of the uranyl salt concentration, some power of the acidity, and some (at present unknown) functions of the surface. The observed activity does not disappear after the maximum is reached because fresh UX_1 continues to arrive at the collecting surface.

This picture is consistent with the facts which have been observed. Thus, if the uranyl concentration is increased (at constant UX_1 and acid concentrations), the time required to reach a maximum is decreased, and the accumulated activity at the maximum is decreased. However, the actual situation is undoubtedly much more complex. For example, at a fixed acidity, UX_1 concentration and uranyl salt concentration, a thicker coating of carbon will adsorb more UX_1 , and the maximum will occur at a higher level of activity and after a longer time than is observed with a thinner coating. The surface is therefore playing a part in the over-all phenomenon. One additional interesting feature of the surface reaction should be mentioned at this point. A number of Lusteroid tubes were coated with the same thickness of graphite (to the extent that this could be achieved by brush application). They were then immersed in 2 N nitric acid solutions of differing concentrations of uranyl nitrate equilibrated with UX_1 . Hence the ratio of uranyl ion to UX_1 was the same in each case, but the absolute concentrations were varied from solution to solution. Each tube was permitted to adsorb its maximum activity. The results are shown in Table I.

It is clear that, although there are differences in (9) G. Friedlander and J. Kennedy, "Introduction to Radiochemistry," John Wiley and Sons, Inc., New York, N. Y., 1949.

	Тав	LE I	
Tube	Concn. of uranyl nitrate, g./l.	Initial activity, c./min., uncor.	Adsorbed activity at maximum: final count — initial count
1	1	420	440
2	2	620	560
3	4	1400	3 80
4	8	1950	550

the amounts adsorbed, they are much smaller than the initial differences in activity. The agreement is surprisingly good when the difficulty in obtaining equal thickness of adsorber is considered. These results suggest that at a fixed acidity, with a fixed ratio of uranyl salt to UX_1 and (an approximately) fixed surface area, the graphite adsorbs practically a constant quantity of UX_1 in the region of the maximum adsorbed activity.

If attention is fixed on the uranyl salt and the UX_1 , there are two areas of interest which appear to merit further investigation. One is the fact that the uranyl compound appears to have a limited efficiency in removing the adsorbed UX_{1} , or, what is equivalent, fails to suppress adsorption except when its concentration is markedly increased relative to that of the UX_1 . This suggests that the abilities of other substances in this direction might well be studied. The second region of interest is concerned with the maximum. If the uranyl salt were simply to remove or displace the adsorbed species so that the resulting particle size was the same as that of the adsorbing species or larger, it is difficult to see why a maximum should be obtained. On the other hand, if the material were removed in such a form that its average particle was smaller than that diffusing toward the counter, it might be expected to diffuse out of the counting volume of the tube more rapidly than the adsorbing species is arriving, and a maximum would be observed. Hence it might be instructive to investigate the effect of uranyl or similar compounds on the particle size of the dispersed UX_1 .

THE PEPTIZATION OF UX₁ BY VARIOUS METALLIC IONS: A POSSIBLE MECHANISM

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Desorption of radiocolloidal $UX_1(Th^{234})$ from graphite by various metallic salts is studied in acid solution. With carrierfree UX_1 and low concentrations of desorbing agents, a high efficiency is noted with thorium, zirconium and hafnium salts (heavier members of the group IVa elements). Other compounds, including those of U(VI), Ce(IV) and Fe(III) show much less desorbing ability at low concentrations, although their efficiency increases with increasing concentration. A third group, typified by aluminum, show no desorbing ability at all. The observed specificity is ascribed to the tendency of certain ions to polymerize and form auto-complexes in acid solution. A mechanism of peptization is advanced which depends upon disruption of the gel by the formation of small hetero-complexes with the peptizing agents. The diffusion coefficient of UX_1 is shown to be almost doubled in the presence of added thorium carrier.

The previous paper¹ has discussed the interaction of radiocolloidal $UX_1(Th^{234})$ with uranyl salts in acid solution. Under the given experimental conditions the entire cycle (which includes colloid

(1) I. Adler and J. Steigman, THIS JOURNAL, 57, 440 (1953).

growth, adsorption on carbon, desorption and diffusion) is admittedly extremely complicated in character. The present paper is concerned with two simpler aspects of this cycle: the interaction of various salts with adsorbed thorium, and the possible effect of a peptizing agent on the particle size of the colloid.

The sorption of UX_1 on blood charcoal has been studied in the presence of various compounds by Freundlich and others, and is discussed in his book.² A number of substances were observed to decrease the extent of sorption and in some cases to prevent it. Thorium nitrate at a concentration of 4 \times 10^{-4} M reduced sorption by 20%, and at a concentration of 4×10^{-3} M prevented it completely. This behavior was reversible, i.e., the order of addition of reagents was not important. On the other hand, compounds like benzoic acid, zirconyl chloride, strychnine nitrate and methylene blue also prevented adsorption, but only if they had been adsorbed before the addition of the UX_1 . Freundlich explained the behavior of the latter group on the basis of saturation of valence forces at the surface of the carbon, and that of the thorium compounds by the Paneth-Fajans rule.³

Zirconyl chloride is one of the substances reported to depress the sorption of UX_1 on blood charcoal only through prior addition. Because of its general chemical similarity to thorium and in order to compare the behavior of other salts with that of uranyl compounds in their interactions with UX_1 , desorption experiments were conducted with thorium and zirconyl salts. Plastic (Lusteroid) tubes were coated with Aquadag and introduced into solutions of uranyl nitrate (pH 3) in radioactive equilibrium with UX_1 . The tubes were permitted to adsorb UX_1 for varying periods of time, up to 48 hours. They were removed, washed with distilled water and placed into the solutions in which desorption was to be studied. The desorption process was followed by introducing a Geiger-Müller tube into the plastic shell, and measuring the change in radioactivity with time. Adsorption studies were performed in the manner previously described.⁴



Fig. 1.—Desorption of adsorbed UX_1 by $ZrOCl_2$ and $Th(NO_3)_4$.

Figure 1 shows the desorption of UX_1 by thorium nitrate and by zirconyl chloride. Before the addition of the salts, each tube with accumulated UX_1 was placed in 0.1 N HCl solution with practically no desorption occurring. After several hours, sufficient thorium and zirconium compounds were added to the appropriate solutions so that each was $10^{-4} M$. In each case, desorption started immediately, and the bulk of the activity was removed in a short time. It should be noted at this point that the action of the zirconyl chloride is contrary to that reported by Freundlich.²

Figure 2 describes desorption experiments conducted in the same manner with 10^{-4} M solutions of $Y(NO_3)_3$ and FeCl₃ in 0.1 M HCl. These substances were chosen because they are notoriously prone to form colloids in dilute aqueous solution, as are most thorium and zirconium compounds. The two runs demonstrate that neither yttrium nor ferric ions are effective desorbing agents, indicating that some degree of specificity beyond a general tendency to form colloids is involved in effective removal or displacement of adsorbed UX₁. At the end of each run (five hours) each solution was made 10^{-3} M in zirconyl chloride. It is clear that the zirconium again was quite effective in removing adsorbed UX₁.



Fig. 2.—Desorption of UX_1 by $Y(NO_3)_3$ and FeCl₃. The effect of $ZrOCl_2$ is shown for comparison.

The effects of a number of other ions in desorbing UX₁ in more strongly acid solution (1 N HCl) were now investigated. These included trivalent and tetravalent titanium, aluminum, trivalent iron and divalent tin. Zirconium and thorium were also run for comparison. All metal ion concentrations were 10^{-4} M. Trivalent titanium was added as the trichloride. Tetravalent titanium was prepared from the trichloride by oxidation with several drops of concentrated nitric acid. It was observed that aluminum was far more effective than the tetravalent ion, that ferric chloride was somewhat

⁽²⁾ H. Freundlich, "Colloid and Capillary Chemistry," Dutton and Company, New York, N. Y., 1922.

⁽³⁾ G. Friedlander and J. Kennedy, "Introduction to Radiochemistry," John Wiley and Sons, Inc., New York, N. Y., 1949.

⁽⁴⁾ I. Adler and J. Steigman, THIS JOUBNAL, 56, 493 (1952).

more effective than in a less acid solution, and that stannous chloride was about as efficient as ferric chloride. What was again most striking was the outstanding desorbing ability of both thorium and zirconium in comparison with the other substances.

The preliminary desorption experiments indicated that some degree of specificity was involved; tentatively this specificity was assigned to the group IVa elements in the Periodic Table. Hafnium is one of the members of this group. The effect of its soluble salts on adsorbed UX_1 was therefore investigated. In the first experiment, a tube containing adsorbed UX_1 was immersed in 0.1 N HCl for several hours. As in previous runs, practically no desorption occurred. Hafnium chloride $(HfOCl_2)$ was then added so that its final concentration was 10^{-5} M in the 0.1 N HCl solution. A very marked desorption of UX_1 started immediately. Since spectroscopic examination showed the presence of zirconium as the major impurity in this specimen of hafnium chloride (purchased from A. B. Mackay) additional experiments were undertaken in order to make certain that the observed effect was due to hafnium. It was assumed that the contamination by zirconium was as high as 10%and a 0.1 M HCl solution which was 10^{-6} M in zirconyl chloride was used for desorption. It was evident that the 10^{-5} M hafnium chloride solution was much more effective than the more dilute zirconium in removing the adsorbed UX_1 . At equal concentrations, both hafnium and zirconium appeared to be approximately equally effective.

Adsorption on aquadag of UX_1 in the presence of a number of salts was conducted in order to see whether effective desorbing compounds would prevent adsorption. Figure 3 shows the results of such studies in the presence of $10^{-2} M$ concentrations of various substances in 0.5 M HCl. Zirconyl chloride completely suppresses the adsorption of UX_1 . Ferric and stannic chlorides cause some decrease in its adsorption. Stannous chloride is more effective than stannic chloride in preventing adsorption. Aluminum chloride, which is ineffective in desorption, is similarly ineffective in decreasing adsorption.

The effects of bismuth and cerium salts on UX_1 desorption were also investigated. Each compound was 10^{-4} M in 1 M HCl. The effect of 10^{-5} M zirconyl chloride was included for comparative purposes. The latter was obviously a much more effective desorbing agent than the more concentrated bismuth and ceric solutions. After 30 hours, the concentrations of bismuth and cerium were increased tenfold. In each case, more marked UX₁ desorption was noted, with the cerium perhaps the more efficient. The results of the various desorption experiments are summarized in Table I.

The preliminary investigation of desorbing efficiency has disclosed a wide range of behavior. The heavier elements of group IVa—zirconium, hafnium and thorium—are remarkably effective even at very low concentrations. Thus, Fig. 4 demonstrates that thorium nitrate will desorb UX₁ even when present at a concentration of $10^{-7} M$ in 0.1 M HCl. A second group of compounds, which in-



Fig. 3.—A, 0.5 N HCl; B, $10^{-2} M$ AlCl₃; C, $10^{-2} M$ SnCl₄; D, $10^{-2} M$ FeCl₃; E, $10^{-2} M$ SnCl₂; F, $10^{-2} M$ ZrOCl₂.

cludes uranyl nitrate, stannous chloride and ceric ammonium nitrate, are rather ineffective at such low concentrations, but begin to function as desorbing agents at higher concentrations. Finally, there is a third group, typified by aluminum chloride, whose members do not appear to exert a noticeable effect even at high concentrations.

TABLE I Action of Acid Solutions of Various Salts on Adsorbed UX_1 Salt Effect $Th(NO_3)_4$ Causes very marked desorption of UX₁. Effective even at $10^{-7} M$ Causes very marked de-HfOCl₂ sorption of UX1. Observed to be effective at 10-6 M ZrOCl₂ Somewhat less effective than hafnyl chloride. Observed to be effective at 10⁻⁶ M Moderately effective at Ti(III) 10-4 M Ti(IV) Much less efficient than trivalent titanium Moderately effective, but U(VI) comparatively high concentrations are required Fe(III), Sn(II), Ce(IV), Somewhat effective, but Y(III), Sn(IV) comparatively high concentrations are required Pb(II), U(IV), Al(III) Ineffective even at higher concentrations In this discussion it is assumed that the adsorbed

In this discussion it is assumed that the adsorbed thorium species is the gel or a hydroxide aggregate. This assumption is made because adsorption was carried out from solutions at the natural pH of dilute uranyl nitrate solutions (pH 3). Other workers have demonstrated that at this pH a very



Fig. 4.—The desorption of adsorbed UX₁ by various concentrations of Th(_V): A, $10^{-9} M_j$; B, $10^{-7} M_j$; C, $10^{-5} M_j$; D, $10^{-3} M$.

high proportion of UX_1 is colloidal.⁵ It is further assumed that the adsorbed species is removed by peptization. It is not yet possible to distinguish between desorption by displacement on the carbon and desorption by peptization (*i.e.*, some form of direct chemical action on the gel or aggregate). The second assumption is admittedly more tenuous than the first. However, it has led to a hypothesis which is experimentally verifiable and which is presented elsewhere in this paper. It does not, of course, mean that a displacement mechanism is excluded. Several mechanisms may be simultaneously operative in this complex process.

Earlier studies, based on macroscopic quantities of thorium hydroxide gel,⁶ have reported that ferric salts, thorium salts, hydrochloric acid, uranyl salts and others, without differentiation, bring about the redispersal of the precipitated hydroxide. The general explanation for peptization has been that a change in the charge of a gel particle takes place by the addition of a hydrogen ion or some other ion, followed by redispersion of the restabilized colloidal particle. The sharp differentiation at radiocolloidal levels, however, among dispersing agents, and in particular the extremely efficient action of the heavier group IVa elements suggests that some other mechanism may be involved.

This mechanism may be related to the conclusions drawn from a number of recent studies of the polymerization of certain inorganic ions in fairly acidic solutions: Bismuth(III), investigated potentiometrically by Graner and Sillen' appears to exist as a mixture of monomeric ion and various polymers in perchloric acid. Cerium(IV), on the basis of deviations from Beer's law, is claimed to

(6) H. B. Weiser, "The Hydrous Oxides," McGraw-Hill Book Co., New York, N. Y., 1926.

(7) F. Graner and L. G. Sillen, Acta Chem. Scand., 1, 631 (1947).

polymerize in acid solution.⁸ Uranium(VI) has been shown by studies of freezing point depressions to be polymerized in aqueous acid solution.⁹ Zirconium(IV), whose extraction by thenoyl trifluoroacetone from 2 M perchloric acid solution is concentration dependent,¹⁰ is thereby assigned a degree of polymerization. If dimers and higher polymers represent the stable forms of existence of such ions in acid solution at various concentrations, then it is possible that a gel may be disrupted by direct attack of, say, a monomeric ion to form a dimeric mixed complex, or a dimer to form a higher mixed polymer. The observed specificity of desorption could then be related to general chemical similarities resulting in isomorphous replacement. In brief, what is being suggested here is the extension of the idea of auto-complexing to hetero-complexing as a mechanism for peptization in certain cases. There are a number of implications associated with this hypothesis. One is that a radiocolloid will not persist—or will be greatly reduced in concentration—in the presence of a macroconcentration of its own or similar ions. This, at least by implication, is borne out in the desorption of UX_1 by very low concentrations of thorium nitrate $(10^{-7} \ M)$. It is also supported by the studies on radiocolloidal yttrium and zirconium reported by Kurbatov and Kurbatov.^{11,12} They found that if inactive yttrium and zirconium salts are added to the respective radiocolloids, the fraction present as colloid decreased as the total concentration of metal ion was increased. The same sort of phenomenon may also be involved in the behavior of zirconium in perchloric acid on extraction with thenoyl trifluoroacetone.¹⁰ At higher zirconium concentrations, the extraction coefficient showed a sharp decrease; this was attributed to polymer formation. However, a decrease was also noted in the concentration region from "carrier-free" or trace to about $10^{-3} M$ zirconium; above this point the coefficient was sensi-The formation of radiocolloids bly constant. could explain the decrease in extraction coefficient. Connick and McVey considered this possibility and rejected it, on the grounds that silicic acid addition did not change the coefficient. The implication was that radiocolloids form essentially by adsorption on extraneous dust particles. However, as Haissinsky has shown,¹³ this is probably a minor factor in the process of radiocolloid formation. It is interesting to note that the concentration region described is the same one in which Kurbatov and Kurbatov found the decrease in colloid fraction with increasing zirconium concentration. A more direct comparison unfortunately cannot be made because of the great difference in the acidities of the solutions which were studied.

(8) E. L. King and M. L. Pandow, J. Am. Chem. Soc., 74, 1966 (1952).

(9) J. Sutton, J. Chem. Soc., Supplementary Issue No. 2, S275 (1949).
(10) (a) R. E. Connick and W. H. Reas, J. Am. Chem. Soc., 73,

(10) (a) R. E. Connick and W. H. Reas, J. Am. Chem. Soc., 73, 1171 (1951); (b) R. E. Connick and W. H. McVey, *ibid.*, 71, 3182 (1949).

(11) J. D. Kurbatov and M. H. Kurbatov, This Journal, 46, 441 (1942).

(12) J. D. Kurbatov and M. H. Kurbatov, J. Chem. Phys., 13, 208 (1945).

(13) M. Haissinsky, "Les Radiocolloids," Hermann et Cie, Paris, 1934.

⁽⁵⁾ M. H. Kurbatev, B. H. Webster and J. D. Kurbatov, THIS JOURNAL, 54, 1239 (1550).



A second implication in this hypothesis, and one which is experimentally verifiable, is this: the diffusion coefficient of UX_1 should increase upon the addition of thorium or zirconium salts. A number of preliminary experiments were run to investigate this point. These studies were conducted in the apparatus shown in Fig. 5. A large alundum extraction thimble of medium porosity was used to create the interface through which diffusion took place. In each run diffusion took place with the same solution inside and outside the diffusion cell. Relative rates of diffusion were measured by means of a dipping Geiger-Müller tube, which was placed inside the cell. Uranyl-free and carrier-free UX₁ was added to a given solution to bring the activity to approximately 2,000 counts per minute. An aliquot of the original solution, free of UX₁, was quickly transferred to the alundum thimble, and the entire cell was quickly immersed in the main solution, which contained the UX_1 . An initial count was taken inside the thimble. Counts were then taken in the same place at 12-hour intervals. The temperature was maintained constant for all comparative runs (to $\pm 0.5^{\circ}$). Since the concentrations of the various salt solutions were quite small in comparison to the acid concentrations, changes in viscosity were considered to be negligible.

Figure 6 shows the increase in activity with time for the following solutions: 0.5 M nitric acid, 0.5 Mnitric acid containing $10^{-4} M$ thorium nitrate, 0.25M nitric acid containing $10^{-4} M$ aluminum chloride, and 0.25 M nitric acid containing $10^{-4} M$ thorium nitrate. It is clear that the rate of increase of activity (and hence, by implication, the UX₁ diffusion rates) are higher in the presence of thorium nitrate. Similar effects were observed with a 0.25 M nitric acid solution and a 0.25 M nitric acid solution containing $10^{-4} M$ zirconyl chloride. It was concluded that at least qualitatively the addition of thorium or zirconium nitrate to UX₁ causes an increase in the diffusion rate of the radiocolloid.



Fig. 6.—A, 0.25 N HNO₃, 10^{-4} M Th(IV); B, 0.5 N HNO₃, 10^{-4} M Th(IV); C, 0.25 N HNO₃, 10^{-4} AlCl₃; D, 0.5 N HNO₃.

The technique described by McBain and Liu¹⁴ was employed for a more quantitative diffusion study. In this method, material diffuses through a liquid which is immobilized in the interstices of a porous diaphragm (usually of sintered glass). The diffusion constants which result from this procedure are relative values, to be compared with that of a substance of known diffusivity measured the in same apparatus.

The diffusion cell was prepared by grinding down the lip of a Jena 46 sintered glass funnel and adding a stopcock to the tapered end. The volume of the cell was determined by weighing the content of distilled water it held. The solution of known diffusion constant which was used to calibrate it was 0.05 M HCl. The concentration of the bulk electrolyte, and the volumes were the same in the upper and lower cells, except for added UX_1 which was initially placed in the upper cell. Prediffusion was allowed to proceed for three hours in order to establish a gradient within the diaphragm. The cell was then transferred to a fresh receiving solution and diffusion was continued for 20 hours. Measurements of the radioactivity were made on the initial solution, and on the solutions in both the upper and lower cells in order to obtain a material balance. In order to correct for radioactive decay, all solutions were counted at the end of the diffusion period. Calculations were made on the basis of Fick's modified definition¹⁵

$$\mathrm{d}q = -DA \, \frac{\partial c}{\partial x} \, \mathrm{d}t$$

in which dq is the quantity of substance diffusing in time dt through a cross-section of area A and thickness ∂x in time dt, and ∂c is the change in concentration over the distance dx. If the initial concentration in the lower cells is taken as zero at zero time, the integrated equation becomes

(14) J. W. McBain and T. H. Liu, J. Am. Chem. Soc., 53, 59 (1931).
(15) A. Weissberger, "Physical Methods of Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1945.

$$D = \frac{\log C^{\circ} - \log \left(C_{u} - 2C_{1}\right)}{Kt}$$

in which D is the diffusion coefficient expressed in cm.²/day, C^0 is the initial concentration of UX₁ expressed in counts per minute, and converted to g./ml., C_u is the concentration after time t in the upper cell, and C_1 is the corresponding concentration in the lower cell. Since some adsorption of UX₁ was found to occur on the glass surfaces, calculations were based on the activity lost from the upper cell. It is realized that the results are but semi-quantitative at best, because of adsorption and because the systems are not molecularly dispersed.

The value of the cell constant \vec{K} (obtained from 0.05 *M* HCl) was 0.243 at 19° (±0.5°), the temperature which was maintained throughout all experiments. Table II is a summary of the data from which the diffusion coefficients of the UX₁ were obtained. The concentrations of UX₁ are expressed as counts/minute/ml. These numbers were converted to grams of UX₁ by means of the empirically determined linear equation

Grams UX₁ = $6.2 \times 10^{-13} \times \text{counts/minute}$

The experimental counting rates in the table represent the averages of three separate mountings of the specimens. Counts were taken with an endwindow tube. The reproducibility was better than 2%. The column entitled loss (in counts/minute) represents the difference between the initial count and the sum of the final counts in the upper and lower cells. The most probable reason for this loss was adsorption on the walls of the diaphragm (which had the greatest area of exposed glass in the system). It is interesting to note that the material balance in the first three runs (made with carrierfree UX₁) is reasonably good, indicating little adsorption.⁴ However, in determinations 4, 5 and 6, made in the presence of added thorium nitrate, a noticeable loss occurred. An attempt was made to minimize this loss by running consecutive experiments without removing the adsorbed activity. Run 7 represents the third of such a series. In this case, the material balance is relatively good.

TABLE	II
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Temp., 19°, 0.25 M nitric acid

•	Added Th $(NO_3)_4$, mg./100					<i>D</i> (cm.²/
	Detn. ml.	C_0	C_{u}	C_1	Loss	day)
1	0	2460	2170	240	50	0.45
2	0	2270	2020	195	40	.39
3	0	2340	2150	220	30	. 35
4	25	2910	2430	345	135	. 76
5	200	3740	3185	295	260	. 67
6	200	3230	2730	330	170	. 80
7	200	2080	1830	185	65	. 64

It can be seen that the diffusion coefficient of UX_1 is almost doubled in the presence of added thorium nitrate. The technique employed here is similar to that used by Schubert,¹⁶ who determined the diffusion coefficients of various fission products in uranyl nitrate solutions. After appropriate corrections for the effects of viscosity on the diffusion coefficients he concluded that a marked change occurring in a constant in the presence of added electrolyte was due to radiocolloid formation, complex formation or re-solution (depending on the direction of the change). The values reported by him are not too dissimilar to those found here.

One effect of the interaction between UX_1 and thorium salts in acid solution appears, therefore, to be a diminution of particle size. The data do not permit any further conclusion at this point. However, the hypothesis that peptizing agents form complexes with radiocolloidal UX_1 is at least qualitatively upheld.

(16) J. Schubert, A.E.C.D. 1910.

THE EFFECT OF LITHIUM HYDROXIDE ON THE ACTIVITY OF CRACKING CATALYSTS

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The addition of lithium hydroxide to four cracking catalysts lowered their activity for the cracking of cetane. The amount of lithium hydroxide required to reduce the conversion of cetane to 10%, appears to represent a measure of the catalyst acids active in the decomposition of paraffins. A silica alumina cracking catalyst which had been rendered inactive for the cracking of cetane by the addition of lithium hydroxide was more active than the original catalyst for the decomposition of disobutylene, and maintained a high proportion of its original activity for the decomposition of cumene. Potassium hydroxide was a more effective poison per mole than lithium hydroxide, but seemed to follow the pattern established for lithium hydroxide.

The effect of alkali metal ions on the activity of cracking catalysts has recently been reported by Bitepazh² and Mills, Boedeker and Oblad.³ The general effect cf alkalies was to lower greatly the activities of cracking catalysts. In our work the

(1) Department of Chemistry, University of Minnesota.

(2) Yu A. Bitepazh, J. Gen. Chem. (U. S. S. R.), 17, 199 (1947).

(3) G. A. Mills, E. R. Boedecker and A. G. Oblad, J. Am. Chem. Soc., 72, 1554 (1950).

effect of lithium hydroxide on the activities of a number of catalysts for the cracking of cetane, and on a single catalyst for the decomposition of isopropylbenzene and diisobutylene was investigated. It appears that the acid components of the catalysts active for cracking paraffins can be determined by the equivalents of lithium hydroxide required to lower the cracking activity for cetane to a value which shows little farther decrease on the addition

50 cc. Socony-Vacuum	synthetic bead	catalyst	, liquid	hourly s	pace velo	city, 2.0,	charge 1	100 ml.	cetane, '	76.6 g.
Temp., °C.	498	498	498	492	498	501	501	495	501	500
Meq. LiOH/g. cat.	0.00	0.021	0.100	0.168	0.250	0.335	0.405	0.59	0.64	$1 \ 15$
Wt. % of charge										1
Gas	29.5	28.0	23.6	18.2	14.4	11.3	8.9	7.1	7.5	3.8
Coke	0.7	0.7	0.5	0.5	0.3	0.2	0.1	0.1	0.1	0.0
Gasoline	6.9	7.7	6.4	7.1	6.0	3.0	1.6	2.9	2.0	2.1
Cetane	60.6	63.4	68.9	72.8	78.5	85.4	88.6	89.4	89.6	94.0
Loss	2.3	0.2	0.6	1.4	0.8	0.1	0.8	0.5	-0.2	0.1
Conversion, loss free	38.0	36.5	30.7	26.2	20.9	14.5	10.7	10. 2	10.5	5.9
Gas composition, vol. %										
<i>i</i> -C ₄ H ₈	10.5	13.4	13.4	15.5	12.6	16.2	12.8	14.3	14.2	9.4
Other olefins	43.0	42.4	45.1	46.7	47.0	48.5	46.4	56.7	46.9	50.1
Residual gas (paraffin s)	46.5	44.2	41.5	37.8	40.4	35.3	40.8	29.0	38.9	40.5
Mol. wt., gas	49.4	46.4	48.5	48.8	51.2	49.6	45.5	45.2	50.5	41.4

TABLE I CONVERSION OF CETANE

of more lithium hydroxide. Catalysts which have been rendered inactive for the cracking of cetane retained a high activity for the decomposition of diisobutylene and cumene.

Materials. Charging Stocks .-- Cetane was the du Pont product. Diisobutylene was purchased from Matheson. Cumene was obtained from Eastman Kodak Co. In each case the purest material offered by the indicated company was used.

Catalysts.-The calcined Socony Vacuum synthetic bead catalyst contained 10% by weight Al_2O_3 coprecipitated with silica. Specifications for this catalyst include the following data

Size of beads (av.)	3 mm. diameter
Bulk density	0.7 g./ml.
Surface area	$420 \text{ m}.^2/\text{g}.$
Composition, %	SiO ₂ , 89.5
• , • -	$Al_2O_3, 10.0$
	H ₂ O. 0.5

The calcined U.O.P. Type B catalyst contained 86.2% silica, 9.4% zirconia and 4.3% alumina. It was in the form of $\frac{1}{8}$ inch pills and had a surface area of $346 \text{ m}.^2/\text{g}.$

Shell silica-magnesia catalyst had the following specifications:

Commercial 3E catalyst powder purchased from Davison Chemical Company, pelleted with Sterotex and white flour, broken to a 8-16 mesh granules, calcined at 565° in air to remove Sterotex and flour.

remove Sterotex and hour. Chemical analysis, ignited basis (percentages): MgO, 31%; Al₂O₃, 0.68; Fe₂O₃, 0.22; CaO, C.19; Na₂O, 0.05; SO₄⁻, 0.04; Cl⁻, 0.05; SiO₂, 68 (by difference). Shell experimental alumina-boria catalyst was received as 8-16 mesh calcined granules. It contained 11.8% B₂O₃ on grade A Alorco alumina. Its bulk density was 0.93 g./cc. and its surface area was 191 m.²/g. The impregnation of catalysts was carried out as follows. Fifty-ml samples of each catalyst ware weighed, put in

Fifty-ml. samples of each catalyst were weighed, put in bottles and covered with distilled water. Lithium hydroxide was added from a buret in an amount necessary to give the desired meq./g. of catalyst. In a representative case samples were prepared to contain 0, 0.1, 0.2, 0.3, 0.4, 0.6 and 1.0 meq./g., although subsequent variations in the amounts were frequently made after the initial results were obtained. The samples were allowed to stand for times which varied from a week to more than two weeks. It was observed that the silica-alumina and silica-alumina-zirconia composites adsorbed the caustic completely (neutral to phenophthalein) up to the point at which the activity for the cracking of cetane had reached a minimum. A portion of additional caustic remained unadsorbed beyond this point. The unadsorbed caustic was decanted and the cata-lyst washed once with distilled water. The effluent liquids were combined and unadsorbed caustic was determined by titration with standard acid.

End-points were easily obtained on the Socony-Vacuum

catalyst and the U.O.P. Type B catalyst and the data on these catalysts are considered accurate.

The Shell Al₂O₃-B₂O₃ catalyst adsorbed the caustie completely up to 0.3 meq./g., but beyond this value the unadsorbed caustic was not accurately determined because the end-point of the titration was difficult to discern. Although the silica-alumina and silica-alumina-zirconia catalysts gave clear solutions on back titration of the excess caustic, the Al₂O₃-B₂O₃ catalyst produced a slight cloud of solid, presumably due to solution of traces of the catalyst in the lithium hydroxide solution. The amounts of adsorbed caustic recorded for this catalyst are the total amounts added, although it is certain that a small undetermined amount remained unadsorbed at the higher concentrations of caustic.

The silica-magnesia catalyst was similar to the aluminaboria catalyst and a fine solid remained suspended in the caustic solution. Magnesium was identified as one of the suspended components. By rapid titration of the decanted solutions, satisfactory end-points were obtained, but more and more acid could be consumed as it dissolved the magne-sium oxide floc. The data from the rapid titrations were used to calculate the total caustic adsorbed, and, while not as accurate as the data for the silica-alumina catalysts, they appear satisfactory.

After decanting and washing, the catalysts were dried at 110°. Each catalyst was allowed to stand overnight in the furnace at the indicated temperature of the run.

Apparatus and Procedure.—An electrically heated graphite block furnace contained a glass reaction tube of 22 mm. diameter vertically placed in the furnace. A 6 in. length of glass chips with an auxiliary preheater was placed above the 50 ml of catalyst which was supported by a lower 6 in. section of glass chips. By means of a sliding thermocouple centrally located in a 7 mm. glass thermocouple well, the temperatures at the top, middle and bottom of the catalyst bed were recorded at each 10-ml. interval of charge. The average of these temperatures has been recorded as the temperature of the run. All runs were made at atmospheric pressure. Liquid was pumped downward through the catalyst bed at a rate of 100 cc. per hour. All runs were of one hour duration. Liquid was condensed in two ice receivers in series and the uncondensed gas was sampled at proportioned intervals in a gas bottle. The condensed liquid was stabilized to a reflux temperature of 20° and the stabilized gas collected in a second gas bottle. In the cetane runs the stabilized liquid was distilled to a reflux temperature of 250°. The overhead was specified as gasoline and the undistilled bottoms as cetane. Gases were anaand the undistilled bottoms as cerane. Gases were ana-lyzed for oxygen (air), isobutylene, other olefins and re-sidual paraffins, and their molecular weights determined by conventional methods. For recording in the tables the composition and molecular weight of the total gas was cal-culated from the above data. The weight of catalyst re-moved was recorded and the per cent. carbon on a small sample of the catalyst was determined by combustion and absorption of the CO₂ in Ascarite.

The reaction by which cumene decomposed to propylene

and benzene in the presence of a cracking catalyst is well established. In the case of cumene decomposition, the percentage decomposed was calculated from the total volume of gas on the assumption that 25 l. of the gas at room conditions represented one mole of propylene. One mole of propylene would result from the decomposition of one mole of cumene.

The activity of the catalyst for the decomposition of diisobutylene was considered proportional to the volume of gas formed. The per cent. conversion of diisobutylene was calculated on the assumption that two moles of C_4 gas would form for each mole of diisobutylene reacting.

Conversion of cetane was calculated as the weight per cent. of gas, gasoline and coke. When coke was less than 0.05%by weight of the charge it was recorded 0.0. Values from 0.05 to 0.1 were recorded as 0.1%. All conversions have been expressed on a loss free basis. The weight percentages of gasoline and cetane were expressed on a loss free basis after each distillation, and the loss expressed in the tables represents material not accounted for originally as gas, liquid product and coke.

Results

The conversions of cetane by four catalyst samples which had been treated with various amounts of lithium hydroxide are shown in Tables I through IV. In Fig. 1 the conversions from these tables have been plotted as cetane conversion versus milliequivalents of lithium hydroxide per gram of catalyst. Data for KOH adsorption on one of these catalysts is included. Although each curve could be drawn as a smooth curve, it seemed that it could properly be divided into two portions. The first portion in the range of high conversions exhibited a straight line decrease with increasing amounts of lithium hydroxide. In the second portion additional lithium hydroxide resulted in little further decrease in conversion. A value of 10% conversion represents the point at which the initial straight line portion of high slope converged with the second portion in which little change in conversion was produced by additional lithium hydroxide. This break in the slope of the curve appears to represent the point at which the catalyst acid, active for the cracking of cetane, has been



Fig. 1.—Conversion of cetane vs. meq. LiOH per g. for several catalysts: A, Socony Vacuum SiO₂-10% Al₂O₃ with KOH; B, Socony Vacuum SiO₂-10% Al₂O₃; C, UOP Type B SiO₂-9.4% ZrO₂-4.3% Al₂O₃; D, SiO₃-31% MgO; E, Al₂O₂-11.8% B₂O₃.

TABLE II

CONVERSION OF CETANE

50 cc. U.O.P. type B catalyst, liquid hourly space velocity, 2.0, charge 100 ml. cetane, 76.6 g.

	0			,	0		
Temp., °C.	487	499	490	500	502	504	511
Meq. LiOH/g, cat.	0.00	0.053	0.10	0.21	0.31	0.41	0.80
Wt. % of charge							
Gas	32.3	29.4	25.8	14.5	7.7	6.3	3.3
Coke	0.9	0.4	0.3	0.3	0.1	0.1	0.0
Gasoline	11.9	10.3	9.7	6.8	5.5	3.5	3.2
Cetane	53.6	56.6	63.1	77.1	84.7	90.0	93.4
Loss	1.3	3.3	1.1	1.3	2.0	0.1	0.1
Conv., loss free	45,7	41.4	36.3	21.9	13.6	9.9	6.5
Gas composition, vol	. %						
$i-C_4H_8$	19.1	19.0	20.2	19.7			
Other olefins	44.5	45.8	58.0	50.3			
Residual gas							
(paraffins)	36.4	35.2	21.8	30.0			
Mol. wt., gas	49.4	49.8	50.0	48.5			

TABLE III

CONVERSION OF CETANE

50 cc. Al₂O₃-B₂O₃ catalyst, liquid houriy space velocity, 2.0, charge 100 ml. cetane, 76.6 g.

,	0				0			
Temperature, °C.	489	490	491	491	493	497	497	
Meq. LiOH/g. cat.	0.00	0.10	0.20	0.30	0.40	0.60	1.00	
Wt. % charge								
Gas	41.9	41.4	27.4	13.1	18.3	9.2	3.4	
Coke	0.5	0.3	0.1	0.0	0.0	0.0	0.0	
Gasoline	16.7	14.5	13.6	8.2	10.3	6.8	4.6	
Cetane	36.3	43.8	55.0	76.1	69.7	82.1	91.7	
Loss	4.6	0.0	3.9	2.6	1.7	1.9	0.3	
Conv., loss free	62.0	56.2	42.8	21.9	29.1	16.8	8.0	
Gas composition, vol.	Gas composition, vol. %							
$i-C_4H_8$	18.4	19.2	19.4	19.1	19.8	26.3	29.0	
Other olefins	43.9	45.9	49.4	47.4	49.7	40.2	35.7	
Residual (paraffins)	37.7	34.9	31.2	33.5	30.5	33.5	35.3	
Mol. wt., gas	47.7	51.4	49.7	47.8	46.2	43.4	39.1	

TABLE IV

CONVERSION OF CETANE

 $50~{\rm cc.~SiO_2-MgO}$ catalyst, liquid hourly space velocity, 2.0, charge 100 ml. cetane, 76.6 g.

-				-		
Temp., °C.	500	490	493	493	496	498
Meq. LiOH/g. cat.	0.00	0.00	0.20	0.30	0.50	1.26
Wt. % charge						
Gas	42.4	36.7	33.7	30.9	23.6	4.6
Coke	0.7	0.5	0.4	0.3	0.0	0.0
Gasoline	24.5	26.2	23.8	21,6	19.9	9.4
Cetane	28.1	32.6	37.8	42.5	53.5	85.7
Loss	4.3	4,0	4.3	4.7	3.0	0.3
Conversion, loss free	70.7	66.1	60.4	55.4	4 4.8	14.1
Gas composition, vol. %						
1-C4H8	18.9	20.0	19.6	19.3	21.1	
Other olefins	46.7	46.3	49.6	49.9	49.9	
Residual (paraffins)	34.4	33.7	30.8	30.8	29.0	
Mol. wt., gas	50.8	52.2	51.4	51.4	52 .1	

neutralized. On this basis the straight line portion of each curve in Fig. 1 has been extended to cross the line of 10% conversion of cetane. The milliequivalents of lithium hydroxide required to reduce the conversion to 10% is considered a measure of the milliequivalents of active catalyst acid originally present. Thus, the milliequivalents of active acid per gram of catalyst can be determined. Since substantially complete adsorption of lithium hydroxide occurred on catalysts showing conversions greater than 10% (except for SiO₂-MgO), it is apparent that the strong acids (*i.e.*, active in the conversion of cetane) were neutralized first, and that only at higher concentrations of caustic would the weaker acid components be neutralized. In the Thomas⁴ method of determining acidities by the reaction of the catalyst with an excess of 0.1 N potassium hydroxide, acid components inactive for the cracking of cetane are also measured.

Thus, the Socony–Vacuum bead catalyst had an acidity greater than 2.0 meq./g. by the Thomas method, but as little as 0.40 meq. LiOH/g. practically eliminated its activity for the cracking of cetane. In view of the proportional decrease in activity for cetane cracking produced by small quantities of LiOH, it seems likely that these decreases are the result of a direct neutralization of the most active components of the catalyst. The choice of 10% conversion as the value upon which the neutralization of the active acid is based presumably depends upon the charging stock and the severity of the cracking conditions. Measured catalyst acidities are compared with calculated acidities in Table V. In calculating the acidities all of the minor component was considered to have reacted to form the acid of the indicated formula. The necessary amounts of water were included in the catalyst weight although it seems likely that the anhydrides of the indicated acids are the active components at cracking temperatures. It was assumed that only the first hydrogen of the polyprotic acids would be active.

TABLE V

	IABI			
Catalyst	Assumed acid formula4	Calcd. acidity, meq./g.	Obsd. acidity, meq./g.	Calcd. acidity, %
Socony-Vacuum				
10% Al ₂ O ₃ on SiO ₂	(HAlSiO ₄) _x	1.93	0.40	20.7
U.O.P. Type B				
9.4% ZrO2	$(H_4Z_rSi_2O_8)_x$	1.55	. 34	21.9
4.3% Al ₂ O ₃ on SiO ₂	$(HAlSiO_4)_x$			
Shell				
11.8% B ₂ O ₃ on Al ₂ O ₃	$(H_{c}AlB_{2}O_{6})_{z}$	1.62	.66	40.6
Shell				
31% MgO on SiO2	$(H_2MgSiO_4)_x$	6.8	1.32	19.4

It is interesting to observe that all three catalysts in which silica represented the component in execss showed acidities approximately 20% of the theoretical value. This agreement between three catalysts of varying composition can be interpreted to indicate that the silica structures in which the active acid or acid anhydride is distributed are similar in porosity and the proportion of total acid that is available.

The observed acidities of the U.O.P. Type B and the Socony Vacuum bead catalyst would be expected to be in the range of acidities determined for other cracking catalysts of similar activity and type. Tamele⁵ has determined an acidity of 0.35 meq./g. for a catalyst containing 10.3% Al₂O₃ on silica by titration with *n*-butylamine in a nonaqueous medium. An active Houdry silica-alumina catalyst was reported to have an acidity of 0.32 meq./g. by titration.⁶ These values of acidity are appreciably below the calculated values of catalyst acidity and appear to fall in the same range as the acidities determined in our investigation.

Mills and Oblad⁶ indicate that the variation in base exchange capacity of a catalyst as ε function of pH

(4) C. L. Thomas, Ind. Eng. Chem., 41, 2564 (1949).

(5) M. W. Tamele, Faraday Soc. Discussion, No. 8 (1950).

(6) G. A. Mills and A. G. Oblad, "Advances in Catalysis," Vol. 111, Academic Press Inc., 1951, pp. 199-247. with the resulting hysteresis effect can be interpreted to mean that the catalyst creates baseexchange capacity while it is being measured, and further state that they believe the only valid demonstration and measurement of the acidity of cracking catalysts has to be based on the observations of chemisorption of basic substances from a non-aqueous base.

It is our opinion that the direct dependence of cracking activity on the amount of lithium hy-droxide adsorbed at the low concentrations of adsorbed caustic indicates that only strong acid hydrogens are exchanged, and that additional base exchange occurs only when an excess of the particular ion over that required for the neutralization of the strong acid is available. We believe that this point has been reached at our higher caustic concentrations where minor quantities of lithium hydroxide remain unadsorbed in the solution in equilibrium with the catalyst. In this range baseexchange capacity has little or no relation to activity. It is considered an important part of our work that in the range in which additional lithium hydroxide caused a direct decrease in conversion no unadsorbed lithium hydroxide remained in the solution in equilibrium with the catalyst. This situation is, of course, different from that in which impregnations are made from higher concentrations of salt solutions.

Preliminary work using KOH in place of LiOH indicates that essentially the same pattern is obtained. Thus the Socony Vacuum catalyst impregnated with 0.05, 0.10 and 0.45 meq. KOH/g. gave cetane conversions of 30.2, 21.2 and 5.9%, respectively. Although the data on KOH are not considered as precise as those for LiOH, it is shown in Fig. 1 that only 0.18 meq. K⁺/g. was required to reduce the cracking activity to 10% on the Socony-Vacuum catalyst. It is not surprising that the potassium ion is more efficient in lowering the catalyst activity, since it covers an area almost five times as large as that covered by a lithium ion.

The data of Mills, Boedecker and Oblad³ show that 0.06 meq. quinoline/g. is chemisorbed on a calcined silica-12.5% alumina catalyst. Assuming that the quinoline molecule lies flat and covers an area of 36 sq. A., approximately 13 sq.m./g. of the catalyst was covered by quinoline. At 0.18 meq./g. for K⁺ and 0.40 meq./g. for Li⁺, the catalyst surface covered is 6.0 and 2.7 sq. m./g., respectively. Since we would not expect significant differences in the base exchange capacity for lithium and potassium ions on a given catalyst, we believe that the greater poisoning effect of potassium ion is primarily a function of the amount of surface covered. Furthermore, the large quinoline molecule seems to be even more effective than the smaller alkali ions in its poisoning effect. The idea that poisoning is a function of area covered is in agreement with the conclusions of Bitepazh.² It is entirely possible on uncalcined catalysts or on calcined catalysts impregnated with solutions containing a high concentration of the metal ion, that base exchange may play a major role. This is not believed to be the case under the conditions of our work.

However, less than 2% of the total catalyst surface has been covered by the lithium and potassium ion and approximately 4% of the total catalyst surface was covered in the work on quinoline. Unless the active acid centers are grouped in clusters at relatively few points on the surface, it is difficult to explain how the covering of such a small per cent. of the surface could render the catalyst inactive, and at the same time show an increase in

poisoning effect when a larger ion of presumably similar basicity and base exchange capacity is used. It is our opinion that the size of the adsorbed ion is an important variable, but additional variables seem to be involved.

Because of its small size the lithium ion would appear to be the most efficient of the alkali ions for the determination of catalyst acidities, although it would not be certain that some lowering of activity due to mechanical covering of the surface would not also occur with lithium ion. The authors have not investigated variables of operation to the extent required to present this method of determining acidities as a recommended procedure. It is our opinior, however, that extrapolation of activity data on catalyst samples impregnated with lithium hydroxide as described in this article can be developed into a quantitative and reproducible method for determining acidities of cracking catalysts.

In a second phase of this investigation the Socony Vacuum bead catalyst, which had been made inactive for cetane cracking by the addition of lithium hydroxide, was tested for its activity in the decomposition of diisobutylene and cumene. Such catalysts have been reported to be more active than the original, for the decomposition of butyric acid and acetor.⁷

Conversions of cumene for various amounts of lithium hydroxide are shown in Table VI. Although some lowering in activity resulted from the addition of lithium hydroxide to the catalyst, it is observed that the catalysts containing 0.48 and 0.71 meq. LiOH/g. continue to give two-thirds of the conversion observed on the original catalyst.

TABLE VI

Conversion of Isopropylbenzene

50 cc. Socony-Vacuum synthetic bead catalyst, liquid hourly space velocity, 2.0, charge 100 ml. isopropylbenzene (86.1 g., 0.718 mole)

Temp., °C.	478	475	478	477	477
Meq. LiOH/g. cat.	0.00	0.10	0.246	0.478	0.707
Gas volume, l.	10.84	10.50	9.01	7.69	7.38
Conversion, %	60.3	58.4	50.0	42.7	40.7

In Table VII an apparent increase is observed in the decomposition of diisobutylene by a catalyst containing as much 1.34 meq. LiOH/g. Similar

(7) M. Demorest, D. Mooberry and J. D. Danforth, Ind. Eng. Chem., 43, 2569 (1951).

TABLE VII

CONVERSION OF DIISOBUTYLENE

50 cc. Socony-Vacuum synthetic bead catalyst, liquid hourly space velocity, 2.0, charge 100 ml. diisobutylene (71.5 g., 0.638 mole)

Temp., °C.	402	397	395	398
Meq. LiOH/g. cat.	0.00	0.246	0.715	1.34
Gas volume, I.	25.4	27.1	27.1	27.2
Conversion, %	79.8	85.0	85.0	85.4

results were obtained on a catalyst which had been impregnated with 0.45 meq. KOH/g. This latter catalyst was quite inactive for the cracking of cetane, giving a conversion of only 5.9%, but it gave a conversion of diisobutylene of 77% which was approximately the conversion shown in Table VII for the untreated catalyst. It has been clearly shown that catalysts which have been rendered inactive for the cracking of cetane by the presumed neutralization of active catalyst acid, still retain a high activity for other reactions which are usually considered to be acid catalyzed. These data support clearly the supposition that paraffins are cracked by strong acids, but it is more difficult to explain how a catalyst which has remained in contact with an alkaline solution for periods greater than one week, can maintain such a high activity in the decomposition of diisobutylene and cumene.

To be consistent with the current theory of acid catalysis in these reactions,⁶ it can be assumed that weak acids are not neutralized by the amounts of caustic added, and these acids are sufficiently active to promote the decomposition of olefins and alkylaromatics which are much stronger Lewis bases than the paraffin hydrocarbons. However, since acidic oxides as weak as carbon dioxide would be neutralized at the equilibrium pH attained on neutralizing several of the catalysts, it may be worthwhile to consider an activity for these composites that is not directly associated with their acidity.

Summary

The acidity of cracking catalysts responsible for the cracking of cetane can be determined by the amount of lithium hydroxide required to reduce the conversion of cetane to a value which shows little further decrease on the addition of more lithium hydroxide. Catalysts which have been rendered inactive for cetane cracking by the adsorption of lithium hydroxide exhibit an increased activity for the decomposition of diisobutylene, and retain a surprisingly high proportion of their activity for the decomposition of cumene. Less complete data indicate that potassium hydroxide is more effective in poisoning the catalyst, but appears to follow a pattern similar to that observed with lithium hydroxide.

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VELOCITY OF SOUND IN LIQUIDS AND MOLECULAR WEIGHT

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A close examination of Rao's² formula $v^{1/s}(M/\rho) = R$ reveals that in a modified form, it could be made use of in the determination of sound velocities in organic liquids. In the present work, it has been shown that if, instead of $v^{1/s}(M/\rho) = R$ against M, only $v^{1/s}/\rho$ is plotted against M, a family of curves is obtained for the homologous series. The general equation for the family of curves is of the type $v^{1/s}/\rho = A + B/M$ where A = 13.56 is constant for all the series and B varies from series to series, while a plot of $v^{1/s}/\rho$ against 1/M shows that curves are transformed to straight lines, which diverge from the same point (0, 13.56). It has been tested for some homologous series. The calculated values of sound velocity from the new formulas have been compared with the observed values. The modified form suggests some remarkable regularities in the curves of different homologous series.

Introduction

In 1938, as a result of extensive work on sound velocity, Parthasarathy¹ derived a few empirical rules relating to sound velocity and chemical constitution. Later, Rao² in 1940 on the basis of Parthasarathy's work in organic liquids, put forward an empirical formula $v^{1/*}(M/\rho) = R$ between sound velocity v, molecular weight M and the density ρ . R, termed the molecular sound velocity by Lagemann,³ when plotted against M, gave a parallel set of straight lines. As R is a function of the molecular volume and cube root of sound velocity and as $v^{1/*}$ also does not vary much from member to member in every series, it was thought desirable to examine the relationship eliminating M from both sides of the above equation.

Results and Discussion

Rao,² from his formula, *viz.*, $v^{1/2}(M/\rho) = R$ found that R was a constant, independent of temperature for the same compound. He deduced values for different elements and bonds on an analogy of parachor and showed that R is an additive function. This is evident from the formula itself since molecular volume V is involved in the formula.

It was of interest to examine the behavior of the formula if the factor M is removed from the left hand side, *i.e.*, the modified form of the formula becomes $(v^{1/4}/\rho) = K$, a temperature independent constant different from Rao's R. This could well be derived from the ratio of the temperature coefficient of sound velocity and temperature coefficient of volume expansion. According to Rao,⁴ this ratio, *i.e.*

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$$(1/v)(dv/dt)/(1/v)(dv/dt) = -3$$

(1/v)(dv/dt)/(1/e)(de/dt) = +3 (as $V = M/\rho$)

i.e., the ratio of the temperature coefficient of sound velocity to that of the temperature coefficient of density is a constant equal to +3. This constant (K) behaves in an entirely different manner. Whereas *R* increased in every series with an increase in the molecular chain, *K* does not necessarily behave so. In some series, it increases with the

(1) S. Parthasarathy, several papers in the Proc. Ind. Acad. Sci. and Curr. Sci.; Bergmann's "Der Ultraschall," 1949.

(2) M. R. Rao, Ind. J. Phys., 14, 109 (1940).

(3) R. T. Lagemann and W. S. Ducbar, THIS JOURNAL, 49, 428 (1945).

(4) M. R. Rao, J. Chem. Phys., 9, 682 (1941).

increase in the length of the chain and in some cases it decreases with the increase in the length of the chain.

When $v^{1/4}/\rho$ is plotted against $1 \times 10^3/M$ a set of straight lines diverging from a point (0, 13.56) is obtained (see Fig. 1). Their slopes are in the order aliphatic hydrocarbons > 1-olefins, where the series indicates the magnitude of the slope till it comes to aliphatic alcohols for which the line runs approximately parallel to the x-axis. For the other series the gradient changes its sign and follows the order aromatic hydrocarbons > alkyl chlorides > fatty acids. This indicates that the intercept for all the curves is the same whereas the slope varies for each curve.



A general equation of the type $v^{1/2}/\rho = A + (B/M)$

can be ascribed to these lines where

- v
- = velocity of sound at temperature t° = density of the liquid at temperature t°
- M = molecular weight of the liquid
- A = a constant which is the same for all the series
- studied, and B = constant for the same homologous series but is different for different series.

From the above formula, we have calculated B the characteristic constant for each of the homologous series. They are given below

	TABLE I							
	Series	A	B $ imes$ 10 $^{-3}$					
1	Aliphatic hydrocarbons	13.56	176					
2	1-Olefins	13.56	135					
3	Aliphatic alcohols	13.56	- 15.0					
4	Aromatic hydrocarbons	13.56	- 79.56					
5	Alkyl chlorides	13.56	-157					
6	Fatty acids	13.56	-215.2					

The above formula has been used in predicting the values of velocities of sound for different liquids of the homologous series given in Table II. Knowing the values of ρ , M and B for a homologous series as shown in Table I the values of v are calculated. In Table II (i to vi) are tabulated the observed and the calculated values of sound velocity obtained in this manner. How well they agree can be seen from the tables. Hence knowing the values of ρ , M and B for a series, the sound velocity could be predicted with sufficient accuracy by the above formula.

TABLE II

Liquid (i) Aliphatic hydrocarbo	Obsd. values v in m/s from Bergmann Dns: $v = 13.56$ -	Calcd. values v in m/s + (176/M)
Pentane	1008	1007
<i>n</i> -Hexane	1083	1088
<i>n</i> -Heptane	1162	1150
n-Octane	1197	1194
n-Nonane	1248	1233
(ii) 1-Olefins: v	= 13.56 + (135)	(M)
1-Heptene	1128	1129
1-Octene	1184	1189
1-Nonene	1218	1231
1-Decene	1250	1256
1-Undecene	1275	1 27 9
1-Tridecene	1313	1319
1-Pentadecene	1351	1359

(iii) Aliphatic alcoh	ols: $v = 13.56$ -	(15.0/M)
Methyl	1123	1112
Ethyl	1180	1140
n-Propyl	1223	1224
n-Butyl	1268	1255
n-Amyl	1294	1305
n-Hexyl	1322	1324
n-Heptyl	1341	1351
n-Octyl	1358	1373
n-Nonyl	1391	1384
n-Decyl	1402	1395
(iv) Aromatic hydrocar	bons: $v = 13.56$	- (79.56/ <i>M</i>)
Benzene	1310	1309
Toluene	1320	1317
Xylene	1330	1328
(v) Alkyl chloride	es: $v = 13.56 - ($	157/M)
n-Propyl	1091	1088
n-Butyl	1133	1153
n-Hexyl	1221	1222
n-Octyl	1280	1297
n-Decyl	1318	1321
(vi) Fatty acids:	v = 13.56 - (21)	5.2/M)
Acetic	1150	1146
Propionic	1176	1179
Butyric	1203	1209
Valeric	1244	1256
Caproic	1280	1286
Oenanthic	1312	1320
Caprylic	1331	1323

As regards the constant "A," it is remarkable to observe that it has the same value in all the series studied. The significance of this constant is still not clear. As an example illustrating further the importance of "A," it can be mentioned that in another paper⁵ (under publication) on viscosity and sound velocity, the same constant has appeared in their relationship. Further exploratory work is needed before one can give any meaning to "A." Work along these lines is being continued in other directions and it is hoped that an insight into intermolecular forces may be obtained through "A."

(5) Relation between velocity of sound and viscosity in liquids, S. Parthasarathy and N. N. Bakhshi. (Under publication in the Proceedings of the Physical Society of London).
SURFACE ROUGHNESS AS RELATED TO HYSTERESIS OF CONTACT ANGLES. II. THE SYSTEMS PARAFFIN-3 MOLAR CALCIUM CHLORIDE SOLUTION-AIR AND PARAFFIN-GLYCEROL-AIR¹

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Paraffin surfaces of controlled roughness were prepared as previously described by ruling in such a manner as to produce on the surface regular pyramids of height h and angle of inclination ϕ of the faces. As with the system paraffin-water-air previously reported upon, so also in the systems paraffin-3 M calcium chloride-air and paraffin-glycerol-air, contact angle values were unaffected by changes in the height h. For the system paraffin-3 M calcium chloride-air, both the apparent advancing and the apparent receding contact angle values increased for an increase in ϕ . For the system paraffin-glycerolair, the apparent advancing contact angle values increased, while the apparent receding contact angle values decreased for an increase in ϕ . Hysteresis values for both systems studied increased with an increase in the angle of inclination, but were relatively independent of changes in the height of the asperities. Wenzel's theory was found to be inapplicable to the data obtained for the paraffin systems involving water, 3 M calcium chloride, and glycerol. It was demonstrated that the contact angle and resultant drop shape are determined at the line of contact of the solid-liquid-air interface and are not altered by surface irregularities beneath the bulk of the drop.

Discussion

It was shown in a previous paper³ that the physical structure of a paraffin surface can considerably enhance its non-wettability when the liquid involved is water. In the present investigation the effect of the physical structure of the paraffin surface, *i.e.*, surface roughness, on wetting by two other liquids has been studied. One of these liquids, 3 M calcium chloride solution, exhibits on a smooth paraffin surface, a contact angle greater than that shown by water, while the other liquid, glycerol, gives a contact angle less than that of water.

The surfaces used in this research were prepared from blocks of the same paraffin melt used in the previous work. Smooth surfaces were obtained by pressing the block against a clean plate glass surface. A series of rough surfaces was prepared by ruling as previously described³ so as to produce surfaces composed of a large number of regular pyramids. By fixing the angle of inclination ϕ of the faces of the pyramids, and the height hof the pyramids, one completely defines the geometry of the surface. Surfaces were ruled at angles of inclination ϕ , of 30. 45 and 60°. For a given angle of inclination a series of surfaces was produced with different pyramid heights or groove depths. The method and apparatus used for determining contact angles of liquids on these surfaces have been described.⁴

Materials Used.—A 3 M calcium chloride solution was prepared from reagent grade calcium chloride and distilled water. The water was distilled from an alkaline permanganate solution in an all Pyrex still. The surface tension of the distilled water was 72 dynes/cm. The surface tension of the solution saturated with paraffin was 84.5 dynes/cm.

Reagent grade glycerol was distilled under vacuum in a twenty-stage Brunn column. The middle fraction was collected and used after saturation with paraffin. The surface tension of the glycerol saturated with paraffin was 63.2 dynes/cm.

All surface tensions were determined by the Pendent Drop Method.⁴

The data obtained for the systems studied are presented in Tables I and II. For both the 3 Mcalcium chloride and the glycerol systems the apparent advancing and receding angles were relatively independent of the height h. An increase in the angle of inclination ϕ of the pyramid faces produced an increase in both the apparent advancing and the apparent receding contact angles observed for the paraffin-3 M calcium chloride-air system. For the paraffin-glycerol-air system an increase in ϕ resulted in an increase in the apparent advancing contact angle but produced a decrease in the apparent receding contact angle. In contrast to these alterations of the apparent receding contact angles with increase in the angle of inclination, the previously reported water receding angles remained relatively unchanged with increase of angle of inclination. The hysteresis observed for both the systems studied in the present research increased with an increase in ϕ .

TABLE I

PARAFFIN-3 M CALCIUM CHLORIDE SOLUTION-AIR CONTACT

		ANG	LES		
Surface	Spacing, in.	h, in.	$\theta_{,\mathbf{B}}$ degrees	θ, r degrees	$\theta^{L} = \theta^{r},$ degrees
Smooth s	urface		119	109	10
$\phi = 30^{\circ}$	0.01	0.002 9	138 ± 3	114 ± 3	24
	.02	.0058	134 ± 1	115 ± 2	19
	.03	.008 6	137 ± 1	113 ± 1	24
				Av	. 22
$\phi = 45^{\circ}$	0.01	0.005	150 ± 2	117 ± 1	33
	. 02	.010	150 ± 2	115 ± 3	35
	. 03	.015	148 ± 2	114 ± 2	34
				Av	. 34
$\phi = 60^{\circ}$	0.01	0.017	173 ± 3	126 ± 1	47
	.02	.035	175 ± 1	124 ± 2	51
	.03	.052	174 ± 2	124 ± 2	50
				Av	49

^a For each type of grooving, measurements of contact angles were made with each liquid upon each of at least two different surfaces. The \pm sign and accompanying numeral indicate the maximum deviation of the measured values from the average value for the system indicated.

⁽¹⁾ The data in this paper were taken from a portion of a thesis by J. W. Shepard, submitted to the School of Graduate Studies of the University of Michigan in partial fulfillment of the requirements for the Ph.D. degree, August, 1952.

⁽²⁾ Minnesota Mining and Manufacturing Fellow, 1951-1952.

⁽³⁾ F. E. Bartell and J. W. Shepard, THIS JOURNAL, 57, 211 (1953).

⁽⁴⁾ J. M. Andreas, E. A. Hauser and W. B. Tucker, *ibid.*, **42**, 1001 (1938).

TABLE II

Para	AFFIN-GLI	rcerol-A	IR CONTA	CT ANGLE	s
Surface	Spacing, in.	h, in.	$\theta^{\mathbf{a}}$, degrees	θ^r , degrees	$\theta^{a} - \theta^{r}$, degrees
Smooth su	irface		97	90	7
$\phi = 30^{\circ}$	0.01	0.0029	115	93 ± 2	22
	. 02	.0058	115	92 ± 1	23
	. 33	.0086	114	92 ± 1	22
					-
				Av.	22
$\phi = 45^{\circ}$	0.01	0.005	129 ± 3	84 ± 3	45
	.02	.010	126 ± 1	83 ± 3	43
	. 03	.015	126	81	45
					-
				Av.	44
$\phi = 60^{\circ}$	0.31	0.017	145	69 ± 1	77 ± 1
7 00	12	035	145 + 1	69 + 3	76 + 4
	. 52	.000			
	. J3	.052	$144 \pm$	00	18 ± 1
				Av.	77

The 3 M calcium chloride drops were exceptionally mobile on the rough surfaces and air bubbles were entrapped beneath the drops on the surfaces ruled at $\phi = 60^{\circ}$ and at $\phi = 45^{\circ}$. No apparent air entrapment was observed on the surfaces ruled at $\phi = 30^{\circ}$. Glycerol, because of its viscosity, moved rather slowly when it was being advanced across the rough surfaces. On the surfaces ruled at $\phi = 30^{\circ}$ the glycerol drops became octagonal in shape when advancing. With glycerol, as compared with other liquids studied, more time was required for the drop periphery to come to rest after addition or removal of liquid. There appeared to be some initial air bubble entrapment beneath the glycerol on the $\phi = 45^{\circ}$ and on the $\phi = 60^{\circ}$ surfaces, but on standing the bubbles disappeared. The previously described mechanism³ for the entrapment of air bubbles beneath an advancing drop can be applied to the systems of the present study also. When the contact angle is nearly 90° or greater, air bubble entrapment beneath the drop takes place. The angle of inclination ϕ is the determining factor in this air entrapment. As the drop advances on the steeper slopes, the drop surface comes into contact with the face of the opposite pyramid before the periphery reaches the bottom of the groove, thus entrapping a bubble of air. The new liquid drop edge formed at the point of contact of the drop surface with the opposite pyramid face immediately moves to the top of the pyramid. In the case of a viscous liquid such as glycerol the dynamic advancing angle, because of resistance to movement along the solid surface, is sufficiently large to entrap air initially. Once a static condition is reached the liquid advances to wet the surface beneath the bubble and allows the bubble to escape from the solid surface.

In both the calcium chloride solution system and the glycerol system when the liquids were advanced across the rough surfaces the drop did not come to rest on the pyramid faces oriented toward the drop but was observed always to run over to the faces of the pyramids oriented away from the drop. When glycerol was being advanced, though it moved slowly because of its viscosity, there was a momentary increase in the rate of advancement as the liquid moved up the face of the pyramids oriented toward the drop and when this movement stopped the periphery was observed to have run over to the far face. These observations support the concept presented in the previous paper³ that in a liquid-advancing system the drop periphery must come to rest on the faces of the pyramids oriented away from the drop in order to satisfy the condition for minimum free surface energy in the system.

In liquid-receding systems the periphery of the drop was observed to come to rest on the faces of the pyramids oriented toward the drop. This observation suggests that in the receding drop system there exists a condition for minimum free surface energy analogous to that for the advancing drop system. With removal of liquid from the drop the center of gravity is lowered and the curvature of the drop surface is altered. The conditions for equilibrium in the receding drop system, *i.e.*, the formation of a stable contact angle and the attainment of minimum free surface energy for the liquid-air interface, cannot be reached when the drop periphery is located on the faces of the pyramids oriented away from the drop center. As a result the liquid periphery of the receding drop will tend to move to the faces of the pyramids oriented toward the drop.

When glycerol was withdrawn from surfaces ruled at $\phi = 45^{\circ}$ and at $\phi = 60^{\circ}$ an examination of the surface revealed that a film and droplets of liquid remained behind, outlining the periphery of maximum advancement of the drop. On closer scrutiny at $10 \times$ magnification small droplets were observed entrapped in the grooves on some of the $\phi = 45^{\circ}$ and $\phi = 60^{\circ}$ surfaces. No films or droplets left by a receding drop were apparent on the surfaces ruled at $\phi = 30^{\circ}$ nor on smooth surfaces. It seems probable that because of its viscosity and the resistance to its movement on the surfaces, the dynamic receding angle for glycerol is less than 90°. As the liquid is receded, the drop periphery moves down the faces of the pyramids oriented toward the drop. Before the periphery reaches the bottom, the peaks of the next row of pyramids break through the liquid surface and the periphery formed at the new point of contact immediately recedes to those faces of the newly uncovered pyramids oriented toward the drop (see Fig. 1). A portion of the liquid is left behind to collect in the groove. Because of their low volatility the glycerol droplets do not evaporate but remain to be detected.

Wenzel⁵ has presented a theory for the effect of surface roughness on contact angles which has been widely accepted. He points out that within a given geometrical area a roughened surface will contain more actual surface area than will a smooth surface. Wenzel therefore contends that for a rough surface the Young Equation must be modified by multiplying the energy change by a roughness factor, r, which is the ratio of actual surface area to the geometrical surface area. The roughness factor is always greater than one except in the case of an ideally smooth surface when it is equal to

(5) R. N. Wenzel, Ind. Eng. Chem., 28, 988 (1936); THIS JOURNAL, 53, 1466 (1949).



one. Wenzel's modification of the Young Equation is

$$r(\gamma_{a} - \gamma_{ai}) = \gamma_{1} \cos \theta' \qquad (1)$$

where r is the roughness factor, γ_{s} is the surface tension of the solid surface, γ_{sl} is the surface tension of the solid-liquid interface, γ_{l} is the surface tension of the liquid, and θ' , is the contact angle. The contact angle θ observed on a smooth surface is related to the contact angle θ' observed on a roughened surface in the following manner

$$r\left(\cos\theta\right) = \cos\theta' \tag{2}$$

From this relation one would conclude that if the contact angle on a smooth surface was greater than 90° , roughening the surface would increase the observed contact angle. Conversely, if the contact angle for a smooth surface was less than 90° , roughening would decrease the observed contact angle.

Calculations using equation (2) taken from Wenzel's treatment have indicated a lack of applicability of this theory to the data obtained in this research.

For these calculations the advancing and receding contact angles for smooth paraffin surfaces were used together with the roughness factor, r, which for paraffin surfaces is equal to sec. ϕ . For advancing angles deviations ranging from 13 to 40° were found between calculated and observed values. Though the three systems studied all had contact angles on smooth surfaces equal to 90° or greater, and according to Wenzel's theory should have shown contact angle increases as the surface was roughened, the receding angle values for the paraffin-3 M calcium chloride-air system increased with an increase in the roughness factor, r, the receding angle values for the paraffin-water-air system remained nearly unchanged with an increase in r, while the receding angle values for the paraffin-glycerol-air system decreased with an increase in r. The lack of applicability of the theory to the data indicates that Wenzel's theory does not apply to roughnesses of the order of magnitude used in this research.

The theories of capillarity in their earlier development and in the modern treatment are based on the concept that for a given solid-liquid system in which a contact angle is formed, there is one characteristic contact angle formed between the surface of the liquid and the surface of the solid, and that the forces which bring about equilibrium at the line of contact between the two surfaces operate over a limited range. Young⁶ is generally credited as the first to state the relationship between the contact angle and the forces operating at the interface. This relationship was postulated on the basis of resultant forces in the form of vectors constant in magnitude and operating in the directions of the surfaces involved. Young's Equation states the condition for equilibrium between these forces which have been termed surface tensions, *i.e.*

$$\gamma_{\rm s} - \gamma_{\rm sl} = \gamma_{\rm l} \cos\theta \qquad (3)$$

where the terms are as previously defined. For a liquid the surface tension is numerically equal to the free surface energy. For a solid such a relationship may not be strictly valid. However, because of the equivalence of free surface energy and surface tension for a liquid, it is possible to calculate, from the surface tension of the liquid and the value of the contact angle, the energy change on the wetting of a solid by the liquid.

It is difficult to reconcile Wenzel's theory with these concepts. Unless the roughness were of such a magnitude that it would increase the amount of surface located within the range of effectiveness of the forces producing the equilibrium at the solidliquid-air interface, an increase in the surface area produced by roughening would have no direct effect on this equilibrium. The range of the forces involved is exceedingly small and, consequently, the roughness would have to be of molecular dimensions to alter the equilibrium conditions. If the roughness were of greater coarseness it could have no direct effect.

This can be demonstrated by a rather simple experiment. On a smooth paraffin surface obtained by pressing the paraffin against a clean plate glass surface the advancing angle for a glycerol drop was found to be 98°. The glycerol drop was removed and another area on the smooth paraffin surface was cross-hatched with grooves to produce a very rough surface. Another glycerol drop was formed on the roughened area and the average apparent advancing angle for the liquid on this portion of the surface was found to be 148° . Liquid was added to the second drop so that this drop was caused to advance uniformly over the roughened area until the periphery was located just beyond the boundary of the roughened area on the smooth portion of the surface. The drop was advanced until approximately the same volume of liquid was in the drop as had been present in the first drop when measurements were made before roughening part of the surface. The advancing angle obtained under these conditions was 97°, identical within experimental error with that observed previous to roughening the area beneath the drop. One difference was noted. Because of air entrapment beneath the drop and because of

⁽⁶⁾ T. Young, Phil. Trans., 96A, 65 (1805).

the volume increase caused by the roughened area, the drop diameter was greater for approximately the same volume of liquid. However, the drop shape was the same as before roughening. The drop shape changed when the drop edge advanced from the rough to the smooth portion of the surface. The center of gravity of the drop with its periphery on the rough surface was considerably higher than that of the drop with its periphery on the smooth surface. This caused some difficulty since if the drop edge did not move uniformly from the rough to the smooth area, liquid would run off the rough area onto the smooth part of the surface wherever contact was first made with the smooth surface.

The results of this experiment indicate that the contact angle and resultant drop shape are determined at the solid-liquid-air interface and that increasing the surface area beneath the drop by roughening does not alter the contact angle. One must conclude, therefore, that Wenzel's modification of the Young Equation is not justified for roughness of a microscopic or macroscopic magnitude.

A consideration of the nature of the measured contact angle should be informative. The forces involved in producing the equilibrium at the solidliquid-air interface are short range forces effective over a distance of several molecular diameters at most. It is not possible to measure the contact angle in the region where these forces are effective and, indeed, if one could obtain sufficient resolution, the problem of locating the plane of the surfaces involved would make the measurement impossible. The condition for equilibrium is given by the

Young Equation (3) which is a general equation. Equilibrium will be established at the interface when the liquid makes the appropriate angle of contact with the surface of the solid at the interface, regardless of the orientation of this portion of the solid surface with respect to the horizontal direction of the surface. At any point on an actual surface, the plane of the solid surface may be oriented at any of a range of angles with respect to the horizontal direction of the surface. The contact angle is measured at a definite distance from the interface and with respect to an arbitrary plane of reference, the horizontal plane of the solid surface. The resultant contact angle is then the mean of all the angles being made, with respect to the plane of reference, along the line of contact. On a smooth or polished surface the mean angular deviation of the actual plane of the solid surface, along the line of contact, from the arbitrary plane of reference may be slight, but on a roughened surface the mean angular deviation may be considerable. The effect of roughness becomes evident, and no modification of the Young Equation is necessary to explain the effect of roughness. Further discussion on the effect of roughness will be presented in a succeeding paper, together with additional data for liquids which give contact angles of less than 90° with smooth paraffin surfaces.

SURFACE ROUGHNESS AS RELATED TO HYSTERESIS OF CONTACT ANGLES. III. THE SYSTEMS PARAFFIN–ETHYLENE GLYCOL–AIR, PARAFFIN–METHYL CELLOSOLVE–AIR AND PARAFFIN–METHANOL– AIR¹

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Paraffin surfaces of controlled roughness were prepared, as previously described, so as to produce thereon regular pyramids of height h and angle of inclination ϕ of the pyramid faces. These surfaces were used to study the effect of roughness on contact angles formed by liquids which on a smooth paraffin surface formed contact angles less than 90°. For ethylene glycol and for methyl cellosolve on these roughened paraffin surfaces, as the angle of inclination ϕ of the pyramid faces increased, the apparent advancing contact angle values increased, while the apparent receding contact angle values decreased. For methanol on these surfaces, as the angle ϕ increased, the apparent receding contact angle cecreased while the apparent receding contact angle became zero. The hysteresis observed increased with an increase in ϕ except for methanol for which the hysteresis observed decreased. Changes in the height h had no effect on the observed contact angles nor on hysteresis. Wenzel's theory was found inapplicable to these systems. On the basis of these and previous results an explanation of the effect of surface roughness is proposed.

Recent communications from this Laboratory^{3.4} have shown that changes in the physical structure, or roughness, of paraffin surfaces can alter the apparent wetting properties. The present investigation had as its major aim the study of the effect of

(1) The data in this paper were taken from a portion of a thesis by J. W. Shepard, submitted to the School of Graduate Studies of the University of Michigan in partial fulfillment of the requirements for the Ph.D. degree, August, 1952.

(2) Minnesota Mining and Manufacturing Fellow 1951-52. Present address, Minnesota Mining and Manufacturing Company, Saint Paul, Minnesota.

(3) F. E. Bartell and J. W. Shepard, THIS JOURNAL, 56, 211 (1953).
(4) F. E. Bartell and J. W. Shepard, *ibid.*, 56, 455 (1953).

roughness on the wetting of paraffin by a series of liquids which formed contact angles of less than 90° on smooth paraffin surfaces. Previous studies have dealt with liquids which formed contact angles greater than 90° on such surfaces.

Surfaces were ruled so as to have pyramids with angles of inclination ϕ of 30, 45, or 60° and, for a given angle of inclination, with three different heights h. These were prepared from paraffin blocks cast from the same melt as used in previous work.

In the methyl cellosolve and methanol systems

studied in this investigation the liquid drops became rectangular in outline when increased in size and caused to move across the rough surfaces. Gibson,⁵ studying the validity of the equation derived by Poisson for large sessile drops, used rectangular shaped drops and found that for drops greater than 4.0 cm. along the edge, a simplified form of the Poisson equation applied, *i.e.*, the correction terms for horizontal and vertical curvature could be neglected. Accordingly, for the liquid drops which deviated from a circular outline, the following modification of Poisson's equation was used to calculate the contact angle.

$$\cos \theta' = \frac{H}{2\left(\frac{\gamma}{(\rho_{\rm L} - \rho_{\rm a})_{\rm g}}\right)^{1/2}} \tag{1}$$

where H is the height of the drop, γ the surface tension of the liquid, $\rho_{\rm L}$ the density of the liquid, $\rho_{\rm a}$ the density of the air, g the gravitational constant and θ' the contact angle measured through the air.

The values of the contact angle reported are for the angle θ measured through the liquid phase. θ is related to the angle θ' by the expression

 $\theta = 180^{\circ} - \theta' \tag{2}$

Materials Used.—Reagent grade ethylene glycol and methanol, and technical grade methyl cellosolve were freshly distilled in a twenty-stage Brunn column and the respective middle fractions were taken off for use. The methyl cellosolve was distilled twice and the middle fraction was collected each time. The surface tensions of the liquids saturated with paraffin were determined by the Pendent Drop Method⁶ and were found to be 47.4 dyncs/cm. for ethylene glycol, 30.0 dynes/cm. for methyl cellosolve, and 22.6 dynes/cm. for methanol.

Discussion

The data obtained for the three systems (averages of 2 or more experiments) are given in Tables I, II and III. Changes in height h appeared to produce no change in the observed contact angle values for a given ϕ . For the systems involving ethylene glycol and methyl cellosolve, an increase in the angle of inclination ϕ , resulted in an increase in the apparent advancing contact angle θ^{a} values and a decrease in the apparent receding contact angle θ^r values. For the system involving methanol, the apparent advancing contact angle values decreased with an increase in ϕ while the apparent receding angle values were zero for all values of ϕ . Hysteresis increased with an increase in ϕ for the ethylene glycol and the methyl cellosolve systems but decreased for the methanol systems.

When the ethylene glycol drop was withdrawn from paraffin surfaces ruled at $\phi = 60^{\circ}$ and at $\phi = 45^{\circ}$, scattered droplets remained in the grooves, outlining the area of the surface which had been covered by the drop. This phenomenon was not observed on the surfaces ruled at $\phi = 30^{\circ}$ nor on the smooth surfaces. A mechanism for this droplet entrapment has been described in a previous paper⁴ and the present experiments support the concept described therein. Though the ethylene glycol drop when advancing on rough surfaces became octagonal in outline, when receding, it tended to

	TABLE I			
PARAFFIN-ETHYLENE	GLYCOL-AIR	Contact	ANGLES ^a	IN
	Ducuuna			

		DEC	REES		
Surface	Spacing, in.	h, in.	θa	θς	$\theta_a - \theta_r$
Smooth			81	74	7
$\phi = 30^{\circ}$	0.01	0.0029	93 ± 2	67 ± 1	2 6
	.02	.0058	92 ± 1	64 ± 1	28
	.03	.0086	94 ± 1	64 ± 2	30
					Av. 28
$\phi = 45^{\circ}$	0.01	0.005	105	49 ± 1	5 6
	.02	.010	102 ± 3	49 ± 1	53
	.03	.015	99	48 ± 1	51
					Av. 54
$\phi = 60^{\circ}$	0.01	0.017	1 2 3	17 ± 1	106
	.02	. 035	118 ± 1	15 ± 2	103
	.03	.052	119 ± 1	18 ± 1	101
					Av. 103

^a For each type of grooving, measurements of contact angles were made with each liquid upon each of at least two separate surfaces. The \pm sign and accompanying numeral indicate the maximum deviation of the measured values from the average value for the system indicated.

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Paraffin-Methyl Cellosolve-Air Contact Angles in Degrees

Surface	Spacing,	h_{i}	Aa	Ar	6a —
Smooth			60	49	00
Smooth			02	42	20
$\phi = 30^{\circ}$	0.01	0.0029	76 ± 2	13 ± 1	63
	. 02	. 0058	76 ± 3	12 ± 1	64
	. 03	.0086	77 ± 1	11 ± 1	66
					Av. 64
$\phi = 45^{\circ}$	0.01	0.005	81 ± 2	0	81
	. 02	.010	82 ± 2	0	82
	.03	.015	84	0	84
					Av. 82
$\phi = 60^{\circ}$	0.01	0.017	93 ± 3	0	93
,	.02	.035	92	0	92
	02	050	02 1 2	õ	02
	.05	.032	95 ± 3	0	93
					Av. 93

TABLE III

PARAFFIN-METHANOL-AIR CONTACT ANGLES IN DEGREES

	Spacing.	h.			θ —
Surface	in.	in	θ^{n}	θr	0 r
\mathbf{Smooth}			42	27	15
$\phi = 30^{\circ}$	0.01	0.0029	58 ± 2	0	58
	. 02	.0058	60 ± 1	0	60
	. 03	.0086	56 ± 2	0	56
					Av. 58
$\phi = 45^{\circ}$	0.01	0.005	51 ± 3	0	51
	. 02	.010	47	0	47
	.03	.015	51 ± 2	0	51
					-
					Av. 50
$\phi = 60^{\circ}$	0.01	0.017	0	0	0
,	.02	.035	0	0	0
	.03	.052	0	0	0
					-
					Av. 0

⁽⁵⁾ H. S. Gibson, Proc. Roy. Soc. S. Australia, 56, 51 (1932).

⁽⁶⁾ J. M. Andreas, E. A. Hauser and W. B. Tucker, THIS JOURNAL, 42, 1001 (1938).

Liquid	γ. dynes/cm.	Specific gravity ^a g. g./cc.	$\frac{Smooth}{\theta^{a}}$	surface Ør	$\phi = \theta^{a}$	30° в ^т	$\phi = \phi$	45° вт	φ = βa	60° <i>ө</i> т
Water	72	1.00	110°	99°	129°	99 °	142°°	94°°	160°	96 °°
$3 M \text{ CaCl}_2$	84.5	1.236	119	109	136	114	149	115	174	125
Glycerol	63 .2	1.260	97	90	115	92	127	83	145	68
Ethylene glycol	47.5	1.110	81	74	93	65	102	49	120	17
Methyl cellcsolve	30	0.960	62	42	76	12	82	0	93	0
Methanol	22.6	0.8095	42	27	58	0	50	0	0	0

TABLE IV

COMPARISON OF AVERAGE CONTACT ANGLE VALUES IN DEGREES

• At 25° . • The value for the surface ruled at 0.05 inch spacing is not included in these averages. • The value for the surfaces ruled at the 0.01 inch spacings are not included in this average.

become circular. The periphery of the advancing ethylene glycol drop was always located on the pyramid faces oriented away from the drop, while for the receding drop the periphery was located on the faces oriented toward the drop. The liquid tongues in the grooves were extended forward making an acute angle with the horizontal for both advancing and receding drops.

Methyl cellosolve and methanol formed rectangular drops on the roughened surfaces. These liquids when advancing across the surface showed a phenomenon not observed previously. The drops would build up to a maximum height and then would advance along an entire side simultaneously. The drop could then be built up and would advance again only when the same maximum height had been attained. With receding drops, liquid could be removed until the drop surface fell below the peaks of the pyramids without causing recession of the drop periphery. In cases where this occurred the contact angle has been reported as zero. On the surfaces ruled at $\phi = 30^{\circ}$ the methyl cellosolve drop pulled back spontaneously before its surface fell below the peaks. Both on smooth and on rough paraffin surfaces the area which had been beneath a methyl cellosolve drop lost its former translucent appearance and appeared opaque and white after withdrawal of the liquid. Such an effect was not observed for ethylene glycol or methanol.

Table IV presents the average apparent contact angles for the systems studied in this investigation and, for comparison, the average apparent contact angles for the systems previously studied. This summation of data permits some generalization since it includes systems forming a range of contact angles on smooth paraffin surfaces. In general, an increase in the angle of inclination ϕ , produced an increase in the apparent advancing contact angle and a decrease in the apparent receding contact angle. The systems involving 3 M calcium chloride and water as liquids present exceptions to this generalization in the case of the apparent receding angles, while the paraffin-methanol-air system presents an exception to the generalization in the case of the apparent advancing contact angle.

Figure 1 presents the contact angle values on a smooth paraffin surface for the various liquids plotted against their respective surface tension values. Because of the polar nature of the liquids and their similarity of behavior toward paraffin, the points obtained lie along a straight line, though methyl cellosolve and methanol show some deviation from this generalization. This deviation is probably the result of a slight solubility effect with these liquids. The clouding effect of methyl cellosolve on the paraffin surfaces has been mentioned and supports this conclusion.



Fig. 1.—Relation of $\cos \theta$ to surface tensions of liquids used.

Table V presents the average values of the hysteresis of the contact angle observed for the systems studied in this investigation and, for comparison, the average values for the systems previously reported. In general, the hysteresis observed increased with an increase in the angle of inclination ϕ . The paraffin-methanol-air system presents a

TABLE V

Comparison of Average Hysteresis Values in Degrees

Liquid	Smooth surface heta = heta r	$\phi = 30^{\circ}$ $\theta a - \theta r$	$\phi = 45^{\circ}$ $\theta^{a} - \theta^{r}$	$\phi = 60^{\circ}$ $\theta^{a} - \theta^{r}$
Water	11°	30°	48 °ª	64 °°
$3 M \text{ CaCl}_2$	10	24	34	49
Glycerol	7	23	4 4	77
Ethylene glycol	7	28	54	103
Methyl cellosolve	20	64	82	93
Methanol	15	58	50	0

^a The value for the surface ruled at the 0.05 inch spacing is not included in this average. ^b The values for the surfaces ruled at the 0.01 inch spacings are not included in this average.

notable exception to this statement. For this system the hysteresis observed decreased with an increase in ϕ .

The statement in a previous paper⁴ that Wenzel's theory⁷ did not apply to roughness of the order of magnitude used in these investigations is further verified by the lack of applicability of this theory to the data obtained in the present research. For systems which exhibit contact angles less than 90° on smooth paraffin surfaces, Wenzel's treatment predicts a decrease in the observed contact angle as roughness increases, that is, with an increase in ϕ . Experiments showed, however, that in general for the system studied in the present research, the apparent advancing contact angles increased with an increase in ϕ while the apparent receding contact angles decreased to such an extent that numerical agreement with predicted values was poor.

As an explanation for the effect of roughness on contact angles Ray⁸ has offered the postulate that the observed advancing contact angle is the sum of the stable contact angle plus the angle of inclination ϕ of the faces of the asperities, while the observed receding contact angle is the difference between the stable contact angle and the angle of inclination ϕ . The work of Coghill and Andersen⁹ in which they were studying what they termed the "edge effect" offers a partial experimental confirmation of Ray's theory. When the drop edge advancing across a smooth surface encounters a discontinuity in the form of a beveled edge, the drop height must increase to a maximum before the liquid will run down the slope. The apparent advancing angle calculated from this maximum drop height was found to be approximately the sum of the angle obtained on the smooth surface and the angle of inclination of the beveled edge.

Bikerman¹⁰ also observed a raising of the center of gravity of the drop when the drop front climbed over the ridges on his surfaces. This phenomenon was observed during this research in the case of the methyl cellosolve and methanol drops. With both of these liquids it was possible to build the drop up to a measurable maximum height before advancement of the drop edge took place. With the liquids previously studied no build-up to a maximum height prior to advancing was observed; all the liquids advanced uniformly across the roughened surfaces. This maximum height phenomenon in the case of the methyl cellosolve and methanol was probably the result of the rectangular shape which the drop assumed on the surfaces. With such a shape it was impossible for a small portion of the periphery to advance without causing an adjustment at other points along the edge.

Ray's theory is limited to a two-dimensional system, while in experimental systems one must deal with three dimensions and must consider in addition the effect of the liquid surface residing in the grooves between asperities.

(7) R. N. Wenzel, Ind. Eng. Chem., 28, 988 (1936); THIS JOURNAL, 53, 1466 (1949).

(8) B. R. Ray, Thesis, University of Michigan. Supplement IV (1945).

(9) W. H. Coghill and C. O. Anderson, U. S. Bur. Mines Tech. Paper 262, 47 (1923).

(10) J. J. Bikerman, THIS JOURNAL, 54, 653 (1950).

Shuttleworth and Bailey¹¹ have examined the problem of the effect of two dimensional roughness mathematically in some detail. In their treatment they discussed the spreading of a liquid parallel to the grooves in a system composed of parallel grooves separated by ridges. These authors point out that with a system of grooves if the stable contact angle is greater than 90°, the liquid surface will be dented and will not extend as far in the groove as it does on a smooth surface. The tongues of liquid in the grooves will be inclined to the horizontal at an obtuse angle measured through the liquid phase. Oppositely, if the stable angle is less than 90° , the tongues of liquid will extend from the drop along the groove, and for small stable angles the liquid will flow to an unlimited length along the groove. When the stable contact angle is greater than 90° and the groove is deep and narrow, the liquid will not touch the bottom. These conditions were observed to occur in the grooves on the rough surfaces studied in these investigations. For liquids with contact angles on smooth surfaces greater than 90° the liquid tongues in the grooves were inclined at obtuse angles measured through the liquid phase with respect to the horizontal, while for liquids with contact angles on smooth surfaces less than 90° the liquid tongues were inclined at acute angles with respect to the horizontal.

When a large drop rests on a groove system, the surface of the liquid tongues in the grooves must have an approximately zero curvature, equal to that of the drop surface above, and at equilibrium the liquid surface must make the stable contact angle with the walls of the grooves. This condition can be satisfied by a plane inclined to the horizontal at an angle α such that

$$\cos \alpha = \cos \theta \sec \phi \tag{3}$$

 θ being the stable contact angle, and ϕ the angle of inclination of the walls of the groove with respect to the horizontal.

This equation is not a complete solution because the plane would not join smoothly with the rest of the drop. Most of the tongue would have this form, but where it merges into the bulk of the drop the liquid surfaces will have equal and opposite curvatures in perpendicular directions. The approximate length of the tongue in the groove is given by the relationship

$$l = h/\tan\alpha \tag{4}$$

where l represents the length of the tongue, h the depth of the groove, and α the angle described above. When the stable angle is less than 90°, the length of the liquid tongue will increase as the angle of inclination ϕ increases. When ϕ becomes equal to the stable angle θ the liquid will spread continuously up the groove. For the systems involving methanol this spreading of the liquid up the grooves was observed.

Extending their treatment to include three dimensional roughnesses of the type used in this research, Shuttleworth and Bailey describe the spreading as being analogous to spreading parallel to the grooves as outlined above. They suggest

(11) R. Shuttleworth and G. L. J. Bailey, Disc. Faraday Soc., 3, 16 (1948).

that the result would be similar to that described for the two-dimensional case and, accordingly, that the observed contact angle will be determined by the effect of the liquid in the grooves. While their discussion of two-dimensional systems seems quite valid, in extending their theory to three-dimensional systems they neglect to consider adequately the effect of the solid-liquid-air interface located on the faces of the asperities. They do not consider such ε location of the periphery because they feel that the spreading of liquid through the grooves excludes the possibility that the line of contact will lie on the slope of an asperity. The observed location of the periphery in the present investigations shows that this reasoning is not valid.

The surfaces used in this research can be considered as a combination of the two theoretical systems discussed above. The liquid surface makes the stable contact angle with the solid surface along the entire liquid periphery, though the apparent contact angle in the grooves (the angle α described above) differs from the apparent contact angle on the pyramid faces (the sum of the stable angle plus ϕ for an advancing condition and minus ϕ for a receding condition). Because of the complex structure of the solid surface, the liquid surface is irregular near the solid. Further away from the solid the fluidity of the liquid permits the liquid surface to be smooth and to have a shape indicative of a resultant apparent contact angle intermediate between the apparent contact angle in the grooves and the apparent contact angle on the pyramid faces. The observed apparent contact angle is then the result of all the separate apparent angles along the periphery of the drop.

To test this hypothesis, the apparent contact



Fig. 2.—Relation of contact angle, θ^{a} and θ^{r} , values formed on smooth surfaces to those formed on ruled surfaces with $\phi = 30^{\circ}$. O, represents calculated values for θ^{a} on beveled surfaces; Δ , calculated values for θ^{a} on grooved surfaces; \Box , observed θ^{a} values; while \bullet , \blacktriangle and \blacksquare represent corresponding values for receding angles, θ^{r} .

angles of the liquids studied were calculated for the bevel, or pyramid face, system. For this system, the apparent advancing contact angle is the sum of the stable advancing contact angle plus the angle ϕ , and the apparent receding contact angle is the difference between the stable receding contact angle and the angle ϕ . Approximate values for the liquid tongue angles α of the groove systems were calculated also using equation (3). Ob-



Fig. 3.—Relation of contact angle, θ^a and θ^r , values formed on smooth surfaces to those formed on ruled surfaces with $\phi = 45^\circ$. (Significance of symbols the same as in Fig. 2.)



Fig. 4.—Relation of contact angle, θ^{α} and θ^{τ} , values formed on smooth surfaces to those formed on ruled surfaces with $\phi = 60^{\circ}$. (Significance of symbols the same as in Fig. 2.)

served values of the advancing and receding angles on smooth surfaces were used to approximate the respective stable angles in making calculations for both systems. The calculated values for both the bevel and groove systems and the observed apparent contact angle values for rough surfaces have been plotted in Figs. 2-4, as abscissas while the corresponding observed contact angles on the smooth paraffin surface have been plotted as ordinates.

As predicted, the curves for the observed apparent contact angles lie intermediate between the curves for the values calculated for the bevel system and for the groove system. In general, the observed advancing contact angles approach the values for the bevel system, but as the advancing contact angles on the smooth surfaces decrease, they are increasingly influenced by the effect of the liquid in the grooves. For methanol on a groove system, the calculated apparent contact angle α becomes zero when ϕ becomes greater than 42°. For surfaces where $\phi = 45^{\circ}$, therefore, the decrease in the observed apparent methanol advancing contact angle below the value obtained on surfaces ruled at $\phi = 30^{\circ}$ can be accounted for by this pronounced groove effect. This also, then, accounts for the decrease in hysteresis for methanol as the angle ϕ is increased. For paraffin surfaces where $\phi = 60^{\circ}$ the effect of the methanol in the grooves becomes sufficiently pronounced to cause the liquid to spread down the grooves.

The curves for the observed receding angles also lie between the curves for the bevel and groove systems. A study of these curves indicates that the recession of liquids on rough paraffin surfaces is controlled by the movement of liquid through the grooves, though, as the receding contact angle observed for a smooth surface decreases, the effect of the liquid in moving across the beveled faces becomes more important.

One then can conclude that in this research the observed values for the apparent advancing and receding contact angles on the roughened surfaces differ from those obtained for smooth surfaces as a result of the altered physical structure of the surface. The resultant observed contact angle is determined by the orientation of the liquid surface in making the stable contact angle with the solid surface along the entire periphery. When advancing, the movement of the liquid drop across the surface is controlled predominantly by the movement of liquid over the pyramid faces. When receding, the movement of the liquid drop is controlled predominantly by the movement of the periphery in the grooves. The observed hysteresis on paraffin surfaces is then the result of the effect of the physical nature of the surface on the observed contact angle.

ELECTROMOTIVE FORCE STUDIES IN AQUEOUS SOLUTIONS OF HYDROCHLORIC ACID AND GLYCEROL FROM 0 TO 40°

BY SAMUEL B. KNIGHT, H. D. CROCKFORD AND F. W. JAMES

Contribution from the Venable Chemical Laboratory of the University of North Carolina, Chapel Hill, N. C. Received October 30, 1952

Electromotive force measurements on cells of the type $H_2 | HCl(m)$, glycerol (y) | AgCl, Ag were carried out in acid concentrations up to approximately 0.12 m and in 10 and 30% by weight of glycerol. Measurements were made at 5° intervals from 0 to 40°. Standard cell potentials have been calculated for the cells at the various temperatures. The mean activity coefficients of HCl can be calculated from the Debye-Hückel expression using a value of 6.6 Å, for the ion-size parameter. The calculated values agree closely with the experimental values.

The work reported on in this paper is a continuation of the studies being carried on in this Laboratory on the effect of mixed solvents on the thermodynamic properties of hydrochloric acid solutions. In this work electromotive force measurements were made on the cell

$H_2|HCl(m)$, glycerol(x), $H_2O(y)|AgCl-Ag$

from 0 to 40° at 5° intervals in solutions containing 10 and 30% by weight of glycerol and with acid concentrations ranging up to approximately 0.12 m. The activity coefficients of the acid in the various solutions at 25° and the standard cell potentials at the various temperature have been calculated from the data obtained. A study has also been made of the ion size parameter at the various temperatures.

This supplements the work of Harned and Nestler,¹ who studied the same cell in 50% glycerol,

(1) H. S. Harned and F. H. M. Nestler, J. Am. Chem. Soc., 68, 665 (1946).

with acid concentrations up to approximately 0.1 m, and at 5° intervals from 0 to 90°; and Lucasse,² who studied this cell in 3.06 and 21.2% glycerol, with acid concentrations up to 4 m but only at a temperature of 25° .

Experimental

The method of purification of chemicals other than glycerol, the preparation of the electrodes and the experimental procedures, were essentially the same as those of Williams, et $al.^3$

Glycerol.—Reagent grade glycerol was used without further purification, since purification procedures did not seem to improve the quality of the material used and in some cases seemed to induce some slight decomposition. The composition of the glycerol solutions was checked by density measurements using the tables of Bosart and Snoddy.⁴

⁽²⁾ W. W. Lucasse, ibid., 48, 627 (1926).

⁽³⁾ J. P. Williams, S. B. Knight and H. D. Crockford, *ibid.*, **72**, 1277 (1950).

⁽⁴⁾ L. W. Bosart and A. O. Snoddy, Ind. Eng. Chem., 19, 506 (1927).

				TABL	E I				
· · · · · ·				Temper	rature				
m	0°	5°	10°	15°	20°	25°	30°	35°	40°
				10% Gl	ycerol				
0.012981	0.44035v	0.44177v	0.44300v	0.44403v	0.44487v	0.44561v	0.44616v	0.44661v	0.44694
.026730	.40811	. 40893	. 40963	. 41009	.41038	.41036	.41033	.41018	.41000
.050330	.37986	. 38020	.38035	. 38039	.38016	.37978	.37928	.37868	.37797
.061193	.37114	.37134	.37134	.37118	.37085	.37041	.36978	. 36903	. 36806
.074614	. 36244	. 36250	. 36235	. 36202	.36149	. 36090	.36010	.35921	.35822
.094906	.35161	. 35146	. 35114	. 35063	. 34999	.34925	. 34833	. 3470 3	.34601
.11989	$.3{\pm}165$. 34102	. 34051	. 33981	. 33901	.33803	. 33693	. 33565	. 33426
				30% Gl	ycerol				
0.022661	0.40262	0.40343	0.40412	0.40464	0.40501	0.40526	0.40528	0.40522	0.40500
.035571	.38237	.38388	.38324	. 38343	.38346	.38328	.38300	. 38260	.38203
.049297	.36818	. 36843	.36852	.36845	.36821	.36782	.36723	.36652	.36567
.064536	.35620	.35626	.35613	.35587	.35543	.35487	.35418	.35334	.35226
.078708	$.3{igara}742$.34731	.34705	.34661	.34602	.34528	.34435	.34345	.34229
.099 021	.33728	.33700	. 33656	.33595	.33516	.33436	. 33333	.33214	.33081

Vapor Pressures.—Vapor pressures were obtained from large graphs plotted from the data of Carr, Townsend and Badger.⁶

Densities.—All lensities were determined in a pycnometer of about 15-ml. capacity.

Dielectric Constants.—The dielectric constants of the two solutions were calculated at the various temperatures from the following equations of Akerlof.⁶

 $\begin{array}{l} \log D \; (10\% \; \mathrm{glycerol}) = 1.8896 \; - \; 0.00207(t-20) \\ \log D \; (30\% \; \mathrm{glycerol}) = 1.8560 \; - \; 0.00211(t-20) \end{array}$

The electromotive force measurements, corrected to 1 atm. of hydrogen, are averages of at least three cells usually agreeing within ± 0.05 mv. The time necessary for equilibrium at 25°, at which temperature the first determination was always made, was approximately four hours. Approximately one hour was required for a new equilibrium value when the cell temperature was changed. Some of the readings were made by starting the cells at 25°, dropping to 0° by 5° steps, raising the temperature back to 25°, then



Fig. 1.— $E_{exp.}$ vs. temperature, solvent: 10 weight per cent. glycerol.

(5) A. R. Carr, R. E. Townsend and W. L. Badger, Ind. Eng. Chem., 17, 643 (1925).

(6) G. Akerlof, J. Am. Chem. Soc., 54, 4125 (1932).

making readings at 30, 35 and 40°, and then dropping back to 25° for a check on the electromotive force at this temperature. Other measurements were made by the same procedure except that the cell temperature was raised from 25 to 40° in 5° steps, then dropped back to 25°, then changed to 0° at 5° intervals, and finally raised back to 25°. The three readings at 25° agreed within ± 0.05 mv. All electromotive force measurements are expressed in International Volts.

Calculations and Results

The standard electrode potentials were determined by use of the function E' defined by the equation

$$E' = E + 2K \log m - \frac{2KA\sqrt{C}}{1 + \delta B\sqrt{C}} - 2K \log (1 + 0.002mM_{xy}) = E_{m}^{\circ} + f(m) \quad (1)$$

in which E' is the apparent molal potential, E is the observed electromotive force corrected to 1 atm. of hydrogen, m is the molality of the acid, A and B are the Debye-Hückel constants, \hat{a} is the ion size parameter in Å., C is the concentration in moles per liter, M_{xy} is the mean molecular weight of the solvent, and K equals 2.3026 RT/F.

Table I gives the observed electromotive force values for the various molalities at the various temperatures.

Figure 1 shows the manner in which the observed electromotive force changes with temperature for three typical concentrations for the 10% solution. The same typical curves were found for the 30% solutions.

The density values were found to fit an equation of the type

$$d = a + bm$$

The values of a and b for the two concentrations of glycerol at the various temperatures, together with the values of the constants in equation (1) are given in Table II. This table also includes the values of the standard cell potentials at the various temperatures.

The standard cell potentials in Table II were determined by plotting the function E' in equation (1) versus the molality of the acid. Several values of the ion size parameter were tried for the various temperatures in order to determine the best value of &. The E' values obtained in this manner are not presented here as they can all be calculated TABLE II Values of Constants and Standard Cell Potentials

t.

°C.	D	\boldsymbol{A}	В	а	ь	E°
		10%	% Glycer	ol		
0	85.31	0.51294	0.32945	1.0253	0.0188	0.23075
5	83.29	. 51738	. 33040	1.0250	.0190	. 22824
10	81.34	. 52185	. 33134	1.0243	.0190	.22557
15	79.42	. 52708	. 33245	1.0234	.0180	.22274
20	77.53	, 53225	. 33353	1.0222	.0180	.21970
25	75.74	. 53771	.33469	1.0207	.0184	.21650
30	73.95	.54364	.33590	1.0192	.0176	.21315
35	72.21	. 55350	. 33790	1.0173	.0180	. 20965
40	70.50	.44618	. 33847	1.0151	.0194	. 20600
Mxy	19.60					
		3	0% Glyc	erol		
0	79.00	0.57443	0.34211	1.0786	0.0172	0.21684
5	77.22	. 57983	.34321	1.0773	.0170	.21421
10	75.34	. 58532	.34426	1.0758	.0168	. 21141
15	73.55	. 59146	. 34547	1.0741	.0170	, 20851
20	71.78	. 59730	. 34661	1.0722	.0172	.20545
25	70.05	. 60431	. 34793	1.0702	.0172	. 20221
30	68.38	. 61130	. 34929	1.0681	.0166	.19882
35	66.73	.61860	. 35065	1.0658	.0162	.19521
40	65.13	. 626 34	.35215	1.0634	.0160	.19140
M_{XY}	23.81					

from the data given. However, the curves obtained for the various ion size parameters at 25° and for 10^{c7}_{c0} glycerol are given in Fig. 2. The curves obtained for the other solutions were similar to those shown. It is seen that a value of 6.6 A. for the ion size parameter gives a curve that is parallel to the concentration axis up to a molality of approximately 0.07 m. The lowest value of the ion size parameter that gives a straight line over the concentration range studied is about 5.5 Å. No matter what ion size parameter is used the value of the standard cell potential can be considered as correct to ± 0.06 mv. It would appear from the curves shown that the value of the ion size parameter is larger than in pure water solution. A value of 6.6 Å. was found by Williams, et al.,³ for glucose



Fig. 2.—E' vs. molality of HCl at 25° using various values for ionic parameter (a); solvent, 10 weight per cent. glycerol.

solutions and by Crockford and Sakhnovsky' for d-fructose solutions.

The standard cell potentials for the two glycerol concentrations were found to fit the equations

$$E^{\circ}_{m} (10\% \text{ glycerol}) = 0.21650 - 0.000652(t - 25) - 0.0000033(t - 25)^{2}$$
$$E^{\circ}_{m} (30\% \text{ glycerol}) =$$

 $0.20221 - 0.000668(t - 25) - 0.0000034(t - 25)^{2}$

The potentials calculated for the 10% solution agree within ± 0.05 mv. in all temperatures. For the 30% solutions the agreement was equally good except for one temperature with variation 0.06 mv.



Fig. 3.—E°m vs. 1/D, HCl-glycerol-water solutions, 25°.

The standard cell potentials for the two solutions at 25° are plotted versus 1/D in Fig. 3. This curve also includes the point for the 50% solution ob-

TABLE III

MEAN ACTIVITY COEFFICIENTS OF HYDROCHLORIC ACID IN GLYCEROL-WATER MIXTURES AT 25°

GLICEROL WATER MIXTURES AT 20							
Molality	X = 0	X = 10%	X = 30%				
0.005	0.9285	0.928	0.912				
.01	.9048	.903	.884				
.02	.8755	.873	.853				
.03		.854	.834				
.04		.840	. 820				
.05	.8304	.828	, 808				
.06		.818	.798				
.07		.809	. 790				
. 08		.802	.783				
.09		.796	.777				
.10	.7964	.791	.772				

(7) H. D. Crockford and A. A. Sakhnovsky, J. Am. Chem. Soc., 73, 4177 (1951).

tained by Harned and Nestler¹ and the two points for the solutions studied by Lucasse.² A consideration of the data of Lucasse leads us to the conclusion that the dielectric constants for the 21.2 and 3.06% solutions should be 77.1 and 72.5 rather than 76.0 and 66.9 as used by Lucasse. The standard cell potential for the 21.2\% solution has been recalculated to be 0 2084 v.

The mean activity coefficients, $\pm \gamma$, of hydrochloric acid in the two glycerol solutions at 25° were computed from the e.m.f. data by the equation

$$\log \gamma_{\pm} = (E^{\circ}_{\rm m} - E)/0.1183 - \log m \qquad (2)$$

The activity coefficients so calculated were plotted versus m on a large scale and the values at rounded molalities determined. These are given in Table

III together with the values for the acid in pure water as listed by Harned and Owen.⁸

The experimental activity coefficients can be reproduced almost exactly by the Debye equation

$$\log \gamma_{:=} = -\frac{A\sqrt{C}}{1 + \hat{a}B\sqrt{C}} - \log (1 + 0.002mM_{xy}) + C'c$$

in which C' is a constant introduced to account for the "salting out" effect. Using 5.0 Å. for the ion size parameter and C' values of 0.137 and 0.147 for the 10 and 30% glycerol solutions the maximum variation of the activity coefficient from the experimental value was found to be 0.003.

(8) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1943, p. 340.

THE MECHANISM BY WHICH ALUMINUM IONS ALTER THE ELECTROKINETICS OF THE ZINC SULFIDE–WATER INTERFACE^{1,2}

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Data are presented to show the electrokinetics of sphalerite particles as a function of aluminum ion concentration in alkaline, distilled water and acidic media. The effectiveness of the aluminum in altering particle charge depends very much on the medium. At the isoelectric point, in distilled water, the system is highly sensitive to the addition of aluminum ions; whereas, in alkaline medium, the sensitivity is one thousand-fold less. Sensitivity is still less in acid medium. The magnitude of the negative to positive change in electric charge of the sphalerite in the presence of aluminum also depends on the medium. This is greatest in alkali and least in acid. Visible flocculation of the sphalerite at the solids concentration under consideration occurs only in alkaline medium and only at the isoelectric aluminum chloride concentration. These results are most readily explained, not by the direct adsorption of aluminum ions, but by the consideration of aluminum in conjunction with hydroxyl ions at the particle-aqueous medium interface.

Introduction

The results to be described suggest a mechanism for the adsorption and gathering of aluminum ions at the interface between particle and suspending medium, wherein the zeta potential of the particles is determined.

Normally, a suspension of zinc sulfide mineral (sphalerite) in distilled water is negative in charge.^{4,5} Addition of sulfuric acid decreases this negativity so that the isoelectric point is practically reached, but the charge does not become positive even at 0.1 M H₂SO₄.^{4,5} Likewise, a high concentration of NaCl (1 N) causes the zeta potential to be almost zero although not positive, and flocculation⁶ does not occur either with the acid or the salt (the particles being well under one micron in size and at a concentration of 0.0125% by weight⁴).

In direct contrast with the acid and common salt, aluminum chloride does reverse the sign of the

(1) Presented at the National ACS Meeting, Atlantic City, September, 1952, as "The Effect of Aluminum Ions on the Electrokinetics (Flocculation) of Sphalerite Particles."

(2) (a) The data cited in this paper are from M. Bender, Ph.D. Dissertation, New York University (1949); (b) see also ref. 4.

(3) American Cyanamid Company, Calco Chemical Division, Bound Brook, N. J.

(4) M. Bender and H. Mouquin, THIS JOURNAL, 56, 272 (1952).

(5) A. M. Gaudin and S. C. Sun, A.I.M.E. Tech. Pub. No. 2005 (1946).

(6) Flocculation (coagulation) is defined in all this work, as the grouping together of the majority of the "individual" particles of a suspension, which are mostly microscopic and submicroscopic in size, to become macroscopic in size. sphalerite. Also it flocculates it under given conditions. The effectiveness of the aluminum in these actions is markedly dependent on whether the suspension is alkaline, neutral (distilled water), or acidic, extremely low concentrations being involved in the case of the distilled water.

Experimental

Particle charge measurements were made ir. a rectangular modified Northrup-Kunitz cell. The suspensions, which contained 0.0125% by weight of sphalerite, were prepared from the mineral by grinding in a "Diamonite" mortar and pestle. Since most of the particles were less than 0.3 micron (μ) in radius it was necessary to use dark field microscopy to follow them. The temperature at which cataphoretic velocities (C.V.) were determined was that of the room, but the values obtained were corrected to 25° by multiplication by the ratios of the viscosities of water at the corresponding temperatures.

Amount and sign of the particle C.V. was studied as a function of the aluminum concentration in three different media, namely, basic $(0.001 N \text{ Na}_2\text{CO}_3)$, distilled water and acidic $(0.002 N \text{ H}_2\text{SO}_4)$ and Figs. 1,7 2 and 3 are the respective plots. In the alkaline medium the *p*H changes with aluminum concentration and cataphoretic velocity as shown

N AICh			V AICh		
× 104	pН	C.V.	× 104	$p\mathrm{H}$	C.V.
1.00	9.5	-2.79	4.00	7.7	+0.02
3.00	8.5	-1.04	4.25	7.6	-0.06
3.60	7.9	-1.29	4.80	6.9	+2.31
3.75	7.9	-0.30	10.00	5.3	+3.00
3.99	7.8	-0.12			

(7) Figure 1 published in ref. 4.



The distilled water suspensions do not cover so broad a pH range although the aluminum concentrations are over a wide scale:

N AICL			A AlCh		
$\times 10^7$	pH	C.V.	$\times 10^{7}$	p H	C.V.
0	6.6	-1.51	500	5.1	+2.10
2.0	6.2	-2.05	1,000	4.8	+0.04
2.8	5.7	-1.19	1,500	5.0	+1.97
3.2	5.8	-1.35	2,000	4.8	+1.99
3.6	5.7	-1.01	3,000	4.6	+1.11
4.0	6.0	-0.12	4,000	4.4	+1.41
4.4	6.4	-0.19	15,000		+2.28
40.0	5.9	+0.98	300,000	4.0	+2.25

Meanwhile, the pH of all the acid solutions was essentially 2.9.

In Figs. 2 and 3 the log (base 10) of the AlCl₃ normality is plotted instead of the actual concentration to afford representation of the whole concentration range studied. The ordinate (C.V. in μ /sec./volt/cm.) is of the same scale for the three curves, and therefore they all can be visually compared as to the magnitude of changes in electric charge in the three different media considered.

All these suspensions were examined for flocculation. There was no visible flocculation in distilled water⁸ or sulfuric acid medium. In alkaline medium, however, there was flocculation but this occurred only at that aluminum ion concentration corresponding to the isoelectric point.

Note the trace amount of aluminum ion necessary for crossing the isoelectric point when the medium is distilled water. The actual concentration is quite of the same magnitude as the values obtained by Burton⁹ and Svedberg¹⁰ for aluminum sulfate added to a silver sol in "pure" aqueous medium.¹¹ Besides, the steepness of the curve as it decreases in negativity and also the over-all change in C.V. $(-2 \text{ to } +2 \ \mu/\text{sec./volt/cm.})$ are of the same order as the Burton-Svedberg data, despite differences in the systems investigated and in the techniques of measurement. Mattson¹² has reported findings for clay particles with

Mattson¹² has reported findings for clay particles with which the present comparative observations in alkali medium and in acid medium are consistent, namely, that the electrical neutralizing power of aluminum chloride is less in acid medium than in alkaline mecium. Mattson also observed that copper sulfate and salts of iron exhibited similar

(9) E. F. Burtor, Phil. Mag., 12, 472 (1906).

(10) T. Svedberg, Nova Acta Regiae Soc. Sci. Upsaliensis, [4] 2, NI (1907), or "Studien zur Lehre von den Kolloiden Lösungen," Dissertation (1907), translation in Ion, 1. 373 (1909).

(11) Actually, Burton's isoelectric point was at 25×10^{-6} g. Al per liter while Svedberg's was almost 60×10^{-6} .

(12) S. Mattson, THIS JOURNAL, 32, 1532 (1928).

behavior as the aluminum chloride in acid medium compared to alkaline medium.

The present observations that the flocculating conditions for sphalerite are optimum in alkaline medium, are in agreement with data in the literature. For instance, Fahren-wald and Newton¹³ find divalent calcium ion a strong precipitant of quartz only in the presence of hydroxyl ion, *not* in neutral or acid solution. This has been confirmed by Cooke and Digre.¹⁴ Likewise Gaudin and Rizo-Patrón¹⁵ find that barium ion precipitates quartz in alkaline solution, not in acid solution and that effective flotation of the quartz with the barium is obtained in alkaline pulp only. Mattson¹² states that clay flocs formed by AlCl₃ in alkali are much more stable than in AlCl₃ alone or with HCl. Meanwhile, the lesser tendency toward flocculation in the absence of alkali is brought out by Svedberg¹⁰ who in working with the silver sol system already referred to, observed that it was possible to go through the isoelectric point and reverse the charge without flocculation occurring.



Fig. 3.-C.V. vs. N AlCl₃ in 0.002 N H₂SO₄ (sphalerite).

(13) A. W. Fahrenwald and J. Newton, Eng. Min. J., 138, 23 (1937).

(14) S. R. B. Cooke and M. Digre, Mining Eng., 1, 299 (1949).

(15) A. M. Gaudin and A. Rizo-Patrón, Trans. A.I.M.E., 153, 462 (1943).

⁽⁸⁾ However, see footnote 17.

Discussion

The observations made as to the activity of the aluminum being so dependent on the pH, namely: (a) greatest electrokinetic sensitivity to aluminum occurs near the middle of the pH scale; (b) flocculation tendency is less, the less the pH; (c) the magnitude of the negative to positive change in electric charge with aluminum concentration decreases with decrease in pH, are evidently not explainable in terms of *direct* influence by the aluminum ion. For then, it becomes difficult to appreciate the low degree of effectiveness in acid medium where the aluminum exists in its highest cationic polyvalence, *i.e.*, 3.

Since the pH has such a great influence it is not without merit to look to the highly polarizable hydroxyl ion as playing an important part in the adsorption of the aluminum at the interface. The idea of the hydroxyl ion acting as a bridge between the particle and the aluminum has been expressed by Lindenthal (and Weyl)¹⁶ and the present results tend to confirm this view.

For instance the lack of sensitivity to aluminum in the acid medium can be now explained by the low concentration of hydroxyl ions. In alkaline medium, the hydroxyl ion concentration may be high, but the aluminum no longer has sufficiently high cationic polyvalence, since there is too much $OH^$ associated with it. Meanwhile in the distilled water medium there is an optimum of hydroxyl ions and cationic polyvalence so that very small concentrations of aluminum markedly affect the zinc sulfide particle zeta potential. However, note the decreased sensitivity for the higher aluminum concentrations in the distilled water medium where C_{OH} is now appreciably lower. At the same time, sensitivity to Al is enhanced in the alkaline medium at the higher concentrations of AlCl₃ where the middle of the pH scale is approached.

The flocculation is also readily explained for with greater hydroxyl ion concentrations there would be greater tendency for bridging between particles by way of the adsorbed aluminum acting through hydroxyl ions. Actually, it has been shown through quantitative as well as qualitative observations by Bender and Mouquin^{2a,4} that the intensity of the Brownian movement of the particles at the isoelectric point in the aluminum alkaline medium is rela-

(16) J. W. Lindenthal, Office of Naval Research, Technical Report No. 51, May 1952 (The Pennsylvania State College).

(17) Sphalerite at the isoelectric point in alkaline aluminum chloride

tively low as compared with the other media¹⁷ and this should mean less inclination of the particle to break away from a floccule. In this connection it is conceivable that the aluminum-hydroxyl ion bridging is a factor in the reduced Brownian intensity observed for the particles.

The magnitude of the negative to positive change is small for the acid medium because of the scarcity of hydroxyl ions. In alkaline medium the change is greatest due to the abundance of hydroxyl ions. For instance, hydroxyl ions would account for the high negative charge when the aluminum chloride concentration is low. At the high aluminum concentrations there still would be sufficient hydroxyl ions for optimum bridging of the aluminum so that there is a maximum positive charge while at these concentrations in distilled water, the solutions are too acidic. For instance, compare alkaline medium with distilled water medium at about $10^{-3} N$ $AlCl_{3}$.¹⁸

This kind of a mechanism involving hydroxyl ions is evidently applicable to other adsorption and adhesion phenomena not necessarily involving aluminum ions. For instance, the observation made by Bender and Mouquin⁴ of sphalerite particles in acid solution originally fixed to a glass microscope slide (no Brownian movement occurring), and moving with the interface as the liquid between coverglass and slide evaporated, can be explained by hydroxyl ion bridging. Namely, with evaporation, hydroxyl ion bridges holding the particle to the surface combine with hydronium ions and leave as vapor. This results in an unbalanced pull by hydroxyls on the non-evaporated side of the liquidair interface so that the particle remains continuously on the wet side.

(which suspension is flocculated) was quantitatively found to have an appreciably smaller displacement than in alkaline or acid medium with no aluminum chloride (these latter systems being charged and non-flocculated). Qualitative observations indicated the sphalerite in alkaline aluminum chloride at the isoelectric point to be sluggish in Brownian activity compared to that in acid aluminum chloride at isoelectric point concentration (no flocculation occurring) or fairly concentrated (1 N) sodium chloride where the zeta potential of the sphalerite particles was close to zero (no flocculation occurring). In distilled water, sphalerite at the isoelectric point concentration of aluminum chloride, although non-flocculated, was sluggish in Brownian activity compared (qualitatively) to the non-flocculated suspensions already mentioned. Microscope observations did indicate a tendency for flocculation in this suspension, there being a g-cater number of small particle clusters than was usual in the other non-flocculated suspensions.

(18) With respect to the discussion in general, compare the experimental data on the basis of similar AlCh concentrations, similar pH and also C.V.

DEVELOPMENT OF STEPWISE ISOTHERMS ON CARBON BLACK SURFACES¹

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The adsorption isotherms of argon, nitrogen and oxygen on heat-treated carbon blacks at -195° reflect crystallographic structure changes induced in the black by heat treatment. Several types of carbon black were partially graphitized at a series of temperatures up to 2700°. Heat treatment at these temperatures alters the carbon structure as evidenced by X-ray diffraction measurements. Electron micrographs indicate a transition from approximately spherical particles to irregular polyhedra for the graphitized samples. The original carbon samples exhibit the usual sigmoid type isotherms, whereas with increasing degree of graphitization as many as three steps appear in the adsorption isotherms at relative pressures of 0.35, 0.63 and 0.86. Qualitative agreement is obtained with the theoretical equations of Halsey for multilayer adsorption on uniform surfaces. It is believed that these isotherms reflect the transition from heterogeneous to homogeneous surfaces.

Earlier studies of adsorption isotherms and calorimetric heats have demonstrated that there is a considerable degree of heterogeneity in the carbon black surface.² Nitrogen adsorption isotherms were of the usual sigmoid type. The initial heats of adsorption were a little greater than three times the heat of vaporization and decreased rapidly as a function of the fraction of surface covered. It has been assumed that the observed multilayer adsorption is a consequence of surface heterogeneity plus coöperative condensation. Halsey³ has sug-gested that the sigmoid adsorption isotherm may really be the superposition of a number of stepwise adsorptions on a heterogeneous surface.

On the other hand, according to the theories of Fowler and Guggenheim⁴ and the later developments by Halsey and Hill, $^{3,6-7}$ multilayer adsorption on a homogeneous surface should give rise to an isotherm composed of a single series of steps. This is based on the hypothesis that the heat of adsorption in the first layer is greater than that in the second, and so on. Attractive interaction forces exist between neighboring molecules adsorbed on sites of nearly equal energy. When a certain critical pressure is reached, two-dimensional condensation will begin. This will produce an inflection or step in the isotherm. Additional steps should occur upon the completion of each successive layer. Orr,⁸ with the adsorption of non-polar gases on alkali halide crystals, was the first to obtain these steps experimentally. Recently Gulbransen⁹ has published isotherms up to $P/P_0 =$ 0.5 for krypton on graphite which appear to be stepwise isotherms.

Experimental

The standard B.E.T.¹⁰ type apparatus was employed for

(1) Presented before the Division of Colloid Chemistry at the 122nd National Meeting of the American Chemical Society, which was held in Atlantic City, N. J., September, 1952.

(2) R. A. Beebe, J. Biscoe, W. R. Smith and C. B. Wendell, Jr., J. Am. Chem. Soc., 69, 95 (1947).

(3) G. D. Halsey, Jr., J. Chem. Phys., 16, 931 (1948).

(4) R. H. Fowler and E. A. Guggenheim, "Statistical Thermodynamics," Cambridge University Press, Teddington, England, 1939, pp. 426-444.

(5) G. D. Halsey, Jr., J. Am. Chem. Soc., 73, 2693 (1951).
(6) G. D. Halsey, Jr., *ibid.*, 74, 1082 (1952).

(7) T. L. Hill, J. Chem. Phys., 15, 767 (1947).

(8) W. J. C. Orr, Proc. Roy. Soc. (London), A175, 349 (1939).

(9) E. A. Gulbransen and K. F. Andrew, Ind. Eng. Chem., 44, 1039 (1952).

(10) S. Brunauer, P. H. Emmett and E. Teller, J. Am. Chem. Soc., 60, 310 (1938).

these measurements. With a mercury manometer the pressure readings were accurate to ± 0.1 mm. Pressure equilibration was assumed to have been attained when the value did not change more than 0.2 mm. in a 5-minute interval. The time for this equilibration depended both upon the sample and the isotherm region, varying from two minutes to one hour.

The nitrogen, oxygen and argon adsorbates were obtained from Matheson Company and stated to be 99.9% pure. The following commercial grades of carbon black were used

as raw materials: Spheron 6, a medium processing channel black; Sterling R, a semi-reinforcing furnace black; P-33, a fine thermal black; Vulcan 3, a high abrasion furnace black; and Thermax, a medium thermal black. Since the same type of data has been obtained for each black, only the first three will be discussed in the present paper. Each of these carbon blacks had been heat-treated for 2-hour periods in an induction furnace at temperatures ranging from 1000° to 3100° .¹¹ The sample was contained in a graphite crucible. Virtually all air was driven off in the initial heating stages and excluded for the duratior, of the heating period. More complete details of the preparation, X-ray crystallite dimensions and other physical properties of these blacks, are discussed by Schaeffer.12

Results and Discussion

Evacuation Temperature.—Prior to the detailed study of the adsorptive properties of heat-treated carbon blacks, it was essential to determine whether the standard outgassing temperature of 200° would be sufficient to obtain reproducible surfaces. Gulbransen⁹ has reported that there is a marked difference in the isotherm for krypton on graphite if the sample had been outgassed at 950° rather than at room temperature. To test for a similar effect on our samples, a quartz adsorption cell was designed in which the sample could be evacuated at 1000° followed by the normal adsorption determination with no intermediate exposure of the sample to Since this adsorption isotherm checked the air. one following the normal procedure, the 200° evacuation temperature was retained.

Adsorption–Desorption Comparison.—Several complete adsorption-desorption isotherms were carried out on the heat-treated carbon samples. Except in the high relative pressure region, *i.e.*, $P/P_0 > 0.75$, the desorption curve is superimposed on the adsorption curve, indicating that the process is completely reversible. The small hysteresis loop may be due either to slow pressure equilibration or to interparticle condensation.

(11) The heat-treated carbor black samples will be referred to as P-33 (2700°); for example, to indicate a sample of P-33 which has been heated for two hours at 2700°.

(12) W. D. Schaeffer, W. R. Smith and M. H. Polley, Ind. Eng. Chem., forthcoming publication.

Duplication of Isotherms.—Check runs on two separate preparations of Spheron 6 (1000°) indicated excellent duplication of samples and the sensitivity of adsorption measurements to changes in surface morphology. Agreement is estimated to better than $\pm 1\%$.

Surface Area of Samples.—Nitrogen surface area values are listed in Table I. It had been stated previously² that "devolatilization" at 927° had little effect on the surface area of carbon black.

TABLE I

Nitrogen Surface Areas of Heat-Treated Carbon Blacks in $m.^2/g.^\alpha$

Carbon	Treatment temperature. °C.							
black	None	1000	1500	2000	2700			
Spheron 6	114	91.1	88.0	85.4	84.1			
Sterling R	27 , 9	26.0	25.5	25 . 2	2 4 . 9			
P-33	15.5	13.1	12.9	12.6	12.5			

^a Determined from the isotherm "b" point, using 16.2 Å.² for the area of the nitrogen molecule. The B.E.T. plots are not linear.

Upon heating the carbon black to 950°, however the evolution of small amounts of hydrogen commences. This leaves a system of narrow pores which collapse on heating the sample to higher temperatures. This will produce a surface area increase at first, followed by a sharp decrease. Electron micrographs of these heat-treated carbon samples indicate a decrease in particle diameter together with a transition from the spherical particle to irregular polyhedra. These two effects would produce a surface area increase, obviously in direct contradiction to the data in Table I. However, an increase in density with increasing temperature of heat treatment, together with an increased tendency toward agglomeration must counteract the effects of particle shrinkage and irregular shape.

Stepwise Isotherms.—Typical argon isotherms for the three types of carbon black are shown in Figs. 1–3. The blacks have a surface average particle diameter of 354, 1222 and 2250 A. respectively, and so provide a wide range of surface areas (see Table I). Scale diagrams of the quasi-graphitic crystallites, which are randomly oriented within the discrete carbon particles, are included for the



Fig. 1.—Isotherms, argon on Spheron 6 carbon black at $-195\,^{\rm o}.$



Fig. 2.—Argon isotherm at -195° on heat-treated Sterling R (2700°).



Fig. 3.—Isotherms, argon on P-33 carbon black at -195°.

original black and each treatment temperature. Thus on comparing the three blacks it may be seen that not only is the growth of the crystallites a function of temperature but also a function of the carbon particle diameter. This crystallite growth is reflected in the shape of the argon isotherms. The slope of the isotherm in the region of the monolayer decreases, while at the second layer an inflection or step appears. This occurs at 0 35 relative pressure with the adsorbate argon. On the more highly heat-treated samples a second step appears at $P/P_0 = 0.63$ and a third at $P/P_0 = 0.86$. These steps correspond to the filling of the 2nd, 3rd and 4th adsorbed layers. Precisely, the steps occur at multiples of $0.85 V_m$ because either the molecules are not close-packed in the first layer or the presence of crystallite edges increases the surface area by 15%.

These stepwise isotherms are believed to be a consequence of increasing surface homogeneity. The electron micrographs showed a gradual transition from the spherical to the irregular polyhedra. The X-ray diffraction measurements indicated growth of the crystallites. In fact, the crystallites for P-33 (2700°) are of the order of 200 Å, and

those oriented on the surface of the particle may be responsible for the "flat-edged" particles seen in the electron micrographs. From the determination of c, twice the interplanar distance within the crystallite, the degree of graphitization may be determined. Whereas untreated carbon blacks have a c-value of 7.3 Å., P-33 (2700°) has a c-value of 6.84 Å., nearly the same as the value for graphite of 6.74 A. Such an ordered system composed of large planar areas on the surface of the carbon black particles should be expected to provide a homogeneous surface for coöperative condensation.

It was noted earlier that the magnitude as well as the number of steps appear to be a function of crystallite dimension for a given sample. If the isotherms are plotted as fraction of surface covered against relative pressure, samples having similar crystallite sizes should have similar isotherms. The two samples, Sterling R (2700°) and P-33 (2000°) , have vastly different particle diameters but almost the same degree of graphitization. The two isotherms are coincident up to P/P_0 = 0.4 and only slightly displaced at higher relative pressures. The isotherm of a sample of P-33 (1000°), a less highly graphitized black, when similarly plotted, is nearly a sigmoid type isotherm. The slope of each of these isotherms in the region of $P/P_0 = 0.35$ illustrates the differences between the two states of graphitization. The value of the slope at the 0.35 relative pressure region was calculated for all the experimental argon isotherms and plotted as a function of both the L_{a} and L_{c} crystallite dimensions. This is a linear correlation as far as $L_a = 46$ Å. and $L_c = 18$ Å., whereupon there is a sharp break, forming a step that extends to $L_a = 93$ Å. and $L_c = 45$ A. Further increase in crystallite dimensions has no effect upon the isotherm slope at 0.35 P/P_0 . Use of such a correlation curve provides a rapid means of estimating crystallite dimensions for new carbon samples. Adsorption of argon at -195° in the region from $P/P_0 = 0.25$ to 0.50 is sufficient to determine the degree of graphitization of that sample.

It had been called to our attention¹³ that these stepwise isotherms may be due to a freezing point lowering of the adsorbed argon, since the isotherms were determined well below the freezing point of the argon. Consequently, both nitrogen and oxygen isotherms at -195° were determined on many of these same carbon samples. A typical set of isotherms for the three adsorbates on P-33 (2700°) is shown in Fig. 4. The size of the first isotherm step is proportional to the interaction energy of the adsorbed gas, nitrogen having the lowest interaction energy. If the isotherm steps are a result of a freezing point phenomenon, the extent of surface homogeneity must play an important part.

Comparison with Halsey's Equations.—Several equations have been developed by Halsey^{3,5,6} describing multilayer adsorption isotherms. With the assumption that exp $\{-\Delta E_0/E_m\} = 0.2$ and $\Delta E_m/RT = 4$ using equation 13 given in the second paper,⁵ or that $\Delta E_B/\Delta E_m = 2$ and $\Delta E_m/RT = 4$ using equation 8 of the latest paper,⁶ stepwise isotherms are obtained. A comparison of these

(13) J A. Morrison, private communication.





two theoretical equations with the experimental isotherm for argon on Thermax (3100°) is shown in Fig. 5. Correct choice of the variable parameters in the Halsey equations will produce a gradual transition from the sigmoid to the stepwise isotherm. Neither of the two theoretical equations precisely describes the experimental data but both predict steps at the completion of each adsorbed layer occurring at relative pressures of 0.35, 0.75 and 0.87.



Fig. 5.—Comparison of theoretical and experimental isotherms: equation 13, ---; equation 8, ---; Thermax $(3100^\circ), ---O$.

Conclusions

Several series of carbon black adsorbents have been prepared which demonstrate a gradual transition from a heterogeneous to a homogeneous surface. It is gratifying to observe that the degree of homogeneity developed is sufficient to provide experimental confirmation of the stepwise isotherms predicted for a uniform surface.

THE APPLICATION OF THE BJERRUM ION ASSOCIATION THEORY TO THE BINDING OF ANIONS BY PROTEINS

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It is shown that partial shielding of an ion pair from a polar solvent results in increased electrostatic interaction. Application of the Bjerrum theory to the binding of chloride by serum albumin with the assumption of shielding by the protein molecule gives results essentially in accord with the thermodynamics of this reaction. Proper dielectric environment is suggested as an important distinguishing feature of a protein binding site.

Introduction

Ever since experimental evidence made necessary the distinction between the isoelectric and the isoionic points of proteins, it has been apparent that proteins are capable of combining with most anions and many cations to form stable complexes. Much information about the nature of this combination has been gained from the quantitative binding studies of Scatchard, Karush, Klotz and others.² For example, there appear to be two distinct types of binding. The first is operative on heavy metal cations and has been connected with the ability of imidazole residues to form complexes with the cation in question.³ The second type, on which this investigation is focused, does not appear to depend on specific chemical interaction. It has been shown that virtually all anions and many dipolar molecules are capable of combining with proteins, particularly serum albumin, and that in general these compete with one another for sites on the protein molecule.^{4,5} The generality of anionic binding suggests that electrostatic interactions are involved in the combination, an idea which is strengthened by the observation that the acetylation of the amino groups of serum albumin diminishes its power to combine with anionic dyes.⁶ Van der Waals interactions are evidently of importance also since the strength of binding usually increases with the size of the non-polar residue of the anion.

There remain, however, many unexplained features of anionic binding. Most outstanding are: (1) Simple ions like chloride are readily bound by proteins though there is little tendency for them to associate with either free ions or amino acids in aqueous solution. (2) It is not known what characterizes a protein charge as a binding site since there seems to be little connection between the number and nature of known protein charges and the number and strength of binding sites. In particular, one wonders what structural features of the serum albumin molecule account for its remarkable binding properties. Karush has suggested that the serum albumin molecule, because of its looseness of structure, can adapt its configuration to accommodate the bound molecule or ion.⁷ Klotz

(6) I. M. Klotz and J. M. Urquhart, ibid., 71, 1597 (1949).

believes that hydroxyl groups are capable of tying up potential binding sites and that albumin binds strongly because it has a comparatively small number of hydroxyl groups.⁶ Other possibilities will be suggested below. (3) The association is usually accompanied by a large positive entropy change.

That ions of opposite sign will associate under certain conditions was first suggested by Bjerrum⁸ and his theory has been successfully applied by Fuoss and Kraus to the properties of non-aqueous solutions of ionic substances.⁹ It will be assumed in all that follows that the association of anions with proteins involves electrostatic forces only and can be explained by the Bjerrum association theory in suitably modified form. Since this theory applies only to spherically symmetric ions, the calculations will be restricted to the binding of chloride, in which the complicating factor of van der Waals interaction is minimized.

There are only two parameters in the Bjerrum theory, and if its applicability is to be justified, the special binding properties of protein charges must be related to special values of one or both of these parameters. These are the distance of closest approach of the two charges, which is not expected to change when one of the charges is attached to a protein, and the dielectric constant. Here a change might be expected since the large protein molecule will shield the ion pair to a certain extent from the solvent. The effect of such shielding on electrostatic interactions will now be considered.

Electrostatic Calculations.—The electrostatic energy of interaction of two charges separated by a distance d in an infinite dielectric medium is given by the expression

$$W = \frac{e_1 e_2}{\epsilon d} \tag{1}$$

where e_1 and e_2 are the two charges and ϵ is the dielectric constant. If, however, the charges are in the neighborhood of a surface of discontinuity, say an infinite plane separating two materials of different dielectric constant, the situation becomes more complex. A charge is repelled from such a surface if it is in the medium of greater dielectric constant and is attracted if it is in the medium of lower dielectric constant. These forces give rise to additional terms in the interaction energy which

⁽¹⁾ U. S. Public Health research fellow of the National Cancer Institute.

⁽²⁾ A bibliography of binding studies with titles may be found in I. M. Klotz, Cold Spring Harbor Symposia on Quantitative Biology, 14, 97 (1950).

⁽³⁾ C. Tanford, J. ∠m. Chem. Soc., 74, 211 (1952).

⁽⁴⁾ I. M. Klotz, ibid., 68, 2299 (1946).

⁽⁵⁾ F. Karush, ibid., 72, 2714 (1950).

⁽⁷⁾ F. Karush, ibid., 72, 2705 (1950).

⁽⁸⁾ N. Bjerrum, Kgl. Danske Vidensk. Selskab, 7, No. 9 (1926). The theory is also developed in ref. 9.

⁽⁹⁾ R. M. Fuoss and C. A. Kraus, J. Am. Chem. Soc., 55, 1019 (1933).

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can be most readily evaluated using the method of images.¹⁰ We consider a plane boundary between two regions A and B and wish to evaluate the potential in both regions produced by a point charge in A (Fig. 1). It is assumed that ϕ_A , the potential in A, may be represented as the sum of two terms: one arising from the true charge ϵ_1 , the other arising from a charge e_1' , which is the image of e_1 in the plane. This charge may differ in sign and magnitude from the true charge. $\phi_{\rm B}$ is assumed to consist of one term arising from a charge in the same position as the true charge, but differing from it in magnitude. Application of the usual electrostatic boundary conditions (continuity of potential and the normal component of the displacement at the interface) permits the evaluation of the two hypothetical charges. The potentials found in this manner are

$$\phi_{\rm A} = \frac{e_1}{\epsilon_{\Lambda} r} + \frac{(\epsilon_{\Lambda} - \epsilon_{\rm B})}{\epsilon_{\Lambda} (\epsilon_{\rm A} + \epsilon_{\rm B})} \times \frac{e_1}{r'} \qquad (2a)$$

$$\phi_{\rm B} = \frac{2}{\epsilon_{\rm A} + \epsilon_{\rm B}} \frac{e_{\rm I}}{r} \tag{2b}$$

r is the distance of a field point from the true charge, r' the distance from the image charge. It will be noted that the image charge possesses the same sign as the true charge if $\epsilon_A > \epsilon_B$, the opposite sign if $\epsilon_A < \epsilon_B$, and that it vanishes when $\epsilon_A = \epsilon_B$.

We now introduce a second charge, also in region A. Each will produce a potential given by (2). e_1 will be fixed at a distance *a* from the plane boundary and the work required to bring e_2 to a distance *d* from the first charge will be calculated. This can be done without much difficulty for any position of the second charge, but to simplify the discussion, only the case in which the two charges are on a line perpendicular to the interface will be considered (Fig. 2). In calculating the total electrostatic energy *W* care must be exercised in adding the interactions of charges with their images since the latter are not true charges. Ambiguity can be avoided by using the equation

$$W = \frac{1}{2} \left(p_{11}e_1^2 + 2p_{12}e_1e_2 + p_{22}e_2^2 \right) \tag{3}$$

which is more general than the elementary definitions and applies to potentials expressed in terms of images.¹¹ The p_{ij} 's are the coefficients of potential and are defined as the ratio of the potential at charge i caused by charge j to the charge j. In our case these coefficients are given by

$$p_{11} = \frac{\epsilon_{\rm A} - \epsilon_{\rm B}}{\epsilon_{\rm A}(\epsilon_{\rm A} + \epsilon_{\rm B})} \times \frac{1}{2a} \qquad (4a)$$

$$p_{12} = \frac{1}{\epsilon_{A}d} + \frac{\epsilon_{A} - \epsilon_{B}}{\epsilon_{A}(\epsilon_{A} + \epsilon_{B})} \times \frac{1}{2a+d}$$
(4b)

$$p_{22} = \frac{(\epsilon_{\rm A} - \epsilon_{\rm B})}{\epsilon_{\rm A}(\epsilon_{\rm A} + \epsilon_{\rm B})} \times \frac{1}{2(a+d)}$$
(4c)

The self energy of the charges, *i.e.*, the work required to concentrate a finite charge to a point, is infinite and has been deleted. The first term in (3) is the work required to bring the first charge to a distance a from the interface; it must be sub-

(10) W. R. Smythe, "Static and Dynamic Electricity," McGraw-Hill Book Co., New York, N. Y., 1950, or any other text on electrostatics.

(11) Reference 10, p. 36.



Fig. 1.—Two dimensional representation of a charge *e* in the neighborhood of a planar interface and its image *e'* illustrating distances in eq. 2.



Fig. 2.—Two charges and their images illustrating distances in eq. 5.

tracted since e_1 was fixed in this position before the approach of the second charge. Making this sub-traction the total work is then

$$W = \frac{e_1 e_2}{\epsilon_{\rm A} d} + \frac{\epsilon_{\rm A} - \epsilon_{\rm B}}{\epsilon_{\rm A} (\epsilon_{\rm A} + \epsilon_{\rm B})} \frac{e_1 e_2}{2a + d} + \frac{\epsilon_{\rm A} - \epsilon_{\rm B}}{\epsilon_{\rm A} (\epsilon_{\rm A} + \epsilon_{\rm B})} \frac{e_2^2}{4(a + d)}$$
(5)

If $e_1 = e = -e_2$ and the parameter g = a/d is introduced, (5) may be rearranged giving

$$W = -\frac{e^2}{d} \left[\frac{1}{\epsilon_{\rm A}} + \frac{\epsilon_{\rm A} - \epsilon_{\rm B}}{\epsilon_{\rm A}(\epsilon_{\rm A} + \epsilon_{\rm B})} \left(\frac{1}{2g+1} - \frac{1}{4(g+1)} \right) \right]$$
$$\equiv -\frac{e^2}{d} \left[\frac{1}{\epsilon_{\rm eff}} \right] \quad (6)$$

(6) has now the same form as (1). The term in brackets may be regarded as the reciprocal of an effective dielectric constant, *i.e.*, that value of the dielectric constant which when introduced in (1) gives the correct energy of interaction.

 ϵ_{eff} is seen to be a function of the two dielectric constants and g, the ratio of a to d. The variation of ϵ_{eff} with g is illustrated in Fig. 3. In the construction of the curve the values of ϵ_A and ϵ_B were taken to be 80 and 5, respectively. Values for negative g (the first charge in region B) are also shown. These were computed from an equation similar to (6) but derived with e_1 in region B. This curve shows how the potential energy of two opposite charges at a distance d from one another varies with the distance of e_1 from the dielectric interface. It is seen to be a minimum when e_1 is at the interface. When e_1 is far out in region A the shielding effect of B is diminished; when e_1 is too far imbedded in region B, the repulsion of e_2 by region B itself becomes predominant.



If $\epsilon_A \gg \epsilon_B$, (6) may be simplified further to

$$W = -\frac{e^2}{d\epsilon_A} \left[1 + \left(\frac{1}{2g+1} - \frac{1}{4(g+1)} \right) \right] = \frac{-e^2}{d\epsilon_A} f(g)$$
(7)

where f(g) is a purely geometrical factor. If e_2 is not restricted to the line in Fig. 2, f is a more complicated function of a, d and the angle between d and the boundary plane.

The Electrostatic Environment of Protein Charges.—In order to connect the purely electrostatic calculations of the previous section with protein chemistry, a simple electrostatic model of a protein must be adopted. A model which conforms with most modern views of the structure of globular proteins is an ellipsoid of revolution studded with a large number of positive and negative charges. In aqueous solution these charges must be at or near the surface of the protein since they are most stable when surrounded by an aqueous medium and are readily available for titration. One would expect that the protein charges are largely shielded from the bulk of the solvent water on one side by the protein molecule itself and that a protein charge will differ from a free ion in its electrostatic environment to the extent that the protein molecule differs in polarizability from an equivalent volume of water. (It will be assumed that a protein molecule is sufficiently large so that its polarizability may be described in terms of a dielectric constant. The extension concept of dielectric constant to molecular dimensions has been successful in theories of solvation of ions and of the dissociation constants of poly-electrolytes.)^{12,13} There is evidence that a protein molecule will behave like a medium of low dielectric

(12) M. Born, Z. Paysik, 1, 45 (1920).

(13) J. G. Kirkwooc and F. H. Westheimer, J. Chem. Phys., 6, 506 (1938).

constant since most of the polar groups it contains are fixed in configuration and cannot conform to an electric field. The fact that the optical rotation of most globular proteins varies only slightly with considerable changes of pH and temperature indicates that the peptide backbone is quite rigid; the large water content of proteins will not greatly enhance their polarizability since it is chiefly "frozen" water already electrically saturated by the protein charges. These facts suggest that a protein charge will not differ greatly from the e_1 of Figs. 1 and 2 and will therefore have enhanced interactions with other charges. Since a protein molecule can only be crudely represented as a smooth homogeneous ellipsoid, the magnitude of this effect cannot be computed with any degree of certainty and no attempt will be made to correct the results for the curvature of the protein surface. The large size of the protein molecule ensures that the qualitative features of Fig. 3 will remain intact. In view of the above considerations the dielectric constant of a globular protein should not greatly exceed the square of its refractive index. A reasonable estimate is 5, the value of ϵ_B used in constructing Fig. 3, with $\epsilon_A = 80$ representing water.

Shielding by the protein molecule will also shift the pK's of ionizing protein groups—toward higher pH for acidic groups and toward lower pH for basic groups. A rough calculation using Born's equation for the free energy of ions in solution¹² yields $\Delta pK = 1.5$ for an ion of radius 2 Å, and an effective dielectric constant of 40. This effect will be difficult to observe since the pK is also influenced by total protein charge¹⁴ and the configuration of adjacent protein charges.

The Binding of Chloride to Serum Albumin.— In an attempt to account for the severe deviations of electrolyte solutions from the limiting law of Debye and Hückel, Bjerrum suggested that ions might associate to form stable pairs.⁸ In his theory all ions of opposite charge within a distance $q = e_1e_2/2\epsilon kT$ are considered to be associated. A straightforward application of statistical mechanics gives for the association constant

$$K = \frac{N}{1000} \int_0^{2\pi} \int_0^{\pi} \int_a^8 e^{-\frac{W_1 z}{kT}} r^2 \sin\theta d\tau d\theta d\phi \quad (8)$$

where a is the distance of closest approach of the two ions, W_{12} is the free energy of interaction of the two charges at a distance r from one another and the other symbols have their usual significance. If the two charges are equal in magnitude and only coulombic forces are operative, $W_{12} = -e^2/\epsilon r$, the angular integrations give a factor of 4π , and (8) can be simplified to

$$K = \frac{4\pi N}{1000} a^3 b^3 Q(b)$$
 (9)

where 15

$$b = \frac{e^2}{a\epsilon kT}, \quad \mathbf{Q}(b) = \int_2^b e^{-y} y^{-4} \mathrm{d} y$$

(14) E. J. Cohn and John T. Edsall, "Proteins, Amino Acids and Peptides," Reinhold Publ. Corp., New York, N. Y., 1943, Chapter 20.

⁽¹⁵⁾ Values of Q(b) are tabulated in H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1950, p. 123.

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(10)

If this equation is to be applied to the binding of a spherical ion to a protein charge, two modifications must be made. (1) The protein surface will restrict the angular position of the bound ion to a solid angle of approximately 2π rather than 4π . (2) ϵ is a function of both r and θ and must be replaced by an average effective dielectric constant $\langle \epsilon_{\text{eff}} \rangle$ if the integral is to be reduced to the simple form of (9). With these changes we have

where

$$b = \frac{e^z}{\langle \epsilon_{\rm eff} \rangle akT}$$

 $K = \frac{2\pi N}{1000} a^3 b^3 Q(b)$

A simple test case of whether the binding of simple anions can be regarded as Bjerrum association promoted by a reduced effective dielectric is presented by the interaction of the chloride ion with serum albumin, which has been carefully investigated by Scatchard.¹⁶ As previously stated it is not possible to compute the actual effective dielectric constant with any precision. Instead the alternate procedure of taking the value of the association constant found by Scatchard, K = 44, and solving for the average effective dielectric constant has been adopted. Using a = 3.3 Å., the NH_{4} -Cl⁻ distance in crystalline ammonium chloride, graphical solution of eq. 10 gives 28 as the average effective dielectric constant. This is lower than the minimum in Fig. 3. The discrepancy is probably caused by the use of Coulomb's law in calculating the energy of association. This cannot be expected to hold in the intense electric fields in the immediate vicinity of ions which have the dual effect of rupturing the structure of and electrically saturating the solvent. For this reason the Bjerrum theory in its present form can be expected to give only a qualitative description of the binding of ions to proteins. Fuoss and Kraus have shown that for each ion pair there exists a critical dielectric constant above which the associa-tion constant vanishes.⁹ This suggests the possibility that protein shielding makes association possible in aqueous solution by reducing the effective dielectric constant below this critical value.

The heat of association can be calculated from the equations

$$\Delta H = -R \frac{\partial \ln K}{\partial^{1}/T} = -R \left(\frac{3b^{2}Q(b) + b^{3} \frac{dQ}{db}}{b^{3}Q(b)} \right) \left(\frac{\partial b}{\partial 1/T} \right)$$
(11)
$$\frac{\partial b}{\partial 1/T} = \frac{Tb}{\langle \epsilon_{\text{eff}} \rangle} \frac{\partial \langle \langle \epsilon_{\text{eff}} \rangle T \rangle}{\partial T}$$
(12)

resulting in

$$\Delta H = -\frac{RT}{\langle \epsilon_{\text{eff}} \rangle} \left(3 + \frac{e^b}{b^3 Q(b)}\right) \left(\frac{\partial(\langle \epsilon_{\text{eff}} \rangle T)}{\partial T}\right) \quad (13)$$

It is seen that the sign of ΔH is dependent on the sign of $\partial(\langle \epsilon \rangle T)/\partial T$. For ordinary polar and nonpolar liquids this derivative is positive and favors association; for a few highly associated liquids, particularly water, the derivative is negative and the reaction is endothermic. The case of an ion

(16) G. Scatchard, I. H. Scheinberg and S. H. Armstrong, J. Am. Chem. Soc., 72, 535 (1950).

pair partially shielded by a protein molecule is intermediate, the heat is small, and the association is largely an entropy effect. In fact, if $\langle \epsilon_{\rm eff} \rangle =$ $28/80\epsilon_{\rm H_{2O}}$ is substituted in (13), a positive heat of 900 cal./mole is obtained which is within the range reported by Scatchard of 430 ± 540 cal. This should not be taken too seriously as a quantitative calculation but does serve to show that (13) is in conformity with experimental observation.

The source of the positive entropy both found by experiment and predicted by the Bjerrum theory is solvent entropy. It may be defined as¹⁷

$$\Delta S = \left[\int \frac{\partial \epsilon}{\partial T} E^2 dv \right]_{\text{charges}}_{\text{charges}} - \left[\int \frac{\partial \epsilon}{\partial T} E^2 dv \right]_{\text{separated}}_{\text{charges}}$$
(14)

where E is the electric field intensity. It is usually positive since $\partial \epsilon / \partial T$ is negative or zero for all liquids and the first integral is less than the second owing to the cancellation of the fields. It is increased further when one of the charges is brought from aqueous solution to a less polar region since

$$\left|\frac{\partial \epsilon}{\partial T}\right|_{\rm H_{2O}} > \left|\frac{\partial \epsilon}{\partial T}\right|_{\rm polar}$$
(15)

This explanation of the positive entropy corresponds closely to the "liberation of water of hydration" already postulated to account for the positive entropies of association of charged molecules with proteins.

Discussion

The important parameters in (10) are a and $\langle \epsilon \rangle$. The association constant decreases rapidly with increasing $\langle \epsilon \rangle$, which suggests that proper dielectric environment may be an important distinguishing feature of binding sites. In particular the unique binding properties of serum albumin might be ascribed to a number of well shielded charges. Another factor which cannot be excluded is the presence of adjacent protein charges which can either aid or hinder association by their interactions with the bound ion.

The association constant should also increase with decreasing a and therefore with decreasing ionic radius. The experiments of Scatchard and Black have shown, however, that the trend is in the opposite direction.¹⁸ This anomaly probably arises from the use of the Coulombic potential in the derivation of (10) and is evidently related to the finding that apparent radii in electrolyte solutions, as determined by the Debye-Hückel theory, frequently bear an inverse relationship with the crystal radii. The failure of the Coulombic potential is most easily seen with the strongly hydrated cations such as Na⁺ and K⁺. These are reluctant to lose their first hydration shell and are therefore barred from close approach to other ions by repulsive forces ignored in this treatment. This is a plausible explanation for their failure to bind with serum albumin.

Acknowledgment.—The author wishes to express his gratitude to Dr. Rufus Lumry for many stimulating discussions on this and related subjects.

⁽¹⁷⁾ M. Abraham and R. Becker, "The Classical Theory of Electricity and Magnetism," Blackie and Son, London, 1932, Chapter 11, (18) G. Scatchard and E. Black, THIS JOURNAL, 53, 88 (1949).

DIFFUSION OF DISSOLVED MATERIALS THROUGH WOOD

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The theoretical equations derived by Stamm's to describe diffusion in softwoods were checked by two methods involving the measurement of diffusion of sodium chloride and of naphthalene through wood disks and into blocks of wood. Results indicate that the equations are tenable. Possible deductions concerning wood structure are presented.

A study of the diffusion of solutes through solvent impregnated porous media is of theoretical and practical importance in a widely diverse group of phenomena involving the passive transport of substances in solution into and across such porous structures as animal and plant membranes or tissues, rocks, soils, gels, aggregates, etc. Wood is an example of such a porous solid wherein the pores through which diffusion can take place are organized with respect to the dimensions of the solid. Fairly accurate estimates of the dimensions and numbers of pores per unit cross section of wood in the various directions through the specimen can be made microscopically. Wood thus serves as a useful experimental material for the study of the dependence of diffusion on the structure of a porous solid.

Although the diffusion of various materials into wood is important in the chemical pulping processes and in wood preservation procedures, it has been but little studied. Lusby and Maass² investigated the diffusion of sodium chloride, hydrochloric acid and sodium hydroxide into black spruce heartwood. They concluded that the rate of longitudinal diffusion is about the same as the rate in either of the two transverse directions for sodium hydroxide and found the longitudinal rate to be 3.2 times the average rate in the two transverse directions for sodium chloride or hydrochloric acid. Cady and Williams³ studied diffusion restricted to one structural direction of the wood. In this work lactose, urea or glycerol was allowed to diffuse into white fir, western red cedar, white pine or western hemlock. They found three types of diffusion which they called "free," "hindered" and "stirred" diffusion. The type found for a particular species was attributable to the magnitude of the pore sizes occurring in the wood. Christensen⁴ has studied the variables affecting movement of sodium chloride through Eucalyptus obliqua.

A purpose of the present work was to check the theoretical equations derived by Stamm⁵ to describe longitudinal and transverse diffusion through wood and to measure the effects of some of the terms in his equations which are determined by the

sizes of the structural elements of the wood. Stamm derived these equations from an analogy to the laws of electrical conductance concerned with the relationship of resistances to passage of current, namely, that total resistance of conductors in series is equal to the sum of the resistances while in parallel the reciprocal of the total is equal to the sum of the reciprocals of the individual resistances. Stamm combined the resistances to diffusion, as offered by various wood structural elements, to form equations (1) and (2) describing longitudinal and transverse diffusion, respectively.

$$D_{\rm L} = D_{\theta} \left(1 \middle/ \frac{1}{A_{\rm m}} + \frac{n_{\rm w}}{\frac{1}{L_{\rm p}/(q_{\rm L} + q_{\rm m}) + (L_{\rm m}q_{\rm p})} + \frac{Q_{\rm L}}{L_{\rm m}}} \right) + \frac{(1 - A_{\rm m})S_{\rm L}}{(1 - A_{\rm m})S_{\rm L}}$$

and

$$D_{\rm T} = D_0 \left(1 / 1 + \frac{n_{\rm T}}{\frac{1}{L_{\rm p}/(q_{\rm T} + q_{\rm m}) + (L_{\rm m}/q_{\rm p})} + \frac{Q_{\rm T}}{L_{\rm m}}} \right) + \frac{1}{L_{\rm m} n_{\rm T} S_{\rm T}}$$
(2)

where

- $D_{\rm L}$ = the diffusion constant effective in the completely solvent filled wood in the longitudinal direction per unit dimensions of wood
- $D_{\rm T}$ = the diffusion constant effective in the completely solvent filled wood in the transverse direction per unit dimensions of wood
- D_0 = the normal diffusion constant of the solute per unit
- dimensions of the solvent of the cross sectional $A_{\rm m}$ = the fractional void volume and cross sectional area of fiber cavities of swollen wood
- $n_{\rm w}$ = the number of pit membranes or double cell walls traversed in series when the length in the fiber direction is one centimeter
- $n_{\rm T}$ = the average number of fibers traversed per centimeter in radial and tangential directions in swollen wood
- $L_{\rm p}$ = the average pit membrane thickness $L_{\rm m}$ = the average thickness of the double cell walls of swollen wood
- = the fractional area of the tangential walls of the $q_{\mathbf{D}}$ fibers covered by pits
- q_L = the effective fractional cross-sectional area of permanent pit membrane pores for longitudinal passage
- = the fractional cross-section of the transient pit membrane-capillaries of solvent-swollen wood for the passage of molecules the size of water molecules, exclusive of permanent pores $q_{\rm T}$ = the effective fractional cross-sectional area of the
- permanent pit-membrane pores for transverse passage
- $Q_{\rm L}$ = the fractional cross-section of transient cell wall capillaries of solvent-swollen wood effective for passage of molecules the size of the water molecule in the longitudinal direction from one fiber cavity to another
- $Q_{\rm T}$ = the fractional cross-section of the transient cell wall capillaries of solvent-swollen wood effective for the passage of molecules the size of water molecules in the transverse direction from one fiber cavity to another

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⁽³⁾ L. C. Cady and J. W. Williams, THIS JOURNAL, 39, 87 (1935). (4) G. N. Christensen, J. Council Sci. Ind. Res. Australia, 18, 407 (1945)

⁽⁵⁾ A. J. Stamm, U S. Dept. Agri. Tech. Bull., 929 (1946).

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- $S_{\rm L}$ = the fractional cross-section of transient cell wall capillaries of solvent-swollen wood effective for passage of molecules the size of water molecules in fiber direction
- $S_{\rm T}$ = the fractional cross-section of the transient cell wall capillaries of solvent-swollen wood effective for passage of molecules the size of water molecules at right angles to the fiber direction

In the present investigation, the diffusion rates of sodium chloride in water impregnated and swollen wood and of naphthalene in benzene impregnated (non-swollen) wood were measured in both the longitudinal and transverse directions for samples of various soft woods. Measurements of the values of $A_{\rm m}$, $n_{\rm w}$, $n_{\rm T}$ and $L_{\rm m}$ were also made on each wood employed. The measured relative diffusions were compared with the corresponding values calculated from wood dimensions according to equations (1) and (2).

Methods and Materials

The cell used for measurement of diffusion through a disk of wood was patterned after that used by Mouquin and Cathcart.⁶ It was constructed from a piece of flanged Pyrex pipe (1.5 inch diameter). The pipe was cut in two, ground flat on the flanges, and a six millimeter bore stopcock was sealed to the non-flanged ends of each piece. The volumes of each section so obtained were approximately equal. A heavy brass clamp was fitted to each section near the ground edge so that a wood disk under observation could be clamped tightly between the sections. The cell was mounted on a support so that it could be revolved about an axis through the wood disk. Glass bulbs of appropriate specific gravity were contained in each chamber of the cell so that when the cell was revolved they moved through the solution within that chamber and stirred it. Stationary diffusion experi-ments where the cell was held with the solution placed in the upper cell half and distilled water in the lower half gave the same results as when the whole cell was rotated at one revolution per minute. The cell was immersed in a water-bath held at $20 \pm 0.01^{\circ}$ during measurements of the diffusion of sodium chloride and in an air-bath when the diffusion of naphthalene was being measured

Prior to a measurement of diffusion in an aqueous medium the disk of wood to be tested was allowed to come to equilibrium with water vapor saturated air to allow swelling to accur and eliminate cracking when the disk was later evacu-ated under the 1 M sodium chloride solution. In the case of the naphthalene diffusion runs, the disks were first dried in a vacuum oven at 50°. They were then extracted for three or four days with thiophene-free benzene to remove soluble extractives that might interfere with the analysis of naphthalene solutions after completion of a test. Thev were then impregnated with a 0.1 M naphthalene solution in benzene. Edges of the disks were sealed with a vinyl resin coating for the sodium chloride measurements and with the sodium salt of carboxymethyl cellulose for those with naphthalene.

After mounting the disk of wood in the cell, the standardized solution was placed in the upper cell and distilled water or benzene, for the particular case at hand, in the lower. Diffusion was allowed to proceed until a steady state was reached, as shown by equal quantities of solute diffusing through the disk in the same time interval. New solutions through the disk in the same time interval. New solutions were then placed in the cell and diffusion allowed to continue for a time to permit enough solute to pass through the disk to allow for accurate analysis. Sodium chloride in the diffusate was analyzed for by the Mohr method. Naphthalene in diffusates was determined by measurement of its ultraviolet absorption at a wave length of 3120 Å. in the benzene solutions.

A second method which was used in a few experiments for determining the relative diffusion in wood samples was that of allowing a solution to diffuse into blocks of the wood and then sectioning the blocks and analyzing the layers. The procedure followed is described by Burr and Stamm.⁷

Where possible to do so, the magnitude of each term to be employed in equations (1) and (2) was measured for each Thin sections of the wood were cut with the aid of wood. a sliding microtome and photomicrographs were made of these, after staining and mounting. The dimensions of the various wood structures were then obtained from an enlargement of the photograph. Other samples of wood were macerated to release the individual tracheids in order that the length of each enclude be macerated. From 200 to 500 that the length of each could be measured. From 300 to 500 tracheids, under a microscope equipped with an eyepiece micrometer, were measured for each wood sample through which the relative diffusion was determined.

The woods used in the work were of the following species: northern white cedar, *Thuja occidentalis*, L., balsam fir, *Abies balsamea*, (L) Miller, Sitka spruce, *Picea Sitchensis* (Cangard) Carriere, Douglas fir, *Psuedotsuga taxifolia* (La Marck) Brit., and tamarack, *Larix laricina* (Du Roi) Kock. All specimens were heart wood unless otherwise designated in the Tables of results and all samples were air seasoned.

Results

The diffusion coefficient, per unit dimensions of wood, of a solute through a disk of wood saturated with solvent is obtained by substituting in equation (3).

$$D = \frac{2.303hV_{u}V_{1}}{A_{4}(V_{u} + V_{1})}\log\frac{C_{u}^{0}}{C_{u}^{0} - C_{1}(1 + V_{1}/V_{u})}$$
(3)

where

- D = the diffusion coefficient, per unit dimensions of wood, of the solute (cm.²/day) h = the thickness of the wooden disk, cm.
- A = the area of wood disk exposed to solution in cell, cm.²

- t = time of diffusion, days $V_v = \text{volume of upper cell-half, cm.}^3$ $V_1 = \text{volume of lower cell-half, cm.}^3$ $C_n^a = \text{concentration of the upper solution at start of a biffusion are space are litter.}$ diffusion run, moles per liter.
- C_1 = concentration of lower solution at finish of a dif-fusion run, moles per liter.

The diffusion coefficient, as found by equation (3), divided by 1.175, the diffusion coefficient $(cm.^2/day)$ of sodium chloride in water at 20° or by 1.180, the diffusion coefficient (cm.²/day) of naphthalene in benzene at 20° yields the relative diffusion of the solute in the wood impregnated with the corresponding solvent.

Relative diffusions obtained from the measurements and calculations are shown in Tables I, II and III. In Tables I and II, the calculated values of the relative diffusion of sodium chloride as obtained by substituting the various wood dimensions reported by Stamm⁵ into equations (1) and (2), together with the values similarly calculated but

TABLE I

COMPARISON OF MEASURED AND CALCULATED LONGITUDINAL Relative Diffusion Rates of Sodium Chloride through VARIOUS SOFTWOODS

			Relative diffusion				
Section of wood	No. of	Specific gravity, (av.) oven dry weight- green volume	Meas-	Calcd.	Calcd. from wood struc- ture meas- ure- ments		
Northorn white addar	7	0.980	0 643	0.73	0 71		
Northern white cedar	(0.280	0.043	0.10	0.71		
Balsam fir	5	.314	. 603	.70	. 65		
Sitka spruce	6	. 339	. 588	.68	. 63		
Douglas fir	4	.453	.470	.57	. 53		
Douglas fir sapwood	3	. 502	. 429				
Tamarack	5	.465	.437	.56	.48		
Douglas fir	4	.464	. 466	. 56			

⁽⁶⁾ H. Mouquin and W. H. Cathcart, J. Am. Chem. Soc., 57, 1791 (1935).

⁽⁷⁾ H. K. Burr and A. J. Stamm, THIS JOURNAL, 51, 240 (1946).

TABLE II

Comparison of Measured and Calculated Tangential Relative Rates of Diffusion of Sodium Chloride through Various Softwoods

		Relative diffusion				
		Specific			Calcd.	
		gravity,			from	
		(av.)			wood	
		oven			struc-	
		dry			ture	
	No.	weight-		Caled.	meas-	
	of	green	Meas-	by	ure-	
Species of wood	disks	volume	ured	Stamm ⁶	ments	
Northern white cedar	5	0.301	0.0159	0.053	0.059	
Balsam fir	4	. 337	. 0129	. 050	. 039	
Sitka spruce	5	. 340	.0146	. 050	.045	
Douglas fir	5	. 396	. 0108	. 045	. 034	
Douglas fir sapwood	3	. 495	.012			
Tamarack	5	.485	.0112	.035	.034	

TABLE III

RELATIVE DIFFUSION OF NAPHTHALENE IN BENZENE THROUGH VARIOUS SOFTWOOD HEARTWOODS

Species of wood	No. of disks	Specific gravity, oven dry weight- oven dry volume, av.	Relative Meas- ured	diffusion Calcd. by Stamm ²
Long	itudina	al diffusion	I	
Sitka spruce	3	0.392	0.440	0.66
Northern white cedar	4	.331	. 554	.72
Douglas fir	4	. 531	. 255	.56
Tan	gentia	l diffusion		

Northern white cedar 2 .341 .006

by Stamm were employed for all species, although it is probable that these will vary from one wood to another. Table III shows the measured values of the relative diffusion of naphthalene and corresponding values calculated by Stamm.⁵

The relative diffusion values, calculated according to equations (1) and (2), are in reasonably good agreement with measured values. In the longitudinal diffusion measurements with sodium chloride (Table I) the least deviation of the values determined experimentally from those calculated by Stamm⁵ was with northern white cedar. 12%, and the greatest was with tamarack, 22%. In all cases the experimental values were lower than those calculated by Stamm. Calculated values obtained by substituting, in part, microscopically measured dimensions for the actual samples of wood under test into equation (1) are in better agreement with measured values than are the calculated values of Stamm, which were obtained by using average dimensional values for all softwoods. In the tangential diffusion measurements with sodium chloride (Table II) the measured values for relative diffusion amount to only one third to one fifth of the values calculated by Stamm although the order of magnitude of the measured and calculated values are comparable. Calculated values obtained by employing in equation (2) the measured dimensions of the actual wood samples tested remained similar to those obtained by Stamm using average dimensions of all softwoods.

TABLE IV

DIMENSIONS OF WOOD ELEMENTS SUBSTITUTED IN EQUATIONS (1) AND (2) TO OBTAIN CALCULATED RELATIVE DIFFUSION

terms	white cedar	Balsam fir	sitka spruce	Douglas fir	Tamarack	Source of value for terms
.4 m	0.72	0.65	0.64	0.54	0.48	By direct measurement on photomicro- graphs
n	3.53	2.54	2.32	3.76	4.00	From $1/L_e - 1$
$L_{\rm p}$, cm.	0.0001	0.0001	0.0001	0.0001	0.0001	Microscopical estimate (from Stamm ⁵)
<i>q</i> l	0.0038	0.0038	0.0038	0.0038	0.0038	Electroendosmotic measurements (from Stamm ⁵)
$q_{\mathbf{m}}$	0.00011	0.00011	0.00011	0.00011	0.00011	From $q_{\rm P} S_{\rm T}$ (from Stamm ⁵)
(/p	0.014	0.014	0.014	0.014	0.014	Microscopical estimate (from Stamm ⁵)
L_{m} , cm.	0.0004	0.00079	0.00073	0.00092	0.00131	By direct measurements on photomicro- graphs
Q_{L}	0.101	0.101	0.101	0.101	0.101	Stamm's ⁵ value
S_{L}	0.0154	0.0154	0.0154	0.0154	0.0154	Stamm's ^s value
ΝT	330	340	300	300	330	By measurement and count on photo- micrographs
$Q_{\mathbf{T}}$	0.0063	0.0063	0.0063	0,0063	0.0063	Stamm's ⁶ value
qт	0.00052	0.00052	0.00052	0.00052	0.00052	Electro-osmotic measurements by Stamm ⁵
ST	0.0078	0.0078	0.0078	0.0078	0.0078	Stamm's ^s value
Le, cm.	0.278	0.282	0.342	0.210	0.200	Average effective fiber cavity length- from $L_{\rm f}$ and fiber overlap
$L_{\rm f}$, cm.	0.295	0.377	0.402	0.352	0.275	Average fiber length—from measurements on macerated wood

using, where possible, the measured dimensions of the specimens of wood actually employed in the present experiments, can be compared with the experimentally measured values. Table IV lists the dimensions employed in the latter calculated values and shows the sources from which these dimensions were obtained. For those dimensions which are too small to be estimated by photomicrographic procedures the average values given Certain of the terms in equations (1) and (2) are eliminated for the case of a non-swelling solvent, such as benzene, because the openings they represent are present only when the wood is in a swelling medium. Table III shows that the observed values of the relative diffusion in non-swollen wood lie again below the calculated values. The deviation is least for northern white cedar.

A comparison of several methods of measuring

the diffusion coefficient of sodium chloride in wood is made in Table V. These data indicate that the experimental methods used in this work for measuring diffusion coefficients in wood check well with one another. The glass cell diffusion method also gave values for the diffusion coefficient of sodium chloride through various species of wood that are close to those found by an indirect method of measurement, conductivity, and by another wood disk method.

TABLE V

COMPARISON OF RELATIVE DIFFUSION COEFFICIENT OF SODIUM CHLORIDE IN VARIOUS SOFTWOODS AS MEASURED BY DIFFERENT METHODS

		Diele			
Species	Direction of diffusion	and glass cell ^a	$Block^b$	Conduc- tivity ^c	\mathbf{Disk}^d
Douglas fir	Longitudinal	0.47		0.43	
Douglas fir	Tangential	.0064	0.006	.022	
Sitka spruce	Longitudinal	. 59		. 56	
Sitka spruce	Tangential	.0146	.0128		
Eucalyptus					

oblique Tangential .01 ... 0.0109 ^a As described in this work. ^b Method of Burr and Stamm⁷ used in this work. ^c Method and value reported by Burr and Stamm.⁷ ^d Method and value reported by G. N. Christensen, in "Progress reports on factors governing the rate of diffusion of salts into green timber," 1945-1947, Australian Council for Scientific and Industrial Research.

Discussion

Comparison of relative diffusion values obtained by direct measurement with those calculated from wood dimensions should serve to substantiate or refute the theoretical equations of Stamm and might reveal further explanation of various phenomena connected with the passage of liquids through wood.

Although the agreement of the comparable measured and calculated relative diffusion constants may not appear to be good by chemical standards, they are reasonably good considering the variability of wood. As was noted by Burr,⁷ if the two or threefold variation in the diameter of the softwood elements such as tracheids is considered, the experimental values fall within the limits of Stamm's⁵ theoretical curves as allowed for by this diameter variation.

For longitudinal diffusion of sodium chloride in the solvent swollen woods, the theoretical and experimental curves, obtained by plotting the relative diffusions *versus* the specific gravity of the dry wood, are found to be parallel. The deviations between the curves remain relatively constant for all the species studied.

For transverse diffusion of sodium chloride in solvent swollen woods the experimentally determined values of relative diffusion lie considerably below those calculated according to equation (2) from measured and estimated structural dimensions of the wood. The experimental and calculated values, as in the case of longitudinal diffusion, vary in a parallel manner with varying wood specific gravity.

It is likely that the more marked divergence of observed values from calculated values for tangential diffusion exists because of the inexactness of

some of the terms used in equation (2). For instance the effective area of the permanent pit membrane pores for passage of molecules the size of water molecules has never been determined for many of the species used in this work and is subject to considerable error in its measurement where it has been accomplished. The size and number of transient capillaries in the pit membranes and cell walls which are effective for passage of solute molecules are also uncertain. If the value of $L_{\rm p}$, the thickness of the pit membrane, is halved there will be a 19.4% decrease in the calculated transverse diffusion coefficient. The pit membrane is so thin that its thickness can only be estimated. Other terms in equation (2), q_{T} , S_{T} , q_{m} , q_{p} , Q_{T} , also have appreciable effects in determining the value of the relative transverse diffusion and cannot be measured as accurately as the effective terms (primarily A_m) in equation (1). Possible errors in the accurate determination of the dimensions of wood structural elements do not affect seriously the value for the longitudinal diffusion coefficient. For example, if the value of L_p is halved, the calculated relative longitudinal diffusion is reduced by only 1%. Examination of equation (1) indicates that the fractional cross-sectional area of the fiber cavities of the swollen wood is the most important term in its evaluation. This term can be measured with considerable accuracy from photomicrographs of a transverse section of the swollen wood.

During the process of diffusion, molecules of the solute move from a point of high to one of low concentration. In longitudinal diffusion where a species such as northern white cedar is involved, the chances of the diffusing molecule entering into a tracheid lumen are good because this species has thin cell walls and much open space per unit of area. In Douglas fir or tamarack, though, the cross sectional area contains much more wood substance than in the case of northern white cedar: therefore, there is much less chance of unrestricted movement of the sodium chloride through these denser woods. Thus, the percentage of open area of the wood is of great importance in determining the relative longitudinal diffusion coefficient. The specific gravity of wood is an indication cf the amount of actual wood substance present and this bears a relation to the cross sectional area composed of wood substance. The relative longitudinal diffusion through a piece of wood increases, therefore, more or less linearly with decreasing specific gravity. In the diffusion of sodium chloride radially or tangentially through a softwood, the diameters of the cell lumina are not of such importance because the diffusing molecule must pass through approximately one hundred times as many cell walls or pit membranes for the same thickness of wood as when it is moving longitudinally.

It was found that heartwood and sapwood of the same tree (Douglas fir) gave nearly the same longitudinal relative diffusion coefficients with sodium chloride where specific gravity was the same. Structural data for this wood⁸ indicate that the pit membrane pores of an average sample of

(8) Alfred J. Stamm, THIS JOURNAL. 36, 312 (1932).

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Douglas fir sapwood are five times larger in diameter than those of the heartwood and the pore area 25 times larger. In spite of this great increase in pore area of the sapwood over the heartwood, the longitudinal relative diffusion coefficients are still of equal magnitude. This is another indication that the most resistance to longitudinal diffusion in softwoods is due to the cell walls themselves, and not to the size of the smallest passageways from one cell to another as in the case of pressure permeability. In tangential diffusion, by contrast, the size of the pit membrane pores is important in determining the relative diffusion and the smaller size heartwood pores may explain an observed 25%greater tangential diffusion coefficient for Douglas fir sapwood over heartwood.

These results and considerations support the conclusion that the use of equations (1) and (2) is warranted when longitudinal and transverse diffusion coefficients are being estimated from measured structural dimensions of a swollen wood specimen. Because of a greater dependence upon small and difficultly measurable structural dimensions of the wood, however, results achieved through calculations involving equation (2) are subject to a greater probable error than those attained with equation (1).

For longitudinal diffusion through wood of a substance dissolved in a non-swelling solvent, equation (1) becomes simplified by omitting all terms for wood openings that exist only in swollen wood. Table III shows that the experimental values all lie below the calculated values, approaching more closely in the samples of lower specific gravity, *i.e.*, for northern white cedar. It is possible that this lack of parallelism in the curves (relative diffusion versus wood specific gravity) is a result of a greater lcss of extractives by the cedar or it may be due to the variation in the fractional open area of the wood because of the variation in the diameter of the tracheid lumina. The experimental results are still in fair agreement with the calculated ones and it may be concluded that longitudinal diffusion in non-swelling solvents is adequately described by equation (1) with proper deletions.

It is believed that the longitudinal diffusion of naphthalene ir. benzene through the various softwoods presents a case for the existence of permanent pit membrane openings. Since the cell wall does not swell, no transient capillaries would exist in either pit membranes or in the cell walls. Yet the naphthalene molecules pass through unswollen woods at a rate comparable to that for electrolytes through swollen woods. If the absence of per-

manent cell wall pores is accepted—and there is no histological evidence for their presence—it must be concluded that permanent openings exist in the pit membranes which are at least large enough to permit naphthalene molecules to pass.

In the tangential direction the relative diffusion of a solute into heartwood saturated with a nonswelling solvent is only about 40% of that for a swelling solvent. Transient capillaries do not exist in the cell walls of dry wood saturated with benzene. It was previously mentioned how important these transient capillaries are in tangential diffusion. They do not constitute a diffusion pathway in non-swollen wood.

The experimental value for relative diffusion of naphthalene tangentially through northern white cedar was found to be about one-third of the calculated value. Aside from the experimental error in wood dimension estimation, this difference may be partly explained by the fact that the theoretical equations were postulated for diffusion of molecules the size of water molecules whereas the measurements here were made with naphthalene, the molecular diameter of which is seven times that of a water molecule. No tangential diffusion at all could be measured for naphthalene in benzene through Sitka spruce or Douglas fir. A possible explanation is that the permanent pit membrane pores are too small to allow passage of the naphthalene molecules. In determining tangential diffusion rates in non-swelling solvents the size of the pit membrane pores is important. Using the values of the terms given by Stamm⁵ for Sitka spruce in the swollen condition one obtains by equation (2) a relative diffusion of 0.013. If, however, the effective fractional cross-sectional area of the permanent pit-membrane pores for tangential passage were only one-hundredth the value for swollen wood, which is conceivable if many pits were so tightly aspirated in a nonswelling solvent as to render them impassable, the relative tangential diffusion would only be 0.00016. This may mean that in a non-swelling solvent some species of softwood contain bordered pits that remain tightly sealed, whereas in a swelling solvent, effective passageways are opened which allow diffusion. It could also mean that the direct passage through transient capillaries of the cell wall is an important medium for diffusion of electrolytes in a swelling solvent, and passage through the pit membrane pores is secondary in the case of Douglas fir and Sitka spruce. Such being the case, tangential diffusion through these species in nonswelling solvents is virtually nil because of the absence of cell wall capillaries.

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