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## THE JOURNAL OF

# PHYSICAL CHEMISTRY

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## THE JOURNAL OF PHYSICAL CHEMISTRY

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## HEATS OF ADSORPTION AND ADSORPTION ISOTHERMS FOR LOW BOILING GASES ADSORBED ON GRAPHON

BY E. L. PACE AND A. R. SIEBERT

Morley Chemical Laboratory, Western Reserve University, Cleveland, Ohio

Received July 7, 1959

The results of a calorimetric investigation of the equilibrium pressures and differential heats of adsorption for nitrogen argon, neon, orthodeuterium, parahydrogen and helium (He<sup>4</sup>) adsorbed on Graphon in the neighborhood of their respective boiling points are presented.

#### Introduction

A number of recent papers have directed attention to the fact that anomalously high surface areas are obtained when the BET<sup>1</sup> multilayer theory is used with gases with very low boiling points. Schaeffer, *et al.*,<sup>2</sup> report a surface area with helium adsorbed on carbon black which is two to threefold greater than that obtained with nitrogen. This result has been confirmed<sup>3</sup> for both He<sup>3</sup> and He<sup>4</sup> on activated charcoal. Tykodi and Aston<sup>4</sup> also report unexpectedly high areas for the case of neon adsorbed on titanium dioxide.

The present investigation was undertaken' in part to make a comprehensive study of the anomaly for all readily available low boiling gases on a surface of reasonably well-known structure. As a result, areas by the BET method have been determined from equilibrium pressures of nitrogen, argon, neon, orthodeuterium, parahydrogen and helium (He<sup>4</sup>) adsorbed on the same surface at the normal boiling point of each gas. Graphon was used as an adsorbent because it has a high area surface endowed with an unusually high degree of uniformity.

Since the magnitude of the interaction of adsorbed molecules with the adsorbent surface and with each other is of interest, differential heats of adsorption were measured calorimetrically and cor-

(4) R. J. Tykodi, J. G. Aston and G. D. Schreiner, J. Am. Chem. Soc., 77, 2168 (1955). related with the results from the equilibrium pressure measurements.

#### Experimental

The gases which were used in the investigation were commercially available with purities of 99.5% or greater. The helium was further purified by passage over activated charcoal at liquid nitrogen temperatures. The hydrogen and deuterium were converted to approximately 95% parahydrogen and orthodeuterium prior to use.

The calorimetric apparatus and procedure has been described previously.<sup>5,6</sup>

The sample of Graphon was obtained from Godfrey L. Cabot Laboratories, Boston, Massachusetts. The preparation and general characteristics of Graphon have been given by Schaeffer and co-workers.<sup>7</sup> X-Ray diffraction measurements conducted on the particular sample used here gave a  $\bar{c}$  spacing of 6.96 Å. as compared to 6.70 for true graphite.

Excepting for one helium isotherm at  $4.2^{\circ}$ K., all the experimental data were taken with a 31.3-g. portion of the above sample. For the determination of the helium isotherm at  $4.2^{\circ}$ K., a separate 3.25-g. portion of the sample was placed in a small monel container which was joined to the gas-sampling and high vacuum systems by means of a 1.5 mm. monel tube. The container was immersed in liquid helium while the equilibrium pressure measurements were being made. It was assumed that the conversion of the results for the helium isotherm to the same basis as all the other results involved merely the ratio of the weights of the two samples of Graphon.

The calorimetric heats of adsorption were determined for cumulative quantities of each gas until the total coverage exceeded the monolayer value. For all the gases except helium, it was possible to carry out these determinations

(5) E. L. Pace, L. Pierce and K. S. Dennis, *Rev. Sci. Instr.*, **26**, 20 (1955).

(6) E. L. Pace, E. L. Heric and K. S. Dennis, J. Chem. Phys., 21, 1225 (1953).

(7) W. D. Schaeffer, W. R. Smith and M. H. Polley, Ind. Eng. Chem., 45, 1721 (1953).

<sup>(1)</sup> S. Brunauer, P. H. Emmett and E. Teller, J. Am. Chem. Soc., 60, 309 (1938).

<sup>(2)</sup> W. D. Schaeffer, W. R. Smith and C. B. Wendell, *ibid.*, 71, 863 (1949).

<sup>(3)</sup> C. J. Hoffman, F. J. Edeskuty and E. F. Hammel, J. Chem. Phys., 24, 124 (1956).



Fig. 1.-Heat of adsorption of nitrogen on Graphon.



Fig. 2.-Heat of adsorption of argon on Graphon.

at average temperatures corresponding to the normal boiling point of the gas. For helium, the calorimetric measurement was limited to temperatures obtainable with liquid hydrogen as the refrigerant.

Equilibrium pressures of the adsorbate as a function of coverage were determined either as individual isotherms in the neighborhood of the normal boiling points or from observations at essentially constant coverage while the temperature of the calorimeter was varied. Isosteric heats



Fig. 3.—Heat of adsorption of neon on Graphon.



Fig. 4.—Heat of adsorption of deuterium on Graphon.

of adsorption then were evaluated at specific coverages from the data by the use of the Clausius-Clapeyron equation or graphically from plots of  $\ln p \ vs. 1/T$ . In the case of helium, the isosteric heats were evaluated from one isotherm at 11.8°K. determined with a 31.3-g. portion of Graphon and a second isotherm at 4.2°K. determined with a separate 3.25-g. portion.

#### **Results and Discussion**

The results of the equilibrium pressure measurements have been correlated by means of the equation

• 
$$p/v(p_0 - p) = 1/v_{\rm m}c + [(c - 1)/v_{\rm m}c](p/p_0)$$
 (1)

which is evolved from the BET<sup>1</sup> multilayer theory. The values of the two parameters, c and  $v_{\rm m}$ , for the systems which were studied appear in Table I. The surface areas in each case which were calculated from  $v_{\rm m}$  assuming liquid packing of the molecules in single layer on the surface are given in the last column of Table I.

TABLE I

SURFACE AREAS FROM THE BET PLOTS FOR THE VARIOUS GASES ON GRAPHON

	<b>a</b> 1015	<sup>n</sup> m, monolayer		Area of inolecule from liq.	Surface area,
Gas	$T$ , $^{\circ}$ K.	in moles	с	density, A.*	sq. m./g.
Ar	87.5	0.0311	443	14.4	86.1
$N_2$	77.4	.0275	688	16.2	85.9
Ne	27.3	. 0486	329	10.0	93.4
$D_2$	23.5	. 0703	55	12.9	174.3
$H_2$	20.4	.0620	168	14.2	169.3
He	4.2	$.00934^{a}$	150	15.4	266.6
<sup>a</sup> For	3 25 g of	Graphon.			

The differential heats of adsorption which were determined calorimetrically and the isosteric heats of adsorption which were evaluated from equilibrium pressure data are summarized in graphs of these quantities as a function of the amount adsorbed. Figure 1, 2, 3, 4, 5 and 6 present the results, respectively, for nitrogen, argon, neon, orthodeuterium, parahydrogen and helium. The open circles represent the calorimetric data while the solid or half-solid circles represent the values from equilibrium pressure data.

In those cases where precise measurements of the differential heats of adsorption of the systems have been made, there is good agreement despite the wide variety in the nature of the graphitic surfaces which have been used. The results of Aston and Greyson<sup>8</sup> with neon and helium adsorbed on graphitized carbon (P-33, 2700°) and of Young and co-workers<sup>9-11</sup> with argon adsorbed on graphite and Graphon correspond well with the results of the present investigation.

Acknowledgment.—We are indebted to Dr. W. D. Schaeffer of Godfrey Cabot Laboratories, Boston, Massachusetts, for the sample of Graphon and pertinent structural data. Mr. Robert Shepard of the National Carbon Company, Cleveland,

(8) J. G. Aston and J. Greyson, This JOURNAL, 61, 613 (1957). (9) D. H. Everett and D. M. Young, Trans. Faraday Soc., 48, 1164 (1952).



Fig. 5.—Heat of adsorption of hydrogen on Graphon.



Fig. 6. --Heat of adsorption of helium on Graphon.

Ohio, made the liquid helium which was used in the experiments available to us. The research has been carried out with the support of the Atomic Energy Commission under Contract No. AT(30-1)-824.

<sup>(10)</sup> A. D. Crowell and D. M. Young, ibid., 49, 1081 (1953).

<sup>(11)</sup> R. A. Beebe and D. M. Young, This JOURNAL, 58, 93 (1954).

### THE DECOMPOSITION OF METHANE IN SHOCK WAVES<sup>1</sup>

BY V. KEVORKIAN, C. E. HEATH AND M. BOUDART<sup>2</sup>

Esso Research and Engineering Company Received July 15, 1959

The decomposition of methane in the temperature range  $1656-1965^{\circ}$ K. was studied in a single pulse shock tube reactor. The reaction was found to follow first-order kinetics with the rate constant  $k = 1.32 \times 10^{14} e^{-93,000} / RT$  sec.<sup>-1</sup>. The homogeneous, high temperature reaction is not inhibited by hydrogen. A reaction mechanism involving the decomposition of methane to methylene is postulated to explain the major observations.

#### Introduction

About thirty years ago, Kassel carried out a detailed kinetic study of methane decomposition in the temperature interval 750-1000°.3 He concluded that the reaction is homogeneous, is first order, has an activation energy of 79.4 kcal., and is inhibited by hydrogen. Since that time many other investigators have studied the reaction but have agreed on neither the kinetics nor the mechanism.4-7 Recently, Shantarovich and Pavlov carefully studied the reaction, placing particular attention on its initial stages.<sup>8</sup> They confirmed that methane decomposition at 850-1000° is first order and homogeneous as suggested by Kassel, but found the activation energy to be 85 kcal. They further concluded that the reaction is severely inhibited by  $H_2$ , an observation since confirmed by Germain and Vaniscotte.9

The chemical shock tube reactor provides a new way of studying these high temperature reactions. The shock tube generates a shock wave that homogeneously heats the reactants almost instantaneously and is followed by an expansion wave that cools at a relatively high rate  $(10^{5\circ} \text{K./sec.})$ . The reaction is quenched before diffusion to the walls Therefore, it is studied free of surface occurs. effects.

The extent of possible wall reactions can be calculated from the kinetic theory of gases. On the basis of these calculations, it is concluded that wall reactions do not play a significant part in the reaction. From the equation.

$$\overline{x^2} = \frac{4c_A l_A t}{3} \tag{1}$$

where

- $c_{\rm A}$  = root mean square velocity
- $l_{\rm A}$  = mean free path t = time

and the geometry of the reactor, the number of molecules (or radicals) that can diffuse to the walls is calculated. This is compared with the number of molecules (or radicals) that react in the gas phase

(1) Presented before the 135th Meeting of the American Chemical Society, April, 1959.

(2) Dept. of Chemical Engineering, Princeton University, Princeton, N. J.

(3) L. Kassel, J. Am. Chem. Soc., 54, 3949 (1932).

(4) D. Rudder and H. Biedermann, Bull. soc. chim. France, 47, 710 (1930).

(5) R. V. Wheeler and W. L. Wood, Fuel, 9, 567 (1930).

(6) H. H. Storch, Ind. Eng. Chem., 26, 56 (1934).

(7) H. Tropsch and G. Egloff, ibid., 27, 1063 (1935).

(8) P. S. Shantarovich and B. V. Pavlov, Zhur. Fiz. Khim., 30, 811 (1956).

(9) J. E. Germain and C. Vaniscotte, Bull. soc. chim. France, 319 (1958).

during the shock wave heating pulse. It is assumed that the reaction rate can be given by the normal collision frequency. Using this approach it can be shown that 10<sup>6</sup> homogeneous phase collisions occur for every molecule or radical that collides with the wall. Because most of these homogeneous phase collisions will result in reaction, any contribution of surface to the over-all kinetics will be negligible.

The reaction time is clearly defined and the products recovered are representative of reactions at known conditions. As a result of these advantages, the shock tube was used in the experiments on the thermal decomposition of methane described in this paper. These data provide new information on the chemistry of methane at 1650-2040°K.

The shock tube used in these studies was similar to the "chemical shock tube" of Glick, et al.<sup>10</sup> In this single pulse shock tube, all the reaction occurs behind a single reflected shock wave (Fig. 1). Temperatures and pressures in the reactant behind the reflected shock wave were calculated from equations using the measured velocities of the incident and reflected shock waves. These equations are derived from the laws of conservation of mass, momentum and energy. They were solved using the ideal gas equation of state and extrapolated enthalpy properties from the National Bureau of Standards Tables. The techniques have been described in the literature.<sup>11</sup>

It was necessary to dilute the methane heavily in these experiments with argon in order to obtain valid kinetic data. Temperature changes caused by chemical reaction in the adiabatic environment behind the reflected shock front are kept negligible by the large amounts of argon. Deviations from ideal shock wave theory are also minimized by a high degree of argon dilution. Finally, argon permits the attainment of high temperatures with relatively weak shocks, because of its low heat capacity which remains constant with increasing temperature.

#### Experimental

Mixtures of reactant and argon were pyrolyzed in a 3" i.d. stainless steel single pulse shock tube. The low pressure, or reactant, section was 12 feet long and the high was attached at the high pressure end to a vacuum tank having a volume of 100 cubic feet. The two sections of the shock tube and the tank were all separated by metal diaphragms which were constructed either of stainless steel,

(10) H. S. Glick, W. Squire and A. Hertzberg, "Fifth Symposium (International) on Combustion," Reinhold Publ. Corp., New York, N. Y., pp. 393-402.

(11) A. H. Shapiro, "The Dynamics and Thermodynamics of Compressible Fluid Flow," Vol. II, The Ronald Press Co., New York, N. Y., 1954.

 $<sup>\</sup>overline{x^2}$  = mean square displacement of a molecule

type 302, 0.018 in. thick; aluminum, type 2024-T3, 0.020 in. thick; Alclad aluminum, type 2024-T3, 0.016 in. thick; or magnesium, FS-1-H24, 0.025 in. thick, depending on the difference between driver gas pressure and reactant gas pressure. These materials provide for a range of pressure differentials from 90 to 3 atmospheres.

Before a run, the shock tube is evacuated and premixed mixtures of 90% argon-10% reactant or 98% argon-2%reactant are charged to the reactor. The reactant section is re-evacuated and then recharged with the methaneargon mixture. Helium is added to the high pressure section to a pressure precalculated to give the desired shock conditions. The tank remains evacuated at 65 mm. pressure. After the reactor was charged, a shock wave was set off by rupturing the diaphragm between the driver and the reactant sections with a plunger. This plunger is actuated by firing a small auxiliary shock tube which generates a shock wave that sets the plunger in motion. The small shock tube also actuates a second plunger, a controlled instant later. The second plunger ruptures the diaphragm between the high pressure section and the vacuum tank. The reflected shock wave heats the reactant to the desired temperature and the gases are cooled rapidly at the end of the reaction period by the cooling wave generated from the vacuum tank.

The velocities and pressures of the incident shock and expansion waves are measured at two points along the shock tube by SLM quartz pressure transducers which are spaced eight and a half feet apart with the downstream one six inches from the end plate. Similar information is obtained for the reflected shock wave from the transducer adjacent to the end plate. The signals from these transducers are displayed on a model 152A Hewlett-Packard oscilloscope. The histories of these signals are recorded by a Polaroid camera to provide the data needed to calculate experimental conditions.

Following the run, a vacuum line is opened to the reactant section and samples of the products are withdrawn. These samples are analyzed for methane, argon and helium by mass spectrometry. The argon provides a material balance. The presence of large amounts of helium in the sample indicates either mixing across the contact discontinuity between reactant and driver or turbulent mixing due to poor intersection of the reflected shock wave and contact discontinuity. Such runs were rejected and not used for kinetic calculations.

Two series of experiments were carried out. The first was done with  $CH_4$ -Ar mixtures in the temperature range 1656-1965°K. The second series was done with  $CH_4$ - $H_2$ -Ar mixtures between 1650 and 2040°K. Compressed gases were purchased from the Matheson Company and used without further purification.  $CH_4$ ,  $H_2$ , He and Ar all had purities greater than 09.0, 99.9, 90.99 and 09.998%, respectively. All gases were analyzed by mass spectrometry prior to use.

#### Results

A study of the reaction kinetics is dependent on an accurate estimate of the time during which the high temperature and pressure were maintained. Special considerations are necessary to determine time in a shock tube study, because it decreases throughout the sample with increasing distance from the end of the shock tube. This is evident from Fig. 1. At the end of the run, segments of gas sample having different residence times become mixed, and a composite sample is therefore withdrawn for analysis. Consequently, the conversion determined by product analysis will represent a composite of conversions from a series of reaction volumes having residence times varying from the endplate residence time,  $\tau$ , to a residence time of zero. Therefore, reaction rate constants cannot be explicitly calculated from the over-all conversions and the endplate time or some average residence time. Expressions which take the varying residence times into account can be derived



to provide the rate constants from the shock tube data.

The expressions show that the observed rate constant is lower than the true constant. For a first-order reaction the relation between concentrations and true constants is given by

$$c = \frac{c_0 (1 - e^{-k\tau})}{k\tau}$$
(2)

where

c = concentration

k = reaction rate constant

For a second-order reaction, the corresponding equation is

$$c = \frac{1}{k\tau} \ln \left( 1 + c_0 k\tau \right) \tag{3}$$

The results of the first series of experiments at temperatures from  $1656-1965^{\circ}$ K. were used to calculate both first- and second-order reaction rate constants using the expressions derived above. Equation 2 also was used to calculate the effect of hydrogen on methane pyrolysis in the temperature range  $1650-2040^{\circ}$ K. These data collected at a variety of temperatures, pressures and conversions, are given in Table I.

The "tailored-interface" technique<sup>12</sup> was not employed in these experiments. Any error consequently introduced in the reaction times is, however, believed to be small, because the wave diagrams of the experiments showed the contact discontinuity, reflected shock wave and cooling waves to intersect either in, or close to, a point. The transducer histories also showed no significant pressure changes due to either secondary shock or expansion waves reflected back into the reacting gases when the reflected shock wave intersected the contact discontinuity. These secondary waves, therefore, had to have a negligible effect in comparison to the strong cooling wave generated from the vacuum tank.

The first- and second-order reaction rate constants were fitted graphically to Arrhenius functions

$$k = A e^{-E/RT} \tag{4}$$

An excellent correlation of the shock tube data was obtained using an Arrhenius plot based on firstorder reaction rate constant. The scatter was small in spite of the wide variation in experimental

(12) H. S. Glick, J. J. Klein and W. Squire, J. Chem. Phys., 27, 850 (1957).

TABLE I						
Shock	Тиве	Pyrolysis	OF	METHANE		

reed compn.									
Vol. % CH <sub>1</sub>	2							2	
Vol. % H2									•
Vol. % A	÷		· · · · · · · · · · · · · · · · · · ·	)()				98	
React. press., p.s.i.a.	1.25	1.25	1.25	1.25	1.25	1.25	4.1	4.4	3.3
Driver press., p.s.i.a.	125	125	125	125	125	125	215	215	215
Shock press., p.s.i.a.	13	13	13	14	13	13	38	42	33
Refl. shock press., p.s.i.a.	53	50	50	56	53	50	156	174	140
Reactant temp., °K.	•••••	•••••			300				<b></b>
Driver temp., °K.		•••••		<b>-</b>	300				
Shock temp., °K.	1005	972	972	1029	1002	979	960	975	1008
Refl. shock temp., °K.	1701	1656	1656	1750	1707	1671	1701	1680	1813
Shock wave vel., ft./sec.	3148	3091	3091	3208	3148	3091	2931	2962	3038
Contact discontinuity vel., ft./sec.	2143	2094	2094	2195	2145	2094	1940	1960	2007
End plate res. time, millisec.	1.6	1.9	2.4	1.7	1.8	1.8	1.4	1.5	1.8
Total material bal., $\frac{C}{10}$	98.6	99.5	98.8	99.3	99.9	99.4	99.2	99.4	99.8
H <sub>2</sub> material bal., $\%$	94.3	98.1	95.3	97.2	98.8	97.7	96.9	97.5	99.3
Methane conv., %	10.4	8.8	12.5	13.0	9.1	7.6	21.2	13.7	48.8
Feed compn.									
Vol. % CH₄		2	0	9	••••••		0.9		
Vol. % H2						0.6			
Vol. % A	······	8			· · · · · · · · · · · · · · · · · · ·	- 98.5			
React. press., p.s.i.a.	<b>2.6</b>	2.15	4.1	<b>2.9</b>	2.5	2.3	2.2	2.2	3.1
Driver press., p.s.i.a.	215	215	215	215	215	215	215	215	215
Shock press., p.s.i.a.	26	24	33	28	25	25	24	24	29
Refl. shock press., p.s.i.a.	113	103	130	117	106	108	105	105	120
Reactant temp., °K.	300				298	••••••			
Driver temp., °K.	300	•••••			298				
Shock temp., °K.	1032	1073	864	969	1013	1064	1076	1076	954
Refl. shock temp., °K.	1875	1965	1650	1870	1860	1960	2040	2040	1790
Shock wave vel., ft./sec.	3078	3172	2424	2972	3047	3148	3184	3184	2931
Contact discontinuity vel., ft./sec.	2040	2140	1800	1980	2025	2110	2130	2130	1950
End plate res. time, millisec.	2.1	1.5	1.3	2.0	1.6	1.8	1.5	1.6	1.4
Total material bal., %	98.8	100.0	125.1	129.0	120.8	113.2	120.3	124.6	115.3
H <sub>2</sub> material bal., %	95.5	100.1	111.2	117.6	117.8	108.4	128.6	118.7	107.4
Methane conv., 76	75.0	86.2	22.0	79.5	50.0	79.8	93.1	88.1	54.0

conditions. Furthermore, when the correlation was extended to the low temperatures at which Shantarovich and Pavlov carried out their studies,<sup>8</sup> an excellent fit of their data was obtained, as shown in Fig. 2. This is good evidence for the selection of first-order kinetics. Pressure provides additional evidence. The Arrhenius plot data of Shantarovich and Pavlov were obtained at CH<sub>4</sub> pressures of 100 mm. The data of this investigation were obtained at methane partial pressures up to 290 mm. and total pressures of about 100 p.s.i.a. The insensitivity of the rate constant to a threefold increase in methane partial pressure also tends to indicate that the reaction is first order.

The data were further tested by assuming that the reaction could be second order. Second-order reaction rate constants were calculated and fitted to an Arrhenius line. When plotted in this fashion, the shock tube data gave an empirical activation energy of 133 kcal./mole. This activation energy is considerably greater than that required to break the strongest bond strength in reacting methane by such a large amount. The data of Shantarovich and Pavlov,<sup>8</sup> recalculated on the assumption of second-order kinetics, failed to fall on the experimental line extended from the shock tube data. On the basis of these observations, the possibility that the reaction is second order is discounted.

While it is possible that the reaction follows fractional order kinetics, the shock tube technique does not permit resolution from the nearest integral order over the variable ranges covered in this study.

The excellent fit of the data to a first-order Arrhenius function, the insensitivity of the system to changes in methane pressure, and the demonstration that the reaction is not second order, leads to the conclusion that the homogeneous decomposition of methane follows first-order kinetics over a wide range of conditions.

The first-order rate constant fitted to the combined high and low temperature data has a value of  $1.32 \times 10^{14}e^{-93,000/RT}$  sec.<sup>-1</sup>. The measured frequency factor agrees with the value predicted by the kinetic theory of gases for a unimolecular reaction,  $10^{13}-10^{14}$  sec.<sup>-1</sup>. The measured activation energy is also in substantial agreement with the values, 78–95 kcal./mole, reported by other investigators for the reaction at lower temperatures.<sup>13</sup>

The activation energy for methane pyrolysis measured in this study may be in error because of several reasons. It is essential that measurements of the incident and reflected shock velocities be correct, for the reaction temperature is calculated from these data. The rise time of the SLM transducers to a step increase in pressure, about 15  $\mu$ seconds, does not introduce any error because the shock velocities are calculated from the measured time delays of the arrivals of the shock fronts at the transducer locations. The measured wave velocities would, therefore, be the same if the transducer rise times, which do not differ, were 0 or 15  $\mu$ seconds. Error may be introduced, however, because of the difference in rise times of the calibrators used in the transducer circuits. A difference of  $\pm$  20  $\mu$ seconds would cause the activation energy to vary between 92 and 96 kcal.

In shock wave experiments, it is not possible to determine precisely the temperature at which all of the reaction occurs, because some takes place during the cooling process. This would cause the observed conversions at the calculated "reaction temperatures" to be high, which in turn would cause the reaction rate constants to be overestimated. To determine this effect on the activation energy, cooling rates were calculated from the transducer pressure time histories, assuming an adiabatic expansion. These cooling rates varied from about 200°K./millisec. for the lower temperature experiments to 300°K./millisec. for the higher temperature ones. The additional conversion which occurred after the arrival of the cooling wave at the end plate was determined from these cooling rates, the measured rate expression,  $k = 1.32 \times 10^{14} e^{-93,000/RT}$ , short time increments, and equation 2. The calculations, made at three temperature levels: 1650, 1750 and 1950°-K., were continued until the conversions became constant, signifying that the reactions were "stopped." The actual conversion at the reflected shock ("reaction") temperature then was calculated, permitting new rate constants to be derived. Using these new rate values and the low temperature rate data of Shantarovich and Pavlov,<sup>8</sup> an Arrhenius plot was made which resulted in an activation energy of 91 kcal.

Because the chief sources of error, as discussed above, cause a total uncertainty of less than 5 kcal., it is believed, therefore, that the reported activation energy is likely accurate to within  $\pm 10\%$ .

The strong effect of hydrogen inhibition, reported in the literature, has not been observed at the high temperature conditions of this study. The work of Shantarovich and Pavlov<sup>s</sup> indicated that at a conversion level of 40%, the ratio of the rate of the reaction inhibited by hydrogen to the initial uninhibited reaction rate would be 0.04. Mixtures of hydrogen and methane of 0.64 mole ratio were pyrolyzed in the shock tube to determine whether hydrogen inhibits the reaction at high temperatures. The operating conditions for these runs are listed in Table I. In an experiment at 2040°K., 93% of the methane was converted. If the inhibition reported by Shantarovich and Pavlov<sup>8</sup> is used to calculate the extent of the in-

(13) B. Brooks, C. Boord, S. Kurtz and L. Schmerling, "The Chemistry of Petroleum Hydrocarbons," Vol. II, Reinhold Publ. Corp., New York, N. Y., 1955, p. 71.



Fig. 2.—Plot of  $\log K$  as a function of temperature showing the data of this investigation and the low temperature data of Shantarovich and Pavlov.

hibited reaction at these temperatures, only 10% conversion would have been predicted (Table II).

#### TABLE II

#### METHANE CONVERSION, %

Measured	No H <sub>2</sub> inhibition <sup>a</sup>	H2 inhibition b
50.0	61.8	4.4
79.5	79.5	9.3
93.0	95.0	9.7

 $^a$  Calculated from this study.  $^b$  Calculated from Shantarovich and Pavlov.

Several experiments were carried out in which deuterium was added to the methane-argon mixture. Because the deuterium concentration was low and because of interference in the mass spectrometer caused by water, it was not possible to measure the deuterated methane that might have been in the reaction product. HD was found, however.

#### Discussion

The kinetics of the thermal decomposition of methane have been defined over the temperature range 1656–1965°K. While the kinetics are in substantial agreement with other studies made at lower temperatures, the high temperature reaction exhibits a feature that is distinctly different. The high temperature, homogeneous reaction is not inhibited by hydrogen as might be expected.

The absence of high temperature hydrogen inhibition may be due to either of two causes. The one which first suggests itself is that the hydrogen inhibition step in the reaction sequence is a heterogeneous one, as found by Germain and Vaniscotte.<sup>9</sup> Because wall reactions are of no significance in a shock tube, hydrogen inhibition would therefore not occur when methane is pyrolyzed in such a reactor. Skinner and Ruehrwein<sup>14</sup> pyrolyzed methane in a shock tube at temperatures between 1430 and 1785°K. Although their highest temperature experiment resulted in a CH<sub>4</sub> conversion of about 50%, they noticed no inhibitory effect of hydrogen.

A second possible explanation is that a different termination step predominates under the homogeneous high temperature conditions of the shock tube, resulting in no hydrogen inhibition. If such a termination step is assumed, and it is further assumed that the primary step in methane pyrolysis is the formation of methylene radicals,  $CH_2$ , then a reaction sequence may be written which explains both the low temperature, conventional reactor studies, and the present high temperature shock tube study.

Such an assumption finds support in the literature as noted below. Although the data presented in this paper are not sufficient to establish the proposed mechanism, it is believed that such a mechanism explains the observations made in this as well as more conventional studies better than a methyl radical mechanism. It is hoped that the results and proposed interpretation will stimulate others in this field to identify the elusive and highly reactive  $CH_2$  radical.

The mechanism proposed in this study involves free radical reactions as required by the deuterium experiment. The HD observed in the products probably arises from the reactions

$$\begin{array}{c} H + D_2 \longrightarrow HD + D \\ D + CH_4 \longrightarrow HD + CH_3 \\ CH_3 + D_2 \longrightarrow CH_3D + D \end{array}$$

The reaction seems to have a negligible chain length. Greene, et al.,<sup>15</sup> added some NO to ethane before pyrolyzing it at a high temperature in a shock tube, and apparently noted no effect on the reaction rate. If the chain length is sufficiently short, the measured kinetics would represent those of the primary step. This primary step may be decomposition of methane to either CH<sub>3</sub> or CH<sub>2</sub> radicals. The decomposition to CH<sub>3</sub> would require an activation energy of at least 101 kcal. The decomposition to  $CH_2$  would be endothermic by 85 kcal.<sup>16</sup> and have an energy barrier of 9 kcal.<sup>8</sup> Therefore, if the pyrolysis of methane at shock tube conditions involves a non-chain process whose primary step is the decomposition of  $CH_4$  to  $CH_2$ , the over-all activation energy would be about 94 kcal. The measured experimental activation energy of 93 kcal, tends to agree with the decomposition to methylene radicals, although the higher activation

(14) G. B. Skinner and R. A. Ruchrwein, THIS JOURNAL, **63**, 1736 (1959).

(15) E. F. Greene, R. L. Taylor and W. L. Patterson, Jr., *ibid.*, **62**, 238 (1958).

(16) N. N. Semenov, "Some Problems in Chemical Kinetics and Reactivity," Vol. I. Princeton University Press, Princeton, N. J., 1958. energy for reaction to methyl radicals may be within the experimental error.

The opening step of the proposed mechanism is thus assumed to involve the decomposition of methane to methylene radicals. The reaction products arise from the subsequent reactions of  $CH_3$  formed by the abstraction reaction of  $CH_2$ and methane. The inhibition of methane decomposition arises from reaction 9 which is exothermic.

Primary rupture 
$$CH_4 \longrightarrow CH_2 + H_2$$
 (5)  
Reaction  $CH_2 + CH_4 \longrightarrow CH_2 + CH_3$  (6)  
 $CH_3 + CH_3 \longrightarrow C_2H_6$  (7)  
 $C_2H_6 \longrightarrow Products$  (8)  
Termination  $CH_2 + H_2 \longrightarrow CH_4$  (9)  
 $CH_2 + H_2 \longrightarrow CH_3 + H$  (10)  
 $CH_4 + H \longrightarrow CH_3 + H_2$  (11)

This step may have both heterogeneous and homogeneous components. Germain and Vaniscotte<sup>9</sup> concluded that hydrogen inhibition involves both homogeneous and heterogeneous reactions. At the higher temperature, homogeneous conditions in the shock tube, an endothermic termination step  $CH_2 + H_2 \rightarrow CH_3 + H$  may become important. Consequently, the system should reflect a change from one termination step to the other as conditions change. This is apparent from the rate expressions which can be written for the reaction on the customary basis of steady-state approximation of radical concentrations.

Over-all reaction rate

$$-\frac{d(CH_4)}{dt} = k_5(CH_4) \left[ 1 + \frac{k_6(CH_4) + (k_{10} - k_9)(H_2)}{k_6(CH_4) + (k_{10} + k_9)(H_2)} \right]$$
(12)

Hydrogen inhibited— $k_2 \gg k_{10}$ 

$$-\frac{\mathrm{d}(\mathrm{CH}_4)}{\mathrm{d}t} = \frac{2k_3(\mathrm{CH}_4)}{1 + \frac{k_9(\mathrm{H}_2)}{k_6(\mathrm{CH}_4)}} \tag{13}$$

Non-inhibited  $-k_{10} \gg k_{2}$ 

$$-\frac{\mathrm{d}(\mathrm{CH}_4)}{\mathrm{d}t} = 2k_5(\mathrm{CH}_4) \tag{14}$$

The hydrogen inhibited expression is identical to the equation proposed by Shantarovich and Pavlov<sup>8</sup> to correlate their data at high conversions. Furthermore, at low conversions, where  $H_2$  inhibition is not important, equation 13 reduces to a first-order expression in agreement with the noninhibited equation 14. Equation 14 predicts first order kinetics and shows no  $H_2$  inhibition. This agrees with the shock tube findings.

In conclusion, it is believed that these studies define the kinetics of the thermal decomposition of methane at temperatures below 2000°K. The data further indicate that the high temperature, homogeneous reaction is not hydrogen inhibited. Finally, the kinetics and energetics of methane decomposition determined in this work provide a new view into the behavior of hydrocarbons at very high temperatures.

## RADIOLYSIS OF LIQUID CYCLOHEXANE

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Radiolysis of liquid cyclohexane results in the formation of three major products—hydrogen, cyclohexene and dicyclohexyl—in amounts that vary with the total radiation adsorbed. Examination of the reactions with three free-radical scaveness—butyl disulfide, butyl mercaptan and cyclohexene—demonstrates the formation of thermal hydrogen radicals and shows that hydrogen-radical reactions account for about 40% of hydrogen production. Radiolysis of  $C_6H_{12}$ – $C_6D_{12}$  mixtures gave an upper limit of about 25% for direct detachment of hydrogen. The remaining 35 to 60% of the hydrogen must form by other non-radical processes.

#### Introduction

Radiolysis of cyclohexane has been studied with 170 Kv. cathode rays,<sup>1</sup> high-energy electrons,<sup>2,3</sup>  $\gamma$ -radiation,<sup>4,5</sup> and heavy-particle radiation.<sup>5</sup> Three major products result: hydrogen, cyclohexene and dicyclohexyl. The yields of these products are independent of linear energy transfer<sup>6</sup> and temperature<sup>3</sup>; variations in yield reported with  $\gamma$ radiation have been ascribed to dose-rate effects.<sup>4,5</sup> Solutes also affect yield: iodine reduces hydrogen yield, but, except under special conditions,<sup>7</sup> little or none of the expected hydrogen iodide is formed,<sup>8,9</sup> benzene also reduces hydrogen yield,<sup>7</sup> and both reduce the yield of cyclohexene,<sup>3,6</sup> as does oxygen.<sup>3</sup> Total yields of free radicals from cyclohexane have been determined by scavenging with iodine<sup>9</sup> and with diphenylpicrylhydrazyl<sup>10</sup> are in agreement.

In spite of these investigations, the radiation chemistry of cyclohexane remains inadequately defined. Reported distributions of liquid products differ,<sup>4</sup> and the mechanism of hydrogen formation in this system is still open to speculation.<sup>8</sup>

Three approaches have been used to clarify the complex radiation chemistry of cyclohexane. Radiolysis of cyclohexane was examined over a range of total radiation doses, and the product distribution was extrapolated back to low total dose to determine the initial radiolysis products. Three free-radical scavengers—butyl disulfide, butyl mercaptan and cyclohexene—were used to determine yields of thermal and epithermal hydrogen radicals. Radiolysis of cyclohexane and cyclohexane and cyclohexane- $d_{12}$  mixtures was used to investigate the production of non-radical hydrogen. Results from these experiments have been used to formulate a partial mechanism.

#### Experimental

Cyclohexane was research grade and freshly distilled from sodium. Cyclohexane- $d_{12}$  containing 9.8% cyclohexane- $d_{11}$ 

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(3) H. A. Dewhurst, This Journal, 63, 813 (1959).

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- (6) R. H. Schuler and A. O. Allen, ibid., 77, 507 (1955).
- (7) G. Meshitsuka and M. Burton, Radiation Research, 10, 499 (1959).
- (8) M. Burton, J. Chang, S. Lipsky and M. P. Reddy, J. Chem. Phys., 26, 1337 (1957).

(9) R. W. Fessenden and R. H. Schuler, J. Am. Chem. Soc., 79, 273 (1957).

(10) A. Prevost-Bernas, A. Chapiro, C. Cousin, Y. Landler and M. Magat, Disc. Faraday Soc., 12, 98 (1952).

(Merck), cyclohexene, *n*-butyl mercaptan and butyl disulfide were used without purification. Samples for radiolysis were degassed, sealed into glass

Samples for radiolysis were degassed, sealed into glass tubes under high vacuum, and subjected to  $\gamma$ -radiation from spent uranium fuel slugs at Argonne National Laboratory. The dosimetry, supplied by Argonne, was based on a ferrous oxidation yield of 15.5; dose rate was approximately  $10^{18}$  e.v./g./mir. After radiolysis, the samples were opened into a vacuum system and the hydrogen pressure was measured in a calibrated volume. The vapor pressure of cyclohexane was compensated for by a differential manometer.

Infrared absorption at 13.94  $\mu$  was used to measure the cyclohexene content. Gas chromatography was used to detect the products and to determine the amount of dicyclohexyl formed. An estimate of the accuracy of the determination of cyclohexene and dicyclohexyl is shown in Fig. 1. Mercaptan content was determined by potentiometric titration with silver nitrate.<sup>11</sup> Disulfide was determined by refluxing the radiolysis mixtures with zinc and acetic acid and analyzing an aliquot of the resulting solution for increased mercaptan content. Sulfide was determined from the ultraviolet absorption of the sulfide-iodine complex.<sup>12</sup> Deuterium compounds were analyzed with a mass spectrometer.

**Product Distribution.**—Formation of the three major identifiable products—hydrogen, cyclohexene and dicyclohexyl—might appear to result from simple free radical reactions

$$C_6H_{12} \longrightarrow C_6H_{11} \cdot + H \cdot \tag{1}$$

$$\begin{array}{ccc} H_{\cdot} + C_{6}H_{12} \longrightarrow C_{6}H_{11} + H_{2} \\ 2C_{6}H_{11} \longrightarrow C_{6}H_{12} + C_{6}H_{10} \\ \end{array}$$
(2) (3)

$$C_{6}\Pi_{11} \longrightarrow C_{6}\Pi_{12} + C_{6}\Pi_{10}$$
(3)

$$2\mathbb{C}_6\Pi_{11} \longrightarrow (\mathbb{C}_6\Pi_{11})_2 \tag{4}$$

Although these reactions probably occur, other equally important reactions also may take place. The distribution of three major products was studied over a ten-fold range in radiation dose. *G*-values of hydrogen, cyclohexene and dicyclohexyl are shown in Fig. 1 as functions of adsorbed radiation. The reduced hydrogen formation with increased radiation doses below about  $10^{20}$  e.v./g. confirms a previous study<sup>13</sup> and also agrees with our observed decrease in *G*(cyclohexene) and increase in *G*(dicyclohexyl). Though *G*(cyclohexene) grows smaller, accumulating cyclohexene diminishes *G*(H<sub>2</sub>)

$$C_6H_{10} + H \cdot \longrightarrow C_6H_{11} \cdot$$
 (5)

This higher cyclohexene concentration may also produce more dicyclohexyl radical

$$C_6H_{10} + C_6H_{11} \cdot \longrightarrow C_{12}H_{21} \cdot \tag{6}$$

The rise in G(dicyclohexyl) can be attributed to reaction 6 followed by hydrogen abstraction or disproportionation.

(11) M. W. Tamele and L. B. Ryland, Anal. Chem., 8, 16 (1936).

(12) S. H. Hastings, ibid., 25, 420 (1953).

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<sup>(1)</sup> C. S. Schoepfle and C. H. Fellows, Ind. Eng. Chem., 23, 1396 (1931).



In Fig. 1, the product yields extrapolated to zero dose give a very poor hydrogen balance. Approximately 30% of the total hydrogen is not accounted for by formation of cyclohexene and dicyclohexyl. Some products boiling higher than dicyclohexyl—possibly cyclohexadiene polymers<sup>4</sup>—must have been formed, even though they were not detected by high-temperature gas chromatography. In addition, traces of hexenes and a minor product tentatively identified as cyclohexylcyclohexene were found. Methylcyclopentane also was found in traces and had been detected in previous studies with electrons<sup>2,3</sup>; in studies with  $\gamma$ -radiation, it was reported as a major product.<sup>4</sup>

The G-values for cyclohexene and dicyclohexyl level out above about  $10^{20}$  e.v./g. and are between those obtained by cobalt-60  $\gamma$ -radiation<sup>5</sup> and those obtained by 800-kv. electrons<sup>3</sup>

		Co-60	Electrons
Dose rate, e.v./g. min. $\times 10^{-17}$	10	$^{2}$	900
Total dose, e.v./g. $ imes$ $10^{-21}$	0.2-0.5	6	2-6
G(cyclohexene)	2.2	1.1	2.5
G(dicyclohexyl)	1.5	0.8	2.0

These data support the view that differences observed result from dose-rate changes rather than from differences between the linear energy transfer of 800-kv. electrons and of  $\gamma$ -radiation.<sup>5</sup>

**Effect** of Scavengers.—Free-radical scavengers were used to detect thermal hydrogen radical and to estimate a maximum and a minimum  $G(\mathbf{H} \cdot)$ .

The presence of thermal hydrogen radical has been detected with iodine scavenging.<sup>7</sup> This result agrees with our findings that the radiolysis of cyclohexane with butyl disulfide produces small amounts of butyl mercaptan

RSSR, moles/l.	Total dose, e.v./g. × 10 <sup>-20</sup>	G(RSH)
0.06	3.6	0.3
.06	3.3	. 3
.03	1.7	. 4
. 03	3.6	. 1
.015	1.2	.2

Free radicals attack butyl disulfide by displacement of mercaptide radical so that thermal hydrogen radical should produce mercaptan



 $H \cdot + RSSR \longrightarrow RS \cdot + RSH$ 

The mercaptan produced also reacts with radicals, so that a true G(thermal  $H \cdot)$  could not be obtained.

A maximum yield of hydrogen radical was obtained by determining free-radical yields from cyclohexane with butyl mercaptan as a radical scavenger. The concentration of sulfide and disulfide, the products of mercaptan scavenging, are plotted as a function of radiation in Fig. 2. G(RSSR) and G(RSR) are proportional to the slope of the line, and  $G(R\cdot)$  is equal to twice their sum.<sup>14</sup> The G-value for total radicals produced, 5.6, confirms the 5.7 reported for iodine scavenging.<sup>9</sup> Because a maximum of one hydrogen radical was produced for each alkyl radical, the maximum hydrogen yield from hydrogen radicals is half the total radical yield; thus,  $G(H_2 \text{ from } H \cdot)$  can be no greater than 2.8.

The minimum hydrogen-radical yield was determined by cyclohexene scavenging. As was shown in Fig. 1, cyclohexene produced during the radiolysis of cyclohexane apparently lowers the  $G(H_2)$  from 6.6 to 4.8. Figure 3 shows that adding gross amounts of cyclohexene reduces  $G(H_2)$  to about 4.2. If the total reduction in hydrogen yield is due to scavenging hydrogen radical by cyclohexene and not to an unknown protection mechanism,  $G(H_2 \text{ from } H \cdot)$  can be no greater than 2.4. This value agrees with a previous observation with high-energy electrons,<sup>3</sup> supports the maximum value of  $G(H \cdot)$  obtained in the mercaptan experiments, and indicates that about 35% of the hydrogen is formed by reaction of thermal hydrogen radical. The yield of epithermal hydrogen radical must be less than the difference between that of total hydrogen radical and the decrease in hydrogen yield from scavenging; that is,  $G(\text{Epithermal } H_{\cdot})$  must be less than 0.4, or

about 5% of the total hydrogen yield. Non-radical Hydrogen.—The nature of the 60% of the hydrogen not formed from hydrogen radical was examined by radiolysis of mixtures of cyclohexane and cyclohexane- $d_{12}$  and measurement of the amount of hydrogen, hydrogen deuteride and deuterium produced. Hydrogen produced by reaction 2 should be randomly mixed; that is, to a reasonable first approximation

$$\frac{(\mathrm{HD})^2}{(\mathrm{H}_2) \, (\mathrm{D}_2)} \cong 4$$

Non-random hydrogen and deuterium formed dur-

(14) T. D. Nevitt, W. A. Wilson and H. S. Scelig, Ind. Eng. Chem., 51, 311 (1959).

August, 1960

ing the radiolysis can be calculated<sup>15</sup> from the expression

$$X = 1 - \left[\frac{(\text{HD})^2}{4(\text{H}_2)(\text{D}_2)}\right]^{1/2}$$

where X is the fraction of non-random hydrogen and deuterium. As shown in Table I, more hydrogen and deuterium were formed than calculated for random mixing. The non-random hydrogen and deuterium account for less than 25% of the total if the results are extrapolated back to low total radiation absorbed. Introduction of an aromatic, benzene, did not change this value, although total reaction decreased.

#### TABLE I

C6H12/ C6D12	Radiation dose $\times 10^{-20}$ , e.v./g.	Iso H2	otopic anal 11D	ysis D2	Fraction non- random H <sub>2</sub> + D <sub>2</sub>
0.95	3.3	0.44	0.39	0.16	0.26
1.11	5.5	.50	.37	.13	.27
0.45	5.2	.37	.39	.23	.33
0.87	11	.47	.37	.16	.32
$1.58^{a}$	11	.48	. 39	.13	. 22
	T				

<sup>a</sup> 20% C<sub>6</sub>D<sub>6</sub> present.

Formation of non-random excess hydrogen and deuterium can be explained by direct detachment of molecular hydrogen<sup>15</sup>

#### $C_6H_{12} \longrightarrow C_6H_{10} + H_2$

Thus, up to 25% of the reaction might occur by decomposition of excited cyclohexane molecules to hydrogen and cyclohexene. Results based on oxygen scavenging gave a value of about 15%.<sup>3</sup> In the presence of benzene, reduction of the total yield of hydrogen isotopes without a change in the ratio among them supports the view that benzene decreases both radical and non-radical hydrogen formation.<sup>7</sup>

If direct detachment of hydrogen occurs, formation of the remaining 35% random-mixed unscavenged hydrogen remains to be accounted for in terms of mechanisms involving ions or excited molecules. For example, hydrogen may form by the reaction of cyclohexane molecule-ion on its first

(15) L. M. Dorfman, This JOURNAL, 60, 826 (1956).



collision, with subsequent decomposition of the ionic intermediate

$$\begin{array}{c} C_{6}H_{12}^{-}+C_{6}H_{12} \longrightarrow C_{6}H_{13}^{+}+C_{6}H_{11} \\ C_{6}H_{13}^{+}+e^{-} \longrightarrow C_{6}H_{11} + H_{2} \end{array}$$

On the other hand, because decomposition of the  $C_6H_{13}$  + species also may not be random, non-random excess hydrogen need not form from cyclohexane by direct detachment of molecular hydrogen. Although similar ionic mechanisms have been suggested,<sup>14,16</sup> reactions of such ions in a liquid phase hydrocarbon system are difficult to demonstrate.<sup>17</sup> Thus, postulation of hydrogen formation through any particular ionic species or excited molecule is highly speculative.

#### Conclusion

Despite the formation of only three major products, the radiation chemistry of cyclohexane is complex. Products of radical reactions account for less than 40% of the total. No more than about 25% of the reaction can occur by direct molecular detachment of hydrogen to form cyclohexene. By inference, 35 to 60% of the product must be formed by undefined processes.

(16) For example, see H. A. Dewhurst, J. Am. Chem. Soc., 80, 5607
 (1958); P. C. Chang, N. C. Yang and C. D. Wagner, *ibid.*, 81, 2060
 (1959).

(17) However, see E. Collinson, F. S. Dainton and H. A. Gillis, THIS JOURNAL, 63, 909 (1959).

## A DILATOMETRIC STUDY OF THE CYCLOHEXANE–ANILINE SYSTEM NEAR ITS CRITICAL SEPARATION TEMPERATURE<sup>1</sup>

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It is shown that the coefficient of expansion of the homogeneous mixture of cyclohexane and aniline has a normal value just above the critical temperature. The change of volume which occurs on mixing two phases, which were in equilibrium slightly below the critical temperature and which have been warmed to slightly above the critical temperature is, however, much smaller than expected. The results are discussed in terms of the mechanism of mixing in the immediate neighborhood of the critical point, with due regard for the probability that the interfacial tension between the two phases vanishes while the phases still differ in composition.

The density of coexisting phases of the cyclohexane-aniline system and of the homogeneous mixture just above the critical solution temperature have been measured by Atack and Rice,<sup>2,3</sup> using a submerged float suspended by a quartz fiber spring. These measurements indicated a possibility that the homogeneous liquid just above the critical temperature had a rather large negative coefficient of expansion, although the temperature range was so narrow that the actual changes in density were so small that they had to be regarded as within the possible limits of error. The presently reported measurements were begun to check on the possibility of an anomalous coefficient of expansion. It was also desired to ascertain whether there was a sudden change of density at the critical temperature. There appears to be a range of critical compositions in the cyclohexane-aniline system<sup>2-4</sup> corresponding to a flat horizontal section of the coexistence curve, and Atack and Rice<sup>3</sup> found a sudden change in the density of the upper portion of the mixture on lowering the temperature past the critical temperature, resulting, they believed, from the sudden appearance at the critical temperature of two phases of distinctly different composition. If the density of the homogeneous liquid just above the critical temperature is not exactly the mean (properly weighted according to the amounts of the phases) of the densities of the two phases just below, passing through this temperature would cause a sudden change in the volume of the entire system.

We have accordingly made measurements of the volume of a mixture in the critical range, using a dilatometric method. Direct measurements of the position of the meniscus in the capillary of a dilatometer were made. We also made some measurements in which the system was cooled just below the critical temperature, so that two phases were present. The system then was heated just above the critical temperature without stirring, so that two phases were still present, and the change of the position of the meniscus upon stirring then was recorded as a function of the temperature to which it had been cooled.

It will be noted that our motivation was somewhat different from that of earlier workers who have made similar measurements,<sup>5</sup> and our measurements have been largely, although not entirely, confined to temperatures very close to the critical.

#### **Experimental Details**

Materials.—The cyclohexane was from the National Bureau of Standards, sample No. 209a-25, with 0.010  $\pm$  0.006 mole % impurity, and was used without further purification. The aniline, part of a special cut provided by National Aniline, was thrice distilled, the last two times in an aspirator vacuum, discarding the first and last 10 cc. and collecting the distillate over zinc dust. The resulting purified aniline was twice recrystallized, then distilled four times in a high vacuum system and sealed in an ampoule under vacuum. Two 9.5-cc. samples, each 0.451 mole fraction aniline, were prepared for the final sample, and were exhaustively dried, as described in earlier work from this Laboratory,<sup>2-4</sup> by successive distillations over calcined calcium oxide. The composition chosen was within the critical range of the cyclohexane-aniline system, and the phase boundary always appeared slightly above the middle of the tube.

The dilatometer consisted of a bulb containing a magnetic stirrer leaving a volume of  $14.8 \pm 0.3$  cm available to the liquid, connected through precision capillary tubing (Fischer and Porter) with inside diameter  $0.0820 \pm 0.0008$  cm, to a reservoir, as shown in Fig. 1.

The purified samples were combined and distilled into the reservoir, which then was sealed off with the sample frozen. With the sample thoroughly mixed and held above the critical temperature, it was poured through the capillary into the dilatometer bulb. When the capillary was completely filled at 32.5°, it was found that the liquid level was conveniently centered in the capillary upon lowering the temperature to the critical temperature. The dilatometer, containing the proper amount of liquid, was sealed off at the top of the capillary. This was accomplished by blowing streams of liquid nitrogen against the capillary at the point where the menicus stood, thus forming a frozen plug to scal the liquid in the dilatometer. At the same time warm jets of air were directed at the capillary, immediately above the cold jets, to prevent more liquid from the reservoir from condensing into the capillary.

The dilatometer was held firmly in place in a waterbath by a simple brass rack. The liquid level in the capillary was measured with respect to a reference mark fused onto the capillary wall, using a Gaertner Scientific Corporation micrometer slide cathetometer capable of measuring vertical displacements up to 2.5 cm. accurate to at least 0.001 cm. Our actual reproducibility was about 0.002 cm.

cm. Temperature Control and Measurement.—The dilatometer was immersed in a bath whose temperature was controlled to about  $\pm 0.001^{\circ}$ . The temperature was measured by a platinum resistance thermometer and Mueller bridge assembly. We found that the effect of room temperature on the unthermostatted coils of the Mueller bridge was a disturbing influence, and in this case we have no control by simultaneous comparison of different tubes in the same bath, as in previous studies. Direct observation indicated that around 26°, a change of 1° in room temperature would pro-

<sup>(1)</sup> Work supported by the Office of Ordnance Research, U. S. Army.

<sup>(2)</sup> D. Atack and O. K. Rice, Disc. Faraday Soc., 15, 210 (1953).

<sup>(3)</sup> D. Atack and O. K. Rice, J. Chem. Phys., 22, 382 (1954).
(4) R. W. Rowden and O. K. Rice, "Changements de Phases,"

<sup>(4)</sup> R. W. Rowden and O. K. Rice, Changements de Phases, Compt. rend. 2<sup>e</sup> Réunion Annuelle, Société de Chimie Physique, Paris, 1952, p. 78.

<sup>(5)</sup> See, e.g., G. Jura, D. Fraga, G. Maki and J. H. Hildebrand, Proc. Natl. Acad. Sci. U. S., **39**, 19 (1953); I. R. Krichevskii, N. E. Khazanova and L. R. Linshits, *Zhur. Fiz. Khim.*, **29**, 547 (1955).



Fig. 1.-Sketch of dilatometer, with arrangement for filling.

duce a change of  $0.0025^{\circ}$  in the reading of the resistance thermometer. All readings were reduced to 26°. The room temperature was always within 2° of 26°, and usually within 1°.

#### Results

A number of checks were made on the transition temperature of the mixture in the dilatometer. Exact reproducibility was not obtained, perhaps because of difficulties in observation of the fairly large sample, possibly in part due to difficulties of temperature regulation or equilibration of the large sample, and perhaps in part due to personal differences of two different observers. Various observations gave temperatures ranging from 29.529 to 29.533°, on the scale used. The mean, 29.531°, is, in any case, within 0.002° of the extremes.

A series of readings was made on the level of the liquid in the capillary. These were made by allowing the dilatometer to come to equilibrium at some temperature, then slowly changing the temperature, allowing sufficient time for equilibration between readings. These results are displayed in Fig. 2. In order to avoid a great multiplicity of figures, the readings for the different series of runs are displaced vertically with respect to each other, the scale for each series of runs being indicated.

After the series of readings described above were made, some observations of a different character were made. The sample was cooled to a temperature  $T_1$ , usually below the critical temperature, and allowed to come to equilibrium for at least an hour (sometimes overnight). The temperature then was raised to a temperature  $T_2$ , above the critical temperature, and held there about an hour. It then was stirred, and an almost immediate observation was made of the change,  $\Delta l$ , of the height of the liquid in the capillary which occurred as the phase boundary disappeared on stirring. The results of these experiments are shown in Table I. The order of the experiments is given by the first column. The mixture always expanded on stirring.

The last experiment recorded in Table I was a special experiment. The sample was allowed to stand for some days in a refrigerator at 5.0°, was stirred at this temperature, and then allowed to stand for two more days. It then stood at room temperature for over four hours and finally was placed in the bath. It was not stirred and the phase boundary remained sharp and clear, there being no indication of opalescence. The position of the meniscus in the capillary was noted, the results shown in Fig. 3 being obtained; in each case



Fig. 2.—Dilatometric measurements: open circles, one phase present; half black circle, two phase present; circle with line doubtful (meniscus, if present, invisible, on account of opalescence); arrows indicate order in which readings were made If two points are connected with a solid line the mixture was not stirred between readings. A broken line means stirring between readings.



Fig. 3.—Dilatometric measurements over a greater temperature range: half black circles, two phases present, after chilling to  $5.0^{\circ}$  without subsequent stirring; slope of line, 2.6 cm./deg. Open circles, one phase present; slope of line 3.4 cm./ceg. Length of broken line shows change on stirring.

the level remained constant for one-half hour before recording. (The "free length" is the distance from the met iscus to the top of the capillary. A correction had to be made since there was some liquid in the upper part of the capillary, which was not readily dislodged. This had not occurred in the earlier measurements.) After the reading at 30.143° the sample was stirred. At first the volume suddenly contracted until there was some free space in the dilatometer bulb. With further stirring, during the next minute or two, the volume in-

#### TABLE I

	æ	2		$\Delta V/V$		AT/
No.	$I_1$	12	$\Delta t(mm.)$	(av.)	$x_2 - x_1$	ΔV calc/V
1ª	29.548	29.571	0.00			
3 <b>°</b>	29.538	29.562	.00			
4 <sup>a</sup>	29.534	29.565	.00			
6 <sup>b</sup>	29.533	29.552	.00 to 0.01	$2 \times 10^{-7}$	$0.056^{\circ}$	$6.3 imes10^{-6}$
7 <sup>6</sup>	29.533	29.545	.00 to .02	$4 \times 10^{-7}$	. 056 <sup>e</sup>	$6.3 imes10^{-6}$
5'	29.532	29.545	.01 to .02	5 $\times 10^{-7}$	.059 <sup>e</sup>	$7.0  imes 10^{-6}$
$2^{\circ}$	29.530	29.547	.03 to .04	$1.25 imes10^{-6}$	.065°	$8.5 imes10^{-6}$
8°	29.530	29.542	.04 to .05	$1.6  imes 10^{-6}$	.065 <sup>e</sup>	$8.5 imes10^{-6}$
10°	29.528	29.544	. 06	$2.1 \times 10^{-6}$	. 070 <sup>e</sup>	$9.9 imes10^{-6}$
9°	29.524	29.536	. 09	$3.2~ imes~10^{-6}$	. 079 <sup>e</sup>	$1.3 imes10^{-5}$
116	5.0	30 143	39 <sup>d</sup>	$1.39 \times 10^{-3}$	.83'	

<sup>a</sup> No meniscus. <sup>b</sup> Meniscus visible at  $T_2$  before stirring; invisible or doubtful at  $T_1$  because of opalescence. <sup>c</sup> Meniscus visible at  $T_1$  and at  $T_2$  before stirring. <sup>d</sup> Corrected to 29.54°. <sup>e</sup> From Fig. 2 of reference 7, taking  $T_c = 29.533$ , which seemed most consistent with this set of observations. <sup>f</sup> Estimated from Fig. 3 of reference 8.

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creased, reaching the position indicated in Fig. 3, the over-all change in its position being given in Table I, corrected to 29.54°. The other readings on the upper curve were made the next day; again there was one-half hour constancy before the final recording was made.

#### Discussion

It is clear from the above results that there are no very remarkable volumetric effects in the neighborhood of the critical point. The apparent negative expansion coefficient suggested by the results of Atack and Rice is not confirmed. A rough value of the expansion coefficient of the homogeneous phase above the critical temperature, calculated from the dimensions of the apparatus and the slopes of the lines shown in Fig. 2 (weighted as indicated by the circled numbers, this being based mostly on the temperature range involved in each case, secondarily on the number of readings taken) is 1.2  $\times$  $10^{-3}$  per degree, which is in the normal range. From the two extreme points for the one phase system in Fig. 3, the temperature coefficient appears to be  $1.19 \times 10^{-3}$ , in good agreement. The coefficient of expansion for pure cyclohexane at 30° is<sup>6</sup>  $1.22 \times 10^{-3}$ , that for aniline is  $60.85 \times 10^{-3}$ .

To analyze the data of Table I, we will attempt as a preliminary proposition to represent the molal volume as a simple quadratic function of the mole fractions

$$V = V_{\rm c} + a_1(x - x_{\rm c}) + a_2(x - x_{\rm c})^2 \qquad (1)$$

where x represents the mole fraction of aniline and the subscript c refers to a solution at the middle of the critical range. In view of the anomalies in the neighborhood of the critical point we may expect that such a curve would not be valid for the whole range of x; indeed, we shall see that it is not. It may, however, at least give us a norm, in terms of which deviations may be described. It has been shown by Rice<sup>7</sup> that the mole fractions  $x_1$ and  $x_2$  of solutions in equilibrium with each other at temperature  $T_1$  are related by

$$x_2 - x_1 = b(T_c - T_1 + 0.005^\circ)^{1/3}$$
 (2)

where  $T_c$  is the critical temperature (highest temperate at which a meniscus can be observed) and b is a constant. Having effected the separation of

phases at a certain temperature  $T_1$  we now raise the temperature to one just above  $T_c$ , and in this process  $x_2 - x_1$  will not change much, nor will the corresponding difference of molal volumes,  $V_2 - V_1$ . If we have  $n_1$  moles of solution with aniline mole fraction  $x_1$  and  $n_2$  moles with aniline mole fraction  $x_2$  such that  $n_1 + n_2 = 1$ , then the volume before stirring will be, if eq. 1 holds

$$n_1V_1 + n_2V_2 = V_c + n_1a_1(x_1 - x_c) + n_2a_1(z_2 - x_c) + n_1a_2(x_1 - x_c)^2 + n_2a_2(x_2 - x_c)^2$$
(3)

The mole fraction after stirring will be  $n_1x_1 + n_2x_2$ and the total molal volume will be given by

$$= V_{c} + a_{1}[n_{1}(x_{1} - x_{c}) + n_{2}(x_{2} - x_{c})] + a_{2}[n_{1}(x_{1} - x_{c}) + n_{2}(x_{2} - x_{c})]^{2} \quad (4)$$

Subtracting eq. 3 from eq. 4, remembering  $n_1 + n_2 = 1$  we find

$$\Delta V_{\text{cnlc}} = V - n_1 V_1 - n_2 V_2 = -a_2 n_1 n_2 (x_2 - x_1)^2 \quad (5)$$
  
or, by (2)

$$\Delta V_{\text{calc}} = -a_2 b n_1 n_2 (T_c - T_1 + 0.005^\circ)^{2/3}$$

This suggests that we should plot  $\Delta l$ . which is proportional to  $\Delta V$ , against  $(T_c - T_1 + 0.005^{\circ})^{2/3}$ . This is done in Fig. 4, and  $\Delta l$  is also plotted against  $(T_{\rm c} - T_{\rm l})^{2/3}$  which, since  $n_1 n_2$  is almost constant, should give a straight line passing through the origin if there were no flat top to the coexistence curve. It is seen that the latter condition is nearly fulfilled; however, we feel that the independent evidence that the coexistence curve is actually truncated about 0.005° below that would be the top of a rounded curve is very good,<sup>2,3,7</sup> and it would appear much more sensible to find the value of  $x_2$   $x_1$  corresponding to a given  $T_1$  from the available data<sup>7.8</sup> (this is done in Table I) and use this in eq. 5 to find a  $\Delta V_{calc}$  to compare with the experimental  $\Delta V$ .  $\Delta V_{\text{calc}}$  is, of course, a calculated value only in the sense that it is calculated on the basis of a second-degree curve, the constants of which have to be found empirically. Schlegel<sup>9</sup> and Atack and Rice<sup>2,3</sup> have both given densities in the critical region which, combined with densities of the pure liquids, could be used to find a value for  $a_2$ . However, their results are not in good agreement, and it seems best for present purposes to find  $a_2$  from run no. 11 of Table I and use this value to get  $\Delta V_{\rm calc}/V$ . In this way we have found  $\Delta V_{\rm calc}/V$ 

(6)

<sup>(6)</sup> J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier Publishing Co., Inc., Houston, Texas, 1950.

<sup>(7)</sup> O. K. Rice, J. Chem. Phys., 23, 164 (1955).

<sup>(8)</sup> H. Schlegel, J. chim. phys., 31, 517 (1934).

for the other runs listed in Table I, using  $n_1 = n_2 = \frac{1}{2}$ , which is sufficiently close to our experimental conditions, especially since the product  $n_1n_2$ , with  $n_1 + n_2 = 1$ , is quite insensitive to the individual values.

It is seen that in Table I the  $\Delta V$  of mixing is, in all runs except run no. 11, small compared with that calculated using run no. 11 as a basis. The molal volume curve then, as is the case with other thermodynamic properties, must become anomalously flat near the critical composition. This can be given a physical interpretation if the vanishing of the meniscus at  $T_{\rm c}$  occurs because of the vanishing of the interfacial tension between two phases which have not actually become identical.<sup>10,11</sup> We would then really have mixing ("emulsification") of two phases, without their complete mutual solution on a molecular scale, so, just at the critical temperature, there would be little or no change of volume on mixing and there would still be an anomalously small change of volume if the mixing occurred at a temperature  $T_2$  a couple of hundredths of a degree above  $T_{\rm c}$ .

We believe that this effect is real, and not caused by the conditions of the experiment. We assume that temperature equilibrium was achieved before the measurements were made. In run no. 11 this seems fairly certain from the procedure used in the observations. We also assume that there is no equilibration of material between phases on raising the temperature. If there were such equilibration in run no. 11, this presumably would cause  $\Delta l$  to be too small and so would tend to cover up the effect. Equilibration of material in the other runs would lower their  $\Delta l$ 's and so appear to enhance the effect, but it seems quite impossible that there would be appreciable diffusion in an hour of time without stirring. If temperature equilibrium in these cases were incomplete in the hour, and then were suddenly effected by a few seconds stirring, this would



increase  $\Delta l$  and appear to diminish the effect. Also heat produced by the mechanical work of stirring could only increase the expansion. However, the mixing of the phases may result in cooling and contraction, though no tendency was observed for the meniscus to rise further on standing a short time after the first observation, except in the case of run no. 11, in which, as we noted, there was an initial decrease in volume, which may have been due to cooling. In the other runs we may say certainly that the temperature did not decrease enough to bring the mixture to the transition temperature and slow down the rate of mixing. From the expansions observed in Figs. 2 and 3, it is seen that in the case of run no. 9, where  $T_2$  is very close to  $T_c$ , the cooling effect could not be sufficient to change our conclusion that the change of volume on mixing is anomalously small. In any case it is hard to believe that merely a nice counterbalancing of heat effect and true expansion, both of which certainly must decrease as  $T_1$  approaches  $T_c$ , could give the more or less uniform decrease in  $\Delta V$ shown in Table I. We, therefore, believe that we have uncovered a critical phenomenon in the  $\Delta V$  of mixing.

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<sup>(10)</sup> O. K. Rice, J. Chem. Phys., 15, 314 (1947).

<sup>(11)</sup> O. K. Rice, THIS JOURNAL, 1293 54, (1950).

## THE THERMODYNAMICS OF NON-UNIFORM SYSTEMS, AND THE INTERFACIAL TENSION NEAR A CRITICAL POINT<sup>1</sup>

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The interfacial tension between two phases is considered in the framework of the theory developed by Cahn and Hilliard in which the free energy of a non-uniform system is assumed to depend not only on concentrations but on their gradients Explicit account is taken of the observed cubic form of the coexistence curve. A phenomenological theory is developed for the coefficients in the expansion of the free energy in terms of concentrations and their gradients. The coefficients are assumed to depend on the derivatives of the chemical potentials with respect to composition, but it is assumed that as one departs from the critical point, the contributions from derivatives of partial molal energies and entropies can become in a certain sense independent of each other. A plausible argument makes the interfacial tension in a binary liquid system roughly proportional to  $(T_c - T)^{1/2}$  (T = temperature,  $T_c$  = critical temperature), accidentally the same result obtained by Cahn and Hilliard on the basis of other assumptions. In a liquid-vapor system the surface tension is estimated to be proportional to  $(T_c - T)^{1/2}$ , the difference arising because there is no Gibbs-Duhem equation in this case. It is shown that the theory is consistent with Tolman's theory of surface tension. Effects of pressure variations in the transition region are considered. Finally, a general thermodynamic formalism for non-uniform systems is developed.

#### 1. Introduction

Recently Cahn and Hilliard<sup>2</sup> have developed a thermodynamic theory of surfaces which can be used as the framework for a phenomenological study of the interfacial tension near the critical point of a binary liquid system. This theory is based upon the general idea that the free energy per molecule of a small portion of fluid must depend not only upon the concentration at the particular point but also upon the various spatial derivatives of the concentrations. It is our purpose in this paper to consider the effect of the peculiarities of the critical region, and eventually to proceed to some more general considerations.

Following the notation of Cahn and Hilliard, let c be the mole fraction of component B of the binary mixture and let x measure the distance perpendicular to the surface (we will consider only plane surfaces). The free energy per molecule, which the system at any point would have if there were no concentration gradients, will be denoted as  $f_0$ . This is equal to  $(1 - c)\mu_A + c\mu_B$ , where  $\mu_A$  and  $\mu_B$  are the chemical potentials, per molecule, characteristic of a uniform concentration c. The actual molecular free energy, which is a function as well of  $\partial c/\partial x$ ,  $\partial^2 c/\partial x^2$ , . . . will be designated as f. In the two bulk phases in equilibrium with each other we have  $\mu_A = \mu_{A,e}$  and  $\mu_B = \mu_{B,e}$ , where the subscript e denotes the equilibrium value. We now define a quantity  $\Delta f$  which differs from zero only near the interface

$$\Delta f = f_0 - (1 - c)\mu_{A,e} - c\mu_{B,e} = (1 - c)(\mu_A - \mu_{A,e}) + c(\mu_B - \mu_{B,e}) \quad (1.1)$$

All quantities are evaluated at the same temperature. If f were equal to  $f_0$  the interfacial tension  $\sigma'$ would be obtained by integrating  $\Delta f$  across the interface; actually Cahn and Hilliard have shown that

$$\sigma' = N_V \int_{-\infty}^{\infty} \left[ \Delta f + \kappa (\partial c / \partial x)^2 \right] \mathrm{d}x \qquad (1.2)$$

where  $\kappa$  is a coefficient that is a function of c and T, where  $N_{V}$  is the number of molecules per unit volume.  $N_{V}$  can be assumed with good approximation to be constant. A term involving  $\partial^{2}c/\partial x^{2}$  (whose

coefficient, however, as we shall see, is probably zero) can by integration by parts be merged into the term involving  $\partial c/\partial x$ , its coefficient contributing to  $\kappa$ . Higher derivatives and higher powers of  $\partial c/\partial x$ are neglected; they are higher order terms and are small near the critical point where the interface is not too sharp. Terms in the first power of  $\partial c/\partial x$ were eliminated by Cahn and Hilliard on grounds of symmetry, since the effect should not change sign when  $\partial c/\partial x$  does. At the expense of some discontinuity, a possibility which cannot be completely excluded, it might be imagined that f could depend on the absolute value of the first power of  $\partial c/\partial x$ . However, one might expect the effect of a uniform gradient to vanish in the limit of a small gradient, since the effects on the side of greater x would just about cancel those of the side of smaller x, so the quadratic form seems reasonable.

Use of the methods of the calculus of variations to minimize  $\sigma'$  yields the result

$$\Delta f - \kappa (\partial c / \partial x)^2 = \text{const.}$$
(1.3)

and eventually, after a change of variables, the constant in (1.3) being zero because  $\Delta f$  and  $(\partial c/\partial x)^2$ are zero at the concentrations,  $c_{\alpha}$  and  $c_{\beta}$ , of the equilibrium phases, the equation

$$\sigma = 2N_{\rm V} \int_{c\alpha}^{c\beta} (\kappa \Delta f)^{1/2} \,\mathrm{d}c \qquad (1.4)$$

is obtained,  $\sigma$  being the minimized value of  $\sigma'$ .  $\kappa$  and  $\Delta f$  are functions of c and T, so if these functions are known  $\sigma$  can be found. It will be in the evaluation of these quantities that we will differ from Cahn and Hilliard.

2. Evaluation of the Excess Free Energy in a Binary System.—We will now wish to attempt to expand  $\Delta f$  by means of a Taylor expansion about the critical point. We will do this assuming a rounded coexistence or solubility curve. It is probably actually flat at the top,<sup>3</sup> but this "truncation" occurs so close to the critical temperature that it will not be important for interfacial tension measurements.

Preparatory to making this expansion we will write down expressions for various partial derivatives of  $\Delta f$ , the independent variables being T and c, one of these being held constant. In writing down

(3) O. K. Rice, ibid., 23, 164 (1955).

Work supported by the Office of Ordnance Research, U. S. Army.
 J. W. Cahn and J. E. Hilliard, J. Chem. Phys., 28, 258 (1958).

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these expressions we note that  $\mu_{A,e}$  and  $\mu_{B,e}$  depend only on T, not on c. The expressions following an identity sign are obtained from the preceding expression by applying the Gibbs-Duhem relation. The quantity following the arrow gives the value at the critical point, or the designation to be used for the particular quantity at the critical point. These results will be explained below.

$$\frac{\partial \Delta f}{\partial c} = -(\mu_{\rm A} - \mu_{\rm A,e}) + (\mu_{\rm B} - \mu_{\rm B,e}) + (1 - c)\partial\mu_{\rm A}/\partial c + c\partial\mu_{\rm B}/\partial c \equiv -(\mu_{\rm A} - \mu_{\rm A,e}) + (\mu_{\rm B} - \mu_{\rm B,e}) \rightarrow 0 \quad (2.1)$$

$$\partial^2 \Delta f' \partial c^2 = -\partial \mu_{\rm A} / \partial c + \partial \mu_{\rm B} / \partial c \to 0 \qquad (2.2)$$

$$\partial^3 \Delta f / \partial c^3 = -\partial^2 \mu_{\rm A} / \partial c^2 + \partial^2 \mu_{\rm B} / \partial c^2 \rightarrow 0 \quad (2.3)$$

$$O^*\Delta J/OC^* = -O^*\mu_A/OC^* + O^*\mu_B/OC^* \rightarrow 0$$
 (2.4)

$$\partial^{5}\Delta f/\partial c^{5} = -\partial^{4}\mu_{A}/\partial c^{4} + \partial^{4}\mu_{B}/\partial c^{4} \rightarrow (5!)\gamma_{0} \quad (2.5)$$
$$\partial\Delta f/\partial T = (1 - c)(\partial\mu_{A}/\partial T - d\mu_{A,e}/dT)$$

$$+ c(\partial \mu_{B}/\partial T - d\mu_{B,e}/dT) \rightarrow 0 \quad (2.6)$$
  
$$\partial^{2} \Delta f/\partial c \partial T = - (\partial \mu_{A}/\partial T - d\mu_{A,e}/dT)$$

+ 
$$(\partial \mu_B / \partial T - d\mu_{B,e} / dT) \rightarrow 0$$
 (2.7)

$$\partial^3 \Delta f \partial c^2 dT = - \partial^2 \mu_{\rm A} / \partial c \partial T + \partial^2 \mu_{\rm B} / \partial c \partial T \rightarrow 2\beta_0 \quad (2.8)$$

At the critical point  $\mu_A = \mu_{A,e}$  and  $\mu_B = \mu_{B,e}$ , hence the result of eq. 2.1. Also, the general criteria of a critical point are  $\partial \mu_A / \partial c = \partial \mu B / \partial c =$  $\partial^2 \mu_A / \partial c^2 = \partial^2 \mu_B / \partial c^2 = 0$ . These are analogous to the pressure-volume relationships,  $\partial p / \partial V =$  $\partial^2 p / \partial V^2 = 0$ , in a one-component system. If these are the only derivatives which vanish one will find a quadratic coexistence curve. However, in actual practice the coexistence curve for binary liquid systems<sup>4</sup> as well as for liquid-vapor systems<sup>5</sup> turns out to be cubic, *i.e.*, to good approximation we may write, close to the critical point

$$(\Delta c_{\rm e})^3 = \alpha (T_{\rm c} - T) = \alpha \Delta T \qquad (2.9)$$

where  $\Delta c_e = c_e - c_c$  and  $\alpha$  is a constant, which, however, is positive if  $\Delta c_e$  is positive and negative if  $\Delta c_e$ is negative, assuming an upper critical point. The subscript c denotes a value at the critical point. If this is the correct form then one more derivative must vanish,<sup>6</sup> *i.e.*,  $\partial^3 \mu_A / \partial c^3 = \partial^3 \mu_B / \partial c^3 = 0$ , which explains the result of eq. 2.5. It is at this point that we first differ from Cahn and Hilliard, since they did not allow for the vanishing of these derivatives, and thus obtained a quadratic coexistence curve.

As with eq. 2.9, a discontinuity with change in sign must occur in  $\partial^4 \mu_A / \partial c^4$  and  $\partial^4 \mu_B / \partial c^4$  at the critical point; otherwise, since all lower derivatives are zero,  $\mu_A$  and  $\mu_B$  would not decrease and increase, respectively, uniformly with c. Thus in attempting an expansion of  $\Delta t$  about the critical point we really need two expansions, one about each side of the critical point. This is unpleasant, but seems to be the best representation of the experimental facts.  $\gamma_0$  will be positive for  $c > c_c$ , negative for  $c < c_c$ .

Turning now to eq. 2.6 and 2.7 we may write, using the subscript e on a derivative to denote its value at the coexistence curve

$$\mu_{\rm A,e}/{\rm d}T = (\partial \mu_{\rm A}/\partial T)_{\rm e} + (\partial \mu_{\rm A}/\partial c)_{\rm e} \, {\rm d}c_{\rm e}/{\rm d}T \quad (2.10)$$

Since we wish to evaluate the derivatives at the critical point, where c and  $c_{\rm e}$  coincide, we see that the partial derivatives with respect to temperature cancel in eq. 2.6 and 2.7, and  $(\partial \mu_A / \partial c)_{\rm e}$  vanishes at the critical point.  $dc_{\rm e}/dT$ , to be sure, becomes infinite; by eq. 2.9, it is the limit, as  $\Delta c_{\rm e}$  goes to zero, of  $-\alpha/3(\Delta c_{\rm e})^2$ ; however, setting up a Taylor expansion for  $(\partial \mu_A / \partial c)_{\rm e}$  we see that it starts

$$(\partial \mu_{\rm A}/\partial c)_{\rm e} = -(\partial^2 \mu_{\rm A}/\partial c \partial T)_{\rm e} \Delta T +$$

$$\frac{1}{3!} (\partial^4 \mu_{\rm A} / \partial c^4)_{\rm c} (\Delta c_{\rm e})^3 \quad (2.11)$$

so that it goes to zero to a higher order. This will take care of eq. 2.6 and 2.7. If we substitute eq. 2.11 into eq. 2.10, using the value for  $dc_e/dT$ , and substitute the result with its companion equation for  $\mu_B$  into eq. 2.7, we obtain

$$\frac{\partial^{2}\Delta f}{\partial c\partial T} = \left(\frac{\partial \mu_{\Lambda}}{\partial T}\right)_{e} - \frac{\partial \mu_{\Lambda}}{\partial T} - \left(\frac{\partial \mu_{B}}{\partial T}\right)_{e} + \frac{\partial \mu_{B}}{\partial T} - \frac{2}{3}\beta_{0}\Delta c_{e} + \frac{20}{3}\alpha\gamma_{0}\Delta c_{e} \cong 2\beta_{0}(\Delta c - \Delta c_{e}) - \frac{2}{3}\beta_{0}\Delta c_{e} + \frac{20}{3}\alpha\gamma_{0}\Delta c_{e} \quad (2.12)$$

where  $\Delta c = c - c_e$ . A similar reduction can be effected for (2.6).

As soon as we attempt to go to higher derivatives with respect to T infinities appear. This means that the attempt to expand  $\Delta f$  in a Taylor series about the critical point fails. As an alternative we shall expand it about the concentration  $c_c$  at each separate temperature. Even this procedure is fraught with difficulties and cannot be carried out in a completely rigorous fashion, but we will be able to find a plausible solution. We will carry out this calculation on the assumption that  $T_c - T$  is small, and that no coefficient need be carried if the degree of the term involved at  $\Delta c = \Delta c_e$  exceeds that of the leading terms by as much as  $\Delta c_e$  or  $(T_c - T)^{1/3}$ .

The infinities noted above arise from terms containing  $\mu_{A,e}$  and  $\mu_{B,e}$ , coming eventually from the behavior of  $dc_e/dT$ ; terms not containing them will give no difficulty. There is, however, another kind of infinity which appears at the critical point; it comes from the discontinuities in  $\partial^4 \mu_A / \partial c^4$  and  $\partial^4 \mu_{\rm B} / \partial c^4$ , which means that the fifth derivatives are infinite at the critical point. This will also mean that  $\partial^5 \mu_{\rm A} / \partial c^4 \partial T$  and  $\partial^5 \mu_{\rm B} / \partial c^4 \partial T$  will have anomalous values near the critical point, since the discontinuity in the fourth derivatives will not be expected to persist below the critical temperature. The expected behaviors of  $\partial^4 \mu_A / \partial c^4$  at  $T_c$  and just below  $T_c$  are shown in Fig. 1. Clearly what we must do is to ignore the, hopefully small, region where  $\partial^4 \mu_{\rm B} / \partial c^4$  changes rapidly, and assume that outside this region everything behaves normally. Doing this, we assume that  $\partial^5 \Delta f / \partial c^5$  remains roughly fixed as  $(5!)\gamma_0$ , and we start our expansion as though the region of rapid change did not exist. This difficulty should be less with the lower derivatives; from (2.8) we may write

$$(\partial^2 \Delta f / \partial c^2) T_{,ce} = 2\beta_0 (T - T_c) = -2\alpha^{-1}\beta_0 \Delta c_e^3$$
 (2.13)

the subscripts indicating that it is evaluated at temperature T and  $\Delta c = 0$ .

 $\partial \Delta f / \partial c$  vanishes at the critical point, and at a

<sup>(4)</sup> Data summarized by J. D. Cox and E. F. G. Herington, *Trans. Faraday Soc.*, **52**, 926 (1956), who, however, discuss them in terms of an empirical equation which holds over a greater range than eq. 2.9.

<sup>(5)</sup> Data summarized by E. A. Guggenheim, J. Chem. Phys., 13, 253 (1945).

<sup>(6)</sup> O. K. Rice, ibid., 23, 169 (1954).



Fig. 1.—Behavior of  $\partial^4 \mu_A / \partial c^4$  near the critical point.

point near the critical point, with the same concentration it will be given by

$$(\partial \Delta f/\partial c)T_{,cc} = \int_{T_c}^{T} (\partial^2 \Delta f/\partial c \partial T)_{cc} dT = -3\alpha^{-1} \int_{0}^{\Delta ce} (\partial^2 \Delta f/\partial c \partial T)_{cc} \Delta c_c^2 d\Delta c_e \quad (2.14)$$

We may use eq. 2.12 with  $\Delta c = 0$  to evaluate  $(\partial^2 \Delta f / \partial c \partial T)_{cc}$ . (Equation 2.12 depends on eq. 2.11, but the latter is justified if interpreted properly in the light of the discussion just given.) We obtain after integrating

$$(\partial \Delta f / \partial c)_{T,c_c} = \alpha^{-1} (2\beta_0 - 5\alpha\gamma_0) \Delta c_e^4 \qquad (2.15)$$

We can now set up the Taylor expansion for  $\Delta f$  about the point  $\Delta c = 0$ , neglecting terms arising from  $\partial^3 \Delta f / \partial c^3$  and  $\partial^4 \Delta f / \partial c^4$ , since they will be of higher degree

 $\Delta f = \Delta f_{c_{\rm c}} + a(\Delta c_{\rm c})^4 \Delta c - b(\Delta c_{\rm e})^3 (\Delta c)^2 + \gamma_0 (\Delta c)^5 \quad (2.16)$  where

$$a = \alpha^{-1}(2\beta_0 - 5\alpha\gamma_0)$$
  
$$b = \alpha^{-1}\beta_0$$

Since  $\Delta f$  must be zero when  $\Delta c = \Delta c_e$  (see Cahn and Hilliard's Fig. 1), we can readily evaluate  $\Delta f_{c_e}$ , and we thus obtain

$$\Delta f = a(\Delta c_e)^4 (\Delta c - \Delta c_e) - b(\Delta c_e)^2 [(\Delta c)^2 - (\Delta c_e)^2] + \gamma_0 [(\Delta c)^5 - (\Delta c_e)^5]$$
(2.17)

This can also be obtained by evaluating and integrating  $\partial \Delta f / \partial T$ . From the definitions,  $a - 2b + 5\gamma_0 = 0$ , which means that  $(\partial \Delta f / \partial c)_e = 0$ , which is consistent with eq. 2.1.

Because of the discontinuities at  $\Delta c = 0$  we must regard the signs in eq. 2.16 with care. It will be seen that because  $\alpha, \gamma_0$  and  $\Delta c_e$  change sign when  $\Delta c$ does,  $\Delta f$  can always be positive, as it must.

3. Discussion of the Interfacial Tension.—To calculate the interfacial tension we must introduce the expression for  $\Delta f$  into eq. 1.4. Remembering the discontinuity at  $\Delta c = 0$  it will be best to replace eq. 1.4 by

$$\sigma = 4N_{\rm V} \int_0^{\Delta ce} (\kappa \Delta f)^{1/2} \, \mathrm{d}\Delta c \qquad (3.1)$$

where  $\Delta c_{\rm e} > 0$ ; this is at least a good approxima-

tion. If we introduce the variable  $z = \Delta c / \Delta c_e$ , then, by virtue of (2.17), eq. 3.1 becomes

$$\sigma = 4N_{\rm V} \left(\Delta c_{\rm c}\right)^{7/2} \int_0^1 \kappa^{1/2} [a(z-1) - b(z^2 - 1) + \gamma_0(z^6 - 1)]^{1/2} dz \quad (3.2)$$

If we assume with Cahn and Hilliard that  $\kappa$  is approximately constant it appears that  $\sigma$  should vary as  $(\Delta c_e)^{1/2}$  or  $(\Delta T)^{1/6}$ . The appearance of the fractional power in  $(\Delta c_e)^{1/2}$  is of course closely connected with the infinities in the derivatives.

The exponent of  $\Delta T$  is definitely too low for the cyclohexane-aniline system, which is about the only one which has been examined close to the critical point; Atack and Rice<sup>7</sup> found empirically that the surface tension varied about as  $(\Delta T)^{1.39}$ . Cahn and Hilliard, effectively assuming a quadratic coexistence curve, deduced that  $\sigma$  should vary as  $(\Delta T)^{3/2}$ . This agrees within the limits of error. However, since Cahn and Hilliard's result was based on the quadratic coexistence curve, the empirical basis was not correct, and the apparent concordance with the interfacial tension cannot at this point be considered significant.

Atack and Rice made the assumption that the surface entropy was proportional to the "difference" between the two phases, measured by the equivalent of  $\Delta c_{\rm e}$ . Since the surface entropy is equal to  $-d\sigma/dT$ , this gives, with eq. 2.9, the result that  $\sigma$  is proportional to  $(T_{\rm e} - T)^{4/3}$  or to  $(\Delta c_{\rm e})^4$ . This also agrees within the experimental error.

Looking at eq. 3.2 we see that the result of Atack and Rice would be obtained if  $\kappa$  were not constant but vanished at the critical point and either was dependent on temperature, being in first order proportional to  $|\Delta c_{\rm e}|$ , or dependent on concentration, being in first order proportional to  $|\Delta c|$ , or else being a linear combination of such terms. On the other hand, if  $\sigma$  varied as  $(T_{\rm c} - T)^{3/2}$ , then  $\kappa$  must be proportional to  $(\Delta c_{\rm e})^2$ ,  $(\Delta c)^2$ , or  $\Delta c_{\rm e} \Delta c$ .

4. The Coefficients in the Free-Energy Expression.—The suggestion that  $\kappa$  should be zero at the critical point certainly does not seem unreasonable in view of the insensitivity of the free energy there. To see how this might come about we will develop a phenomenological theory of the coefficients in the expression for f.  $\mu_{\rm A}$  represents the increase of free energy when a molecule A is introduced into a uniform environment. f represents an average increase of free energy per molecule when some molecules (composition that of the solution) are introduced into an environment with gradients, aside from the pressure effects which are discussed below. This depends upon the relation of the introduced molecules to their surroundings, upon the possible configurations and upon the energy relations. Furthermore, it must be noted that, on account of the size of the molecules, the neighbors intrude perceptibly on any position. One might say then that a given molecule is affected by its neighbors up to a certain average penetration distance  $\delta x$ , which depends on temperature and concentration (but, we assume, not too strongly), and there will be an effect on this molecule depending upon how much the concentration has changed in this dis-

(7) D. Atack and O. K. Rice, Disc. Faraday Soc., 15, 210 (1953).

tance. The change in mole fraction will be given by

$$\delta c = (\partial c/\partial x) \delta x + \frac{1}{2} (\partial^2 c/\partial x^2) (\delta x)^2 + \dots \quad (4.1)$$

We then might expect f to be affected by the changes of  $\mu_A$  and  $\mu_B$  with  $\delta c$ . These changes should be weighted by the respective mole fractions. Thus we will be interested in the expression

$$(1-c)\partial\mu_A/\partial c + c\partial\mu_B/\partial c$$
 (4.2)

This, however, vanishes on account of the Gibbs-Duhem relation.

We have so far assumed that the effect depends only on the gradients of  $\mu_A$  and  $\mu_B$ . A chemical potential, however, is a composite term, depending upon a partial molecular energy contribution and a partial molecular entropy contribution. The effective  $\delta x$  for energy might be different from that for entropy. However, an equation similar to the Gibbs-Duhem relation holds for all partial molal or molecular quantities. Thus we must conclude that the coefficients of all the terms,  $\partial c/\partial x$ ,  $\partial^2 c/$  $\partial x^2$ , ... must vanish in the expansion for f. It has been concluded already on other grounds that the coefficient of  $\partial c/\partial x$  will vanish, but it now appears that many other coefficients will vanish also. The effect of  $\partial c$  must be at least a second-order effect. We have

$$(\delta c)^2 = (\partial c/\partial x)^2 (\delta x)^2 + \dots \qquad (4.3)$$

and we must expect effects which would be proportional to

$$[(1 - c)\partial^2 \mu_A / \partial c^2 + c \partial^2 \mu_B / \partial c^2] (\delta c)^2 = (\partial \mu_A / \partial c - \partial \mu_B / \partial c) (\delta c)^2 \quad (4.4)$$

the equality arising by differentiation of the Gibbs– Duhem equation. If the effects of the energy and entropy are to some degree dissociated there will be an additional term proportional to

$$[(1 - c)\partial^2 \bar{e}_{\rm A}/\partial c^2 + c\partial^2 \bar{e}_{\rm B}/\partial c^2](\delta c)^2 = (\partial \bar{e}_{\rm A}/\partial c - \partial \bar{e}_{\rm B}/\partial c)(\delta c)^2 \quad (4.5)$$

where  $\bar{e}_{\rm A}$  and  $\bar{e}_{\rm B}$  are the partial molecular energies. The coefficient of  $(\partial c/\partial x)^2$  in the expression for f will thus be proportional to a linear combination of the quantities multiplying  $(\delta c)^2$  in (4.4) and (4.5).

Let us suppose at first that the coefficient depends only on the expression in (4.4). Then we see at once from eq. 2.2 to 2.5 and eq. 2.8, expanding about the critical point, that

$$\kappa \propto 2\beta_0 \Delta T - 20\gamma_0 (\Delta c)^3 \tag{4.6}$$

We would expect  $\kappa$  not only to be proportional to  $\partial \mu_A / \partial c - \partial \mu_B / \partial c$  but to have the same sign. Ordinarily  $\partial \mu_A / \partial c - \partial \mu_B / \partial c$  will be negative, but in the unstable region below the critical temperature,  $\partial \mu_A / \partial c - \partial \mu_B / \partial c$  is positive ( $\beta_0$  is positive). Thus in such a region  $\kappa$  would start out positive at the critical concentration, but the second term in eq. 4.6 would cause it to become negative at concentrations beyond<sup>8</sup>

$$|\Delta c| = \left(\frac{1}{10} \beta_0 / \alpha \gamma_0\right)^{1/4} |\Delta c_c| < |\Delta c_c| \qquad (4.7)$$

If  $\kappa$  were negative there would be no solution to eq. 1.3, and  $\partial c/\partial x$  would tend toward infinity. It would not actually become infinite because of higher order terms, but to our approximation we may consider that we would have a discontinuity. It must be stated that even in a single phase a certain instability would result if  $\kappa$  were negative,<sup>2</sup> for one can always imagine oscillations in concentration which would make  $\partial c/\partial x$  large, and if the "wave length" were short enough this could be accom-plished without much variation in concentration. Indeed  $(\partial \Delta f / \partial c) \kappa c$  always averages zero for a stable phase, so some fluctuations in concentration must be expected; too large a fluctuation would be prevented, especially far from the critical point, by the non-zero value of  $\partial^2 \Delta f / \partial c^2$ . It is not certain that such fluctuations should worry us; indeed, their effect should already be taken into account in calculating the free energy of a stable uniform phase, the fluctuations being a normal property of the phase. In our problem we consider a superimposed gradient, and the occurrence of a near discontinuity in this gradient does not seem impossible. In our approximation the value of  $\Delta c$  would jump from that given by eq. 4.7 to  $\Delta c_e$  itself. In this case we apply the variation problem to the concentrations within the limits<sup>9</sup> given by (4.7). The constant in eq. 1.3 would not be zero but rather equal to the value of  $\Delta f$  at the concentration given by eq. 4.7. The variation problem can be solved and yields an equation of the same dimensionality with respect to  $\Delta c_{\rm e}$  or  $\Delta c$  and the same power of  $\kappa$  as eq. 3.2. Since  $\kappa$  itself now depends on  $(\Delta c_e)^3$ and  $(\Delta c)^3$ , the net effect will be that  $\sigma$  will be proportional to  $(\Delta c_e)^{5}$  or  $(T_c - T)^{5/3}$  which seems too high.

This suggests that we consider possible dissociation of the energy and entropy terms in calculating  $\kappa$ . If they must be considered separately at the critical point, then the leading term in  $\kappa$  is constant, because  $\partial \bar{e}_A / \partial c - \partial \bar{e}_B / \partial c$  is not expected to vanish at the critical point. But just at the critical point we might suppose that the energy and entropy effects would come in together, for here there are large fluctuations, and any concentration or any gradient must be an average over a rather wide range. A particle at a given position finds itself first in one situation, then another, because the fluctuations will bring to it conditions resembling those on one side of it, and conditions resembling those on the other, the frequency of any particular

(9) Since the uniform equilibrium phase already includes the effects of gradients it seems natural to set the value of  $\kappa$  at this concentration equal to zero, and to suppose that the effective value of  $\kappa$  does not depart too greatly from zero in the near discontinuity. Then the contribution to the interfacial tension from the region of the near discontinuity would be approximately.

$$r_{\rm d} \cong N_{\rm V} \int \left[\Delta f + \kappa_n \left(\frac{\partial c}{\partial x}\right)^n\right] {\rm d}x$$

assuming the situation is controlled by a higher power of  $\partial c/\partial x$ ; the minimization condition would be

$$\Delta f - [n - 1] \kappa_n (\partial c / \partial x)^n = 0$$

the constant being zero if one can assume that in actuality, taking into account the higher-power terms, this region merges continuously into the uniform phase. Then

$$\sigma_{\rm d} = [n/(n-1)] N_{\rm V} \int [(n-1)\kappa_n]^{1/n} (\Delta f)^{1-1/n} \, {\rm d}c$$

which would be expected to involve a higher power of  $\Delta c_e$ , and so does not need to be included in our considerations.

<sup>(8)</sup> The inequality in (4.7) follows because when  $\Delta c = \Delta c_e$  we have  $\Delta f - \Delta f_{c_e} = -\Delta f_{c_e} < 0$ . Thus, setting  $\Delta c = \Delta c_e$  in eq. 2.16, we see that if  $\Delta c_e > 0$  (so that  $\alpha$  and  $\gamma_0$  are positive), then  $\alpha - b + \gamma_0 = \alpha^{-1}\beta_0 - 4\gamma_0$  is negative.

situation falling off with the distance at which this particular condition resembles the average one. The molecule thus experiences intimately all the conditions in closely neighboring volume elements. When this is the case it is not surprising if entropy effects and energy effects come in together. The above argument suggests that  $\delta x$  is connected with the fluctuations and that there might be a relation between  $\delta x$  and the dissociation of energy and entropy terms.  $\delta x$  would presumably have a maximum at the critical point where the fluctuations are largest, but probably not a sharp one, so in first order the dependence of  $\sigma$  on T would not be affected. If the dissociation of energy and entropy has a simple minimum which is very nearly zero at the critical point it would behave approximately as  $(\Delta c)^2$  and  $(\Delta c_e)^2$ , giving terms of this order in the expression for  $\kappa$ . These terms would presumably be positive and would eliminate the discontinuity in composition. They would make  $\sigma$  proportional to  $(\Delta c_e)^{3/2}$  or  $(T_e - T)^{3/2}$ , the same result obtained by Cahn and Hilliard, though it is now on a very different basis. On the other hand, it might be that the minimum is very flat and that there is a small amount of dissociation of the energy and entropy effects even at the critical point, and the experimental values of  $\sigma$ , rather than being a simple power, represent some compromise between the  $(T_{c})$  $(T_{c})^{7/6}$  term which would arise thus and the  $(T_{c})^{7/6}$  $(-T)^{3/3}$  contribution obtained from the consideration of eq. 4.4. While we cannot draw any very exact conclusions, the analysis at least shows the factors involved in the temperature dependence of the interfacial tension, and makes the observed behavior appear quite reasonable.

It is also possible that there might be some dissociation of the effects of the two different kinds of molecules, especially if they were very different in size or structure. If this occurred we would not have an expression like (4.2) but one in which the effects of the two species were not proportional to their mole fractions. Thus the Gibbs-Duhem equation would not apply, and the coefficient of  $\partial^2 c / \partial x^2$  in the free-energy expression could have a non-zero value. This must be the situation in a one-component system and this is treated below. It can lead to a lower dependence of  $\kappa$  on  $\Delta c$ . However, this dissociation of effects would also be expected to be practically vanishing at the critical point where the fluctuations are large, and its increase away from the critical point would be superimposed on the other effects. So it seems unlikely that this would give rise to any term of net lower degree in  $\Delta c$  than those already considered.

Our considerations are designed, of course, to apply only in the immediate neighborhood of the critical point. One may wonder whether the values of  $\Delta c_{\rm e}$  which are attained even quite close to the critical point are really "small," since actually the width of a solubility curve is quite appreciable even a very small distance from the critical point. The very fact that  $\Delta c_{\rm e}$  does increase so rapidly with  $\Delta T$ , and that this is connected with the small variation of the chemical potentials in this region, may lend

(9a) We assume that the temperature dependence will be given by  $(\Delta c_e)^2$  if the concentration dependence is  $(\Delta c)^2$ , in analogy to eq. 4.6.

credence to the idea that it can be regarded as a small quantity. On the other hand, the considerations of Widom and Rice<sup>10</sup> concerning equations of state in the critical region indicate that further consideration of this point might be desirable.

It is interesting to note that the thickness of the interface, calculated according to eq. 2.25 of Cahn and Hilliard, turns out to be proportional to  $(T_{c} T)^{-1/6}$  if  $\kappa$  is proportional to  $(\Delta c)^2$  or  $(\Delta c_e)^2$ , a much smaller dependence than given by Cahn and Hilliards' calculation. In any case we would not expect the interface actually to reach an infinite thickness if the coexistence curve is flattened at the top and the interfacial tension vanishes while the phases are still different.

5. Liquid-Vapor Equilibrium.—Though the liquid-vapor equilibrium of a one-component system resembles the solubility equilibrium of a binary liquid system, there are certain differences, which stem from the fact that pressure and pressure gradients are of importance in the liquid-vapor system, and from the fact that there is no Gibbs-Duhem equation in the latter.

Consider a two-phase system in a fixed volume. If the bulk densities of liquid and vapor remained unchanged up to a boundary surface, this surface would divide the system into two volumes each of which was also fixed. The surface tension then is equal to the excess Helmholtz free energy over that which would exist if the properties of liquid and vapor were unchanged up to the boundary surface. Since the Helmholtz free energy per molecule is equal to  $\mu - p/\rho$ , where  $\mu$  is the chemical potential, p is the pressure and  $\rho$  the number density (which plays the same role as c in the preceding theory), we will have for the surface tension arising from any arbitrary distribution

$$\sigma' = \int_{-\infty}^{\infty} \left[ \rho(\mu - \mu_e) - p + p_e \right] \mathrm{d}x \qquad (5.1)$$

where the subscript e indicates the value for the equilibrium phases as before. We now set

$$f = \mu - p/\rho \tag{5.2}$$

f is in general a function of  $\rho$  and its space derivatives. If the space derivatives are zero, then f = $f_0$ . We let

$$\Delta f = f_0 - \mu_e + p_e/\rho = \mu_0 - \mu_e - (p_0 - p_e)/\rho \quad (5.3)$$

and obtain

$$\sigma' = \int_{-\infty}^{\infty} \rho[f - \mu_e + p_e/\rho] dx = \int_{-\infty}^{\infty} \rho[\Delta f + \kappa_1 \partial^2 \rho / \partial x^2 + \kappa_2 (\partial \rho / \partial x)^2 + \dots] dx \quad (5.4)$$

where the last terms come from the expansion of f –  $f_0$  in terms of the space derivatives. The same argument as in Section 1 indicates that the coefficient of  $\partial \rho / \partial x$  should vanish. The equilibrium value  $\sigma$  of the surface tension will be the minimized value of  $\sigma'$ . The factor  $\rho$  plays the role of  $N_V$  in eq. 1.2 but cannot be taken to be constant in this case, although this will still be a good approximation near the critical point. The term in  $\partial^2 \rho / \partial x^2$  can be integrated by parts as before; though we shall see that there is probably a near-discontinuity in  $\rho$ ,

(10) B. Widom and O. K. Rice, J. Chem. Phys., 23, 1250 (1955).

since it is only a near-discontinuity this requires no special attention. We have

$$\int_{-\infty}^{\infty} \rho \kappa_1 (\partial^2 \rho / \partial x^2) dx = \rho \kappa_1 (\partial \rho / \partial x) \Big|_{-\infty}^{\infty} - \int_{-\infty}^{\infty} [\partial (\rho \kappa_1) / \partial \rho] [\partial \rho / \partial x)^2 dx \quad (5.5)$$

 $\partial \rho / \partial x$  vanishes at  $\infty$  and  $-\infty$  thus eq. 5.4 becomes, to terms in  $(\partial \rho / \partial x)^2$ 

$$\sigma' = \int_{-\infty}^{\infty} \rho [\Delta f + \kappa (\partial \rho / \partial x)^2] dx \qquad (5.6)$$

where

$$\rho \kappa = \rho \kappa_2 - \partial(\rho \kappa_1) / \partial \rho \qquad (5.7)$$

Minimization of eq. 5.6 will again give the equivalent of eq. 1.3 even if  $\rho$  is not constant, and if there is only one point of discontinuity the constant of eq. 1.3 will still be zero. The final result will be, if  $\rho = \rho_{\rm l}$  for the bulk liquid and  $\rho = \rho_{\rm v}$  for the bulk vapor

$$\sigma = 2 \int_{\rho_{\mathbf{v}}}^{\rho_1} \rho(\kappa \Delta f)^{1/2} \,\mathrm{d}\rho \qquad (5.8)$$

but with no contributions from the range in concentrations between any gap which may occur.<sup>9</sup>

We will assume<sup>5</sup> that the shape of the coexistence curve near the critical point will be given by 2.9, replacing  $\Delta c_e$  by  $\Delta \rho_e$ . This means that  $\partial^3 p_0 / \partial \rho^4$ .  $\partial \rho^3$  vanishes at the critical point, but not  $\partial^4 p_0 / \partial \rho^4$ . The latter, however, has a discontinuity and changes signs there, like  $\partial^4 \mu_A / \partial c^4$  and  $\partial^4 \mu_B / \partial c^4$ .

6. The Excess Free Energy in the Liquid-Vapor Boundary.—We can now proceed to write down the various derivatives of  $\Delta f$ , noting that  $\mu_e$  is a function of T only, and that, according to the well-known thermodynamic relation

$$(\partial \mu_0 / \partial p_0)_T = \rho^{-1} \tag{6.1}$$

so that

$$\partial \mu_0 / \partial \rho = (\partial \mu_0 / \partial p_0)_T \partial p_0 / \partial \rho = \rho^{-1} \partial p_0 / \partial \rho \qquad (6.2)$$

In writing partial derivatives  $\rho$  and T are generally taken as the independent variables, and if no indication to the contrary is given either  $\rho$  or T is held constant. As before we use the arrow to indicate the value approached at the critical point. We find, writing out only the highest derivative of  $p_0$  in most cases

$$\partial \Delta f / \partial \rho = \rho^{-2} (p_0 - p_e) \rightarrow 0$$
 (6.3)

$$\partial^2 \Delta f / \partial \rho^2 = \rho^{-2} \partial p_0 / \partial \rho - 2 \rho^{-3} (p_0 - p_c) \rightarrow 0 \quad (6.4)$$

$$\partial^3 \Delta f / \partial \rho^3 = \rho^{-2} \partial^2 p_0 / \partial \rho^2 + \dots \to 0 \qquad (6.5)$$

$$\partial^4 \Delta f / \partial \rho^4 = \rho^{-2} \partial^3 p_0 / \partial \rho^3 + \dots \to 0 \tag{6.6}$$

$$\partial^5 \Delta f / \partial \rho^5 = \rho^{-2} \partial^4 p_0 / \partial \rho^4 + \dots \rightarrow (5!) \gamma_0 \quad (6.7)$$

$$\partial \Delta f / \partial T = \partial \mu_0 / \partial T - \mathrm{d} \mu_\mathrm{e} / \mathrm{d} T$$

$$\rho^{-1}(\partial p_0/\partial T - \mathrm{d} p_e/\mathrm{d} T) \to 0 \quad (6.8)$$

(6.12)

$$\partial^{2}\Delta f/\partial\rho \partial T = \rho^{-2}(\partial p_{0}/\partial T - dp_{e}/dT) \rightarrow 0 \quad (6.9)$$
  
$$\partial^{3}\Delta f/\partial\rho^{2}\partial T \rightarrow -2\rho^{-3}(\partial p_{0}/\partial T) - dp_{e}/dT) + \rho^{-2}\partial^{2}p_{0}/\partial\rho \partial T \rightarrow 2\beta_{0} \quad (6.10)$$

Equation 6.9 may be reduced as was 
$$(2.7)$$
. We have

$$dp_e/dT = (\partial p_0/\partial T)_e + (\partial p_0/\partial \rho)_e d\rho_e/dT \quad (6.11)$$
  
xpanding about the critical point

Expanding about the critical poi  $(\partial p_1/\partial \rho)_0 = -(\partial^2 p_0/\partial \rho \partial T)_{\rho_c} \Delta T +$ 

$$\frac{1}{3!} (\partial^4 p_0 / \partial \rho^4)_{\rho e} (\Delta \rho_e)^3 = \rho_e^2 (-2\alpha^{-1}\beta_0 + 20\gamma_0) (\Delta \rho_e)^3$$

which gives

$$\partial^2 \Delta f / \partial \rho \partial T = 2\beta_0 (\Delta \rho - \Delta \rho_e) - \frac{2}{3} \beta_0 \Delta \rho_0 + \frac{20}{3} \alpha \gamma_0 \Delta \rho_0$$
(6.13)

the exact analogy of eq. 2.12. Formally, then, the expansion of  $\Delta f$  looks exactly the same as before, and we finally obtain eq. 2.16, with *c* replaced by  $\rho$ .

7. Evaluation of  $\kappa$  and the Surface Tension.— In considering  $\kappa$  we find one difference from the discussion given in Section 4. In the liquid-vapor case there is no Gibbs-Duhem equation, hence we can expect effects arising from the first-power term,  $\delta\rho$ . Thus we cannot exclude the first-degree terms in  $\rho$ ; the coefficient of  $\partial\rho/\partial x$  is, as we have seen, expected to be zero in any case, but the coefficient of  $\partial^2 \rho/\partial x^2$  will not be. Considering the case where  $\partial\rho/\partial x$  vanishes, we see that a positive value of  $\partial^2 \rho/\partial x^2$ means that a molecule will find itself on the average near a region of concentrations greater than that at its own position, whereas a negative value of  $\partial^2 \rho/\partial x^2$  will have the opposite effect. Thus we may expect a non-zero value of  $\kappa_1$ .

Both  $\kappa_1$  and  $\kappa_2$  should vanish at the critical point, on the basis of the arguments given in Section 4. The dissociation of the energy and entropy effects should, if the phenomenological suggestion of Section 4 is correct, cause them to increase proportionally to  $(\Delta \rho)^2$ . However, we recall that  $\kappa$  depends upon  $\partial \kappa_1 / \partial \rho$  and it will on this basis contain a term proportional to  $\Delta \rho$ . To the approximation that terms of higher degree can be neglected,  $\kappa$  will change sign at  $\Delta \rho = 0$ .

If energy effects predominate over entropy effects, then, because of the attractive forces, the greater the censity the lower the free energy will be. Therefore the sign of the contribution to  $\Delta f$  will be opposite to that of  $\delta \rho$  so that, by eq. 4.1 (with  $\rho$  substituted for c), the sign of  $\kappa_1$  will be negative. This being the case,  $\partial \kappa_1/\partial \rho$  will be negative on the liquid side, positive on the vapor side, and, this being the leading term in  $\kappa$ , the latter will by eq. 5.7 be positive on the liquid side and negative on the vapor side, the dividing concentration being approximately  $\rho_{c}$ . According to the discussion in Section 4 a discontinuity (or near discontinuity) will occur where  $\kappa$  becomes negative, and there will be no concentrations in the range extending approximately from  $\rho_c$  to  $\rho_V$ . So eq. 5.8 takes the form

$$\sigma = 2 \int_{\rho_c}^{\rho_l} \rho_c (\kappa \Delta f)^{1/2} \,\mathrm{d}\rho \qquad (7.1)$$

For our purposes it is sufficient to replace  $\rho$  in the integrand by  $\rho_{\rm c}$ . If we set  $\kappa = \kappa_0 \Delta \rho$ , where  $\kappa_0$  is a constant, use the variable  $z = \Delta \rho / \Delta \rho_{\rm e}$ , and substitute the value of  $\Delta f$  (eq. 2.17) we obtain

$$\sigma = 2\rho_{c} (\Delta \rho_{r})^{4} \int_{0}^{1} \kappa_{0} z^{1/2} [a(z-1) - b(z^{2}-1) + \gamma_{0}(z^{5}-1)]^{1/2} dz \quad (7.2)$$

Thus  $\sigma$  will be proportional to  $(\Delta \rho_e)^4$  or  $(T_e - T)^{4/4}$ . If entropy effects predominate the discontinuity will be on the liquid state, but the results will be otherwise similar.

One cannot perhaps exclude the possibility, though it does not seem too probable, that, in the dissociation of energy and entropy effects, the energy would predominate at high densities and the entropy at the lower densities where the freedom of movement is greater. If this were the case  $\kappa_1$ would change sign at  $\Delta \rho = 0$ , and it would seem natural to suppose it proportional to  $\Delta \rho$ . Then it would contribute a positive term to  $\kappa$  and  $\sigma$  would be proportional to  $(\Delta \rho_{\sigma})^{1/2}$  or  $(T_{\sigma} - T)^{1/4}$ .

be proportional to  $(\Delta \rho_{\rm e})^{7/2}$  or  $(T_{\rm c} - T)^{7/6}$ . In any case, it is very interesting that the lack of the Gibbs-Duhem equation causes the dependence of  $\sigma$  on  $T_c - T$  to be slightly less in the case of the liquid-vapor equilibrium than in the case of the binary solutions. Unfortunately there are hardly any data by means of which to test the results, Guggenheim<sup>5</sup> has shown that for many liquids  $\sigma$  is proportional to  $(T_c - T)^{11/9}$  [instead of  $(T_c - T)^{11/9}$ ], or, what is equivalent, to  $(\Delta \rho_e)^{11/3}$  [instead of  $(\Delta \rho_e)^4$ ; the  $(\Delta \rho_e)^4$  law is the McLeod<sup>11</sup> equation, but it is not exact]. This is based upon data sufficiently far from the critical point so as not to be too significant for our purposes, and is not, in my opinion, to be taken as evidence for a behavior of  $\kappa$ , such as is discussed in the preceding paragraph. Winkler and Maass<sup>12</sup> have measured the surface tensions of dimethyl ether and propylene fairly near their critical points. The data, however, are hardly sufficiently accurate to distinguish between  $(T_c - T)^{11/9}$  and  $(T_c - T)^{4/3}$  near the critical point, and one is handicapped in interpretation by the fact that they did not give the exact value of  $T_{\rm c}$  for the samples used. They did believe that their data for dimethyl ether fit the McLeod equation; their data for propylene, however, did not. Surface tension data very close to the critical point would surely be of great interest, but the experimental difficulties are formidable.

8. Relation to Tolman's Theory.—Tolman<sup>13</sup> developed a theory of surface tension which, when applied to a flat surface, gave this expression for  $\sigma$ 

$$\sigma = \int_{-\infty}^{\infty} (p_{\rm e} - p) \mathrm{d}x \qquad (8.1)$$

The relation of this expression to the expression which we have used is easy to see. Our expression, eq. 5.4, can be written, using eq. 5.2

$$\sigma' = \int_{-\infty}^{\infty} \rho(\mu - p/\rho + \mu_{\rm e} + p_{\rm e}/\rho) \, \mathrm{d}x \quad (8.2)$$

At equilibrium this integral will be a minimum so that, if  $\delta$  denotes a small variation

$$\int_{-\infty}^{\infty} \delta[\rho(\mu - p/\rho + \mu_{\rm e} + p_{\rm e}/\rho)] \mathrm{d}x = 0 \quad (8.3)$$

Since the variation is arbitrary the integrand in (8.3) may be set equal to zero, which gives, since  $\mu_e$  and  $p_e$  are fixed

$$(\delta\rho)(\mu - \mu_{\rm e}) + \rho\delta\mu - \delta p = 0 \qquad (8.4)$$

This is, of course, the beginning of the procedure of the calculus of variations.  $\mu$  and p may depend upon  $\rho$  and its derivatives with respect to x, but if one is prepared to accept the fundamental assumption that it is possible to assign a definite energy and entropy to the particles in any slab of matter, regardless how thin it may be, then (see Section

(12) C. A. Winkler and O. Maass, Can. J. Res., 9, 65 (1933).

9) thermodynamics requires that at fixed temperature  $\rho\delta\mu = \delta p$ , and we see from eq. 8.4 that  $\mu = \mu_{e}$ , which is, of course, the expected equilibrium condition. Under these circumstances  $\epsilon q$ . 8.2 obviously reduces to eq. 8.1.

There is a simple physical interpretation of eq. 8.1. If we attempt to stretch a surface by means of an instrument (say a wire to which the surface clings) there will be a pressure of  $p_e$  all around the instrument except on the side toward the surface. The net force per unit length will be given by the integral of (8.1), which is a pressure difference multiplied by an average width.

The considerations which were valid for a liquidvapor system will also apply to the binary liquid system. In this case the pressure of the two bulk phases can be taken as zero, and where we consider a solution of a non-equilibrium concentration but with no concentration gradient we also deal with a case of zero pressure. Thus we have avoided any mention of pressure in this case, but a pressure (which will be predominantly negative) will develop in the transition layer. We will indeed have

$$f = g - p/N_{\rm V} \tag{8.5}$$

where *g* is the Gibbs free energy per molecule, and is equal to

$$g = (1 - c)\mu_{\rm A} + c\mu_{\rm B} \tag{8.6}$$

Here  $\mu_A$  and  $\mu_B$  are the chemical potentials when there are concentration gradients and c is the mole fraction as before. Again equating the overall chemical potentials throughout the system, we will be left with eq. 8.1.

The equality of the chemical potentials can be deduced in much the same way as before, but in minimizing the integral we must leave  $N_V$  inside the integral instead of taking it out as in eq. 1.2. The minimization condition in this case is

$$\delta \{N_{\mathrm{V}}[(1-c)(\boldsymbol{\mu}_{\mathrm{A}}-\boldsymbol{\mu}_{\mathrm{A},\mathrm{e}})+c(\boldsymbol{\mu}_{\mathrm{B}}-\boldsymbol{\mu}_{\mathrm{B},\mathrm{e}})-(p-p_{\mathrm{e}})/N_{\mathrm{V}}]\}$$

$$= [(1-c)(\boldsymbol{\mu}_{\mathrm{A}}-\boldsymbol{\mu}_{\mathrm{A},\mathrm{e}})+c(\boldsymbol{\mu}_{\mathrm{B}}-\boldsymbol{\mu}_{\mathrm{B},\mathrm{e}})]\delta N_{\mathrm{V}} - N_{\mathrm{V}}(\boldsymbol{\mu}_{\mathrm{A}}-\boldsymbol{\mu}_{\mathrm{A},\mathrm{e}})\delta c + N_{\mathrm{V}}(\boldsymbol{\mu}_{\mathrm{B}}-\boldsymbol{\mu}_{\mathrm{B},\mathrm{e}})\delta c + N_{\mathrm{V}}(\boldsymbol{\mu}_{\mathrm{A}}-\boldsymbol{\mu}_{\mathrm{A},\mathrm{e}})\delta c + N_{\mathrm{V}}(\boldsymbol{\mu}_{\mathrm{A}}+c\delta\boldsymbol{\mu}_{\mathrm{B}}] - \delta p = 0 \quad (8.7)$$

Since  $(1 - c)\delta\mu_{\rm A} + c\delta\mu_{\rm B}$  will be the change in g at constant composition, it must, at fixed temperature, be equal to  $\delta p/N_{\rm V}$ , by the argument used above. Thus, since  $\delta N_{\rm V}$  and  $\delta c$  are both arbitrary, we must have  $\mu_{\rm A} = \mu_{\rm A,e}$  and  $\mu_{\rm B} = \mu_{\rm B,e}$  at equilibrium.

The pressure which develops in a binary liquid system can itself affect the free energy, a fact which has been neglected. We can make an estimate of what this effect will be. According to eq. 8.1 the average difference in pressure,  $\delta p$ , will be given by

$$\delta p \sim -\sigma/l$$
 (8.8)

where l is the thickness of the surface. The effect of this pressure difference on  $\Delta f$  will be roughly

$$\delta \Delta f \sim -\int_{v_0}^{v_0+\delta v} \delta p \mathrm{d}v = -\int_0^{\delta p} \delta p (\partial v/\partial p) \mathrm{d}p \sim -\frac{1}{2} (\partial v/\partial p) (\delta p)^2 \quad (8.9)$$

where  $v_0(\sim N_V^{-1})$  is the original molecular volume, and  $\delta v$  is the change in it produced by the pressure difference  $\delta p$ .

In first approximation the effect may be esti-

<sup>(11)</sup> J. McLeod, Trans. Faraday Soc., 19, 38 (1923).

<sup>(13)</sup> R. C. Tolman, J. Chem. Phys., 16, 758 (1948).

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mated from the equation obtained by substituting eq. 1.3 (with const. = 0) in eq. 1.2

$$\sigma = 2N_{\rm V} \int_{-\infty}^{\infty} \Delta f \mathrm{d}x \qquad (8.10)$$

From eq. 8.9 and 8.10, and then 8.8, we see that

$$\delta\sigma \sim -N_{\rm V}(\partial v/\partial p)(\delta p)^2 l \sim -N_{\rm V}\sigma^2(\partial v/\partial p)/l = \sigma^2\beta/l$$
(8.11)

where  $\beta$  is the compressibility of the liquid mixture. Giving  $\beta$  a typical value of  $10^{-10}$  cm.<sup>2</sup> dyne<sup>-1</sup>, assuming  $l = 5 \times 10^{-8}$  cm., and taking  $\sigma = 1$  dyne  $cm.^{-1}$ , we find

$$\delta\sigma/\sigma \sim 2 \times 10^{-3}$$

Near the critical point where  $\sigma$  is very small the relative change will be still smaller, and it is still essentially negligible even if  $\sigma$  is as great as 10 dyne cm.<sup>-1</sup>.

9. Thermodynamics of Non-uniform Systems. -Conclusions which are formally the same as those of Section 8 may be drawn from a paper by Hart<sup>14</sup> together with a more recent paper of Cahn<sup>15</sup>; these results, however, in contrast to ours and to Tolman's do not give the interfacial tension in terms of the intrinsic pressures of separate elements of volume. Hart defined the intrinsic pressure differently, as a partial coefficient for energy change when molecular volume is changed keeping density gradients and similar derivatives constant, and his intrinsic pressure cannot be used in eq. 8.1. In attempting to consider actual physical processes his definition creates some difficulties, as was noted by Cahn, for it is hard to conceive of a process in which the proper quantities are kept constant. The definition of pressure implied in the foregoing discussion is the more usual operational one: the work which is done by its surroundings on a volume containing certain specified molecules when this volume is changed by an amount  $\delta V$  is equal to  $-p\delta V$ . The interpretation of this statement needs some discussion when it is applied to a very thin slab of material, because in such a case the potential energy of the molecules whose centers are included in the slab is to a significant extent mutual potential energy with molecules outside the slab. This suggests that we must have some means of dividing this potential energy among the various molecules.

This difficulty can be avoided by a more careful formulation. We suppose that there is a certain volume element dv containing certain molecules; we then assume that these molecules are constrained to move in a different volume,  $dv + \delta v$ , thus effectively changing the density in this region while the density elsewhere remains fixed. We then define p by stating that the change of the total energy E of the entire system is given, if no heat flow occurs, by<sup>16</sup>

(14) E. W. Hart. Phys. Rev., 113, 412 (1959).

(15) J. W. Cahn, J. Chem. Phys., 30, 1121 (1959).
(16) G. Bakker (W. Wien and F. Harms, ed., "Handbuch der Experimental Physik," Akademische Verlagsgesellschaft, Leipzig, 1928, Vol. 6, pp. 18 ff.) has claimed that the pressure is different in the directions normal to and parallel to the surface. His "proof" of this contention is obviously incorrect, as may be seen by reading the paper of Tolman,<sup>13</sup> but a disproof is more difficult. If his contention is correct, our arguments will apply to the pressure parallel to the surface (which is then defined as the thermodynamic pressure) with changes in volume

$$\delta E = -p\delta v \tag{9.1}$$

This includes the effect of any density gradients which are introduced or changed, rather than taking them into account explicitly, as was done by Hart. Our procedure results in a simpler formulation, since changes in density gradients cannot be separated from changes in density. It is legitimate, since the effect of a subsequent change in a neighboring volume element will not be changed to the first order of small quantities ( $\delta v \ll dv$ ), and the contributions of different volume elements are therefore additive. The total change of energy in all parts of the system, allowing heat flow, will, if each volume element of the system is in internal equilibrium, be given at constant temperature, by

$$dE = TdS - \int p(\delta v/dv) dv \qquad (9.2)$$

the integral being taken over the whole system. We now define the Gibbs free energy

$$G = E - TS + \int p \mathrm{d}v \tag{9.3}$$

If we allow the introduction of molecules of various kinds (*i.e.*, changes  $\delta n_1$ ,  $\delta n_2$ , ... in the numbers of these molecules) into various volume elements of the system we have, at constant temperature

 $\mathrm{d}G = \int [\delta p + \mu_1(\delta n_1/\mathrm{d}v) + \mu_2(\delta n_2/\mathrm{d}v) + \dots] \,\mathrm{d}v \quad (9.4)$ where

$$u_i = \bar{e}_i - T\bar{s}_i + p\bar{v}_i \tag{9.5}$$

with  $\bar{e}_i = (\partial E/\partial n_i)_{p,T}$ , etc., these quantities being functions of position. The usual properties of a homogeneous function hold. By introducing the different components into the system over the different portions of the fluid in such a way that their densities, proportions, and surroundings remain constant we can assure that  $\delta p = 0$ , and we find

$$G = \int [\mu_1(dn_1/dv) + \mu_2(dn_2/dv) + \dots] dv \quad (9.6)$$

where  $dn_i$  is the total number of molecules of kind i in the volume element dr. Similarly

$$\begin{split} \mathcal{E} &= \int [\bar{e}_1(dn_1/dv) + \bar{v}_2(dn_2/dv) + \dots] \, dv \quad (9.7) \\ S &= \int [\bar{s}_1(dn_1/dv) + \bar{s}_2(dn_2/dv) + \dots] \, dv \quad (9.8) \\ V &= \int [\bar{v}_1(dn_1/dv) + \bar{v}_2(dn_2/dv) + \dots] \, dv \quad (9.9) \end{split}$$

The integrands in eq. 9.6 to 9.9 may be written g(dn/dv), e(dn/dv), s(dn/dv) and v(dn/dv), where g, e, s, v, are contributions of the particular volume element per molecule and dn is the total number of molecules in the volume element, and we see that (9.6) is equivalent to (8.6).

We can now rewrite eq. 9.1 as

$$\delta E = -p\delta V \tag{9.10}$$

since clearly  $\delta v = \delta V$  under the circumstances under which (9.1) holds. Equation 9.10 will be valid either before or after we have added some new molecules of type i to the volume element in question. Hence, also

$$\delta \bar{c}_{i} = -p \delta \bar{v}_{i} \tag{9.11}$$

By a similar argument, we have in general, if heat flow is allowed and the temperature held fixed

confined to those produced by displacements in that direction, this type of displacement being implied in any case in the development below of eq. 9.6 to 9.9. When the whole system is in equilibrium one might argue that the parallel and normal pressures must be equal, otherwise a change in the shape of a volume could produce a net change in the energy of the system at constant entropy: however, this argument is hardly rigorous, since the shape of one volume element could not change without changing that of others,

$$\delta \bar{e}_i = T \delta \bar{s}_i - p \delta \bar{r}_i \qquad (9.12)$$

Hence at constant temperature

$$\delta\mu_i = \bar{v}_i \,\delta p \tag{9.13}$$

which was used in the deductions of Section 8. We have thus achieved a consistent thermodynamic formulation on the basis of the definition of pressure given in eq. 9.1."

I am indebted to Professor J. C. Morrow for an interesting discussion of these thermodynamic questions.

(17) T. L. Hill, J. Chem. Phys., 30, 1521 (1959), has considered the problem of setting up thermodynamic functions in a non-uniform system from the point of view of statistical mechanics.

## LIGHT SCATTERING STUDIES ON THE G-F TRANSFORMATION OF ACTIN

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The G-F transformation of actin, which occurs upon the addition of magnesium ions, was studied by light scattering and sedimentation methods. At constant magnesium concentration the curve of the reduced intensity,  $R_0$ , vs. the actin concentration is divided into two linear regions; one below the critical concentration of actin corresponds to the G-state of actin, and the other above the critical concentration has a much steeper slope which indicates the formation of F-actin. The critical concentration is dependent on the magnesium concentration. F-actin particles can be centrifuged at 100,000 g. The amount of precipitated F-actin increases linearly with the protein concentration above the critical concentration and the z-average radius of gyration (about 800 A.) do not vary with the protein or magnesium concentration. Thus, the rapid increase in turbidity, after the formation of F-actin, obtained by increasing the protein concentration is due to an increase in the number of F-actin particles and not to a gradual growth of F-actin molecules.

#### Introduction

Actin, one of the muscle proteins, exists in a globular form in salt-free solutions, and is converted to a fibrous form by the addition of neutral salts. From our study of this G-F transformation of actin by several experimental methods,<sup>1</sup> we concluded that the transformation can be regarded as a condensation phenomenon. In this paper, some results obtained with light scattering and sedimentation methods are described in detail.

Some light scattering studies have been made on the depolymerization of F-actin<sup>2</sup> at high concentrations of mono-valent salts, e.g., concentrations above 0.1 M KCl, the optimal polymerization concentration, however, we are interested in the polymerization of G-actin to F-actin caused by a small amount of magnesium ions, a specific reagent for actin polymerization.<sup>3</sup> Our finding that F-actin solutions in the intermediate stages of polymerization contain both fibrous molecules (F-actin) and small molecules (G-actin) suggested that the G-F transformation is a condensation phenomenon. Therefore, the size and the molecular weight of Factin in the polymerization process is of great interest. Our light scattering and sedimentation measurements indicate that the F-actin molecules have almost the same molecular weight regardless of the extent of the polymerization.

#### Experimental

Samples.—The crude G-actin solutions, obtained from acetone dried rabbit skeletal muscle from which myosin had been removed by Straub solution (0.6 M KCl pH 6.5) according to Feuer, et al.,<sup>4</sup> were extracted with glass-distilled

water and purified by the procedure by Mommaerts.<sup>5</sup> The solutions, after depolymerization by dialysis for about four days against water containing adenosine triphosphate,  $10^{-4}$  M, were centrifuged at 100,000 g for 5 hours to remove traces of F-actin. The supernatant is our original G-actin solution.

The samples to be measured were made up by the addition of MgCl<sub>2</sub> and veronal-HCl buffer (pH 8.0) to the original G-actin solution. They were stored for 1-2 hours at room temperature and then at 0° for more than one day; if the samples are measured before storage, repro.lucible results are not obtained because of non-equilibrium polymerization. Special attention must be paid to the buffer which converts some of the G-actin to the F-form depending on the amount and the species of ions.<sup>a</sup> e.g., phosphate buffer exerts a marked affect, while that of veronal or tris buffer is relatively weak.

Equipment and Measurements.-The light scattering measurements were carried out with a Shimazu light scattering photometer, and the scattering intensity over the angular range of  $30-135^\circ$  was measured by the use of small cylindrical cells. Light of wave length 546, 436 or 366 m $\mu$ , from a mercury arc was used as the incident beam. Immediately before the measurement each sample was centrifuged at about 20,000 g to remove the large particles suspended in the solution.<sup>7</sup> The refractive index increment, which was measured in a differential refractometer,<sup>8</sup> was dn/dc = 0.18, a value which agrees closely with that of Mommaerts.<sup>9</sup> There was practically no difference between the refractive index increments of G-actin and F-actin. The protein concentration was determined by dry weight and micro-Kjeldahl analysis, and then the refractive index measurement was conventionally employed for the determination of concen-tration. The F-actin solutions were centrifuged with a Spinco Model L Ultracentrifuge for 10 minu at 100,000 g; the gel-like sediment was dissolved in a given volume of water and the concentration  $(C_{gel})$  determined with a differential refractometer. Viscosity measurements were made with a capillary viscometer at a shear rate of several hundred sec. -1.

<sup>(1)</sup> F. Oosawa, S. Asakura, K. Hotta, N. Imai and T. Ooi, J. Polymer Sci., 37, 323 (1959).

<sup>(2)</sup> R. F. Steiner, K. Laki and S. Spicer, ibid., 8, 23 (1952).

<sup>(3)</sup> A. Szent-Györgyi, "Chemistry of Muscular Contraction," (second edition), Academic Press, New York, N. Y., 1951.

<sup>(4)</sup> G. Feuer, M. Molnár, E. Pettko and F. B. Straub, Acta Physiol. Hung., 1, 150 (1948).

<sup>(5)</sup> W. Mommaerts, J. Biol. Chem., 188, 559 (1951).

<sup>(6)</sup> M. Barany, N. A. Bico and J. Molnar, Acta Physiol. Hung., 5, 63 (1954).

<sup>(7)</sup> G. Oster, Anr. Chem., 25, 1165 (1953).

<sup>(8)</sup> G. V. Schulz, O. Bodemann and H. J. Cantow, J. Polymer Sci., 10, 73 (1953).

<sup>(9)</sup> W. Mommaerts, J. Biol. Chem., 198, 445 (1952).

#### Results

The original G-actin solutions are clear and nonviscous; the molecular weight of G-actin determined by our light scattering measurements is 120,000 or less, the value differing from sample to sample; the corresponding intrinsic viscosity is about 0.3.<sup>2,9,10</sup> This molecular weight of G-actin is somewhat larger than that usually reported probably due to the polydispersity of the original solutions which often contain small aggregates of Gactin, e.g., dimer, trimer, etc. Upon the addition of magnesium ions the solutions become turbid and viscous, and the extent of F-actin formation increases with the protein concentration  $C_A$  and the magnesium concentration [Mg]. When  $C_A$  is increased at constant [Mg], the turbidity increases approximately with  $C_A$  below a critical concentration which is depend on [Mg]. Above this critical concentration G-actin turns into gel-like F-actin and a steep linear increase of turbidity is observed. Thus, we obtain turbidity versus  $C_A$  curves which can be divided into two linear regions at the critical concentration; see Fig. 1 in which the scattering intensity from the angle  $\theta$ ,  $R_{\theta}$ , is plotted against  $C_{\rm A}$ .

The critical concentration for F-actin formation becomes lower with increasing [Mg], as shown in Fig. 2 in which the reduced scattering intensity  $(R_0)$  is plotted against  $C_A$  for various magnesium concentrations. This critical concentration, of course, also depends on the buffer and pH. At a magnesium concentration of about 0.2 mM or below (pH 8.0), the G-F transformation is negligible even at very high actin concentrations. Within the  $C_A$  range of our experiments, a remarkable change in the scattering intensity occurred between 0.4 and 0.8 mM [Mg].

The relationship between the scattering intensity and  $M_w$ , the weight average molecular weight, is given by

$$KC/R_0 = 1/M_w + 2BC \tag{1}$$

where B is the second virial coefficient and K = $2\pi^2 n^2 (\mathrm{d}n/\mathrm{d}c)^2/N_0\lambda^4$  (n is the refractive index of the solvent, dn/dc is the refractive index increment,  $N_0$ is Avogadro's number and  $\lambda$  is the wave length of the incident beam).<sup>11</sup> When we replot the data in Fig. 2 in the form  $KC_A/R_0$  vs.  $C_A$ , we obtain curves which are approximately horizontal below the critical concentration and gradually fall off with increasing  $C_{\rm A}$ . These curves suggest that the weight average molecular weight of F-actin increases with  $C_{\rm A}$  or [Mg], but these results may be interpreted in other ways; e.g., the decrease in the  $KC_A/R_0$  vs.  $C_{\rm A}$  curves above the critical concentration may be due to large negative values of B. However, the break in the  $R_0-C_A$  curves at the critical concentration suggests the sudden formation of long F-actin particles, and the subsequent sharp linear rise of the curve points to an increase in the number of such particles. This interpretation is supported by the results of the sedimentation experiments described below.

From the sedimentation experiments, we can estimate the amount of gel-like F-actin in the orig-



Fig. 1.—The relative scattering intensity  $R_{\theta \tau} vs. \sin^2(\theta/2)$ at various protein concentrations: veronal-HCl buffer 6 mM; pH 8.0; [Mg] = 0.6 mM;  $C_{\rm A}$  = 1.5, 1.0, 0.75, 0.5 and 0.25 mg./ml.;  $\lambda$  436 m $\mu$ .



Fig. 2.—The relation between the relative reduced intensity  $R_{0r}$  and the actin concentration  $C_A$ : veronal-HCl buffer 6 mM; pH 8.0; [Mg] = 1.0, 0.8, 0.6, 0.4, 0.2 and 0 mM.

inal F-actin solutions. Above the critical concentration at constant [Mg],  $C_{gel}$  increases linearly with  $C_A$  (Fig. 3), a result which is similar to that obtained from the light scattering measurements. The supernatant after centrifugation contains small actin molecules which can be converted to F-actin by the addition of a sufficient amount of magnesium ions. Thus, the F-actin solutions before centrifugation contain G-actin molecules in equilibrium with F-actin particles. It is remarkable that the centrifugation does not affect the equilibrium between F-actin and G-actin since the G-F transformation of actin is a condensation phenomenon.

In solutions containing both very large molecules and small molecules, we can assume that the scat-

<sup>(10)</sup> T. C. Tsao, Biochem. Biophys. Acta, 11, 227 (1953).

<sup>(11)</sup> P. Doty and J. T. Edsall, "Advances in Protein Chemistry," Vol. IV, Academic Press, New York, N. Y., 1951, p. 37.







Fig. 4.—The relative reduced intensity  $R_{0r}$  rs.  $C_{gel}$ : several experimental runs are plotted;  $\lambda$  366 m $\mu$ : x, 1.4 mM [Mg];  $\bigcirc, \triangle$ , 1.0 mM [Mg];  $\triangle, \otimes, 0.8$  mM [Mg],  $\bigcirc, 0.6$  mM [Mg];  $\square, 0.4$  mM [Mg];  $\bullet, 1.0$  mM [Mg]; 0.8 mM [Mg] and 0.6 mM [Mg].



Fig. 5.—Plot of  $(3\lambda'^2/16\pi^2)(dR_{\theta}/d\sin^2(\theta/2))_{\theta=0}$  *vs.*  $R_{0r}$ : 0, 1.0 m.M [Mg];  $\bullet$ , 0.8 m.M [Mg]; 0, 0.6 m.M [Mg];  $\Delta$ , 0.4 m.M [Mg];  $\lambda = 436$  m. $\mu$ .

tering intensity at small angles is contributed mainly by the larger molecules because of the reduced intensity  $R_0$  and the weight average molecular weight; in the present case, the F-actin particles which form the gel-like sediment make the principal contribution to  $R_0$ . When  $R_0$  was plotted against  $C_{gel}$  without regard for  $C_A$  and [Mg] (Fig. 4), we obtained a straight line which passes through the zero point. The slope of this line gives the molecular weight of the large F-actin molecules: 7,800,000, 8,000,000 and 8,100,000 for the incident beams of wave length 366, 436 and 546 m $\mu$ , respectively. Thus, the F-actin particles have the same weight average molecular weight irrespective of  $C_A$  and [Mg].

The size of the F-actin molecule, which can be derived from the angular dependency of the scattering intensity  $(R_{\theta})$ , was also found to be independent of  $C_{\rm A}$  and [Mg], a result which supports our conclusion that the molecular weight of F-actin is constant. The z-average radius of gyration,  $(\langle r_{\rm g}^2 \rangle)^{1/2}$ , can be determined from the particle scattering factor,  $P(\theta)$ , by the relation<sup>12</sup>

$$P(\theta) = 1 - (16\pi^2/3\lambda'^2) \langle r_g^2 \rangle \sin^2(\theta/2)$$
 (2)

where  $\lambda'$  is the wave length in the medium. Assuming that there is no interaction between particles and that  $R_{\theta} vs. \sin^2(\theta/2)$  gives the size of particles in the solution, we can rewrite equation 2 as

$$dR_{\theta}/d\sin^2(\theta/2))_{\theta=0}/R_{\theta} = 16\pi^2/3\lambda^{\prime 2} \langle r_{\mu}^2 \rangle \qquad (3)$$

Consequently, we can evaluate the z-average radius of gyration from the slope of the line  $3\lambda'^2/16\pi^2$   $(dR_{\theta}/d\sin^2(\theta/2))_{\theta=0}$  vs.  $R_0$  given in Fig. 5 which indicates that  $(\langle r_g^2 \rangle)^{1/2}$  is independent of  $C_A$  and [Mg]. The values obtained were 710, 780 and 930 Å. for the wave lengths 366, 436 and 546 m $\mu$ , respectively.

On the basis of these results we can draw the following conclusions: above the critical concentration which is determined by the magnesium concentration, large F-actin molecules, having a molecular weight of 8,000,000 and a radius of gyration of 800 Å., exist in equilibrium with active G-actin molecules. The amount of F-actin increases linearly with the actin concentration and also increases with the magnesium concentration. Accordingly, the apparent turbidity increment with  $C_A$  and [Mg] is due to an increase in the number of F-actin molecules and not to the gradual growth of individual Factin molecules.

Viscosity measurements usually are employed as a measure of G-F transformation. In our experiments the dependence of the specific viscosity,  $\eta_{\rm sp}$ , on  $C_{\rm A}$  and [Mg] (Fig. 6) corresponds to that of  $R_0$ or  $C_{\text{gel}}$  on  $C_A$  and [Mg]; *i.e.*,  $\eta_{\text{sp}}$  rises linearly with  $C_{\rm A}$  above the critical concentration. If all the actin molecules were active (i.e., if they were all converted to F-actin at high magnesium concentration), the specificity viscosity would be proportional to  $C_{gel}$  since all the protein would be spun down and therefore  $C_A = C_{gel}$ . However, some inactive actin usually is produced by the purification process, for in the majority of cases the amount of total protein which cannot be polymerized by any means is 20-40%; therefore, we estimate the contribution of unit particle to viscosity,  $\eta_{sp}/c_{gel}$ , from the measurements of  $\eta_{sp}$  and  $C_{gel}$ , a valid procedure

(12) P. Debye, THIS JOURNAL, 51, 18 (1947).

since the viscosity increase is attributable to the increase of F-actin, irrespective of the amount of inactive actin.  $\eta_{sp}/C_{gel}$  was found to be nearly 15, the average of the values at various  $C_A$  and [Mg]. From this value and  $\eta_{sp}/C_A$  (where  $\eta_{sp}$  was measured at high [Mg], a few millimoles) we can estimate the activity, *i.e.*, the ratio of active to total protein.

#### Discussion

We assumed that there is no interaction between actin molecules, and that the turbidity is given by the sum of the contribution of individual G-actin or F-actin molecules. The falling off of the  $KC_A/R_0$ vs.  $C_{\rm A}$  curve above the critical concentration means that attraction occurs between actin molecules or that some aggregates are formed. The curves in Fig. 2 ( $R_0 vs. C_A$ ) indicate a kind of phase transition, and the linear increase of  $R_0$  with  $C_A$  above the critical concentration suggest an increase in the number of F-actin molecules of about the same particle weight rather than a gradual growth of particle size. The sedimentation experiments lend strong support to this tentative interpretation of the light scattering data. Nevertheless, it seems strange that the interaction constant between Factin molecules was observed to be nearly zero; to investigate this phenomenon, it is necessary to measure the scattering intensity of more concentrated actin solutions.

The other assumption that the reduced intensity  $R_0$  is mainly due to large molecules in F-actin solution is based on the well-known relation between  $R_0$  and the weight average molecular weight in a polydisperse system

$$R_0/KC_A = M_w = \sum_i M_i f_i \qquad (4)$$

where  $M_i$  is the mass and  $f_i$  the weight fraction of ith molecule. From the sedimentation experiments we can assume roughly that only two kinds of molecules, small molecules  $M_1$  and large F-actin molecules  $M_2$ , are present in the solutions; then, substituting  $C_{gel}$  for  $C_A$ , we can rewrite equation 4 as

$$R_0/KC_{\rm gel} = M_2 - M_1[(C_{\rm A}/C_{\rm gel}) - 1]$$
 (5)

The approximation that  $\sum_{i} M_{i} f_{i} = M_{2}$  implies that

 $M_2$  is much larger than  $\dot{M}_1[(C_A/C_{gel}) - 1]$ . Since  $M_1$  is of the order of G-actin, about 100,000, and  $C_{gel}/C_A$  is usually greater than 0.2, the error in the approximation is less than about 5%, which is comparable to the error caused by the extrapolation of the scattering intensity to zero angle.

Strictly speaking, F-actin solutions must be polydisperse, probably having a narrow distribution around molecular weight 8,000,000, although it is not clear whether the deviations from the straight line in Fig. 5 are due to polydispersity or to experimental error. The molecular weight of F-actin obtained here is nearly three times larger than the values reported by other authors<sup>2,13</sup> who employed 0.1 *M* potassium chloride or iodide, as the polymerization agent, and used more dilute solutions; a possible explanation for this discrepancy is that



Fig. 6.—The relation of the specific viscosity to  $C_A$ : veronal-HCl buffer 6 mM; pH 8.0; O, 1.0 mM [Mg]; x, 0.8 mM [Mg];  $\triangle$ , 0.6 mM [Mg];  $\Box$ , 0.4 mM [Mg].

two or three F-actin fibers are bundled together in concentrated solution and separate on dilution. This explanation is supported by the agreement between our value for the radius of gyration of F-actin and that reported for a much more dilute solution.<sup>2</sup> The observation that F-actin solutions exhibit elastic properties at very low shear rate but flow easily at high shear rate, is consistent with this picture<sup>14</sup>; *i.e.*, F-actin molecules are weakly bound to each other and separate readily upon mechanical agitation.

In regard to the forces binding actin molecules. it is obvious that hydrogen bonding is involved since large amounts of neutral salts or other reagents which tend to prevent the formation of hydrogen bonds (e.g., urea) cause the depolymerization of F-actin<sup>15</sup>; furthermore, the polymerization is accelerated by a decrease in pH. And of course the damping out of electrostatic repulsion caused by the addition of salts is regarded as a major factor in the polymerization. Adenosine triphosphate (ATP) must also play an important role since actin becomes inactive in the absence of ATP<sup>16</sup>; once ATP bound to an actin molecule is freed by heating or dialysis against pure water, the actin molecule loses its ability to polymerize. Furthermore, dephosphorylation always accompanies the poly-merization of G-actin.<sup>17,18</sup> Although quantitative results are lacking, the amount of ATP seems to affect the polymerization rate. The nature of the interaction may well be the key to actin polymerization.

It is notable that the turbidity increment of dilute solutions below the critical concentration increases with [Mg], *i.e.*, the molecular weight before gel formation becomes larger with [Mg]. This initial stage of the polymerization cannot be simply explained by the monomer-dimer transformation of Tsao<sup>11</sup> or the ovoid picture of Szent-Györgyi,<sup>3</sup> the two suggestions which seem to be relevant to the

<sup>(13)</sup> J. Gergely and H. Kohler, Conference on the Chemistry of Muscular Contraction, 17, Igaku Shoin, Tokyo, Japan, 1957.

<sup>(14)</sup> H. Boedtker and P. Doty, THIS JOURNAL, 58, 968 (1954).

<sup>(15)</sup> A. Szent-Györgyi and J. Rosalie, Arch. Biochem., 31, 90 (1951).

<sup>(16)</sup> A. Szent-Györgyi, ibid., 31, 97 (1951).

<sup>(17)</sup> F. B. Straub and G. Fener, Biochim. Biophys. Acta, 4, 445 (1950).

<sup>(18)</sup> W. Mommaerts, J. Biol. Chem., 198, 469 (1952).

problem. Our preliminary results indicate the first and then to polymerize to fibers until a network G-actin monomers are likely to form the dimer is formed. Details will be published e sewhere.

## SOLVENT EXTRACTION OF HEPTAVALENT TECHNETIUM

#### BY G. E. BOYD AND Q. V. LARSON

Contribution from Oak Ridge National Laboratory, Oak Ridge, Tennessee Received October 26, 1959

The extraction of heptavalent technetium, initially contained in aqueous acid, neutral salt and in alkaline solutions, by a wide variety of immiscible organic liquids, including alcohols, ketones, ethers, esters, nitro-compounds, nitriles, amines, hydrocarbons, chloro-hydrocarbons and organo-phosphorus and organo-nitrogen compounds dissolved in non-polar liquids A basic oxygen or nitrogen atom in the organic molecule was necessary to effect a partition. Quantitative was measured. extraction was obtained when the active solvent also possessed an appreciable dielectric constant. Structural effects were evident and with mixtures involving alcohols synergistic actions were observed. The partitioning Tc(VII) species was shown to be the pertechactate ion,  $TcO_4^-$ , for which the molar extraction coefficient was concentration independent up to  $10^{-3} M$ . Extraction generally was much more efficient from acid than from neutral salt or alkaline aqueous phases indicating that the hydronium ion possessed properties especially favoring its distribution. The extraction mechanism with amines dissolved in inactive solvents was anion exchange; with the *n*-alkyl phosphine oxide solutions stoichiometric complexes were formed in the organic phase; with the alcohols, ketones and ethers the formation of a cationic complex appeared to be essential.

Reports of observations on the extraction of technetium from aqueous solutions by organic liquids have been few in number and limited in scope.<sup>2-7</sup> Accordingly, in developing a rapid separation technique for the isolation of the shortlived fission-product technetium isotopes it became necessary to conduct measurements on the extraction of Tc(VII) from acid, neutral and alkaline aqueous solutions. Several new correlations of extractability with the molecular structure of the organic solvent were discovered, and previous observations were greatly extended. These latter may be of interest because pertechnetate ion,  $TcO_4^-$ , is a member of the class of complex ions,  $MX_4$ , which are important in the solution chemistry of a number of the transition elements. The magnitudes of the extraction coefficients for many of these elements present in halide ion solutions are determined by the formation constant and by the intrinsic (Nernst) partition coefficient for the complex ion involved.<sup>8,9</sup> Pertechnetate ion is stable in a wide variety of aqueous media so that measurements of its partition should give information on the intrinsic factor in the solvent extraction of structurally analogous  $MX_4^-$  ions.

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 G. E. Boyd, Q. V. Larson and E. E. Motta, "Observations on the Chemistry of Element 43," (Abstract No. 48), Symposium on the New Elements, Division of Physical and Inorganic Chemistry, American Chemical Society, Syracuse, N. Y., June 28-30, 1948.

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#### Experimental

Observations on the solvent extraction behavior of ultramicro amounts of heptavalent technetium were facilitated micro amounts of heptavalent technetium were facilitated by using the 60 d Tc<sup>95m</sup>  $\gamma$ -ray emitting isotope as tracer. This activity was formed by Mo (p.xn) reactions in metallic molybdenum irradiated with 22 Mev. protons; the amount produced in a typical two-hour bombardment was 6.4 millicuries (yield = 18.2  $\mu\mu$ C./ $\mu$ ahr.). The procedure for separating "carrier-free" Tc<sup>95m</sup> from cyclotron targets has been described.<sup>10</sup> The final step in the isolation consisted in the dissolution of a technetium dioxide electrodeposition in the dissolution of a technetium dioxide electrodeposit on platinum in ammoniacal peroxide. This solution was evaporated to dryness to ensure the formation of  $T_{\rm c}(\rm VII)$  and the residue (NII, $T_{\rm c}O_4$ ) was taken up with distilled water and diluted to give 25.00 ml. of solution. Aliquots (usually  $100 \lambda$ ) were taken from this solution for the extraction measurements.

In several experiments extractions were performed with initial aqueous concentrations of Tc(VII) between  $10^{-4}$  and  $10^{-6}$  M. These solutions were prepared by dissolving a weighed amount of pure KTcO<sub>4</sub> (containing  $2.2 \times 10^5$  y Tc<sup>99µ</sup>) in distilled water. Sixty-day Tc<sup>95m</sup> trazer was added if a radiometric analysis of the equilibrium phases was to be conducted. Alternatively, concentration ratios were determined spectrophotometrically with a Cary Model-14 photoelectric recording spectrophotometer using the ultra-violet absorption band of pertechnetate ion in aqueous solution at 2875 Å.

Organic solvents of the highest purity were obtained from the Eastman Kodak Company or from the Matheson, Coleman and Bell Company (*i.e.*, White Label or Reagent grade); usually they were not purified additionally. Technical grade tri-n-butyl phosphate (TBP), however, was purified by steam distillations.<sup>11</sup> Interferences by impurities in the organic liquids were believed to have been absent. However, reagent grade evelohexanol preparations from different sources gave different technetium extractions even though gas chromatographic analyses showed them both to be quite pure.

Tri-n-octyl phosphine oxide (TOPO) obtained from the Eastman Kodak Company was of high purity as indicated by ultraviolet absorption spectrum measurements on its solutions in "Spectro-grade" cyclohexane.<sup>12</sup> Tri-*n*-octyl-amine (TOA) employed was supplied by Carbon and Carbide Chemicals Company. A differential titration

(10) G. E. Boyd, Q. V. Larson and E. E. Motta, J. Am. Chem. Soc., 82, 809 (1960).

(11) K. Alcock, S. S. Grimley, T. V. Healy, J. Kennedy and H. A. C. McKay, Trans. Faraday Soc., 52, 39 (1956).

(12) The authors are indebted to J. C. White for the pure preparations of TOPO used in the initial stages of this work.

<sup>(1)</sup> Presented before the Division of Physical Chemistry, 133rd National Meeting, American Chemical Society, San Francisco, California, April 13-18, 1958.

revealed its tertiary amine content to be greater than 97%.<sup>13</sup> Dimethyldidodecenylammonium chloride (DDA) was obtained from the Rohm and Haas Chemical Company and was greater than 98.5% pure.

Extractions were performed in the survey measurements (Table II) by equilibrating initially equal volumes of aqueous and organic phase at room temperature. Ten ml. of each phase (with the technetium in the aqueous layer) was added to a 30-ml. glass-stoppered separatory funnel equipped with a Teflon stopcock, and was shaken together on a mechanical shaker for 15-30 minutes. Phase separation was effected by a brief centrifugation using a Size 1, Type SD International Centrifuge wherein the temperature remained close to  $25^{\circ}$ .<sup>14</sup> Equilibrium phase volumes were estimated to  $\pm 0.1$  ml. by draining each from the separatory funnel into 15-ml. graduated centrifuge tubes. The ratio of aqueous to organic volume,  $V_a/V_o$ , was reproducible to better than 5%, and in no case did the sum differ from that for the initial phases by more than 5%. In the extraction mechanism studies the aqueous and organic phases were pre-equilibrated with one another before the addition of Tc(VII) tracer to the aqueous phase so that here  $V_a/V_o$  always was close to unity.

 $V_{\rm e}/V_{\rm o}$  always was close to unity. The entire volume of each phase was assayed for its  $\gamma$ -radioactivity with a  $4\pi$  geometry ionization chamber filled with 40 atm. of argon gas.<sup>15</sup> This instrument was exceptionally stable, and its response was linear over a wide range of intensities. Using the ion chamber efficiency- $\gamma$ -ray energy calibration and the decay scheme<sup>16</sup> for 60 d Tc<sup>ssim</sup> it was possible to convert the radioactivity assay readings into absolute disintegration rates and thence into concentrations of pertechnetate ion. Thus, in the technetium tracer experiments the initial concentration in the aqueous phase between  $10^{-11}$  and  $10^{-10}$  mole liter<sup>-1</sup>. Radioactivity balances which differed by no more than 3% from the activity added to the aqueous phase before extraction were obtained in all the measurements reported. This result suggested that errors such as those caused by the adsorption of pertechnetate ion onto the walls of the separatory funnel, etc., were absent.

Molar distribution ratios, or extraction coefficients,  $E_{a}^{\circ}$  were computed from the radioactivity (or spectrophotometric) and volume measurements using the definition

$$E_{a}^{\circ} = \frac{\text{Activity in total organic phase}}{\text{Activity in total aqueous phase}} \begin{pmatrix} V_{a} \\ V_{o} \end{pmatrix}$$

Generally,  $E_{\rm a}^{\circ}$  was determined with a precision of  $\pm 5\%$ or better. However, when  $E_{\rm a}^{\circ}$  was quite small (*i.e.*, < 0.01) or quite large (*i.e.*, > 100) the precision was no better than  $\pm 15\%$  because of difficulties in the phase separations (*i.e.*, occlusion of phases), because of statistical errors in the estimation of the minute quantities of radioactivity in one of the phases, and sometimes because a few tenths of a per cent. of the technetium tracer apparently was nonextractable. The spectrophotometric estimations of  $E_{\rm a}^{\circ}$ were less precise and were restricted to a more narrow range (*i.e.*, 0.1 <  $E_{\rm a}^{\circ}$  < 10) than were the values obtained using the radiometric method. Under favorable circumstances, however, the former procedure may be more reliable in that changes in the intensity of the unique ultraviolet absorption spectrum of pertechnetate ion are assayed, rather than a gross radioactivity assumed to reside entirely in the TcO<sub>4</sub><sup>-</sup> ion.

Studies of the reversibility of the extraction showed, when the phases were in complete equilibrium, that the value of  $E_a^{\circ}$  was independent of whether pertechnetate ion was present initially in the aqueous or in the organic phase. The extraction coefficient was also independent of the relative volumes of the two equilibrium phases.

The temperature variation of  $E_{a}^{\circ}$  was measured to determine the need for maintaining constant temperature. In these experiments the immiscible phases were stirred in a tube immersed in a water-bath controlled to within  $\pm 0.1^{\circ}$  of the desired temperature. Samples from each



Fig. 1.—Ultraviolet absorption spectra of pertechnetate ion in (A) water and in various organic phases: (B) cyclohexanol, (C) 0.1 M tri-*n*-octyl phosphine oxide, TOPO, in cyclohexane, (D) 0.1 M tri-*n*-octylamine, TOA, in cyclohexane, and (E) dimethyldidodeeenylammonium chloride, DDA, in cyclohexane. Molar absorbancy indices for aqueous solutions at 2440 and 2880 Å. and 6055 and 2290, respectively.

phase were taken after a sufficient time to allow for complete phase separation by gravity on cessation of stirring. At 25° the variation of  $E_{a}^{\circ}$  was 35% per degree for 1 hexanol and 5.2% per degree for a 10% w./v. solution of trinoctyl phosphine oxide in a hydrocarbon diluent, corresponding to apparent partial molar heats of extraction at 25° of -5.8 and -).2 kcal. mole<sup>-1</sup>, respectively. Because of this relatively small temperature dependence, all extractions were performed at room temperature (*i.e.*, 25 ± 1°).

Spectrophotometric examinations of the organic phases from several extraction experiments showed that pertechnetate ion,  $\text{TeO}_4^-$ , was the partitioning Tc(VII) species. The characteristic (Fig. 1) ultraviolet absorption spectrum exhibited in aqueous solutions was found with all the organic solutions. A comparison of the spectra for the aqueous and cyclohexanol solutions with those for the cyclohexane solutions of TOPO, TOA and DDA revealed a 15  $\pm$  5 Å. shift to the red in the absorption maximum with the latter; the vibrational "fine structure" of the electronic bands also was enhanced. The blurring of the structure in the water and cyclohexanol solutions may be explained in terms of

<sup>(13)</sup> Private communication, K. B. Brown, 1957.

<sup>(14)</sup> In an interesting recent study C. E. Higgins and W. H. Baldwin of this Laboratory have shown that temperature rises as large as 12° can be obtained in lengthy centrifugations, *cf.*, *Anal. Chem.*, **32**, 236 (1960).

<sup>(15)</sup> C. J. Borkovski, ibid., 21, 348 (1949).

<sup>(16)</sup> H. Medicus, Helv. Phys. Acta, 23, 299 (1950).



Fig. 2.—Extraction of Tc(VII) from normal acid, neutral salt and alkaline solutions by straight chain alcohols.

Franck-Condon strain and the relaxation time of the solvent cage.<sup>17</sup> In non-polar solvents such as cyclohexane where strain is absent, vibrational structure was preserved.

Experiments also were conducted to determine if  $E_{a^{\circ}}$ were independent of the pertechnetate ion concentration. The radiometric method was employed using  $Tc^{35m}$  tracer in solutions of KTcO<sub>4</sub> made up to the desired concentration with fission-product  $Tc^{39g}$ . For extraction from 2 N nitric acid solution with cyclohexanol, cyclohexanone and with a dilute solution of methyldioct. Vlamine (MDOA) in benzene the data (Table I) show that  $E_a^{\circ}$  was concentration independent from  $10^{-10}$  to  $10^{-3}$  M. This result is consistent with the hypothesis that Tc(VII) did not occur in a polymeric species in the organic phases.

#### TABLE I

CONCENTRATION DEPENDENCE OF EXTRACTION COEFFICIENTS FOR Tc(VII) IN AQUEOUS 2 N HNO<sub>3</sub> Solutions

Initia ion co	l TcO₄- ncn., M	Cyclo- hexanol	Cyclo- hexanone	5% w./v. MDOA in C6H6
ca. 1.5	$\times 10^{-10}$	8.16	8.74	9.31
<b>2</b>	$\times 10^{-8}$	7.98	7.95	8.99
<b>2</b>	× 10⁻7	8.07	8.56	9.22
<b>2</b>	$\times 10^{-6}$	8.52	8.55	9.03
2	$\times$ 10 <sup>-5</sup>	7.88	8.12	(7.37)
<b>2</b>	$\times$ 10 <sup>-4</sup>	8.16	8.61	8.78
<b>2</b>	$\times$ 10 <sup>-3</sup>	8.28	9.09	9.41
	Av.	$8.15 \pm 0.15$	$\frac{1}{8.52 \pm 0.27}$	$\frac{1}{9.12 \pm 0.19}$

### Experimental Results and Discussion

Survey Measurements.—The extraction of tracer quantities of Tc(VII) from normal sulfuric acid, sodium sulfate and sodium hydroxide solutions, respectively, was measured using 75 different organic liquids or solutions. The extraction coefficients,  $E_{a}^{o}$ , derived from these measurements are summarized in Table II which also presents value for the static dielectric constants for the moisture-free liquids taken from the literature,<sup>18</sup> unless otherwise noted. The following generaliza-

(17) N. S. Bayliss and E. G. McRac, THIS JOURNAL, 58, 1002 (1954).

tions based on Table II may be of interest.

(1) The extraction of pertechnetate ion by aliphatic and aromatic hydrocarbons and chlorohydrocarbons was negligible even when the latter possessed relatively large dielectric constants (viz., 1,2-dichloroethane). A necessary condition for efficient extraction by a pure liquid appeared to be the presence of an electron donor atom in its molecules (e.g., a basic oxygen or nitrogen atom).

(2) The presence of donor atoms in the molecules of the organic liquid was not a sufficient condition for extraction. Such measures of solvent basicity as are given by infrared frequency shifts<sup>19</sup> or by heat of mixing determinations<sup>20</sup> have indicated ethers and esters to be more strongly basic than ketones or nitro-compounds; yet, pertechnetate ion was poorly extracted by the former and efficiently by the latter classes of solvents. The possession of an appreciable dielectric constant favored extraction by a liquid even when only weak donor atoms were present in it (viz., the organonitro compounds). Increasing the dielectric constant of diethyl ether by substituting strongly electronegative atoms (see  $\beta$ , $\beta'$ -dichlorodiethyl ether) markedly enhanced extraction despite indications<sup>19</sup> of a significant decrease in basicity thereform.

(3) The extraction of Tc(VII) decreased within an homologous series on increasing the hydrocarbon character of the molecules. This dependence for alcohols, ketones and ethers could be correlated with the O:C atom ratio for the molecule (Fig. 2).<sup>21</sup> Increasing the hydrocarbon portion of an *n*-alkyl alcohol lowers the number of donor oxygen atoms per unit volume of organic phase because of the increased molecular weight and because of change in density. If the basicity of the carbinol groups is not changed by increasing chain length it should be possible to vary the O:C ratio, and hence  $E_{\mathbf{a}}^{\circ}$ , by adding a pure hydrocarbon liquid to an alcohol. The results presented in Fig. 3 appeared to confirm this expectation and to suggest that it was the polar group concentration which governed the extraction. The data given in Fig. 3 also yielded a linear relationship when log  $E_a^{\circ}$ was plotted against the mole fraction of hexane, as did extraction data (not shown) taken with 2hexanone in the same inactive solvent. A thermodynamic justification for this latter behavior, first observed in the extraction of indium tracer from 0.2-0.5 N HBr by solutions of methyl isopropyl ketone in cyclohexane and benzene, has been given.22

(4) Significant differences in the basicity of cyclo-

(18) A. A. Maryott and E. R. Smith, "Table of Dielectric Constants of Pure Liquids," NBS Circular 514, 1951; A. J. Petro, "Table of Dielectric Constants and Dipole Moments," Publication 503, National Research Council, 1955, p. 29. Dielectric constants for which literature values could not be found were measured in this work using a simple, tuned-circuit, radio-frequency bridge.

(19) W. Gordy and S. C. Stanford, J. Chem. Phys., 8, 170 (1940).

(20) C. S. Marvel, M. J. Copley and E. Ginsberg, J. Am. Chem. Soc., **62**, 3109 (1940).

(21) A similar correlation in the extraction of uranyl nitrate by ethers has been noted by E. Glueckauf, H. A. C. McKay an I. A. R. Mathieson, *Trans. Faraday Soc.*, **47**, 428 (1951). When the C:C atom ratio becomes larger than ca. 0.25 the extraction coefficient decreases because of the increasing miscibility of the aqueous and organic phases.

(22) H. Irving and F. J. C. Rossotti, J. Chem. Soc., 2475 (1956).

	TA	ABLE II			
EXTRACTION OF TC(	VII)	FROM	VARIOUS	1 N A	QUEOUS
S	OLUT	IONS AT	25°		
		Dielcc-			
	0:C	tric con-			
Organic liquid	ratio	stant	$H_2SO_4$	Na <sub>2</sub> SO <sub>4</sub>	NaOH
	A	Icohols			
1-Pentanol 2 Mathul 1 hutanal	1:5	13.9	4.0	1.5	0.10
2-Methyl-1-butanol	1:5	14.1	3.6	1 2	. 080
2-Pentanol	1:5	14.2	7.6	3.2	.26
3-Pentanol	1:5	13.6 <sup>a</sup>	9.5	3.1	. 24
2-Methyl-2-butanol	1:5	5.8 10.0	10.4	4.0	.73
1-Hexanol 2 Hexanol	1:0	13.3	2.1	0.10	.045
2-Methyl-2-pentanol	1:6		3.7	.21	. 062
Cyclohexanol	1:6	15.0	32	3.6	. 77
$Cyclohexanol^b$	1:6		0.003		
1-Heptanol	1:7	12.1	.95	0.068	.020
4-Heptanoi Benzyl alcohol	1:7	6.2 13.1	.43	. 046	13
1 Outanal	1.8	0.8	0.0	047	015
2-Ethyl-1-hexanol	1:8	7.2 <sup>n</sup>	. 24	.006	. 003
2-Octanol	1:8	7.8	. 62	. 021	. 008
2,6-Dimethyl-4-heptanol	1:9		.10	. 002	.002
1-Decanol	1:10	8.1	.22	. 020	. 008
	К	etones			
2-Butanone	1:4	18.5	20	12	7.9
2-Pentanone	1:5	15.4	38	32	15
3-Pentanone	1:5	17.0	35	6.2	2.5
3-Methyl-2-butanone	1:5	(15.5)	33	21	(2.2)
2-Hexanone	1:6	14.6	14	3.6	1.2
4-Methyl-2-pentanone	1:6	13.1	14	1.7	0.79
Cyclohexanone Cyclohexanone <sup>b</sup>	1:0	18.5	93 0.002	1.4	0.7
2-Hentanone	1:7	11.9	4.6	1.0	0.42
3-Heptanone	1:7		2.4	0.35	0.21
4-Heptanone	1:7		0.26		
2,4-Dimethyl-3-		10.0	0.1	0.00	
pentanone	1:7	12.0	2.1	0.20	
2-Octanone	1:8	10.4	1.7	6.0	5.2
2-Nonanone	1:9		0.72	0.068	0.015
2,6-Dimethyl-4-					
heptanonc	1:9	••	0.15	.041	.019
	I	Ethers			
Dibutoxytetracthylene					
glycol	5:16	$5.9^{a}$	6.5	.50	.32
Dibutoxydicthylene					
glycol	1:4	$4.6^{n}$	0.19	.015	.004
Di-ethyl	1:4	4.3	0.029	.003	.002
$\beta,\beta'$ -Dichloro-dictity.	1:4	21.2	0.002	.073	.05
Glycol dibutyl ether	1:5	$3.8^{a}$	.024	.004	.003
Disisonropyl ether	1:6	3.9	.012	.002	.001
Anisola	1:7	4.3	.001	.00-1	< .01
Di-z-butyl ether	1:8	3.1	.012	.003	.002
Thiophene		2.8	.028		. 036
Imophene		Vatore			
	0.7	LSLEIN	001	019	014
Amyl acetate	2:7	4.0	.060	.018	.014
Isthyl benzoate	2:9	0.0	.000	. 000	
Organo	-phos	phorus	compoun	ds	
Tributyl phosphate		7.9	44	8.3	7.5
Tributyl phosphate"			0.21	0.002	0.001
oxide <sup>b</sup>			46	.051	. 017
Tri-octylphosphine				-	
oxide <sup>b</sup>			41	.017	. 013
Tri-decylphosphine oxide <sup>b</sup>			-19		. 023
Tris-(2-ethylhexyl)					
phosphine oxide <sup>6</sup>		••	1.4	.002	. 003
Di-(2-ethylhexyl)			0.011		.019
phospholic acm					

Organo-nitrogen compounds						
Nitromethanc	35.9	3.0	2.5	0.50		
Nitrobenzene	34.8	1.2	0.086	0.057		
Benzonitrile	25.2	5.1	. 56	1.6		
Primary <i>l</i> -amine						
(JM-T) <sup>b</sup>		12	.002			
Secondary amine						
(9D-178) <sup>b</sup>		70	. 020	. 003		
Di-n-decylamine <sup>b</sup>		47	. 036	. 003		
Tri-n-octylaminc <sup>b</sup>		110	.004	. 002		
Tri-iso-octylamine <sup>b</sup>		72	.003	.002		
Methyl di-n-octylar_ineb		30	3.3	.18		
Tribenzylamine		8.3	0.004	. 002		
Pyridine <sup>b</sup>	12.3			180		
Cetvldimethylbenzyl-						
ammonium chloride <sup>d</sup>		105	18	1.1.1		
Dimethyldidodecenyl-						
ammonium chloride <sup>d</sup>		100	65	99		
Tributyllauryl-						
ammonium bromide <sup>d</sup>		6.0	0.34	0.004		
Hydrocarbo	ons and cl	hlorocarb	ons			
1.2-Dichloroethane	10.4	< 0.01	< .01	< 01		
1,1-Dichloroethane	10.0		< .01	< .01		
Dichloromethane	9.1	< .01	< .01	< .01		
Chloroform	4.8	< .001	< .001	< .001		
Trichloroethylene	3.4	< .001	< .001	< . 001		
Xylene	2.5		< . 001	< .001		
Toluene	2.4	.057	< .01	< .01		
Benzene	2.3	.017	< .01	< .001		
Carbon tetrachloride	2.2	< .001	< .001	< .001		
Cyclohexane	2.0	. 004	< 01	< .01		
<i>n</i> -Hexane	1.9	.005	. 003	. 003		
<sup>a</sup> This work. <sup>b</sup> 0.1 M	in cycloł	nexane.	° 0.1 M	in kero-		

sine.  $^{d}$  0.1 M in toluene.

hexanol, cyclohexanone,  $\beta_{\beta}\beta'$ -dichlorodiethyl ether tri-n-octylphosphine oxide (TOPO) and tri-noctylamine (TOA) were demonstrated by measurements (Table II) of the extraction effected by their 0.1 M solutions in cyclohexane. The enormously greater effective basicity of TOPO and TOA when compared under circumstances where the dielectric constant and stoichiometric concentrations of "donor atoms" remained unchanged is evident. The results in Table II also afford other compari-sons at constant "donor atom" concentration. A plot of  $\log E_a^{\circ}$  against polar group molarity for the homologous methyl ketones and secondary nalkyl alcohols showed the former compounds to be the more efficient extractants. However, the latter compounds are usually considered the more strongly basic; possibly the effective basicity of the alcohols is reduced by hydrogen bonding.

(5) Experiments with mixtures of 4-heptanol and 4-heptanone also suggested that extensive molecular association may be one of the causes for the relatively low solvent extraction power of alcohols. Values of  $E_{a}^{\circ}$  for extraction from 1 N H<sub>2</sub>SO<sub>4</sub> solutions by the aforementioned pure compounds were nearly the same (*viz.*, 0.43 and 0.26, respectively): however, the addition of 10, 25, 50 and 75% v./v. of ketone to alcohol increased the extraction coefficients to 0.74, 1.80, 1.51 and 0.88, respectively. The initial additions of ketone to alcohol presumably caused dissociation of the latter thereby increasing the thermodynamic activity of the alcohol and hence the extraction.<sup>23</sup>

(6) Within any one class of compounds  $E_{a}^{o}$  appeared to depend on the structure of the molecule.

(23) An analogous synergistic effect in the extraction of Pa(V) from concentrated HCl has been reported quite recently: A. T. Casey and A. G. Madduck, J. Inorg. and Nucl. Chem., **10**, 289 (1959).



Fig. 3.—Comparison of the extraction of Tc(VII) from  $N H_2SO_4$  by pure alcohols (open circles) with solutions of 1-hexanol in *n*-hexane (filled circles).

This finding was not unexpected as molecular structure controls the density and hence the donor group concentration in an organic liquid, its diclectric constant and influences the basicity of the donor groups in its molecules.

Alcohols.—(a) Tertiary alcohols were better extractants than secondary or primary alcohols of the same O:C atom ratio. Presumably, the tertiary alcohols are less hydrogen-bonded and hence more basic. (b) Aromatic substituted or cyclic aliphatic alcohols showed higher  $E_{\rm a}^{\circ}$  values than straight-chain alcohols of the same O:C atom ratio. (c) The distance of branching from the carbinol group in the *n*-alcohols was important; branching at the end of a straight chain did not alter  $E_{\rm a}^{\circ}$ ; branching at the  $\alpha$ -carbon atom reduced the extraction coefficient.

Ketones.—(a) Among a series of isomers  $E_{a}^{\circ}$  varied with the position of the carbonyl group along a straight chain; methyl ketones showed the largest and symmetric ketones the smallest extraction efficiency. (b) Aromatic substituted or cyclic aliphatic ketones showed higher  $E_{a}^{\circ}$  values than the *n*-aliphatic ketones of the same O:C atom ratio. The substantially greater basicity of cyclohexanone<sup>19</sup> compared with 2-hexanone may have been the cause for the large  $E_{a}^{\circ}$  observed with the cyclic ketone.

**Ethers.**—Poly-ethers were more effective extractants than normal ethers of the same O:C atom ratio. The former compounds also showed a much lower miscibility with aqueous solutions than the latter. Among the poly-ethers there was a correlation (not shown) of log  $E_{a}^{\circ}$  with the O:C atom ratio. This correlation suggested that the oxygen atoms in these compounds act independently with the CH<sub>2</sub>-groups behaving simply as diluents.

Organo-phosphorus Compounds.—(a) The ester of phosphoric acid, tri-*n*-butyl phosphate (TBP) was greatly superior to any of the carboxylic acid esters examined. This superiority appeared to result from the much greater basicity of the oxygen atoms in TBP; the large size and polar nature of this molecule probably were important in addition. (b) Compared with TBP at equal concentrations in an inactive solvent the more strongly basic tri-*n*-alkyl phosphine oxides were substantially more effective. (c) Changes in the size of the phosphine oxide molecule appeared unimportant as demonstrated by the values of  $E_{a}^{\circ}$  for tri-*n*-hexyl, tri-*n*-octyl and tri-*n*-decyl phosphine oxides. Branching in the straight chain of tri-alkyl phosphine oxide, however, reduced  $E_{a}^{\circ}$ (cf., TOPO and tris-(2-ethylhexyl)-phosphine oxide).

Organo-nitrogen Compounds.—(a) The magnitude of  $E_{a}^{\circ}$  for extraction from acid solutions increased in going from primary to secondary to tertiary amine solutions in cyclohexane. (b) Among the tertiary amines decreased basicity was accompanied by decreased extraction coefficients (cf., TOA and tri-benzylamine). (c) Quaternary ammonium salts dissolved in inert solvents gave an efficient extraction not only from acid but also from neutral and alkaline solutions.

An hypothesis consistent with all of the results from the survey measurements on the partition of heptavalent technetium is that the necessary and sufficient condition for extraction is that a cationic complex exists in the organic phase and that an ion association pair or cluster involving this cation and an essentially unsolvated  $TcO_4$ -ion be formed.<sup>24</sup> The stability of the complex may be high and its composition definite when substituted ammonium ions are the active reagents in an organic solution, less so when the basic phosphine oxides and phosphoric acid esters are employed, and probably the complex is only poorly defined in the pure solvents. For the latter the complex may possess a stoichiometry consistent with either  $H_3O^+(H_2O)_mS_nTcO_4^-$  or  $SH^+(H_2O)_pS_qTcO_4^-$ . Recently evidence has been adduced supporting the first of these formulas with m = 3.25 Increasing cation size will promote extraction so that the larger the value of n (or q) the larger  $E_{\mathbf{a}}^{\circ}$  will be, provided the dielectric constant is not decreased unduly. Thus, the fact that tri-*n*-octylamine gave a larger extraction from  $N H_2 SO_4$  than did methyldi-n-octylamine (Table II) may be considered a consequence of the larger size of the former, if the difference in shape can be neglected.

Extraction from Acid Solutions.—Further investigations with acid solutions seemed desirable as one of the interesting facts revealed by Table I was that while the extraction of Tc(VII) from neutral salt and alkaline aqueous solutions was quite incomplete with acid solutions quantitative extraction was observed. Results from measurements with normal solutions of several strong acids showed (Table III) that a correlation for a variety of solvents existed between the extraction of pertechnetate ion and the nature of the acid anion. Acid extraction into cyclohexanol was

(24) See for example the discussion by G. H. Morrison and II. Freiser, "Solvent Extraction in Analytical Chemistry," John Wiley and Sons. Inc., New York, N. Y., 1957, p. 30.

(25) R. M. Diamond, This JOURNAL, 63, 659 (1959).

Extra	CTION OF TC(VII) FI	ROM NORMAL	SOLUTIONS OF	VARIOUS ST	RONG ACIDS,	Eao	
Solvent	H <sub>4</sub> PO <sub>4</sub>	H₂SO₄	HCI	HBr	HNO.	HIP	HClO4
Cyclohexanol	210	32	15	12	8.8	5.5	4.3
	$0.027^{c}$	0.05°	0.18 <sup>e</sup>	C.29°	$0.41^{c}$	0.59°	$0.48^{c}$
Cyclohexanone	130	93	51	25	14	5.1	2.6
$\beta,\beta'$ -Dichlorodiethyl ether		1.5	0.40	0.12	0.031	0.074	0.001
Tributyl phosphate		44	120	91	29	70	5.6
Tri-octylphosphine oxide <sup>a</sup>	130	51	48	25	0.46	65	0.24
Tri-octylamine <sup>a</sup>	74	110	580	74	26	3.6	0.44

TABLE III

 $^{\circ}$  0.1 M in cyclohexane.  $^{\circ}$  Even at quite small concentrations pertechnetate ion is thermodynamically unstable toward reduction by N HI. Possibly the valence state extracted from this acid was Tc(V).  $^{\circ}$  Extraction coefficient for acid.

measured also, and the  $E_a^{\circ}$  values are given in the second row of Table III. With this solvent at least, the extraction of pertechnetate ion decreased as that of the acid increased. An anion-exchange mechanism between  $\text{TcO}_4^-$  ion and the anion of the acid was involved in the extractions effected by tri-*n*-octylamine solutions. A similar dependence on the nature of the acid anion was shown by the other extractants; possibly they also extract Tc(VII) by an ion-exchange mechanism.

The dependence of the extraction of Tc(VII)on the concentration of acid initially in the aqueous phase was determined. With pure cyclohexanol (Fig. 4) the extraction increased rapidly upon the addition of small amounts of acid, and, after a maximum  $E_{a}^{o}$  value was reached at, or below, 1 N, an exponential decrease set in.<sup>26</sup> Curves similar to those in Fig. 4 also were observed with cyclohexanone, with pure tri-n-butyl phosphate and with solutions of TBP in a liquid hydrocarbon; maxima in the values of  $E_a^{\circ}$  were exhibited at significantly lower acidities, however. The rate of decrease in the extraction coefficient for cyclohexanone with acid concentration past the maximum was much greater than for either cyclohexanol or TBP. Presumably, such behavior reflects the increased miscibility of the ketone with strongly acid aqueous phases. In other work<sup>27,28</sup> it also has appeared that decreases in  $E_{a}^{\circ}$  always coincide with gross changes in phase volumes on equilibration.

Complications because of interphase solubilities may be minimized if dilute solutions of strongly basic extractants in hydrocarbon or other inactive liquids are employed. Accordingly, measurements of the acid concentration dependence of Tc(VII) were performed with deci-molar solutions of tri-n-octylphosphine oxide, tri-n-octylamine and dimethyldidodecenylammonium nitrate in cyclohexane. Maxima in the variations of  $E_{a}^{\circ}$  with acid molarity were observed with the first two compounds for concentrations of acid at and below 0.1 N (Figs. 5 and 6). In the case of the amine the decrease below ca. 0.05 N was probably a consequence of the hydrolysis of its (nitrate) salt; the decrease above this concentration reflected the exchange of  $TcO_4^-$  by the competing No maximum was found with  $0.0\overline{1}$  $NO_3^-$  ion.

(26) The variation of  $E_{\rm a}{}^{\rm o}$  shown for HCl solutions above 5 N does not represent the behavior of Tc(VII). At and above this concentration increasing amounts of Tc(V) were formed by the reduction of pertechnetate ion by chloridc ion.

(27) H. Irving and F. J. C. Rossotti, Analyst, 77, 801 (1952).

(28) D. E. Metzler and R. J. Myers, J. Am. Chem. Soc., 72, 3776 (1950).



Fig. 4.—Acid concentration dependence of the extraction of Tc(VII) from aqueous acid solutions by cyclohexanol.

M solutions of the quaternary ammonium salt dissolved in toluene (Fig. 6).<sup>29</sup>

A qualitative explanation for the linear decrease in log  $E_{\rm a}^{\circ}$  for TcO<sub>4</sub><sup>-</sup> ion concentrations less than  $10^{-5}$  M with the log of the acid concentration (Fig. 6), and for the linear increase with the log of the tri-n-octylammonium nitrate (or dimethyldidodecenylammonium nitrate) concentration in the organic phase (Table IV) can be based on the assumption that a mass law governed anion exchange equilibrium occurred

$$\overline{\mathrm{R}_{4}\mathrm{N}^{+}\mathrm{N}\mathrm{O}_{4}^{-}} - \mathrm{Te}\mathrm{O}_{4}^{-} \rightleftharpoons \overline{\mathrm{R}_{4}\mathrm{N}^{+}\mathrm{Te}\mathrm{O}_{4}^{-}} + \mathrm{N}\mathrm{O}_{4}^{-} \quad (1)$$

where the bar denotes the organic phase. The equilibrium concentration product quotient is then

$$Q = \frac{\overline{C}_{\text{TcO4}^-} C_{\text{NO3}^-}}{\overline{C}_{\text{NO3}^-} C_{\text{TcO4}^-}} = E_{a}^{\circ} \left( \frac{C_{\text{HNO3}}}{\overline{C}_{\text{R4NNO3}}} \right)$$
(2)

and, for a constant nitrate ion concentration in the organic phase,  $E_{a}^{\circ}$  will decrease inversely as the

<sup>(29)</sup> The departures from a straight line of unit negative slope below  $0.05 \ N \ HNO_3$  in Fig. 6 are believed to have been caused by minute amounts of technetium irreversibly adsorbed on CuS and other colloidal impurities in the radio-tracer preparation.







Fig. 6.—Extraction of Tc(VII) from aqueous nitric acid solutions by 0.01 M tri-*n*-octylamine (TOA) in cyclohexane and by 0.01 M dimethyldidodeccnylammonium chloride (DDA) in toluene.

first power of the nitrate concentration in the aqueous phase provided thermodynamic activity coefficient variations may be ignored. The failure of this latter approximation may be the cause for the departures of the points at the highest concentrations in Fig. 6 from the unit slope straight

TABLE	IV
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EXTRACTION OF PERTECHNETATE ION AT TRACER CON-CENTRATIONS IN AQUEOUS NITRIC ACID SOLUTIONS BY PRE-EQUILIBRATED ORGANIC SOLUTIONS OF AMMONIUM SALTS Molarity  $E_{s^0}$  Q

A. Dimethyldidodecenylammonium nitrate in toluene:  $1 N HNO_3$ 

$C_{\rm DDA}$		
0.0005	0.40	802
.00075	.63	842
. 001	.76	756
.0025	2.00	800
.005	3.59	718
.01	6.39	639
.05	26.3	526
.10	45.3	453

B. Tri-n-octylammonium nitrate in a hydrocarbon solvent: 2 N HNO<sub>3</sub>

Стол		
0.015	0.90	120
.0283	2.01	144
.0283	2.21	156
. 06	3.92	131
. 14	9.60	137
. 25	18.7	149
. 43	<b>3</b> 9. <b>7</b>	185
. 65	41.7	128
85	67.8	160

lines. In addition, excess nitric acid over that needed to form ammonium salt in the organic phase was found to be extracted; alternatively, this may have been the cause of the deviation.

In applying the mass law to systems wherein the concentration of ammonium salt in the organic phase was varied, it was assumed that the species  $R_4N+NO_3^-$  or  $R_3NH+NO_3^-$  were monomeric. No direct measurements supporting this assumption have been reported; however, light scattering and other studies with solutions of tri-*n*-octylammonium sulfate in benzene have indicated this salt to be molecularly dispersed.<sup>30</sup> It seems less likely that dimethyldidodecenylammonium nitrate would be unassociated even in organic solutions after considering the extensive researches of Kraus<sup>31</sup> on similar compounds. The decrease of Q with increasing DDA concentration shown in Table IV may therefore be a result of an increasingly complex organic solution.

The dielectric constant of the inactive organic solvent for ammonium and other salt-type compounds may influence their efficiency for extraction if electrolytic dissociation can occur in the organic phase. The measurements reported in Table V show that the extraction of pertechnetate ion was the most complete when solvents of high dielectric constant were used. A similar dependence was observed with solutions of tri-*n*octylphosphine oxide although with this compound chloroform probably is not an inactive diluent.

Non-ideal behavior by the foregoing organic solutions may sometimes govern their solvent

(30) K. A. Allen, This JOURNAL, 62, 1119 (1958).

(31) C. A. Kraus, ibid., 60, 129 (1956).
Extraction of Tc(VII) from  $1 \ N H_2SO_4$  by Solutions of Tri-n-octyl Phosphine Oxide (TOPO), Tri-n-octylamine (TOA) and Dimethyldidodecenylammonium Sulfate (DDA) in Various Inert Solvents

	Extra	action coeffici	ient —
Diluent	TOPOa	TOAª	DDA b
1,2-Dichloroethane	27	200	190
Chloroform	0.077	120	120
Benzene	. 63	110	40
Carbon tetrachloride	. 13	110	17
Di-isopropyl ether	.91	100	15
Cyclohexane	. 41	81	8.6
Hexane	. 57	96	8.2
<sup>a</sup> 0.01 N solutions.	<sup>b</sup> 0.001 N solut	tions.	

extraction efficiency. Thus, association of the solute to give low molecular weight micelles will lower the thermodynamic activity of the salt and reduce extraction. The molecular structure of the amine (cf. Table II) may determine the degree of its interaction with the solvent as well as its tendency to form micelles, and hence the extraction efficiency of the solutions of its salts.<sup>32</sup>

Assuming that the extraction of pertechnetate ion by organic solutions of TOPO (and tributyl phosphate) involved the formation of complex which reacted according to

$$H^+ + TcO_4^- + qTOPO \longrightarrow HTcO_4 \cdot qTOPO$$
 (3)

application of the law of mass gives

 $\log E_{a^{\circ}} = \log K + \log [\mathrm{H}^{+}] + q \log [\mathrm{TOPO}] \quad (4)$ 

where [TOPO] is the thermodynamic activity of the uncomplexed reagent which may be taken as monomeric.<sup>33</sup> Concentrations may be employed instead of activities for sufficiently dilute TOPO solutions; when this was done (Table VI), the extraction data were found consistent with q = 2. Adduct numbers of two have been reported<sup>34</sup> for the extraction of dichromate, Zr(IV), Mo(VI), U(VI), Ti(IV) and Sn(IV) from acid aqueous chloride, sulfate and nitrate solutions. The extraction of Th(IV) with TOPO appears to be exceptional; here, q = 3.

The increase in extraction of heptavalent technetium with increasing acidity at low concentrations observed with alcohols (Fig. 4) and ketones may be explained by assuming that increasing amounts of salt (*i.e.*, ion pairs) were formed in the organic phase by reaction of the basic solvent S with acid

$$H_{3}O^{+} + NO_{3}^{-} + nH_{2}O + mS \underset{H_{3}O^{+} \cdot (H_{2}O)_{n}S_{m} \cdot NO_{3}^{-}}{\longrightarrow} (5)$$

This salt, which alternatively may be  $SH^+$  ( $H_{2^-}O)_pS_q \cdot NO_3^-$ , may then react with trace amounts of pertechnetate ion in aqueous solution by ion exchange to give  $H_3O^+$  ( $H_2O)_nS_m \cdot TcO_4^-$ . When only small amounts of  $HNO_3$  are in the organic phase it is expected that the concentration of salt will be linearly proportional to the nitric acid activity in

(32) See also C. F. Coleman, K. B. Brown, J. G. Moore and K. A. Allen, Proceedings of the 2nd International Conference on the Peaceful Uses of Atomic Energy, Geneva, Switzerland, 1958.

(33) C. F. Baes, Jr., Oak Ridge National Laboratory Unclassified Report, ORNL-2737, July 2, 1959.

(34) J. C. White, "Solvent Extraction in the Analysis of Metals," ASTM STP 238, Am. Soc. for Testing Materials, Philadelphia, Pa., 1958.





#### TABLE VI

EXTRACTION OF PERTECHNETATE ION AT TRACER CONCEN-TRATIONS IN AQUEOUS ACID SOLUTIONS BY PRE-EQUILI-BRATED ORGANIC SOLUTIONS OF TRI-*n*-octylphosphine

	OAIDD	
Molarity	$E_{a^{lpha}}$	$E_{a^{o}}/(C \operatorname{topo}^{2}C \operatorname{hxo}_{3})$
TOPO in	n hydrocarbon solve	ent: $2 N HNO_3$
0.0215	0.0188	20.3
. 043	.0307	8.30
. 086	.0967	6.54
. 17	. 569	9.84
. 23	1.02	9.64
.35	3.42	13.9
TOPO	n carbon tetrachlo	ride: 1 N HCl <sup>a</sup>
0.0041	0.0129	767
.0103	.0514	485
. 0207	.093	217
.031	.241	251
.0413	. 420	246
1033	2.25	211
. 2066	9.37	220
<sup>a</sup> Extraction	by pure CCl <sub>4</sub> gave E	$a^{\circ} = 0.003.$

the aqueous phase. If the aqueous nitrate ion concentration is held constant  $E_{\rm a}^{\circ}$  for Tc(VII) should increase linearly with the concentration of  ${\rm H}_{3}{\rm O}^+$  (H<sub>2</sub>O)<sub>n</sub>S<sub>m</sub>NO<sub>3</sub><sup>-</sup>, and hence with the aqueous acid concentration. This expectation appeared to be confirmed by measurements of the extraction of technetium from constant ionic strength aqueous solutions by pure cyclohexanol (Fig. 7).

Extraction from Salt Solutions.—Relative to acid solutions Tc(VII) was poorly extracted from normal neutral salt and strong-base solutions (Table II). Nonetheless, an examination of the factors which appeared to govern the partition with the latter seemed worth while. Measurements with strongly basic extractants dissolved in non-polar organic liquids were not carried out, because it was considered that the extraction mechanism with



Fig. 8.—Extraction of heptavalent technetium from aqueous salt solutions by cyclohexanol.



Fig. 9.—Extraction of heptavalent technetium from aqueous salt solutions by tri-n-butyl phosphate (TBP).

them was simple ion exchange. It did not seem probable, however, that the extraction of Tc(VII) by pure alcohols, ketones, nitro-compounds and by tributyl phosphate from neutral and alkaline solutions occurred by such a process. Data presented in Figs. 8 and 9 for cyclohexanol and tri-n-butyl phosphate, respectively, show the dependence of pertechnetate ion extraction on the anion of the salt and on the concentration. Heptavalent technetium, with all solvents, including methyl ethyl ketone and cyclohexanone for which data are not shown, was extracted to the greatest extent from sodium sulfate and least from sodium nitrate or sodium perchlorate solutions. Maxima in the variations of  $E_{\mathbf{a}}^{o}$  with salt concentration were absent except possibly in the extractions from sodium perchlorate solutions by tri-*n*-butyl phosphate and from sodium hydroxide solutions by cyclohexanol. The relatively efficient extractions from Na<sub>2</sub>SO<sub>4</sub> solutions could have resulted if small amounts of free acid had been present; pH measurements always showed these solutions to be close to neutral, however.

The data in Fig. 9 appear to be consistent with

information on the solubilities of the various sodium salts in pure TBP.<sup>35</sup> For example, the solubility of  $Na_2SO_4$  in the TBP is extremely small (0.00022) molal) compared with  $NaClO_4$  (1.11 molal). Further the sequence of extractability of the sodium salts from their aqueous solutions into TBP at  $25^{\circ}$  is: NaClO<sub>4</sub> > NaNO<sub>3</sub> > NaCl. Sodium pertechnetate, by analogy with NaClO<sub>4</sub>, should be appreciably soluble in TBP and should be extracted efficiently by this solvent from its own pure aqueous solutions. In the extraction of microamounts of pertechnetate ion from concentrated salt solutions "salting-out" effects in the aqueous phase and competition in the formation of TBPsalt complexes in the organic phase must occur. The initial rapid increase of  $E_{a^{\circ}}$  with increasing salt concentration shown in Figs. 8 and 9 was probably the consequence, however, of the increasing sodium ion concentration. If the salt in the aqueous solution in which pertechnetate ion is contained possesses a high thermodynamic activity  $E_{a}^{\circ}$ should be increased. Thus, for example, if LiNO<sub>3</sub> were the salt a higher pertechnetate ion extraction would be expected than if KNO<sub>3</sub> were used. Distribution measurements showed that such differences did occur between electrolytes in the anticipated order but that these were significantly larger than was expected (Table VII). This outcome suggested that the extent of cation solvation and ion-pair dissociation in the organic phase was likely to be important. The data presented in Table VIII, in contrast to those in Table VII, may be taken to indicate that the relative contributions from these two factors may be different: With TBP strong solvation forces favoring the small cations may be involved, whereas because of the high dielectric constant of nitromethane<sup>36</sup> all the alkali pertechnetates must be ionized extensively in the organic phase. In the latter case salts with large cations should extract better than those with small cations of a similar structure.

### TABLE VII

EXTRACTION OF TC(VII) FROM 1 M NITRATE SOLUTIONS BY TRI-n-BUTYL PHOSPHATE

Aqueous soln.	Eao	Aqueous soln.	Ear
HNO3	28.3	KNO3	1.1
$LiNO_3$	14.7	$Ca(NO_3)_2$	15.6
NH <sub>4</sub> NO <sub>3</sub>	4.6	$\mathrm{Cu}(\mathrm{NO}_3)_2$	5.4
NaNO3	2.2	$Al(NO_3)_3$	4.4

#### Table VIII

Extraction of Tc(VII) into Nitromethane from Neutral, Molar Aqueous Solutions of the Alkali Chlo

	RIC	DES	
Salt	Eao	Salt	Enº
LiCl	0.55	KCl	2.1
NaCl	1.2	RbCl	2.5
HCl	1.6	CsCl	3.7

(35) T. V. Healy and P. E. Brown, "Extraction of Alkali Salts into Organic Solvents," AERE-E/R-1970, Harwell, Berks., England, June 6, 1956.

(36) H. L. Friedman and G. R. Haugen, J. Am. Chem. Soc., 76, 2060 (1954).

# ON THE ENERGETICS OF PHYSICALLY ADSORBED FILMS, WITH PARTICULAR REFERENCE TO THE USE OF KRYPTON FOR SURFACE AREA MEASUREMENT

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Some simple considerations of the energetics of adsorbed films suggest that fairly complete monolayers of gases such as krypton should be formed before the onset of significant multilayer formation. Such monolayer formation should be experimentally observable by the Brunauer-Emmett-Teller method. It is noted that the experimentally observed variations in the molecular area parameters used to calculate areas may reflect differences in the adsorption energetics for different adsorbent systems. On the basis of these considerations, together with our experimental results for krypton adsorption, it is concluded that recent criticisms of the use of krypton in the BET surface area method are not justified.

If a gas is adsorbed on a solid surface in a nearly complete monomolecular layer before the onset of multilayer adsorption, and if the point at which this first monolayer is completed can be evaluated from the experimental observations, a method for surface area measurement is available. This, of course, is the basis of such widely-used techniques as that due to Brunauer, Emmett and Teller.

Krypton is used extensively for the measurement of surface areas of solids by the BET method.<sup>1-3</sup> Malden and Marsh<sup>4</sup> have recently suggested that this is unwise, since they have obtained curved BET plots in some of their measurements. Ifonig and Reyerson<sup>5</sup> have also suggested, on theoretical grounds, that nitrogen is to be preferred to other gases for surface area measurements. On the basis of a large number of surface area determinations performed in this Laboratory over the past several years, we do not feel that these criticisms are justified.

Some rather simple considerations of the energetics of an adsorbed film, which we present below, lead us to conclude that under conditions normally found in surface area measurement, fairly complete monomolecular layers will be formed. This is so for krypton as well as the other commonly used measuring gases, such as nitrogen and argon.

It should be emphasized that our consideration of the BET method here deals only with the question of its utility for determining surface areas. The validity of the assumptions underlying the BET theory and the applicability of the isotherm equation are pertinent to the present discussion only insofar as they affect the method of determining surface area and the significance of the results obtained. As will be apparent, however, this does *not* constitute treating the method as a purely empirical approach; to do so, in our opinion, vitiates much of its utility and casts doubt on the physical significance of the surface area values measured.

The range of applicability of the BET equation is commonly quoted in terms of a relative pressure

(1) R. A. Beebe, J. B. Beckwith and J. M. Honig, J. Am. Chem. Soc., 67, 1554 (1945).

(4) P. J. Malden and J. D. F. Marsh, THIS JOURNAL. 63, 1309 (1959).

(5) J. M. Honig and L. H. Reyerson, Can. J. Chem., 34, 1101 (1956).

range (specifically  $0.05 < p/p_0 < 0.35$ ), but this seems to us to obscure the physical implications of the equation: a more direct reference to monolayer formation seems to be in order, and several authors<sup>6,7</sup> have indeed pointed out that the range of applicability would better be discussed in terms of coverage. Meyer<sup>8</sup> has observed that the BET equation itself contains a criterion for consistency in this sense, since at monolayer coverage, the relative pressure of measuring vapor has a definite relation to the energy parameter c. We have preferred to use this criterion in the form

$$\frac{p}{p_0}\Big|_{v_{\rm m}} = \frac{1}{1 + \sqrt{c}}$$

It is also instructive to consider the range of relative pressures which will correspond to given values of surface coverage,  $\theta$ , for various magnitudes of c. Some values computed from the BET equation

$$\theta = \frac{v}{v_{\rm m}} = \frac{cp}{(p_0 - p) \left[1 + (c - 1)\frac{p}{p_0}\right]}$$

are presented in the second and third columns of Table I.

TABLE I

Monolayer Relative Pressures and Thermodynamic Functions, Calculated from the BET Equation (T = 77.4 °K)

			)		
с	$p/p_0 v_m$	$p/p_0$ range, $\theta = 0.8-1.2$	$\begin{array}{c} E_1 - E_L \\ (= RT \\ \ln c) \end{array}$	$ \begin{array}{l} \Delta F \\ (= RT \\ \ln p/p_{0}) \end{array} $	$\begin{array}{c} -\Delta S \\ (\sim (\Delta E \\ -\Delta F))/T \end{array}$
10	0.240	0.167-0.315	355	95.4	3.4
30	.154	.084245	533	125.1	5.3
100	.091	.033199	710	160.3	7.1
300	.055	.012179	888	194.0	9.0
1000	.031	.004171	1065	232.3	10.8

If we are to require, therefore, that a BET plot be linear over a given range of surface coverage in the vicinity of the first monolayer, it is apparent that both the position and length of this linear region, in terms of relative pressure, will vary for different substrates. These statements are true regardless of the gas being used.

Let us now consider the nature of a sorbed film. In order that the completion of a monolayer shall be detectable, there must be some change in the

- (6) M. L. Corrin, This JOURNAL, 59, 313 (1955).
- (7) D. S. MacIver and P. H. Emmett, ibid., 60, 824 (1956).
- (8) L. Meyer, Z. physik. Chem. (N.F.), 16, 331 (1958).

<sup>(2)</sup> R. A. W. Haul, Angew. Chem., 68, 238 (1956).

<sup>(3)</sup> A. J. Rosenberg, J. Am. Chem. Soc., 78, 2929 (1956).

rate of increase of enthalpy of the adsorbed film with respect to the amount adsorbed. Such a change is assumed in the BET theory, since in the terms commonly used in that theory,  $E_1 \neq E_L$ . In this connection, Meyer<sup>8</sup> suggested that  $v_m$ should be considered the volume of gas adsorbed over the range of enthalpies  $(\Delta H_{\rm f} - \Delta H_{\rm l})$  greater than RT, where  $H_{\rm f}$  and  $H_{\rm l}$  are the enthalpies of sorbed film and bulk liquid adsorbate, respectively, per mole. He suggested that since this quantity is larger than RT considerably beyond  $\theta = 1$  for the adsorption of helium, helium forms multilayers and therefore cannot indicate the formation of a monolayer. If a sharp (or fairly sharp) monolayer is to exist, the surface must possess a good deal of ordering power for the gas involved. To borrow the terms of information theory, the surface must have a considerable negentropy which can be expended in forming the monofilm, and which is sufficient to hold the gas in an ordered way (we wish to imply by "ordered" a state in which the p-v-tbehavior is significantly different from that of the gas or vapor above it). Now the quantity  $(\Delta H_{\rm f} \Delta H_1$ ) is indeed a measure of such negentropy, but at coverages below the monolayer we must remember that  $\Delta H_1$ , the enthalpy of vaporization of bulk liquid sorbate, is not the best standard against which to judge the excess negentropy. If we consider only nearest neighbor interactions (consistent with the general idea of the short-range nature of the forces governing the physical adsorption of molecularly small species), the lateral forces in a monomolecular film result in a heat of sorbate-sorbate interaction only one-half as big as the heat of three-dimensional liquefaction of the vapor. Now sorbate-sorbent interactions must be (within the first layer) larger than the sorbatesorbate interactions, or we shall not form a monolayer, but rather condense the sorbate in a bulk form on the substrate.

The smallest sorbate-sorbent interactions that one can reasonably expect are those exhibited by gases sorbing on the basal plane of certain covalently-bonded layer structures (e.g., graphite,<sup>9a</sup>  $MoS_{2}$ ,<sup>96</sup> etc.), and this fact has been used to permit studies of sorbate-sorbate interactions below the critical liquid temperature of the sorbate. As a result of such studies, the lateral interaction energies have indeed been found to be equal to, or less than, one-half of  $\Delta H_1$  at  $\theta \simeq 1$ . Bearing in mind the magnitude of the maximum observed sorbate-sorbate interactions then we would propose use of the criterion  $(\Delta H_{\rm f} - 1/2 \Delta H_{\rm l}) \ge$  some constant, for the range up to one monolayer, in order that the first monolayer may be clearly observed.

Let us now consider how large  $(\Delta H_{\rm f} - 1/2 \Delta H_{\rm l})$ must be in order that the measuring gas will be successful in indicating the monolayer point. The configurational entropy of the film,  $\Delta S_{\rm c} = k \ln \Omega$ , which is cognate with the entropy of mixing in a three-dimensional system, will contribute to the total interaction but this contribution cannot exceed (*RT* ln 2) cal./mole adsorbed, which would

(9) (a) C. H. Amberg, W. B. Spencer and R. A. Beebe. Can. J. Chem., 53, 305 (1955); (b) P. Cannon, THIS JOURNAL, 64, 858 (1960).

correspond to complete randomness. However, this may be enough to cause the anomalous behavior of helium cited by Meyer<sup>8</sup> since the entropy of vaporization of helium,  $\Delta H_1/T_v \sim 5$  cal. mole<sup>-1</sup> deg.<sup>-1</sup>, and in this case then  $(1/2)(\Delta H_1/T_v) + R$ ln  $2 \simeq \Delta H_1/T_v$ ; consequently a two dimensional monofilm of He at 4.2°K. is thermodynamically unstable, and multilayers will be formed spontaneously. On the other hand, the physical adsorption of krypton  $(\Delta H_1/T_v = 180 \text{ cal. mole}^{-1}$ deg.<sup>-1</sup>) and nitrogen  $(\Delta H_1/T_v = 17.6 \text{ cal. mole}^{-1}$ deg.<sup>-1</sup>) could not be expected to be controlled by the same mechanism. The point here is simply that if the net increase in enthalpy for the adsorption of one monolayer of gas is less than  $RT \ln 2$ for any gas-solid pair, the entropy gain associated with configurational randomness will lower the threshold for macrocondensation to the point that a true monolayer measurement will be impossible.

The only example which is well known in which this case obtains is that for helium,<sup>8</sup> where the increase in enthalpy associated with the transfer of atoms from a bulk liquid phase to an adsorbed, well defined monofilm is given by  $(\Delta H_{\rm f} - \Delta H_{\rm l})$ +  $(1/2)\Delta H_{\rm l}$ , which is approximately equal to RTln 2. We advance this as evidence that the use of our criterion may be justified, and as a plausible new explanation for the anomalous behavior observed with He. In the cases with which we are concerned, however, 10 < c < 1000, with  $c \cong \exp(\Delta H_{\rm f} - \Delta H_{\rm l})/RT$ .

However, multilayer formation does begin in some of these cases; those sorbate particles going into the second and third layers do count in the heat or entropy of the sorbed phase per statistical monolayer, and it can be seen in the last column of Table I that in order to achieve a statistical monolayer coverage at c < 300 with the sorbed atoms having a cross section very nearly that of those atoms in the corresponding liquid, a second layer will have to start to form, since  $-\Delta S$  for a true monolayer of either Kr or N2 is 9 e.u./mole adsorbed, and a surface with c < 300 has an intrinsic negentropy or ordering power of <9 e.u. It is thus apparent that if a preliminary estimate of the surface energy of the solid is available, it is possible to choose a suitable measuring gas, provided its heat of vaporization is known. In the context of our present set of definitions, a suitable measuring gas is one whose cross section in the sorbed phase is (i) not very different from that in the corresponding liquid and (ii) constant from substrate to substrate. We have shown above that these requirements place certain restrictions on the relative magnitudes of  $(\Delta H_{\rm f} - \Delta H_{\rm l})/RT$  and  $\Delta S^{\rm v}$ . It comes then as no surprise that Ar, Kr, N<sub>2</sub> and even O<sub>2</sub> should be acceptable as measuring gases in the majority of cases, since their standard liquid entropies are about 18 e.u. Even Ne with  $\Delta H_1/T_{\gamma} = 17.5$  e.u. would serve for area measurements on substrates having c values greater than 3 against such gases. For lower energy solids, hydrogen at its boiling point might be used, since  $\Delta H_1/T_v$  for hydrogen is 10.6 e.u. Here, the efficient range cf negentropy would run from 5.3 to 3.3 e.u., allowing measurement at rather low partial pressures of  $H_2$ . It is

readily recognized that the highest energy solids present no problem: the higher c becomes, the larger the intrinsic negentropy available at coverages up to  $r_{\rm in}$  (*i.e.*, the more nearly perfect an adsorbed monof.lm). It is entertaining to consider how large c would have to be in order that the monolayer of krypton would constitute a perfectly still "crystal": c would have to be in excess of  $10^6$ and the monolayer would be complete at  $p/p_0 < 10^{-6}$ .

We have implied the possibility that  $(\Delta H_{\rm f})$  –  $\Delta H_1$ ) may become smaller than RT before the completion of the first monolayer, and it is quite possible that under these circumstances there may be differences not only between gases but between different surfaces and the same gas. If this were to happen very much before the completion of the monolayer, however, it should be reflected in the value of c: as Brunauer<sup>10</sup> has pointed out, c is to be associated with the less-active part of the surface. This is of course a necessary result of fitting the BET equation near monolayer coverage, where it is the less-active part of the surface which is being filled. The failure of an isotherm calculated from the BET equation to fit the experimental points at low relative pressures is generally acknowledged to be due to surface heterogeneity. One of us already has remarked<sup>11</sup> that the applicability of the BET method to systems with widely varying degrees of gas-solid interaction is a reflection of the energetic "smoothing" of the surface by the gas molecules adsorbed at low coverage. If  $(\Delta H_{\rm f} - \Delta H_{\rm l})$  should approach RT at  $\theta$  equal to a small fraction of 1, c would have to have a value not much greater than 3; it is well known that when the adsorbent-adsorbate interaction is as weak as this, satisfactory BET surface areas are not obtained (cf. Emmett<sup>12</sup>).

Another point, however, must be considered in this connection. It is well known that there is uncertainty about the cross-sectional area per molecule,  $\sigma$ , to be used in calculating surface areas from  $v_{\rm m}$  values. For nitrogen, values of  $\sigma$  from 15.4 Å.<sup>2,13</sup> to 16.2 Å.<sup>2</sup> (both by calculation from the liquid density<sup>14</sup> and by experimental measurements<sup>15</sup>) have been proposed. For other gases, even wider ranges have been found; for krypton individual experiments have given  $\sigma$  values from 17.7 Å.<sup>2,1</sup> to 22.0 Å.<sup>2,16</sup> while the (extrapolated) liquid density leads to a value of 15.0 Å.<sup>2</sup>. These variations have been interpreted in terms of differences in packing of the adsorbed molecules.<sup>17</sup> This argument, however, leads to a number of difficulties. One would expect, for example, that for a given group of solids, an adsorbate composed

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- (14) P. H. Emmett and S. Brunauer, J. Am. Chem. Soc., 59, 1553 (1937).
- (15) W. D. Harkins and G. Jura, ibid., 66, 1366 (1944).

(16) R. T. Davis, Jr., T. W. DeWitt and P. H. Emmett, THIS JOURNAL, **51**, 1232 (1947).

(17) W. C. Walker and A. C. Zettlemoyer, ibid., 57, 182 (1953).

of small spherical molecules would show less variation in packing than one containing molecules of any other shape. Particularly, an elongated molecule like  $N_2$ , which might be adsorbed either standing up or lying down, should exhibit a wider range of apparent molecular areas than those found for rare gas atoms. In terms of Meyer's interpretation, however, these variations might stem from a fairly sharp decrease in  $(\Delta H_{\rm f} - \Delta H_{\rm l})$  from a high value over most of the first monolayer to a value less than RT at a coverage not quite equal to the complete monolayer. In Table II, some estimated parameters related to  $(\Delta H_{\rm f} - \Delta H_{\rm l})$  are compared with the experimentally found  $\sigma$  variations (expressed as monolayer density compared to liquid density, *i.e.*,  $(\sigma_{\text{liq}}/\sigma_{\text{exptl}}))$ . For these gases, at least, it appears that when a stronger adsorption force is combined with a lower value of  $\Delta H_1$ , apparent monolayer density equals or exceeds the liquid density; when the liquid has a high heat of vaporization, and the adsorption force is low,  $(\Delta H_{\rm f} - \Delta H_{\rm f})$  would be expected to be smaller, and the apparent monolayer density is low and more variable.

TABLE II

FACTORS AFFECTING OBSERVED CROSS-SECTIONAL AREAS

Gas	Adsorption forces (to produce Δ <i>Πf</i> )	Δ <i>H1</i> , a keal./ mole	ExptJ. monolayer density (relative to liquid packing)
$N_2$	Quadrupole + dispersion	1.38	1.0 -1.05
Ar	Dispersion only	1.63	0.84-0.96
Kr	Dispersion only	2.61	0.68-0.85

 $^{\rm a}$  Estimated from vapor pressures of liquid near 77.4°, by Clausius–Clapeyron equation.

All of these considerations suggest that the widespread applicability of the BET method should not be considered as merely an empirical fact. If properly evaluated, and confirmed by the checks inherent in the BET equation, the value of  $v_{\mathbf{m}}$  is of real physical significance. If this is then converted to a surface area through the use of a significant  $\sigma$  value, appropriate to the solid at hand, the result also is significant. We have seen that  $\sigma$ may not have a unique value, but may vary. However, the experimental results so far reported suggest that this variation is generally not great. For krypton, for example, measurements on materials as different as metals and oxides,1,3,16 aluminosilicates,<sup>18</sup> graphite,<sup>19</sup> silica<sup>20</sup> and organic materials<sup>21</sup> have yielded surface areas in reasonable agreement with the values determined by other methods, if  $\sigma_{Kr}$  is taken to be 19.5  $\pm$  1 A.<sup>2</sup> Further confirmation of the ability of krypton adsorption data on a variety of substrates to yield good linear BET plots in the monolayer region is given by Fig. 1, where typical plots obtained in this Laboratory are presented. (Table III gives the sample data and the parameters obtained from the plots shown.)

(20) K. Wheatley, J. Appl. Chem., 9, 159 (1959).

<sup>(10)</sup> S. Brunauer, "The Adsorption of Gases and Vapors. I. Physical Adsorption," Princeton University Press, Princeton, N. J., 1945, p. 158.

<sup>(11)</sup> G. L. Gaines, Jr., THIS JOURNAL, 62, 1526 (1958).

<sup>(12)</sup> P. H. Emmett, "Catalysis," Vol. 1, Reinhold Publ. Corp., New York, N. Y., 1954, p. 52.

<sup>(18)</sup> G. L. Gaines, Jr., and C. P. Rutkowski, *ibid.*, 62, 1521 (1958).
(19) H. L. McDermot and B. E. Lawton, *Can. J. Chem.*, 37, 54 (1959).

<sup>(21)</sup> A. C. Zettlemoyer, A. Chand and E. Gamble, J. Am. Chem. Soc., 72, 2752 (1950).



Fig. 1.—BET plots for krypton adsorption at  $77.4^{\circ}$ K. on various solids (crosses indicate monolayer coverage evaluated from c) (see Table III).

TABLE III

DATA SHOWN IN FIGURE 1

Curve	Sample	Wt. of sample, g.	Surface area, m. <sup>2</sup> /g.a	с
1	Sintered Ag	34.30	0.0085	52
<b>2</b>	Glass powder	6.24	0.11	80
3	Mica paper	1.00	1.92	15
4	$MoS_2$	0.170	8.31	64
5	W powder	1.70	0.90	215
• Witł	$\sigma_{\rm Kr} = 19.5 {\rm \AA}.^2$			

Malden and Marsh<sup>4</sup> have criticized the use of krypton on the basis of lack of general utility. We feel from our own results and those cited in this paper that the general applicability has been amply demonstrated. Furthermore, the use of the rare gases eliminates the possibility of chemisorption, which recently has been found to occur with  $N_2$  at low temperatures on certain metals, e.g., Ni<sup>22</sup> and W.<sup>23</sup> Of course, krypton and argon adsorption can be affected by the presence of chemisorbed or strongly physically adsorbed surface contamination,<sup>24,25</sup> but one usually attempts to measure surface areas in the absence of contamination. The presence of phase changes in adsorbed films, appearing as discontinuities in the isotherms, might have been thought to cause poor surface area results,<sup>12</sup> but this has been shown not to be the case for krypton.<sup>19,26</sup> It is of course also well known that with certain types of adsorbents, different gases will measure different areas; for example, a zeolite such as Molecular Sieve 4A (Linde Co.) adsorbs krypton only on the external surfaces,<sup>27</sup> while admitting oxygen into the lattice<sup>28</sup> with a spectacular difference in apparent area.

For these reasons, therefore, it is certainly necessary to consider the nature of the adsorbent and possible interactions between it and the adsorbate before selecting a gas for surface area measurement. If there is uncertainty about the likelihood of such specific effects, it is probably wisest to make measurements with more than one adsorbate.

We are indebted to Miss C. P. Rutkowski, who performed all of the adsorption measurements described, and to Dr. B. H. Zimm for a critical review of the manuscript.

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# A NEW APPARATUS FOR MEASURING THE SORET EFFECT

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A simple conductimetric method of measuring the Soret effect in dilute aqueous solutions of electrolytes is reported. The construction and operation of the thermal diffusion cell are described, and results for dilute solutions of  $CdSO_4$ ,  $AgNO_3$ , NaBr and  $Tl_2SO_4$  are given. These are in satisfactory agreement with results obtained by other methods.

## Introduction

Information about the Soret effect in *dilute* aqueous solutions of electrolytes is sparse. For solutions of higher concentration, methods based on optical interferometry have been developed, most recently by Longsworth.<sup>2</sup> In dilute solutions such methods are insufficiently sensitive, and other techniques must be devised for measuring the concentration changes. Agar and Breck<sup>3</sup> followed

(1) Dept. of Chemical Engineering. University of Cambridge, Pembroke St., Cambridge, England. the concentration changes by measuring the e.m.f. of a non-isothermal cell, but this method is applicable to only a few systems. Measurements of conduction offer good prospects and we shall describe here a simple conductimetric cell (cell A) which gives a clear demonstration of the Soret effect in dilute solutions. Details of a different design of cell (Cell B) are given elsewhere<sup>4</sup> and (3) J. N. Agar and W. G. Breck, *Trans. Faraday Soc.*, **53**, 167 (1957).

(4) (a) J. N. Agar and J. C. R. Turner, *Proc. Roy. Soc. (London)*, **255 A**, 307 (19(0); (b) J. C. R. Turner, Ph.D. Thesis, University of Cambridge.

<sup>(2)</sup> L. G. Longsworth, This JOURNAL, 61, 1557 (1957).

further results obtained with a later cell will be forthcoming

Apparatus .- The cell (Fig. 1) consists of two rectangular silver end-plates (Ag) screwed to a Perspex block (P). The solution (S) is contained between the plates in a cylindrical hole in the Perspex, thin rubber gaskets being used to make a liquid-tight joint between the plates and the Perspex. A narrow-bore filling hole (F) is used for filling and emptying the cell. The four platinum wires (E) of diameter  $\frac{1}{4}$  mm. and protruding about  $\frac{1}{2}$  mm. into the solution compartment, are used as conductance electrodes. A satisfactory seal between these wires and the Perspex (superior to that obtained with adhesives) was made by heating them and forcing them through the Perspex while hot. The protruding ends of the wires were platinized

before the end-plates were attached. To commence a run, the cell, containing the desired solution, was placed between two copper cylinders main-tained at 20 and 30° by circulating water from two thermostats. To minimize convection, the top of the cell was kept at the higher temperature  $(30^\circ)$ , the sides were lagged, and the cell was accurately levelled. The resistances of the solution between the top pair and between the bottom pair of electrodes were measured at intervals using an audio-frequency bridge sensitive to 1 part in 10<sup>4</sup>. The steady *temperature* distribution is established in about 12 minutes, and during this period there are large changes in the meas-ured resistances. To ensure that subsequent resistance changes are due to changes of concentration and not to further changes of temperature, it is necessary to keep the temperatures constant to within 0.01°

# Theory of the Method

During the approach to the steady state the molality (m) at time (t) and distance (x) from the lower plate should be given to a sufficiently good approximation<sup>5,6</sup> by

$$\frac{-\ln(m/m_0)}{\sigma\Delta T} \simeq \frac{m_c - m}{\sigma\Delta T m_0} = \left(\frac{x}{a} - \frac{1}{2}\right) + \frac{4}{\pi^2}\cos\frac{\pi x}{a} \times e^{-t/\theta} \quad (1)$$

provided  $t > \theta/3$ . In this equation

 $m_0$  = initial uniform molality

= total height of cell a

- = Soret coefficient
- $\Delta T$  = temp. difference between the ends  $\theta = a^2/\pi^2 D$ , the characteristic time
- D = diffusion coefficient

For times less than  $\theta/3$ , additional terms are required.<sup>5,6</sup> The derivation of (1) assumes a uniform temperature gradient and ignores the temperature dependence of D and  $\sigma$ . "Warming-up" corrections<sup>6</sup> are small and also have been ignored in this work.

The measured resistance (R) of either pair of electrodes is proportional to the specific resistance  $(\rho)$  at the relevant height in the cell, and changes in R,  $\rho$  and m can be related by

$$d \ln R = d \ln \rho = -B d \ln m$$
 (2)

where

$$B = \left(1 + \frac{\partial \ln \Lambda}{\partial \ln c}\right)_T \times \left(\frac{\partial \ln c}{\partial \ln m}\right)_T$$

and  $\Lambda$  is the equivalent conductance. The coefficient B can be calculated from published data and can be treated as constant over the ranges of temperature and molality occurring in any one experiment. Since d  $\ln m$  is small we may write

$$\frac{R-R_0}{R_0} = -\frac{B(m-m_0)}{m_0}$$
(3)

(6) J. N. Agar, Trans. Faraday Soc., 56, 776 (1960).



-Cell A3 (height =  $1.34_4$  cm.), approximately to Fig. 1.-Dimensions of cells A1 and A2 are similar except for scale. their heights (see Table I).

where  $R_0$  is the resistance at t = 0 (uniform solution). Equation 1 thus becomes

$$\frac{R-R_0}{B\sigma\Delta TR_0} = \left(\frac{x}{a} - \frac{1}{2}\right) + \frac{4}{\pi^2}\cos\frac{\pi x}{a} \times e^{-t/\theta} \quad (4)$$

where x now refers to the effective position of one or the other electrode pair.

For the steady state  $(t \rightarrow \infty)$ , we obtain

$$\frac{R_{\infty} - R_0}{B\sigma\Delta T R_0} = \left(\frac{x}{a} - \frac{1}{2}\right) \tag{5}$$

and (4) can thus be rewritten in the form

 $\ln |R - R_{\infty}| = \ln |R_0 - R_{\infty}| +$  $\ln \left[ \frac{4 \cos(\pi x/a)}{\pi^2 \left(\frac{1}{2} - \frac{x}{a}\right)} \right] - \frac{t}{\theta} \quad (6)$ 

The effective positions of the electrodes may be deduced from resistance measurements with a uniform solution in the cell under the following conditions: (a) isothermal at  $20^{\circ}$  ( $T_1$ ), (b) isothermal at 30°  $(T_2)$ , (c) with the upper end plate at  $T_2$  and the lower at  $T_1$ .

By interpolation, the effective temperatures at the electrodes under the usual operating conditions (c) can be determined. A small correction is necessary for non-linearity in the temperature-conductance relationship. Assuming a uniform temperature gradient, the effective positions x then follow.

The resistance measurement (c) varies with time due to thermal diffusion in the solution. It is thus necessary to extrapolate back to zero time to obtain the resistance appropriate to a uniform solution, bearing in mind that the unsteady temperature distribution in the first few minutes renders useless any readings in that period. We have used free-hand extrapolation and this introduces an uncertainty into the value of x/a deduced from the resistance readings.

The possibility of error in the extrapolation is clearly reduced if the Soret coefficient is small; with this in view we have used 0.02 m solutions of NaCl, KCl and LiCl and, in these cases at least, graphical extrapolation is quite adequate. For cell A3 the preferred values of x/a by this method are 0.852 and 0.186. All measurements (using the three solutions mentioned above and some others) lie within  $\pm 0.005$  of these values, and the error due to the extrapolation seems to be within  $\pm 0.001$ .

Longsworth<sup>2,7</sup> found that the temperature gradient in his cells was not uniform, which implies some lateral flow of heat through the walls. This

1.015 1.010 ELECTRODES 1.000 1.005 1.000 ELECTRODES .995 .995 .995 .990 .985

Fig. 2.–0.045 *m* cadmium sulfate; 0–24 hours, thermal diffusion run  $(30-20^{\circ})$   $r = (obsd. resistance)/(resistance extrapd. to zero hr.); 24-48 hours, isothermal return run <math>(20^{\circ})$   $r = (obsd. resistance)/(resistance with uniform soln. at <math>20^{\circ}$ ).

Time, hr.

16

24

32

40

-18

8

is less likely to occur in our cells, since the thermal conductivity of their Perspex walls is much less than that of the glass walls used in Longsworth's cells. We therefore think that the assumption of uniform temperature gradient is unlikely to introduce serious errors into our estimates of x/a. As far as steady-state observations are concerned, the point is in any case unimportant, because the difference in  $\ln m$  between the two electrode pairs is governed by the difference in T rather than that in x.

# Results

Figure 2 shows the results of an experiment using  $0.045 \ m$  CdSO<sub>4</sub>. As the solute diffused from the upper (hot) part of the cell to the lower (cold) part, the resistance of the upper pair of electrodes rose and that of the lower pair fell. After 24 hours the "steady state" was nearly achieved, in which thermal diffusion was balanced by ordinary diffusion in the opposite direction.

The cell was then brought to an isothermal state by holding the temperature of the lower end-plate at 20° and cautiously reducing that of the upper end-plate from 30 to 20°. The concentration gradient thereafter collapsed by ordinary isothermal diffusion, as shown by the right-hand plot of Fig. 2.

In general, it is difficult to avoid convective mixing when changing the temperature gradient, but in the case of  $0.045 \ m \ CdSO_4$  the liquid is stabilized by the density gradient associated with the Soret concentration changes and it is possible to bring the cell to an isothermal state without convection provided the process is carried out slowly (30 minutes).

The observations on CdSO<sub>4</sub> and other solutions agree well with equations 4 and 6, except for slight anomalies in the early stages of a run, which cannot be explained by the omission of higher exponential terms from (1) and are perhaps due to local irregularities in the diffusion field near the electrodes. These anomalies vary from one cell to another. It is worth noting that the next term in the series that should replace the single time-dependent term in (1) is

$$\frac{1}{9}\cos\frac{3\pi x}{a}\;e^{-9t/\theta}$$

which vanishes when x/a = 1/6 or 5/6 and very nearly vanishes when x/a = 0.186 or 0.852, as in cell A3 (*cf.* Harned and French<sup>8</sup>).

In an experiment of sufficiently long duration the observed R approaches  $R_{\infty}$  closely. In order to save time, it is more convenient to extrapolate the observed R to  $t = \infty$  with the aid of (4). Using a rough estimate of  $\theta$ , a plot of R against  $e^{-t/\theta}$  is constructed and extrapolated to  $e^{-t/\theta} =$ 0. The intercept  $(R_{\infty})$  is insensitive to errors in  $\theta$ .

When  $R_{\infty}$  has been determined,  $\theta$  may be found from a plot of  $\ln |R - R_{\infty}|$  against t (see (6)), although accurate values of  $\theta$ cannot be obtained in cases where the Soret coefficient is small—for example, 0.02 m NaBr (Table I). Equation 6 also

shows that  $|R_0 - R_{\infty}|$  (and hence  $R_0$ ) may be estimated by extrapolation of the linear part of the  $\ln |R - \tilde{R}_{\infty}| vs. t$  graph to t = 0.

Alternatively,  $R_0$  may be obtained by a freehand extrapolation of the R vs. t curve to t = 0; the values of  $|R_0 - R_{\infty}|$  obtained in this way are always slightly greater than those obtained by the log plot, although the resulting differences in  $\sigma$  do not exceed  $0.2 \times 10^{-3}$  deg.<sup>-1</sup>. The extrapolation of the log plot is not entirely satisfactory owing to the anomalies in the early stages, as mentioned above. We have therefore used the simpler free-hand extrapolation throughout.

TABLE I

Cell height, cni.	Soln., m	θealed min.	θ <sub>meas</sub> min.	10 <sup>3</sup> σ, deg. <sup>-1</sup> , this work	10 <sup>3</sup> σ, deg. <sup>-1</sup> , cell Bf
A1 2.055	0.014 AgNO <sub>3</sub>	$422^{a}$	410	3.33	$\begin{array}{c} 3.30\\ 3.51 \end{array}$
A2 1.520	0.014 AgNO <sub>3</sub>	$230^{a}$	240	3.29	$\frac{3.30}{3.51}$
A3 1.344	0.014 AgNO <sub>3</sub>	$180^a$	184	3.63	3.30 3.51
A3	0.045 CdSO <sub>4</sub>	$500^{b}$	465	7.30	7.41 7.33
A3	0.02 Tl <sub>2</sub> SO <sub>4</sub>		$235^{\circ}$	7.15	7.04
A3	0.02 NaBr	195''	170 <sup>e</sup>	1.83	$\frac{1.76}{2.14}$

<sup>a</sup>  $D = 1.68 \times 10^{-5}$  cm.<sup>2</sup> sec.<sup>-1</sup> extrapolated from results of Harned.<sup>9</sup>  $b D = 0.61 \times 10^{-5}$  cm.<sup>2</sup> sec.<sup>-1</sup> extrapolated from results of Longsworth.<sup>7c</sup> D unknown; this value of  $\theta$  corresponds to  $D = 1.30 \times 10^{-5}$  cm.<sup>2</sup> sec.<sup>-1</sup>. <sup>d</sup> D estimated as  $1.55 \times 10^{-5}$  cm.<sup>2</sup>sec.<sup>-1</sup> from data in Harned and Owen.<sup>10</sup> <sup>c</sup> This value is not accurate because  $\sigma$  is small. <sup>l</sup> Upper figure = steady state value of  $\sigma$ ; lower figure = initial rate value of  $\sigma$  (see Agar and Turner<sup>4n</sup>).

(7) L. G. Longsworth, "The Structure of Electrolytic Solutions," Ed. W. J. Hamer, John Wiley and Sons, Inc., New York, N. Y., 1959, pp. 183-199.

(8) 11. S. Harned and D. M. French, Proc. N. Y. Acad. Sci., 46, 267 (1945).

(9) H. S. Harned and C. L. Hildreth, J. Am. Chem. Soc., 73, 3292 (1951).

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Table I gives a summary of results with cells of different height and with solutions of widely different diffusion coefficients. The tabulated values of  $\sigma$  and  $\theta$  are the means of observations on the top and bottom pairs of electrodes. By taking these means we eliminate changes in resistance due to drift in the mean temperature of the cell. In fact, however, the values of  $\sigma$  and  $\theta$  for the individual electrode pairs usually agree closely  $(e.g., to within 0.2 \times 10^{-3} \text{ deg.}^{-1} \text{ for } \sigma)$ . Values of  $\sigma$  obtained in cell B are given for comparison.

#### Discussion

Although we have used cell B more extensively than cell A (and generally prefer it, especially for low concentrations) the results obtained from cell A are a valuable confirmation of those from cell B. Furthermore, cell A has the advantage of (10) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1958. simpler construction. In cell B the end-plates themselves act as electrodes, and platinumfaced silver plates are required. These specialized and expensive components are not needed in cell A. It also seems possible that cell A will operate satisfactorily at higher concentrations than can be used in cell B, although we have not used either at concentrations above 0.05 m.

Evidence has been presented elsewhere<sup>4a</sup> that convection effects occur in cell B, and the steadystate values of  $\sigma$  (see Table I) are therefore low. The initial rate values of  $\sigma$  from cell B should be free from convection errors. Comparison of the results for cell A and cell B suggests that some convection is also occurring in cell A. It is to be expected that convective mixing will usually be a less serious problem at higher concentrations,<sup>4a</sup> and it is in this region that cell A may prove most useful.

# THE REACTIONS OF WATER VAPOR WITH BERYLLIA AND BERYLLIA– ALUMINA COMPOUNDS<sup>1</sup>

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The reactions of water vapor with BeO, BeO·Al<sub>2</sub>O<sub>3</sub> and BeO·3Al<sub>2</sub>O<sub>3</sub> were studied in the range 1300 to 1575° using a transpiration technique. The equilibrium constants for the reactions per mole of water are given by:  $\log K_p = 1.93 - 9280/T$ ,  $\log K_p = 2.45 - 10800/T$ , and  $\log K_p = 1.55 - 9450/T$ , respectively. Values of  $\Delta F^0$ ,  $\Delta H^0$  and  $\Delta S^0$  are given for these reactions and for solid state reactions involving these materials and alumina.

# Introduction

It has been shown<sup>2-5</sup> that beryllium oxide reacts with water vapor at high temperatures to form a volatile compound, probably  $Be(OH)_2$ .<sup>4</sup> Hutchison and Malm<sup>3</sup> found that beryl is much less reactive with water vapor than is beryllia; this fact led Potter<sup>6</sup> to suggest that the addition of other oxides might sufficiently reduce the chemical potential of beryllia to cause a substantial reduction in the volatility. This study was undertaken to investigate the reactions of water vapor with the two established compounds in the beryllia–alumina system<sup>7.8</sup>: chrysoberyl (BeO·Al<sub>2</sub>O<sub>3</sub>) and the compound BeO·3Al<sub>2</sub>O<sub>3</sub>. The reaction of water vapor with beryllia was studied to test the experimental procedures.

#### Experimental

Materials.—The two beryllia-alumina compounds were prepared from BeO of 0.2  $\mu$  particle size and 99.98% purity, and Al<sub>2</sub>O<sub>3</sub> of 0.3  $\mu$  particle size and 99.9% purity. For

(1) This work was sponsored by the U. S. Atomic Energy Commission under contract AT (11-1)-GEN-8.

(2) M. G. Berkman and S. L. Simon, ANL-4177, July 15, 1948.

(3) C. A. Hutchison, Jr., and J. G. Malm, J. Am. Chem. Soc., 71, 1338 (1949).

(4) L. I. Grossweiner and R. L. Seifert, ibid., 74, 2701 (1952).

(5) G. R. B. Elliott, UCRL-1831, June 1952.

(6) N. D. Potter, NAA-SR-MEMO 2152, November 5, 1957 (AEC Classified Report).

(7) W. R. Foster and H. F. Royal, J. Am. Ceram. Soc, 32, 26 (1949).

(8) S. M. Lang, C. L. Fillmore and L. H. Maxwell, J. Research Natl. Bur. Standards, 48, 298 (1952),

cach compound the two pure oxides were weighed into separate beakers, slurried separately with methanol, quantitatively transferred to a polyethylene bottle, and shaken vigorously for 45 minutes. The mixed slurry was transferred to a Morganite alumina crucible, allowed to air dry, and sintered at 1350° for two eight-hour periods after each of which the sintered mass was crushed and returned to the crucible with a small portion withheld for X-ray powder pattern analysis. The patterns indicated that very little of the 1:3 compound had been formed and that both materials containec appreciable amounts of free alumina. The mixtures then were fired for four hours at 1850°, crushed and analyzed chemically and by powder patterns. The latter indicated that the chrysoberyl sample contained no free alumina or berylia and only a very small amount of the 1:3 compound; the sample of the latter contained no free beryllia and very small amounts of alumina and of chrysoberyl. Chemical analysis yielded BeO/Al<sub>2</sub>O<sub>3</sub> ratios of 1.06  $\pm 0.12$  and 0.318  $\pm 0.035$ . The samples used in the transpiration runs consisted of particles varying in size from 0.25 to 2 mm, in maximum dimension.

The beryllia used in the water vapor-beryllia study was obtained from a high-fired, high-purity crucible supplied by the U. S. Naval Research Laboratory. Spectrochemical analysis of the material gave the values:  $Al_2O_3$ , 0.008%; CaO, 0.003%; SiO<sub>2</sub>, 0.002%; MgO, 0.001%; no detectable amounts of the oxides of Ti, Cr, Mn, Fe, Co, Ni, Cd, Ba and Zn. The samples used consisted of irregular particles from 0.5 to 3 mm. in maximum dimension.

Apparatus.—Steam was generated in a one-liter flask equipped with a capillary vent and heated by a Variac controlled Glas-Col mantle; it was then passed through a Teflon packed, stainless steel, needle valve into the reaction vessel where it was preheated before passing through the inductively heated sample into a condenser and water collection system.

The reaction vessel consisted of a vertical 45 mm. quartz test-tube, 32 cm. long, surrounding the susceptor and crucible which were supported by an alumina tube 6 in. long  $\times$  0.500 in. o.d.  $\times$  0.250 in. i.d. The lower end of the quartz tube was joined to the valve by a 45/50 Vycor and Pyrex ground joint and Pyrex tubing. The lower end of the alumina tube was ground to fit, and supported by a 10/30 Pyrex joint which was ring-sealed to the large Pyrex joint and to 12 mm. Pyrex tubing. The latter was fitted with a side arm and terminated in a Pyrex window below which a front-silvered mirror was fixed for optical temperature measurement.

Water was condensed in a water jacketed condenser connected to the Pyrex side arm and collected in a 25 mm. Pyrex side-arm test-tube. The latter was attached by ground joints to the condenser and a drying tube which was weighed with the collector tube. A second drying tube, also filled with anhydrous magnesium perchlorate, was attached to the first by a ground joint and was used to prevent absorption of atmospheric water vapor.

All tubing between the boiler and the condenser, including the quartz reaction vessel below the induction coil, was maintained at 120 to 150° by heating tapes; all glass-tometal seals were Kovar and all metal-to-metal connections were silver soldered.

The samples were contained in a cylindrical Morganite crucible, 25 mm. high  $\times$  9 mm. i.d. and ground to 0.465 in. o.d. The bottom of the crucible was perforated with seven 0.009 in. holes and ground to fit the flat ground top of the supporting alumina tube. In addition, the lower half of the crucible was ground to a 3° taper so that it could slip within a 0.460 in. annular constriction near the center of the susceptor. The latter was a 2.500 in. length of platinum-10% rhodium tube, 0.500 in o.d. with a wall thickness of 0.015 in. The susceptor was attached with Morganite coment to the alumina supporting tube, the upper  $^{3}/_{4}$  in. of which was ground to 0.469 in diameter. This arrangement prevented the formation of an annular passage around the crucible due to differences in thermal expansion; the fit was such that an appreciable force was required to push the crucible from the susceptor after each run. Alumina crucibles were used rather than platinum because the latter is known to react with water vapor in the presence of beryllia.<sup>4</sup> The non-reactivity of alumina was established by passing water vapor for 3.25 hr. at 1500 l./hr., through 11.5 g. of Morganite thermocouple tubing heated to 1525°; the contact area was 75 cm.<sup>2</sup> and the weight loss, 0.1 mg., was less than the precision of weighing.

Temperatures were measured with a model 75 Micro Optical Pyrometer which was calibrated by observing the filament of a standard tungsten lamp through the mirror, window and alumina tube. After completion of the final run, the calibration was checked by simultaneous pyrometer and thermorouple measurements which agreed to within 3° over the entire range.

Power was supplied by a 10 kc., 15 kw., Tocco motorgenerator unit; the 250-volt output was fed to a parallel resonant circuit in which the coil and susceptor constituted the inductance.

Procedure.-The Morganite crucible was weighed, filled to a depth of 0.5 to 1 cm., reweighed to determine the weight of sample, and placed in the susceptor mounted on the alumina tube. The quartz tube was placed in position and helium, dried by passage through hot zirconium turnings was allowed to flow through the system overnight at 20-30 cm.<sup>3</sup>/min. The sample was heated to a steady temperature and the weighed water collection system was attached to the condenser. The helium flow then was discontinued and the steam valve opened. The temperature of the bottom of the crucible (hence, of the exit gases) was measured frequently and averaged over the length of the run which was taken to be the time between opening and closing of the steam valve; during each run the temperature remained constant to within approximately 10° except for the initial 20 minutes, during which an increase of up to 80° occurred. Water vapor pressure was assumed to be constant at the atmospheric pressure measured at the middle of each run; this pressure varied from 736 to 744 mm. After closing the steam valve, helium was readmitted and allowed to flow until no water was visible on the inner tube of the condenser. The collection system then was removed and reweighed to determine the amount of water which had passed through the sample. The power was shut off and the sample allowed to cool to room temperature with dry helium flowing. The crucible then was removed from the susceptor, reweighed to determine the weight loss of the sample to  $\pm 0.2$  mg., emptied and prepared for the next run.

The partial pressure of the volatile beryllium compound was calculated from the weight data and water vapor pressure assuming that the entire weight loss was BcO, that the volatile product was monomeric  $Be(OH)_2$ , and that all gases behaved ideally.

### **Results and Discussion**

Grossweiner and Seifert<sup>4</sup> have shown that the volatile product of the beryllia-water vapor reaction contains BeO and  $H_2O$  in equimolar amounts and that it is energetically unlikely to be a simple molecular association. Although there are no experimental data on the molecular weight of the product, their assumption that it is monomeric seems reasonable and will be adopted here. Hence, the predominant reaction is assumed to be

$$BeO(s) + H_2O(g) = Be(OH)_2(g)$$
(1)

It is also assumed that the gaseous product is monomeric in the reactions of the two beryllia– alumina compounds with water vapor.

To determine the nature of the solid product of the water vapor-chrysoberyl reaction, the first two runs only were conducted on one sample. The powder patterns obtained from these runs contained no lines attributable to  $Al_2O_3$  alone; comparison of the two patterns showed a progressive and marked increase in the intensity of the pattern of the 1:3 compound and an observable decrease in that of the chrysoberyl pattern Hence, the predominant reaction of water vapor with chrysoberyl is

$$3/2\text{BeO} \cdot \text{Al}_2\text{O}_3(s) + \text{H}_2\text{O}(g) = 1/2\text{BeO} \cdot 3\text{Al}_2\text{O}_3(s) + \text{Be(OH)}_3(g)$$
 (2)

Powder patterns obtained after five preliminary runs, conducted on one portion of BeO·3Al<sub>2</sub>O<sub>3</sub>, showed a progressive increase in the intensity of the alumina pattern, a corresponding decrease in that of the pattern of BeO·2Al<sub>2</sub>O<sub>3</sub>, and essentially zero intensity for the chrysoberyl pattern. Spectrochemical analysis and a powder pattern of a sample of the solid condensate obtained from the alumina tube showed that the condensate consisted of BeO with approximately 1% Al<sub>2</sub>O<sub>3</sub>. The predominant reaction of water vapor with the 1:3 compound is, therefore

 $BeO \cdot 3Al_2O_3(s) + H_2O(g) = 3Al_2O_3(s) + Be(OH)_2(g)$  (3)

It should be noted that the sensitivity of the Xray diffraction method is not sufficient to preclude the possibility of the occurrence of side reactions with reactions 2 and 3. Unfortunately, this source of error could be eliminated only with great difficulty, if at all; the necessity of carrying the reactions to completion under equilibrium conditions would require extremely long runs and would be complicated by diffusion effects in the solid. However, since no solid solutions and no other compounds have been found<sup>7.8</sup> in the aluminarich portion of the beryllia-alumina system, it is unlikely that any side reactions would be of sufficient importance to affect the observed experimental error to an appreciable extent.

For each material a series of measurements was made at 1535 to 1575° with varying flow rates to determine whether equilibrium could be achieved. August, 1960

The results, given in Table I, show no trend in the partial pressure of  $Be(OH)_2$  with variations in the flow rate of fivefold in the case of beryllia, three-fold in the case of chrysoberyl, and sevenfold in the case of the 1:3 compound; in addition, no trend was evident with twofold and threefold variations in the amount of sample for chrysoberyl and the 1:3 compound, respectively. Within the accuracy of the measurements, therefore, equilibrium was attained. The extremes of flow rate at

TABLE ]	Ĺ
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Equilibrium	PARTIAL	PRESSU	) RE	OF	Bc(OH) <sub>2</sub>	IN	WATER
		VAP	OR				
Temp., ± 15°K.	Sample wt., mg.	Wt. loss, mg.	Flo rate 1./h	w e, r.	Run, hr.	Þ	Be(OH)2, 11111.
		For I	3eO				
1822	713.0	5.2	5	. 6	7.80	(	0.553
1839	707.8	12.0	30	. 1	3.20		. 561
1576	698.2	4.3	12	. 7	15.00		.087
1605	691.5	7.6	20	. 1	15.00		.099
1586	683.9	8.4	24	. 2	15.17		.089
1713	675.5	3.4	7	. 1	9.00		.222
1703	672.1	11.7	25	. 5	9.00		.213
For BeO·Al <sub>2</sub> O <sub>3</sub>							
1828	641.6	4.7	9	. 9	7.00	(	0.303
1842	554.1	9.4	30	. 7	5.00		.276
1848 1	163.2	7.9	26	. 6	4.50		. 295
1843	456.2	9.9	33	. 4	5.00		.268
1841	365.2	10.7	24	. 4	7.00		.282
1732	464.9	4.4	21	. 4	8.00		.109
1604 1	195.1	1.9	15	. 4	12.00		.040
1606	564.4	4.1	26	. 1	16.00		.039
	F	or BeO	-3Al	$_{2}O_{3}$			
1791	444.8	2.9	19	.4	4.75	(	0.138
1821	384.1	7.6	50	. 6	3.60		. 186
1813	335.6	9.3	48	. 0	5.00		.172
1808	573.6	9.4	146		2.00		.142
1832	311.4	5.0	19	. 9	6.30		.178
1832	174.4	5.8	63	. 1	2.25		.183
1814	191.9	5.9	67	. 0	2.40		.163
1734	216.0	4.9	48	. 0	6.00		.072
1649	331.3	1.4	8	. 0	12.50		.056
1626	610.5	2.5	50	.7	5.00		. 039

these temperatures correspond to the following linear velocities in the unoccupied portion of the crucible: for beryllia, 13 and 2.4 cm./sec.; for chrysoberyl, 13 and 4.3 cm./sec.; for BeO·3Al<sub>2</sub>O<sub>3</sub>, 64 and 8.5 cm./sec. If it is conservatively assumed that 40% of the volume of the occupied length of the crucible was available for gas flow, these velocities yield contact times of 0.03 to 0.16 sec. for beryllia, 0.02 to 0.06 sec. for chrysoberyl, and 0.004 to 0.03 sec. for the 1:3 compound.

The variation of the equilibrium constant with temperature is given in Fig. 1. No correction was made for the vaporization of BeO, the total vapor pressure of which is only  $3 \times 10^{-7}$  mm. at  $1575^{99}$ ; no correction was made for the pressure of gaseous Al<sub>2</sub>O<sub>3</sub> species in view of the negligible loss observed using alumina thermocouple tubing and the results of Elliott.<sup>5</sup> The straight lines in Fig. 1 were ob-

(9) N. D. Erway and R. L. Scifert, J. Electrochem. Soc., 98, 83 (1951).



Fig. 1.—Log  $K\rho$  vs. 1/T (A<sub>2</sub>O<sub>3</sub> should read Al<sub>2</sub>O<sub>5</sub>).

tained from a least squares treatment of the data, using the method of fractional residuals, and correspond to the expressions

$$\log K_{\rm p} = 1.93 \pm 0.04 - (9280 \pm 80)/T$$
(I)  
$$\log K_{\rm p} = 2.45 \pm 0.07 - (10800 \pm 130)/T$$
(II)

and

$$\log K_{\rm p} = 1.55 \pm 0.10 - (9450 \pm 170)T \quad (\rm III)$$

for reaction 1, 2 and 3, respectively; the dashed line is that obtained by Grossweiner and Seifert<sup>4</sup> for reaction 1 and corresponds to

$$\log K_{\rm p} = 1.63 - 9060/T$$

These equations yield the values given in Table II for A, B,  $\Delta H^0$ ,  $\Delta S^0$ , and  $\Delta F_{1673}^0$  where A and B are constants in the expression

$$\Delta F_{\rm T^0} = 2.303 R (A - BT)$$

The values given for the solid state reactions

$$BeO \cdot Al_2O_3 = 1/3BeO \cdot 3Al_2O_3 + 2/3BeO \qquad (4)$$

and

$$BcO\cdot 3Al_2O_3 = 3Al_2O_3 + BeO$$
(5)

obtained by linear combinations of reactions 1, 2 and 3, were calculated from the results of this work. For all reactions it is assumed that  $\Delta H^0$  is independent of temperature, that the standard state of all gases is one atmosphere, and that the solids are in their standard states.

Combining the above data with free energy values for metal oxides<sup>10</sup> yields the following free energies of formation at 1400°: for gaseous Be(OH)<sub>2</sub>, -111 kcal./mole; for BeO·Al<sub>2</sub>O<sub>3</sub>, -378 kcal./ mole; for BeO·3Al<sub>2</sub>O<sub>3</sub>, -952 kcal./mole. The value of  $\Delta H^0$  for the beryllia-water vapor

The value of  $\Delta H^0$  for the beryllia-water vapor reaction obtained in this work differs from that of (10) A. Glassner, ANL-5750.

	Т	HERMODYN!	MIC PRO	PERTIES	
Reac- tion	.1, °K.	B	∠ <i>H</i> °, kcal.	∆ <i>S</i> ⁰, e.u.	$\Delta F_{1673}$ , kcal.
l <sup>a</sup>	9060	1.63	41.5	7.4	29.0
1	9280	1.93	42.5	8.8	$27.7\pm0.7$
2	10800	2.45	49.4	11.2	$30.7 \pm 1.1$
3	9450	1.55	43.2	7.1	$31.4 \pm 1.5$
-1	1012	0.35	4.6	1.6	$2.0 \pm 1.2$
5	168	-0.38	0.8	-1.7	$3.7 \pm 2.2$
a Das					

TABLE II

From Grossweiner and Seifert 4

Grossweiner and Seifert<sup>4</sup> by only 2.4%, probably within the experimental accuracy of the two studies. However, this difference in  $\Delta H^{0}$  is sufficient to account for nearly one-half of the discrepancy in the values obtained for B, the intercept of the log Kvs. 1/T curve. The remainder probably is due to two factors: it is likely that some water vapor by-passed their samples through the annular space between the sample container and the furnace wall; secondly, and much less important, the contact time in their work was approximately one-third of that of this work. Since each of these factors would lead to lower values for the partial pressure of  $Be(OH)_2$ , the results of this work should be closer to equilibrium values.

The value of  $\Delta S^0$  obtained for the chrysobery water vapor reaction is unusually high for a reaction involving no change in the number of moles of gas; Kubaschewski and Evans,<sup>11</sup> however, list several reactions for which the entropy change is comparable; for example  $\Delta S_{1600}^{0} = 14.1$  e.u. for the reaction

$$Cr(s) + Cl_2(g) = CrCl_2(g)$$

The difference in the slopes obtained for the reactions of chrysoberyl and BeO-3Al<sub>2</sub>O<sub>3</sub> with water vapor is consistent with the requirement of higher temperatures for the formation of the latter than for chrysoberyl, as observed here and by Foster and Royal,<sup>7</sup> and with the fact that, unlike chrysoberyl, it is not a naturally occurring substance. In addition, measurement of the intensities of Xray diffractometer tracings of a sample of BeO. 3Al<sub>2</sub>O<sub>3</sub> before and after heating at 1150° for two weeks showed some disproportionation into chrysoberyl and alumina.

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(11) O. Kubaschewski and E. L. Evans, "Metalluroical Thermochemistry," 3rd edition, Pergamon Press, New York, N. Y., 1958, pp. 336-343.

# DETERMINATION OF PARTICLE SIZE IN SILVER BROMIDE SOLS BY LIGHT SCATTERING<sup>1</sup>

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The average particle size in stable silver bromide sols has been measured by six different light scattering methods. The results are interpreted both by the Mic theory and approximations thereto and compared with particle sizes by electron microscopy. The effect of polydispersity upon light scattering is discussed. The type of average size given by a method depends upon the size distribution and the ratio of the refractive index of the particle to the refractive index of the surround-ing medium. Various average sizes from light scattering agree with the corresponding average size from electron microscopy within electron microscopy. within about 10%. Measurements of specific turbidity of sols of known concentration at two widely spaced wave lengths may be used to estimate the distribution of sizes, in good agreement with the distribution derived from electron microscopy.

#### Introduction

This study was carried on in conjunction with a study of the kinetics of nucleation and growth of silver bromide particles. For the purpose of finding an accurate and reliable light scattering method to apply to aqueous sols of growing particles, several methods were tested on stable sols. The methods useful for the type of sols under consideration are limited by the high refractive index ratio (1.67 to 1.76, depending on wave length) and size of the particles, and also by the polydispersity. Six light scattering methods could be used. Four of the six methods are based directly on Mie theory for spherical particles. Two of these use the absolute intensity of transmitted or scattered light, and two are based on the relative intensities scattered at different angles. The remaining two methods are based upon extension of the Debye approximation

(1) Taken from the Ph.D. thesis of Willard H. Beattie, October, 1958.

for particles with refractive index ratio near unity. A full discussion of the theory may be found elsewhere.<sup>1a</sup> The methods which were investigated are described in the following section.

#### Methods

1. Specific Turbidity.—When light passes through thickness l of non-absorbing scatterers, the turbidity  $\tau$  is given by equation 1

$$\tau = \frac{1}{l} \ln \frac{I_0}{l} \tag{1}$$

in which  $I_0$  and I are incident and transmitted intensities, respectively.  $\tau$  depends upon the number, size, shape and refractive index of the illuminated particles. For spheres of radius r

$$\tau = n\pi r^2 K \tag{2}$$

where n is the number of particles per ml. of suspen-

(1a) H. C. Van de Hulst, "Light Scattering by Small Particles," John Wiley and Sons, Inc., New York, N. Y., 1957.

August, 1960

sion, and K, the scattering coefficient, is the ratio of scattering cross section to geometric cross section. For particles such that  $r < \lambda'/20$ 

$$K = \frac{8}{3} \alpha^4 \left(\frac{m^2 - 1}{m^2 + 2}\right)^2 \tag{3}$$

where  $\alpha = 2\pi r/\lambda'$ ,  $\lambda'$ , wave length in medium surrounding particle,  $= \lambda/\mu_0$ ,  $\lambda$  is wave length *in vacuo*, *m* is  $\mu/\mu_0$ ,  $\mu$  is refractive index of particle, and  $\mu_0$  is refractive index of surrounding medium. For larger spheres, *K* must be calculated from the Mie equations.<sup>1</sup>

Specific turbidity<sup>2</sup> for spheres is given by

$$\frac{\tau}{c} = \frac{3\pi}{2\lambda' D} \times \frac{K}{\alpha} \tag{4}$$

where D is density of particle and c = concentration in g./ml. Specific turbidity depends upon the size and refractive index of the particles but is independent of n. Since the refractive index ratio m is usually known, the specific turbidity may be used as an absolute method to measure particle size. For Rayleigh particles, size may be obtained from equations 3 and 4. For large particles,  $K/\alpha$ is not a simple function and size is best found from graphs of  $K/\alpha vs. \alpha$ .

Scattering coefficients for use with silver bromide sols were obtained by interpolation of tabulated scattering coefficients.<sup>3-5</sup> Graphs of log K vs. m were prepared<sup>6</sup> at each  $\alpha$ . Using interpolated scattering coefficients for m equal to 1.76 and 1.70, corresponding to silver bromide sols at 436 and 546 m $\mu$ , respectively, plots of log  $K/\alpha$  vs.  $\alpha$  were prepared. These are shown in Fig. 1.

2. Specific Scattering Intensity.—When light falls on a suspension of non-absorbing spherical particles, the intensity of light scattered at angle  $\theta$  from the forward direction of the incident beam is

$$R_{\theta_{u}} = V_{\theta_{u}} + H_{\theta_{u}} = \frac{n\lambda^{\prime 2}}{8\pi^{2}} (i_{1} + i_{2})$$
(5)

where  $R_{\theta u}$  is the Rayleigh ratio or reduced intensity,  $= I_{\theta}b^2/I_0$ ,  $I_{\theta}$  = intensity of light scattered per ml. of suspension at angle  $\theta$  from the forward direction of an unpolarized incident beam of intensity  $I_0$ , at a distance b from the scattering volume;  $V_{\theta u}$ and  $H_{\theta u}$  are the vertically and horizontally polarized components of  $R_{\theta u}$ , respectively, and  $i_1$  and  $i_2$ are intensity functions for vertically and horizontally polarized light, respectively. For particles such that  $r < \lambda'/20$ ,  $i_1$  and  $i_2$  are given by

$$i_1 = \alpha^6 \left(\frac{m^2 - 1}{m^2 + 2}\right)^2$$
$$i_2 = \alpha^6 \left(\frac{m^2 - 1}{m^2 + 2}\right)^2 \cos^2 \theta$$

and substitution into equation 5 gives the Rayleigh equation for angularly scattered light. For large

(2) W. Heller and W. J. Pangonis, J. Chem. Phys., 26, 498 (1957).

(5) R. O. Gumprecht and C. M. Sliepeevich, "Tables of Light Scattering Functions for Spherical Particles," Engineering Research Institute, University of Michigan, Ann Arbor, 1951.

(6) W. H. Beattie, Ph.D. Thesis, University of Minnesota, 1958.



Fig. 1.— Specific turbidity as a function of  $\alpha$  for *m* equal to 1.76 and 1.70.

particles, the intensity functions are given by the Mie equations.<sup>1</sup>

Specific scattering is given for the vertical component of unpolarized incident light by

$$\frac{V_{\theta_{u}}}{c} = \frac{3}{4D\lambda'} \times \frac{i_{1}(\theta)}{\alpha^{3}}$$
(6)

For Rayleigh particles, size may be obtained by substitution into equation 6. For larger particles,  $\alpha$  may be found from  $V_{\theta u}/c$  with the aid of graphs of  $i_1(\theta)/\alpha^3 vs. \alpha$ .

Intensity functions for use with silver bromide sols were interpolated graphically<sup>6</sup> from published values.<sup>3-5</sup> Plots of log  $i_1(\theta)/\alpha^3$  vs.  $\alpha$  were prepared (Fig. 2) for *m* equal to 1.76 and 1.70. Figure 2 also includes values for m = 1.55, corresponding to silver bromide in glycerol (vide infra). In both the specific turbidity and specific scattering methods, size is a single valued function of  $K/\alpha$ or  $i/\alpha^3$  only for sizes smaller than the size corresponding to the first maximum in the corresponding function.

**3.** Dissymmetry.—Dissymmetry is defined<sup>7</sup> as the ratio of intensities scattered at two angles symmetrical about 90°. It is a measure of size for particles larger than Rayleigh particles. In the present instance (high m) Mie theory must be used for calculations of dissymmetry. Figure 3 was calculated for angles of 40 and 140°.<sup>3,4</sup>

4. Polarization Ratio.—This is the ratio of intensities scattered with different polarizations at a

(7) P. Debye and E. W. Anacker, THIS JOURNAL, 55, 644 (1951).

<sup>(3)</sup> A. N. Lowan, "Tables of Scattering Functions for Spherical Particles," National Bureau of Standards A.M.S.-4, Washington, D. C., 1948.

<sup>(4)</sup> E. J. Mechan and W. H. Beattie, J. Opt. Soc. Am., 49, 735 (1959).



Fig. 2.—Specific scattering at  $0^{\circ}$  as a function of  $\alpha$  for m equal to 1.76, 1.70 and 1.55.

given angle.<sup>8,9</sup> It may be used to determine the size of isotropic spheres larger than Rayleigh particles. Figure 4, which is a plot of polarization ratio vs.  $\alpha$ , was prepared from tables of light scattering functions.<sup>3,4</sup> Angles of 80 and 90° were found to give maximum sensitivity.

5. Zimm-Dandliker Equation.—The Zimm-Dandliker equation<sup>10</sup> extends the range of the Debye approximation to particles of relatively high m. It is not restricted to spherical particles. The equation is

$$(2K_1 + K_2) \left(\frac{c}{R\theta_v}\right)_{\substack{c=0\\\theta=0}} = \frac{1}{M}$$
(7)

where

$$K_1 = \frac{2\pi^2 \mu_0^2}{N\lambda^4} \left(\frac{\partial \mu}{\partial c}\right)^2, K_2 = \frac{\mu_0^2}{4\lambda'^2 N} \left(\frac{\tau}{c}\right)^2_{c=0}$$

N is Avogadro's number and M is molecular weight or particle weight. For particles with  $m \simeq 1$ ,  $K_2 << K_1$ , and equation 7 reduces to Zimm's well known equation.<sup>11</sup>

6. Extrapolation to Infinite Wave Length.— The Debye approximation is valid when  $2\alpha(m - 1) <<1$ . Since  $\alpha$  becomes small at sufficiently long wave length, the method can be extended to high m when long wave lengths are used. Cashin and

(8) D. Sinclair and V. K. LaMer, Chem. Revs., 44, 245 (1949).

(9) M. Kerker and V. K. LaMer, J. Am. Chem. Soc., 72, 3516 (1950).



Fig. 3.—Dissymmetry (40°, 140°) as a function of  $\alpha$  for m equal to 1.76, 1.70 and 1.54.

Debye<sup>12</sup> derived equation 8, giving molecular or particle weight as a function of turbidity and wave length

$$\left(\frac{Hc}{\tau}\right)_{c=0} = \frac{1}{Q\overline{M}} \tag{8}$$

where  $H = 16\pi K/3$ , and Q is the particle dissipation factor, a function of particle size and wave length.

Billmcycr<sup>13</sup> introduced an expanded form of the particle dissipation factor into equation 8, obtaining

$$\left(\frac{Hc}{\tau}\right)_{c=0} = \frac{1}{M} + \frac{AL^2}{\lambda'^2 M} \tag{9}$$

A is a constant dependent upon the shape of the particle, equal to 3.95 for spheres, and L is major dimension of particle (diameter for spheres). A plot of  $(Hc/\tau)_c = 0$  vs.  $1/\lambda'^2$  extrapolated to infinite wave length gives M.

Refractive Index Relations.—In all the above methods, the refractive index of the particle, relative to that of the surrounding medium, is a parameter. The first four methods require m to be known. The last two methods require the refractive index increment,  $\partial \mu / \partial c$ , to be known. This is usually measured, but for spherical particles it may be calculated from m and scattering intensity.<sup>10</sup> The relation is

$$\frac{\partial \mu}{\partial c} = \frac{3\mu_0 R(i_1^*)}{2\alpha^3 D} \tag{10}$$

<sup>(10)</sup> B. H. Zimm and W. B. Dandliker, THIS JOURNAL, 58, 644 (1954).

<sup>(11)</sup> B. H. Zimm, J. Chem. Phys., 16, 1093, 1099 (1948).

<sup>(12)</sup> W. M. Cashin and P. Debye, Phys. Rev., 75, 1307 (1949).

<sup>(13)</sup> F. W. Billmeyer, Jr., J. Am. Chem. Soc., 76, 4636 (1954).

.1

0.5



Fig. 4.—Polarization ratio ( $\rho$ ) at 80° and 90° for m equal to 1.70.

1.5

1.0

where  $R(i_1^*)$  is the real part of the forward scattering function, as defined by Lowan.<sup>3</sup> For small spheres obeying Rayleigh scattering, the relation becomes

$$\frac{\partial\mu}{\partial c} = \frac{3\mu_0}{2D} \left( \frac{m^2 - 1}{m^2 + 2} \right) \tag{11}$$

a. 2.0

2.5

3.0

# Effect of Polydispersity

1. Calculation of Type Average.—Different light scattering methods give the same size when applied to monodisperse suspensions, but generally give different sizes when applied to polydisperse suspensions. The difference is due to (1) different kinds of averages yielded by different light scattering methods, and (2) different kinds of averages yielded by different size ranges in any given method.

The latter effect arises in the following way. For a monodisperse suspension at a given  $\lambda$ , scattering functions such as K or  $\tau/c$  are proportional to the radius to a power y which may be defined by relation to the scattering cross section S

$$S = k_1 \alpha^y \tag{12}$$

where  $S = \pi r^2 K$ . S represents the total light energy scattered by one spherical particle per second per unit intensity of illumination. In this and the later equations,  $k_1, k_2, \ldots$ , include the numerical constants. K is given by the relation  $K = k_2 \alpha^{y-2}$ .

In a heterodisperse system the values of  $\tau$ , S and concentration c are given by



Fig. 5.—Graphs of K and S as a function of  $\alpha$  for m equal to 1.30, from calculations by Heller and Pangonis.<sup>2</sup>

$$\tau = k_1 \sum_i n_i \alpha_i^y$$
$$S = k_1 \sum_i \alpha_i^y$$
$$c = k_3 \sum_i n_i \alpha_i^3$$

Hence the specific turbidity and average value of  $\alpha^{y-3}$  are

$$\frac{\tau}{c} = k_4 \frac{\sum\limits_{i} n_i \alpha_i^y}{\sum\limits_{i} n_i \alpha_i^3} = k_4 \overline{\alpha^{y-3}}$$
(13)

where  $\alpha^{y-3}$  corresponds to the (y-3)rd average of  $\alpha$ . Figure 5, according to Heller and Pangonis,<sup>2</sup> gives relative values of scattering cross section and scattering coefficient for m = 1.30. Narrow size distributions, *a* to *h*, are indicated on the graph. The corresponding values of *y* are given in Table I. For sizes up to *g*, the effect of large particles in a given distribution becomes continually less. Between *a* and *c*, large particles affect average size more than small, and between *e* and *h*, small particles affect average size more than large.

The value of y, for any  $\alpha$  and m, is obtained as follows. From equations 13 and 4

$$d \log K/\alpha = d \log \tau/c = (y - 3) d \log \alpha \quad (14)$$

A plot of either log  $K/\alpha$  or log  $\tau/c vs$ . log  $\alpha$  has the slope (y - 3) At high m, the irregular variation of K with  $\alpha$  makes the determination of type average

where



Fig. 6.—Graph of (y - z) as a function of average  $\alpha$  for m equal to 1.70. The exponents, y and z, determine the type of average for narrow distributions about an average  $\alpha$ .



Fig. 7.—Graph of x as a function of average  $\alpha$  for m equal to 1.70. The exponent, x, determines the type of average for narrow distributions about an average  $\alpha$ , when applying the Zimm-Dandliker equation to spheres.

TABLE I VARIATION OF y with  $\alpha$ , m = 1.30 (cf. Fig. 5)

Size range	Ex- ponent y	Remarks
a	6	Rayleigh scattering
b	5	
с	4	
d	3	K proportional to $\alpha$
e	$^{2}$	Maximum in $K$
f	1	S proportional to $\alpha$
g	0	Maximum in S
h	$^{2}$	Minimum in K

difficult. With wide distributions of size the value of y changes throughout the distribution, and it is impossible to assign any meaningful type average. For narrow distributions, it is possible to describe the type of average at each  $\alpha$  for the methods used in this paper. Let F represent any light scattering function defined as the ratio of two measurable quantities, such as dissymmetry, or  $\tau/c$ . F is defined as

$$F = \frac{\sum_{i} n_{i} \alpha_{i}^{y}}{\sum_{i} n_{i} \alpha_{i}^{z}} = \overline{\alpha^{y-z}}$$
(15)

As a consequence, d log F = (y - z) d log  $\alpha$ . A plot of log F vs. log  $\alpha$  gives the type average from the average slope over the distribution. If F is  $\tau/c$ , slope is y - 3. Log-log plots were made for the methods used in the paper with m = 1.70. The results, giving type of average as a function of  $\alpha$ , are shown in Fig. 6. The first maximum in F corresponds to an abrupt change in the type of average for particles of high refractive index.

An approximate type of average may be obtained for wide distribution if the largest particles are smaller than the size corresponding to the first maximum. A value of y taken as 5 or 6 is a good approximation for either specific turbidity or specific scattering at 0°. Distributions with larger particles than corresponding to the first maximum will err on the low side if y is taken as 5 or 6.

The type of average given by the Zimm-Dandliker equation (eq. 7) for spherical particles is as follows. The equation may be expressed

$$R_{\theta_{\rm V}} = k_5 n \alpha^6 F(\alpha)$$

$$F(\alpha) = 4\pi^2 \left(\frac{\partial \mu}{\partial c}\right)^2 + \left(\frac{\lambda'}{2}\right)^2 \left(\frac{\tau}{c}\right)^2$$

For a distribution of sizes, the specific scattering is

$$\frac{Rg_{v}}{c} = k_{f} \frac{\sum_{i} n_{i} \alpha_{i}^{*} F(\alpha_{i})}{\sum_{i} n_{i} \alpha_{i}^{*}}$$
(16)

 $F(\alpha)$  has been calculated from tabulated functions for spheres with m = 1.70. To evaluate the type of average obtained it is convenient to define x by the relation

$$F(\alpha) = \alpha^x$$

so that a plot of log F vs. log  $\alpha$  has the slope x. The dependence of x on  $\alpha$  for m = 1.70 is shown in Fig. 7. The type average given by the Zimm-Dandliker equation is

$$\overline{\alpha^{3+x}} = \frac{\sum_{i} n_{i} \alpha_{i}^{5+x}}{\sum_{i} n_{i} \alpha_{i}^{3}}$$

For Rayleigh particles, x = 0, and the weight average of  $\alpha^3$  is obtained. For  $0.5 < \alpha < 1.5$ , the average is constant and slightly higher than that for Rayleigh particles. This is the most useful range of the Zimm-Dandliker equation for m =1.70.

2. Estimation of Distribution of Size.—A number of workers have tried to estimate the degree of polydispersity from light scattering data. Most have confined their attention to systems with  $m \simeq 1$ , so that the Rayleigh-Gans approximation applies. The methods that have been tested for  $m \simeq 1$  are: (a) variation of concentration,<sup>14</sup> later refuted,<sup>15</sup> (b) angular distribution of scattered light,<sup>11,16,17</sup> and (c) angle of minimum intensity.<sup>18,19</sup> Atherton and Peters<sup>20</sup> calculated turbidity, dissymmetry and slope of log  $\tau$  vs. log  $\alpha$  for Gaussian distributions of spheres, using graphical integration. Arrington<sup>21</sup> and Sloan<sup>22</sup> estimated distribution of size using low angle scattering. Ellison<sup>23</sup> used both the Rayleigh Gans and the diffraction approximations to calculate the effect of polydispersity for three types of distributions. Little direct use has been made of the Mie scattering functions to estimate polydispersity. Kerker and LaMer<sup>9</sup> estimated size distributions of two and three component

- (14) B. H. Zimm and P. Doty, J. Chem. Phys., 12, 203 (1944).
- (15) J. Waser, R. M. Badger and V. Shomaker, ibid., 14, 43 (1946).
- (16) P. Doty and R. F. Steiner, ibid., 18, 1211 (1950).
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- (18) W. B. Dandliker, J. Am. Chem. Soc., 72, 5110 (1950).
- (19) F. Bueche, ibid., 74, 2373 (1952).
- (20) E. Atherton and R. H. Feters, Brit. J. Appl. Phys., 4, 366 (1953).
- (21) C. H. Arrington, Jr., Abstr. Papers 125th Meeting Am. Chem. Soc., Kansas City, March, 1954.
  - (22) C. K. Sloan, This Journal, 59, 834 (1955).
- (23) J. McK. Ellison, Brit. J. Appl. Phys., Supplement 3 (1954).

mixtures using the polarization ratio and phase angle methods. Evva<sup>24</sup> calculated average  $K/\alpha$ values for polydisperse spheres with three types of distributions. The  $K/\alpha$  vs.  $\alpha$  curve was shifted to larger  $\alpha$  with a broader distribution of size, but the shape was not much changed. An approach combining light transmission with differential settling according to Stokes' law was used by both Sinclair and LaMer,<sup>8</sup> and Gumprecht and Sliepcevich.<sup>25</sup>

In principle the size distribution for larger than Rayleigh particles can be obtained directly either from accurate transmission measurements over a range of wave lengths, or accurate intensity measurements over a range of angles. This cannot be done for Rayleigh particles, since  $\tau$  depends upon  $\lambda$  in the same way for all sizes, and  $i(\theta)$  depends upon  $\theta$  in the same way for all sizes. For larger than Rayleigh particles, the same dependence that changes the type of average makes possible the calculation of size distribution. The main difficulty, as Ellison<sup>23</sup> found, is that variation of intensity with angle is due mainly to particles larger than the number average. This causes small particles to be masked by large ones.

The distribution may be approximated by assuming a type of distribution, and calculating its average size and width. Kottler<sup>26</sup> has pointed out that the log-normal distribution is a probable one, and this is supported by the data of Loveland and Trivelli<sup>27</sup> for certain silver bromide emulsions. The log-normal distribution<sup>28</sup> is defined by the equation

$$f(r) dr = C \exp\left[-\frac{1}{2} \left(\frac{\log r/r_{g}}{\log \sigma_{g}}\right)^{2}\right] dr \qquad (17)$$

where f(r) dr = number of particles in size range r to r + dr, r = particle radius,  $r_g =$  most frequent size, or geometric mean radius,  $\sigma_g =$  geometric standard deviation, and C = maximal value of f(r). The number average  $(r_n)$ , surface average  $(r_s)$ , and weight average  $(r_w)$  radii are defined by

$$r_{\rm n} = \frac{\sum_{i} n_{i} r_{i}}{\sum_{i} n_{i}} \tag{18}$$

$$r_{\rm s} = \frac{\sum_{i} n_{i} r_{i}^{3}}{\sum_{i} n_{i} r_{i}^{5}}$$
(19)

$$r_{\rm w} = \frac{\sum_{i} n_{i} r_{i}^{4}}{\sum_{i} n_{i} r_{i}^{2}} \tag{20}$$

In a log-normal distribution various averages are related by equations 21–23.

$$\ln(r_{\rm w}/r_{\rm s}) = \ln^2 \sigma_{\rm g} \tag{21}$$

$$\ln(r_{\rm s}/r_{\rm n}) = 2 \ln^2 \sigma_{\rm g} \qquad (22)$$

(24) F. Evva, Z. physik, Chem. (Leipzig), **202**, 208 (1953); **203**, 86 (1954).

(25) R. O. Gumprecht and C. M. Sliepeevich, This JOURNAL, **57**, 95 (1953).

(26) F. Kottler, J. Franklin Inst., 250, 339, 419 (1950).

(27) R. P. Loveland and A. P. H. Trivelli, *ibid.*, **204**, 377 (1927); THIS JOURNAL, **51**, 1004 (1947).

(28) G. Herdan, "Small Particle Statistics," Elsevier, New York, N. Y., 1953.



Fig. 8.— Specific turbidity of silver bromide sols illuminated by light of 450 m $\mu$  as a function of geometric average radius for three distribution widths.

$$\ln(r_{\rm n}/r_{\rm g}) = 0.5 \, \ln^2 \sigma_{\rm g} \tag{23}$$

A log-normal distribution is determined by three parameters: average size, standard deviation and number of particles per unit volume. If the concentration and particle density are known, only two measurements are needed to fix the three parameters.

The distribution can be calculated from results of transmission measurements at two wave lengths as shown. The turbidity of a heterogeneous distribution is

$$\tau = \pi \sum_{i} n_i r_i^2 K_i \tag{24}$$

where  $K_i$  = scattering coefficient for particles of radius  $r_i$ . The concentration (g./ml.) is given by

$$c = \frac{4\pi D}{3} \sum_{i} n_{i} r_{i}^{3}$$
 (25)

If the log-normal distribution is followed and sums replaced by integrals, the specific turbidity is

$$\frac{\tau}{c} = \frac{3}{4D} \frac{\int_0^\infty f(r) r^2 K \, \mathrm{d}r}{\int_0^\infty f(r) r^3 \, \mathrm{d}r}$$
(26)

where f(r) is defined by eq. 17. Numerical integration of eq. 26 was carried out for several distributions of silver bromide sols, based upon measurements at 450 and 800 m $\mu$  (in air). These wave lengths were found to give distinctly different types of averages for the size ranges under consideration, which is advantageous in determining the parameters of the distribution. Typical



Fig. 9.—Same as Fig. 8, but for 800 m $\mu$ .

curves are shown in Figs. 8 and 9. In use, the experimental value of  $\tau/c$  fixes  $r_g$  for each  $\tau_g$ . When  $\tau_g$  is plotted against  $r_g$  for each wave length, the intersection of the two curves gives both  $r_g$  and  $\sigma_g$  (Fig. 12 vide infra).

#### Experimental

1. Preparation and Handling of Sols.—Stock solutions of potassium bromide and silver nitrate were prepared from reagent grade chemicals dried 2 hours at 105°, dissolved in dust-free conductivity water in polyethylene containers and stored in the dark. A non-dialyzed sol A was prepared according to Kolthoff and Bowers.<sup>29</sup> A dialyzed sol C was prepared as follows. A 25-ml. portion of 0.01100 M potassium bromide (25°) was stirred at 900 r.p.m. in a 250-ml. polyethylene beaker, using a 1-inch right angle stirrer. An equal volume of 0.01000 M silver nitrate was added by pipet during 30 seconds and stirring was continued for 40-50 seconds. (The effect of variations of preparation on particle size is discussed in detail in a separate paper.<sup>30</sup> The sol was transferred to dialysis tubing, shielded from light, and 20 gallons of conductivity water was flowed over the tubing during a 2 day period. The concentration of silver bromide in the dialyzed sol was determined by Liebig's method.<sup>31</sup> Five-ml. aliquots were dissolved in potassium cyanide solution and titrated with 0.01 M silver nitrate to a turbidity end-point which was reproducible to 0.5%. Particle size is all the sols studied in this paper had reached constant values by the time the measurements were made; dependence of size on time is discussed elsewhere.<sup>30</sup> All the suspensions were shaken gently before measurement. Scattering by water was negligible compared to the scattering of the most dilute sols even at 25° from the direction of the incident beam. The sols were kept in the dark except during measurement. Separate experiments showed that photochemical reduction of silver bromide during the measurements was negligible. Further precautions are described in detail elsewhere.<sup>6</sup> Two separate preparations according to method C gave sols of practically identical particle sizes.

2. Optical Measurements.—For turbidity and scattering measurements, sols were diluted to  $10^{-4}$  to  $10^{-5}$ M silver bromide. Experiments described elsewhere<sup>30</sup> show that errors in turbidity and in scattering intensity are less than 3% at these concentrations if extrapolation to infinite dilution is omitted. The corresponding error in particle diameter is less than 2%.

Turbidities were measured over the range 436 to 1000  $m_{\mu}$ , using a Beckman DU spectrophotometer with 1, 5 or 10 cm. cells. Following the recommendations of Heller and Tabibian,<sup>32</sup> the cells were painted black on the outside and all measurements were made in a 10 cm. cell compartment fitted with exactly centered aperture plates of 4 mm. diameter aperture at both ends to limit the forward scattered light received by the phototube. Apertures of various diameters were tested in preliminary experiments. The turbidity of a sol containing particles about 0.1  $\mu$  diameter was independent of aperture diameter below 5 mm.

Angular scattering measurements were made with an Aminco Light Scattering Photometer.<sup>33</sup> The transmission scale was calibrated by measuring the transmission of solutions of potassium chromate.<sup>34</sup> Two types of cylindrical cells were used. One was 2.5 cm. in diameter with ground flats for entrance and exit of the beam.<sup>36</sup> This cell was painted black on bottom and back. The other was 4 cm. in diameter with concentric precision ground walls. The instrument was calibrated with both types of cells using Ludox, following precautions outlined by Goring.<sup>36</sup> Correction for reflection of the incident beam was applied in all measurements.<sup>37</sup>

Consideration of all sources of error indicates that the absolute turbidities and scattering intensities should be reliable within 10%.

Dissymmetry (ratio of intensities scattered at 40 and 140°) was measured at 436 and 546 m $\mu$ . These wave lengths were used also for measurement of the polarization ratio  $i_1(\theta)/i_2(\theta)$  at 80 and 90°.

A portion of sol C was diluted 250-fold with glycerol and the angular scattering and polarization ratio was measured at 546 m $\mu$  (4 cm. cclls). The refractive index ratio of silver bromide in this medium at 546 m $\mu$  was 1.54.

Refractive index increment was measured with a Bryce-Phoenix differential refractometer. For undialyzed sols an aqueous solution having the same concentrations of potassium nitrate and bromide as the sol was used as reference. Because of the relatively high turbidity of the sols, corresponding to the high *m* value, the slit image in the refractometer is relatively poorly defined and the error in the measurement of  $\partial \mu / \partial c$  is relatively large. In the sols studied this error is estimated at 10-20% at 546 m $\mu$ , and 30-100% at 436 m $\mu$ , dependent upon particle size. The observed values in an undialyzed sol (Table II) agree within the experimental error with the values calculated from eq. 10 and independent estimates of diameter (*vide infra*).

### TABLE II

OBSERVED AND CALCULATED REFRACTIVE INDEX INCRE-MENT

Wave length, mµ	436	546
Particle diameter," $\mu$	0.111	C.122
Calcd. refractive in-		
dex increment	0.165	0.145
Measd. refractive in-		
dex increment	$0.129 \pm 0.023$	$0.133 \pm 0.010$
<sup>a</sup> From absolute for	ward scattering at 0°	

(32) W. Heller and R. M. Tabibian, J. Colloid Sci., 12, 25 (1957).

(33) G. Oster, Anal. Chem., 25, 1165 (1953).

(34) G. W. Haupt, J. Research Natl. Bur. Standards, 48, 414 (1952).

(35) L. P. Witnauer and H. J. Sherr, Rev. Sci. Instr., 23, 99 (1952).

(36) D. A. I. Goring, M. Senez, B. Melanson and M. H. Huque, J. Colloid Sci., 12, 412 (1957).

(37) H. Sneffer and J. C. Hyde, Can. J. Chem., 30, 817 (1952).

<sup>(29)</sup> J. M. Kolthoff and R. C. Bowers, J. Am. Chem. Soc., 76, 1503 (1954).

<sup>(30)</sup> E. J. Meehan and W. H. Beattie, to be published.

<sup>(31)</sup> I. M. Kolthoff and V. A. Stenger, "Volumetric Analysis," Vol. II, Interscience Publishers, New York, N. Y., 1950, p. 282.

3. Electron Microscopy.—Particle size determination of silver halides by direct electron microscopy is unreliable because of decomposition in the electron beam. Corhon replicas and collodion-chromium replicas of sol C-2 were prepared.<sup>18</sup> Electron micrographs of the replicas were made using an RCA EMU-2 microscope at 7100  $\times$ magnification, calibrated with an accuracy of 5%. Particle diameters were measured at a total magnification of 106,500 Frequency distributions derived from 415 and 341 Χ.  $\times$ . Frequency distributions derived from 415 and 341 particles (carbon and collodion replicas, respectively) are shown in Fig. 10. An approximate estimate of size distri-bution, less reliable than that obtained from replica micro-graphs, was obtained for sol A; the sol was sprayed onto grids and exposed to direct sunlight to reduce it to silver.<sup>29</sup> Micrographs were made at a total magnification of 15,200  $\times$ . Small particles appeared as nearly round individual silver particles, but many large ones appeared as clusters of round or oblong silver particles with a crust-like outline of the orig-inal particle. The crust-like outline appeared only in electron micrographs of non-dialyzed sols and was probably a mixture of potassium nitrate and potassium bromide from the surface of the original particle. Diameters of single silver residues were measured when possible. For broken particles, the crust-like outline was measured and the diameter estimated. Aggregates of particles could not be interpreted, since broken large particles could not be distinguished from small ones. Plates with aggregates, or many oblong particles were not used. A total of 697 particles was measured, and various average diameters calculated. They were corrected to correspond to silver bromide from the molar volumes of silver bromide and silver.

4. Calculations.—Particle diameter was calculated from transmission measurements at 436 and 546 m $\mu$  by use of eq. 4 and Fig. 1. Angular intensities were extrapolated to zero degrees by plotting log  $1/G \sin \theta vs. \sin^2 \theta/2$  where G = microammeter reading, proportional to  $V_{\theta u}$ . Use of the logarithmic function gave a better straight line than the corresponding linear function. Absolute intensities were calculated from the intercept and calibration constants. Particle diameters were found from eq. 6 and Fig. 2. Transmission measurements at long wave lengths were used to calculate particle weight by extrapolation to infinite wave length, using eq. 9. Refractive index increments were calculated from eq. 10 using the size from transmission measurements at 546 m $\mu$ , assuming that m = 1.70 and density = 6.47 g./ml. Extrapolations are shown in Fig. 11. Particle diameter was calculated from both the slope and the intercept of the plots.

Diameters were calculated also from eq. 7 using data at 436 and 546 m $\mu$ . The refractive index increments were calculated as above and also measured for sol C. Diameters were obtained from dissymmetry using Fig. 3 and from polarization ratio using Fig. 4. Finally, diameters were calculated in three ways from the measurements in glycerol: (1) from the extrapolated value of  $i_1(\theta)$ , via Fig. 2 (m = 1.55); (2) from dissymmetry (Fig. 3), and from polarization ratio using graphs (not shown) for m = 1.55.

5. Sources of Error.—Aside from experimental error in measurement of transmitted or absolute scattered intensity, diameters calculated from any of the measurements discussed in this paper may be affected by some of the following sources of error: interpolation of Mie scattering functions to intermediate values of m and  $\alpha$ , effect of true absorption by silver bromide, deviation from spherical shape, and measurement of refractive index increment. The maximum errors in the interpolation of  $i\theta$  and K (consequently in  $i\theta/\alpha^3$  and  $K/\alpha$  are estimated to be less than 5– 10% for the range of  $\alpha$  under consideration. The corresponding maximum error in  $\alpha$  is 2–5%. The value of mis reliable to better than 1%, which corresponds in most cases to a negligible error in  $\alpha$ . Silver bromide absorbs below 450 m $\mu$ , but the error at 436 m $\mu$  is negligible for diameters in the range considered in this paper. Thus for spheres of 0.075 and 0.15  $\mu$  diameter, the values of specific turbidity  $\tau/c$  at 436 m $\mu$  (see Fig. 1, eq. 4) are, respectively, 0.425  $\times$  10<sup>4</sup> and 2.66  $\times$  10<sup>4</sup>. In a measurement in which  $c = 2 \times 10^{-5}$  g./ml. and l = 10 cm., the values of ln  $I_0/I$ , due to scattering, would be, respectively, 0.85 and 5.32. From the absorption coefficient of fused silver bromide<sup>39</sup> it is calculated that the value of ln  $I_0/I$  at the



Fig. 10.—Size frequency distribution for silver bromide sol C-2. Bars show numbers by electron microscopy of carbon replicas (upper graph), and collodion replicas (lower graph) of silver bromide particles. Curves show log normal distribution calculated from specific turbidities.



Fig. 11.—Extrapolation of reciprocal specific turbidities to infinite wave length for sols A and C-2.

above concentration and path length due to true absorption would be only 0.015.

Sizes determined with the electron microscope are reproducible to  $\pm 5\%$ , and the accuracy is usually better than  $\pm 10\%$ . The fact that number average diameters of the collodion and carbon replicas agreed within 4% (vide infra), indicates that no systematic errors were introduced in making the replicas. Measurement of diameter of the projected image was accurate to 1-2 size classes, the greater error for large and irregular particles. Random errors of this type tend to cancel out in the size classes with many particles. At the large end of the distribution random errors in measurement are considerable. This causes considerably larger error in averages highly dependent upon the number of large particles, than with other type averages. This is eviden, from the increasing deviation between

(39) "International Critical Tables," Vol. V, McGraw-Hill Book Co., New York, N. Y., 1926, p. 270.

<sup>(38)</sup> E. J. Meehan and W. H. Beattie, J. Colloid Sci., 15, 183 (1960).

AVERAGE	PARTICLE SIZ	es by Diffe	ERENT METHO	ODS			
	Sol A		Sol (	Sol C-1		Sol C-2	
Measurement	430 mµ	546 mµ	430 Mµ	540 mµ	430 Mµ	540 mµ	
Specific turbidity	<b>.</b>	0.050	0.55	1 975	0.01	1 15	
$\tau/c \times 10^{-4}$	2.21	0.952	2.77	1,375	2.91	1.40	
Diameter, $\mu$	0.142	0.143	0.151	0.172	0,153	0.175	
Specific scattering (extrapolated to 0°)							
$R_{\theta v}/2c = V_{\theta u}/c \ (2.5 \ cm. \ cell)$	4200	1330	4970	2560	4830	2170	
(4 cm. cell)		• • • • •	5810	2540	5030	2230	
(average)	· · · · ·		5390	2550	4930	2200	
Diameter (from average), $\mu$	0.152	0.159	0,162	0.188	0.169	0.180	
Refractive index increment							
Calcd. $(\partial \mu / \partial c)^2$	0.0281	0.0229	0.027	0.0235	0.0185	0.0236	
Measd. $(\partial \mu / \partial c)^2$			0.0006	0.0185			
Zimm-Dandliker equation							
$2K_1$ using calcd. $(\partial \mu / \partial c)^2 \times 10^7$	9.18	3.01	8.9	3.08	8.8	3.14	
$2K_1$ using measd. $(\partial \mu / \partial c)^2 \times 10^7$			0.02	2.46			
$K_2 \times 10^7$	1.92	2.24	3.01	0.467	3.4	0.52	
$M \times 10^9$ using calcd. $(\partial \mu / \partial c)^2$	7.95	8.30	9.2	14.4	8.1	12.0	
Diameter of corresponding sphere, $\mu$	0.158	0.160	0.165	0.192	0.159	0.181	
$M \times 10^{-9}$ using measd. $(\partial \mu / \partial c)^2$			36	17.4			
Diameter of corresponding sphere, $\mu$			$0.28^{a}$	0.204			
Extrapolation to infinite wave length							
$M \times 10^{-9}$ (from intercept)	6.	7			17		
Diameter of corresponding sphere, $\mu$	0.	149			0.20		
Sphere diameter from slope of plot, $\mu$	0.	18°			0.	32 <b>°</b>	
Dissymmetry	6.55	3.70	12.0	6.8	12.5	7.4	
Diameter, $\mu$	0.133	0.154	0.141	0.171	0.143	0.174	
Diameter from polarization ratio							
At 80°. µ	0.148	0.176	0.155	0.190			
At 90°. µ	0.155	0.184	0.157	0.194	0.157	0.193	
<sup>a</sup> Unreliable, see text.							

TABLE III Average Particle Sizes by Different Method

diameters for collodion and carbon replicas as one progresses down Table V (*vide infra*). It appears that average sizes from the electron microscope are accurate to 10-20% depending upon the type of average.

The effect of deviation from spherical shape and uncertainty in the refractive index increment are discussed later.

### Results

Average diameters derived from all the measurements on silver bromide sols in water and in glycerol are collected in Tables III and IV. The various methods yield different values for heterodisperse systems, which accounts for the difference in some of the results. Table V lists average diameters calculated from electron micrographs, and these values are compared in Table VI with values derived from light scattering which give the corresponding average values. Finally, the distribution of diameters has been estimated from light scattering data, assuming the log normal distribution. From the specific turbidities at 450 and Solution. If four the specific turbulties at 450 and 800 m $\mu$ ,  $r_g$  was obtained for 3 assumed values of  $\sigma_g$  at each wave length (Fig. 8, 9). The values of  $r_g$  are plotted against  $\sigma_g$  in Fig. 12 for sols A and C-2. The results for these sols plus C-1 (not shown in Fig. 12) are given in Table VII. Figure 10 shows the calculated distribution (smooth curve) derived solely from light scattering measurements, compared with the distributions measured in the two replica electron micrographs.

With respect to the value of  $d^3$  (first group of Table VI) the agreement between the values de-

#### TABLE IV

Comparison of Diameters from Scattering in Glycerol and in Water, Sol C-1,  $\lambda$  546 m $\mu$ 

Method	Glycerol	Water
Diameter from scattering extrapld. to $0^\circ$ , $\mu$	0.172	0.188
Diameter from dissymmetry, $\mu$	.161	. 171
Diameter from polarization ratio (80°), $\mu$	. 185	. 190

# TABLE V

AVERAGE DIAMETER CALCULATED FROM

	Diameter, Carbon	Sol C-2, $\mu$	Diameter
Average	replica	replica	Sol A, µ
$\overline{d} = \frac{\Sigma n d}{\Sigma n}$	0.119	0.115	0.078
$\bar{d} = \frac{\Sigma n d^4}{\Sigma n d^3}$	. 149	.166	. 140
$\overline{d^3} = \frac{\Sigma n d^6}{\Sigma n d^3}$	.159	.178	. 153
$\overline{d^4} = \frac{\Sigma n d^7}{\Sigma n d^3}$	.163	.185	
$\overline{d}^{2} = \frac{\Sigma n d^{8}}{\Sigma n d^{6}}$	.18	.21	.18

rived from specific turbidity and electron micrographs is excellent. The specific turbidities at two wave lengths yield the same diameter for sol A, which differs by 8% from the microscope value. The diameter of sol C from specific turbidity at 546 m $\mu$  lies between the two diameters from carbon and collodion replicas, which themselves differ by 11%. No reliable estimate of diameter for this sol can be calculated from specific turbidity at 436 m $\mu$  because (cf. Fig. 6) at this wave length some of the particles are larger than  $\alpha = 1.6$ , and the average does not correspond to  $\sum n_i d_i^{+/}$ .

$$\sum n_{i}d_{i}^{3}$$
.

The diameter obtained by extrapolation to infinite wave length is high for sol C which contains larger particles than sol A. The method is not accurately applicable to such particle sizes, because the condition  $2\alpha(m-1) < 1$  is not fulfilled even at the longest usable wave lengths.

In the second group of Table VI the value of  $d^4$ derived from specific scattering at 0° is in excellent agreement with the diameter from electron micrographs. The diameter for sol C by light scattering lies between the diameters of replicas by electron microscopy. Diameters in sol A by light scattering at two wave lengths are in excellent agreement. The value for sol C at 436 m $\mu$  is unreliable for the same reason given above.

#### TABLE VI

COMPARISON OF AVERAGE SIZES

Type of average	Method	Diame Sol A	ter in µ Sol C
$d^3 = \frac{\Sigma n d^6}{\Sigma n d^3}$	$\frac{\tau}{c}(\lambda 546)$	0.143	0.175
	$\frac{\tau}{c}(\lambda 436)$	.142	( .15)
(Wt. average volume)	Extrapolated to $\lambda = \infty$ Electron microscope	. 149 . 153	. 20 . 159 . 178
$d^{\frac{1}{4}} = \frac{\Sigma n d^{7}}{\Sigma n d^{3}}$	$\left(\frac{V}{c}\right)_{\vartheta=0}(\lambda 546)$	. 159	.180
	$\left(\frac{V}{c}\right)_{\theta=0}(\lambda 436)$	.152	( .15)
	Electron microscope		$\left\{ \begin{array}{c} .163 \\ .185 \end{array} \right\}$
$d^{2,5} = \frac{\Sigma n d^{6,5}}{\Sigma n d^3}$	Zimm–Dandliker eq. (λ 546)	. 160	. 181
$\overline{d^2} = \frac{\Sigma n d^8}{\Sigma n d^6}$	Slope of extrap. to $\lambda = \infty$	.18	.32
	Electron microscope	. 18	$\left\{ \begin{array}{c} .18\\ .21 \end{array} \right\}$
$\overline{d} = \frac{\Sigma n d^4}{\Sigma n d^3}$	$\frac{\tau}{c}$ , for log-normal dis-		
	tribution	.131	.164
(Wt. average diameter)	Electron microscope	. 140	{ .149 } { .166 }

The type average given by the Zimm-Dandliker equation indicates that for the diameters under consideration it should give a diameter about half way between that given by turbidity and angular scattering extrapolated to zero degrees. While the diameter obtained at 546 m $\mu$  is somewhat higher than this, the agreement is good. The value found by application of the Zimm-Dandliker equation at 436 m $\mu$  is considerably in error because of the relatively great experimental uncertainty in the measurement of  $\partial \mu / \partial c$  at this wave length. Also in this connection, the calculation of  $\partial \mu / \partial c$  using eq. 10 and an independent estimate of  $\alpha$  is subject to large error if the distribution of size is not narrow. For wide distributions such that  $\partial \mu / \partial c$  is close to



Fig. 12.—Graphical determination of width parameter,  $\sigma_{g}$ . Solid points are for sol A; open points, sol C-2.

its maximum value, the calculated  $\partial \mu / \partial c$  obviously is higher than the average value (cf. Table II).

The diameter given by the slope of the extrapolation to infinite wave length in sol C is in poor agreement with the electron micrograph diameter, again because the condition  $2\alpha(m-1) <<1$  is not fulfilled. The fact that slopes of lines in Fig. 11 cannot be determined accurately makes matters worse. The agreement of values for sol A undoubtedly is coincidental.

The last group in Table VI gives weight average diameters calculated with the assumption that log normal distributions are followed. The agreement with results of electron micrographs is excellent.

The dissymmetry and polarization ratio methods do not give the same type average over the entire distribution. Diameters by these methods can be compared with each other qualitatively using Fig. 6. Large particles ( $\alpha > 1.9$ ) show decreasing dissymmetry with increasing size. At 436 m $\mu$ , but not at 5 $\pm$ 6 m $\mu$ , the large particles in all three sols are larger than  $\alpha = 1.9$ . Therefore dissymmetries and corresponding calculated sizes are lower at 436 than at 546 m $\mu$ . The discrepancy may also be due in part to the finite angular cone of scattered light received by the phototube.

The same thing happens with polarization ratio at both 80 and 90°. At 90° y-z goes to zero at a larger size than at 80°. Therefore, measurements at 90° have greater contributions from large particles than measurements at 80°. Similarly, with polarization ratio at 80°, y-z goes to zero at a larger size than with dissymmetry. Therefore average sizes of broad distributions at either wave length will have the order

# dissymmetry $< \rho_{80} < \rho_{00}$

This agrees with the order of diameters in Talle III.

All the above considerations of types of average apply for m = 1.70-1.75. In glycerol (m = 1.54) different averages are yielded by the same range of  $\alpha$ . From the Mie scattering functions it is found that in glycerol angular scattering extrapolated to zero degrees gives an average defined by  $\overline{d^3} = \sum_i n_i d_i^{\alpha} / \sum_i n_i d_i^{\beta}$ , up to  $\alpha = 2.0$ . At 546 m $\mu$  the entire distribution of sol C gives this average. This is the same type average given by  $\tau/c$  measurements in water at 546 m $\mu$ . The results (Table IV) are in excellent agreement with this prediction. Dissymmetry and polarization ratio in water and glycerol may be compared qualitatively. Both methods give lower types of averages with decreasing m. Results in Table IV are in agreement with this.

The log-normal distribution calculated for sol C-2 is shown in Fig. 10. Allowing for errors in measurements, the calculated distribution is in good agreement with the distributions by electron microscopy.

All the light scattering data discussed above have been interpreted on the basis that the particles are spherical. From electron micrographs it appears that the small particles actually are spherical, but the larger particles begin to show cubic crystal habit. Only the large particles can cause an error, but they contribute most to light intensity scattered. For particles with  $m \simeq 1$ , the scattering at 0° depends only upon the total weight, and is independent of shape. At increasing angle of scat-tering, the particle shape becomes increasingly important. Relative scattering intensities for discs, spheres and rods are known (cf. ref. 1, Chapter VII). At any angle except 0°, rods and discs scatter more than spheres of the same weight. At high m, the effect of shape is not known in general, but to a first approximation the effect with  $m \simeq 1$ should be followed. This would mean that diameters calculated from angular scattering extrapolated to 0° would have little if any error due to deviation from spherical shape, but diameters from dissymmetry and turbidity should be slightly high.

TABLE VII

PA	RAMETERS OF	LOG NORM	IAL DISTRIBU	JTION
Sul	<i>τ</i> g, μ	σε	<i>d</i> υ, μ	dw,μ
A	0.044	1.40	0.094	0.131
C-1	.051	1.41	. 108	.154
C-2	.059	1.36	. 124	. 164

In order to see whether the relatively small discrepancies between diameters from scattering and the appropriate average from electron micrographs could be due to the effect of deviation from spherical shape, the specific forward scattering and the dissymmetry were calculated for the size distribution of sol C-2 given by electron microscopy. The counts of collodion and carbon replicas were combined to give a large sample. The results were

Function	Calculated	Measured
$V_{\theta u}/c$	1810	2200
Dissymmetry	7.05	7.4

Comparison of results shows that the measured values are about 22 and 5% higher than the respective calculated values. The deviations are opposite to the direction expected for non-spherical particles. Therefore these deviations cannot be attributed to non-spherical shape.

In summary, the results reported here show that reliable estimates of size and size distribution for heterodisperse systems of high refractive index ratio can be obtained by light scattering methods. For suspensions with the values of m and  $\alpha$  studied in the present work, the most suitable methods from the practical viewpoint are specific turbidity and specific scattering extrapolated to zero degrees. Both must be interpreted by use of the Mie theory. Of the two, specific turbidity is preferred because of the simplicity of measurement, the choice of wave lengths, and the instrumental accuracy. Measurements of dissymmetry and polarization ratio are satisfactory only for narrow distributions. The simplicity of these measurements may make them desirable methods in some cases. If concentration is not known, they may be the best methods to determine size.

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# THE INITIAL STAGES OF OXIDATION OF GERMANIUM

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The initial stages of oxidation on a germanium surface freed of combined and adsorbed oxygen by reduction with carbon monoxide at 600° was studied with a vacuum microbalance sensitive to  $\frac{1}{100}$ th of a GeO<sub>2</sub> layer. These experiments were done at an oxygen pressure of 75 mm, and at temperatures from 25 to 400°. The oxidation laws were found to change with temperature and the extent of oxidation. The initial oxygen uptake is consistent with the viewpoint that the surfaces prepared by reduction in carbon monoxide behave as if they are atomically clean. The first oxygen layer, as one oxygen per surface germanium atom forms according to the logarithmic rate law in agreement with the results of Green and Kafalas. Subsequent oxidation beyond the second layer is not logarithmic but obeys a Mott and Cabrera thin film-type equation. At temperatures about 250° the second layer forms in less than one minute. The subsequent oxidation rates beyond the second layer forms in less than one minute. The subsequent oxidation rates beyond the second layer forms in less than one minute. The subsequent oxidation rates beyond the second layer forms in less than one minute. The subsequent oxidation there only GeO<sub>2</sub> is formed, are very slow and even at 400° only 17.5 Å. of GeO<sub>2</sub> formed in three hours. Activation energies for the logarithmic law and for the Mott and Cabrera equations were calculated.

#### Introduction

Most oxidation studies have been concerned with the growth of oxide films on pre-existing thinner films and most theories of oxidation treat such systems.<sup>1</sup> The first stages of oxidation would be concerned with the following problems: given an initial condition a metal surface free of oxide and adsorbed gases, how would the first monolayer of oxide be formed? Would oxygen react with such a surface to produce a monolayer of the oxide directly or would this first layer form by some less direct path? The first experimental answer to these questions was provided by Lanyon and Trapnell<sup>2</sup> in the course of a study of the oxygen uptake by evaporated metal films. It was found that for a number of metals the oxygen first very rapidly formed a monolayer of one oxygen atom per surface metal atom followed by a very much slower formation of a second monolayer of one to two oxygen atoms per original metal surface atom. The rate of formation for the second monolayer was found to be proportional to the square root of the oxygen pressure and the activation energy for the process varied linearly with the uptake of this second monolayer.<sup>3</sup> Cabrera<sup>4</sup> has suggested that this latter slow uptake is due to the formation of a chemisorbed oxygen monolayer which when completed is able to transform by some nucleation mechanism to the first monolayer of the stable oxide upon which the normal oxidation could proceed by the high field Mott and Cabrera<sup>5</sup> mechanism.

The oxygen uptake by clean germanium surfaces which were formed by crushing single crystals *in vacuo*, has been studied by Green, Kafalas and

(5) N. F. Mott, Trans. Faraday Soc., 43, 429 (1947); N. Cabrera, Phil. Mag., 40, 175 (1949); N. Cabrera and N. F. Mott, Rep. Prog. in Phys., 12, 163 (1949). Robinson<sup>6</sup> and for ion bombarded and baked surfaces by Wolsky.<sup>7</sup> Green found that an initial uptake occurred in less than six seconds to form a monolayer of one oxygen atom for every surface germanium atom. This was followed by a much slower rate forming a second layer proceeding according to the logarithmic law.

Since the second layer forms so slowly it was decided to increase the rate by increasing the temperature. By raising the temperature while holding the pressure constant the slowest process will be accelerated and any new phenomenon will be observed in shorter periods of time.

The experiments to be described were carried out with a vacuum microbalance and germanium powder. This technique was chosen because of its direct nature and sensitivity. Further, oxidations with rates which depend on pressure can be followed most conveniently by this technique. The precision of the experiments was 1/300th of a monolayer as the amorphous form of germanium dioxide (6.47  $\times$  15<sup>-11</sup> g./cm.<sup>2</sup>). The germanium surface was freed of oxide by reducing the powder in carbon monoxide at temperatures from 580 to 615°. After outgassing the powder in vacuo, oxygen was admitted to the powder at a pressure of 75 mm, and at temperatures from 25 to  $400^{\circ}$ . The reaction course was followed by measuring the increase in weight of the powder. The powder area was measured by adsorbing nitrogen at 77°K. and applying the BET method. By interspersing an area determination with a reduction and oxidation it was found that the area remained con-Ten oxidations were performed, and stant. throughout the temperature range oxidation was both slow and slight compared to most metals. Even after three hours at 400° an oxide film of only five layers (17.5 Å.) thick was formed.

Initially, in less than one minute, a monolayer of one oxygen atom per surface germanium atom<sup>8</sup> was formed. After this first monolayer a second layer formed following the logarithmic law. The logarithmic law was obeyed up to the completion of this second layer at which point oxidation stopped for a time interval. The time interval was dependent on the temperature of the system. After

<sup>(1)</sup> K. Hauffe, "Oxydation von Metallen und Metallegierungen," Springer-Verlag, Berlin, 1956; T. B. Grimley, "Chemistry of the Solid State, (Ed. W. E. Garner), Academic Press, New York, N. Y., 1955; O. K. Kubaschewski and B. E. Hopkins, "Oxidation of Metals and Alloys," Academic Press, New York, N. Y., 1953.

<sup>(2)</sup> M. A. H. Lanyon and B. M. W. Trapnell, Proc. Roy. Soc. (London), **A227**, 387 (1954).

<sup>(3)</sup> The equation is  $\theta = A \exp[-(\Delta E_0 + \theta \Delta E_1)/RT]$ , where  $\theta$  is the coverage and the  $\Delta E$ 's are activation energies. It is usually referred to as the Elovich, or less commonly as the Roginsky-Zeldovich equation. In its integrated form the equation is  $\theta = \beta \ln (t/t_0 + 1)$  where *t* is time. Hereafter this type of uptake will be called the logarithmic law.

<sup>(4)</sup> N. Cabrera, "Semiconductor Surface Physics," University of Pennsylvania Press, Philadelphia, Penna., 1957, p. 327.

<sup>(6)</sup> M. Green, J. A. Kafalas and P. H. Robinson, ref. 4, p. 349.

<sup>(7)</sup> S. P. Wolsky J. Phys. Chem. Solids, 8, 114 (1959).
(8) Assuming the reduced surface to consist of atoms with [111] layer spacings.

this induction period, the oxidation proceeded at a rate which obeyed the Mott and Cabrera equation.

# **Experimental Technique**

The vacuum microbalance used in this study is a modified version of the apparatus described by Gulbransen.9

Load on the balance in these experiments was about 0.4 g. The sensitivity was  $1.107 \times 10^{-7}$  g./ $10^{-4}$  cm., with a period of 13 seconds. Beam arrests on the frame allowed a total deflection of 2 cm. so that the working range was about 2 mg.

The germanium powder and its counterweight were car-The germanium powder and its counterweight were car-ried on quartz pans. These pans, matched to 20  $\mu$ g., weighed about 125 mg., and were attached to the balance by 60 cm. long, 50  $\mu$  diameter platinum wires. One pan was loaded with 257 mg. of germanium powder. The counterweight pan carried a solid piece of germanium matched in weight to the powder within 20  $\mu$ g. The balance was mounted in a cylindrical glass case pro-vided with quartz hangdown wells. The interior of the

vided with quartz hangdown wells. The interior of the case was coated with a transparent conducting coating of tin oxide. The exterior of the case hangdown wells was coated with Aquadag. Addition of an  $\alpha$ -ray source in the vicinity of the balance and grounding eliminated all static charging.

Damping of oscillatory motions of the beam was accomplished by hanging a Cunife magnet 1 cm. long,  $250 \mu$  in diameter from each hangdown. By activating a solenoid placed around one of the hangdown wells it was possible to stop the most violent motions within 2 to 3 periods

The vacuum system was equipped with a liquid nitro-gen trap filled with copper foil. All gases used passed through this trap before contacting the germanium powder. Liquid nitrogen was maintained around the trap during the course of the entire experiment. A titanium getter bulb was used to reduce the partial pressure of any oxidizing gases in vacuo during the outgassing of the powder prior to admission of oxygen.

Temperatures of the powder were determined by setting up a dummy experiment without the balance. A chromelalumel thermocouple was buried in the germanium powder carried by the silica pan and the temperature in the interior of the powder was compared with the temperature in the annular space between the oven and hangdown well, in vacuo and in the presence of gas. Oven temperatures were maintained with a Foxboro Potentiometer Controller.

Germanium powder was prepared by crushing a 4 ohmcm. N-type crystal with a mortar and pestle. After passing the powder through a 300 mesh screen, the silica pan was loaded and hung on the balance. All the experiments were done on one loading of powder.

The carbon monoxide and oxygen gas used were Air Reduction Company reagent gases.

The powder area was measured by applying the BET method to the adsorption isotherm of nitrogen on the powder at 77° K. as determined by the microbalance. Using 15.4 Å.<sup>2</sup> for the area of adsorbed nitrogen molecule<sup>10</sup> and the BET equation, the powder area was found to be 898  $\pm$  4 cm.<sup>2</sup>. Three separate determinations were made and were interspersed with one to two reductions and oxidations which established the independence of the area on these treatments.

A typical experiment was done in the following manner: the powder was outgassed in a titanium gettered vacuum of from  $3 \times 10^{-7}$  to  $10^{-6}$  mm. at a temperature of 530°. from  $3 \times 10^{-7}$  to  $10^{-9}$  mm, at a temperature of  $30^{\circ}$ . Carbon monoxide was admitted to the powder by way of a copper foil filled trap kept at 77° K. after the vacuum reached its lowest point. At  $530^{\circ}$  GeO volatilizes at a rapid rate so that when it was desired to measure the amount of material lost in a CO reduction the reducing gas was admitted at temperatures below 500°. Carbon monoxide pressures were usually 40 to 100 mm and reduction temperatures ranged from 530 to 615°. The reduction usually began immediately except for some rare instances occurring at the lower temperatures, where the reduction was preceded by an induction period. After a more or less abrupt cessation of weight loss which signalled the end of the reduction, the reduction conditions were maintained for an additional 10 to 20 minutes. The powders always

remained unchanged in weight during this period. After this check the carbon monoxide was pumped out of the system while keeping the powder at the reduction temperaafter the pressure dropped to  $10^{-4}$  mm. The powders did not suffer any further change in weight after evacuating the carbon monoxide. The reduction temperatures were maintained until the vacuum reached its lowest value. After this the powder temperature was dropped to the level desired for the oxidation. The system was allowed around 15 minutes to reach equilibrium after which oxygen was admitted to the powder through the trap at pressures aver-aging 75 mm. The first reading was taken one minute after the admission of oxygen. In order to check on any desorption the oxidation was usually stopped after about three hours by evacuating the system without changing the powder temperature. The powder would remain *in vacuo* until the next experiment whereupon the sequence described would be repeated.

# **Experimental Results**

The results of carbon monoxide cleaning of the germanium surfaces are presented first.

Most of the reductions began with a vacuum bake up to the reduction temperature after which carbon monoxide was admitted. A number of more informative reductions were done that did not include a vacuum bake. In these experiments CO was admitted to the powder at 150°. The temperature then was increased to the reduction temperature. The reduction always started with appreciable velocity at 530° and needed about one hour per monolayer at 580° under the conditions of this experiment. The reduction was assumed terminated when less than  $10^{-7}$  g. weight loss was observed in about 20 minutes. This corresponds to an evaporation rate less than  $10^{-13}$  g./cm.<sup>2</sup>-sec., a value of the order of extrapolated published values for the evaporation rate of germanium at these temperatures.<sup>11</sup>

The appearance of an appreciable reduction rate at 530° is a clue to some of the mechanisms operating in the reduction process. There is a "rule" in solid state chemistry<sup>12</sup> that the lowest temperature at which a solid will be expected to enter a solidstate reaction at an appreciable rate occurs approximately at a temperature one-half the melting point of the solid on the absolute scale  $(T_M)$ . The basis for this rule is that bulk diffusion processes become appreciable at  $0.5T_{\rm M}$  and above. The melting point of  $GeO_2$  in the hexagonal form is  $1389^{\circ}K$ . Then  $0.5T_{\rm M}$  is 421° or greater so that the reduction rate is established by some sort of bulk diffusion reaction at least when more than a monolayer of oxide is involved. A further clue to the reduction mechanism is obtained from a plot of the total weight loss observed on reduction against weight of oxygen on the surface before reduction as in Fig. 1. The points can be represented by two intersecting straight lines. The line of smallest slope has a range of zero to one monolayer of oxide calculated as oxygen in one layer of amorphous oxide and has a slope of unity. This slope would correspond to the reaction

<sup>(9)</sup> E. A. Gulbransen, Rev. Sci. Instr., 15, 201 (1944).

<sup>(10)</sup> H. K. Livingston, J. Colloid Sci., 4, 447 (1949).

<sup>(11)</sup> S. Dushman, "Vacuum Technique," John Wiley and Sons, Inc.,

<sup>(12)</sup> A. J. E. Welsch, "Chemistry of the Solid State," Academic Press, Inc., New York, N. Y., 1955, p. 307; A. L. G. Rees, "Chemistry of the Defect Solid State," John Wiley and Sons, Inc., New York, N. Y. 1955, p. 307; A. L. G. Rees, "Chemistry of the Defect Solid State," John Wiley and Sons, Inc., New York, N. Y. 1955, p. 307; A. L. Sons, Inc., New York, N. Y. 1955, p. 307; A. L. Sons, Inc., New York, N. Y. 1955, p. 307; A. L. Sons, Inc., New York, N. Y. 1955, p. 307; A. L. Sons, Inc., New York, N. Y. 1955, p. 307; A. L. Sons, Inc., New York, N. Y. 1955, p. 307; A. Sons, Inc., New York, N. N. Y., 1955, p. 120.

$$1/_{2}GeO_{2}(s) + CO(g) = 1/_{2}Ge(s) + CO_{2}(g)$$

That is, the oxygen in the germanium dioxide is being lost to the carbon monoxide. The line of larger slope ranging from one monolayer of oxide as oxygen and up has a slope of 5.54 and corresponds to the reaction

$$\frac{1}{2}Ge(s) + \frac{1}{2}GeO_2(s) = GeO(g)$$

so that the oxygen is being lost as germanium monoxide

$$M_{\rm GeO_2}/M_0 = 88.6/16 = 5.54$$

The reduction mechanism in these thin oxide films appears to be a reaction between carbon monoxide and the outer layer of germanium dioxide to form germanium and carbon dioxide. Germanium freed by this reduction reacts with the underlying dioxide to form germanium monoxide which is volatile at these temperatures. Simultaneously, there must be a diffusion of germanium from the germanium-oxide interface through the oxide film to replenish the germanium atoms lost at the germanium monoxide generating interface. Therefore, this layer of germanium must act as a barrier to the further action of carbon monoxide.

Nothing has been said that precludes the possibility of obtaining an oxygen-free germanium surface from a simple vacuum bake by virtue of the solid-state germanium-germanium dioxide reaction. A vacuum bake at 500° was tried before the titanium getter bulb was added to the vacuum system. A calculated pressure of oxygen of  $4 \times 10^{-10}$  mm. was found to be sufficient to account for an observed weight loss at the rate of  $1.2 \times 10^{-11}$  g./ cm.<sup>2</sup>-sec. Upon the admission of oxygen, the germanium surface was found to be covered to the extent of one-half of a monolayer of oxygen as one oxygen atom per surface germanium atom. A higher temperature, say above 530°, and a lower partial pressure of oxygen than used in the above experiment might be sufficient conditions to attain an oxygen free germanium surface.

On completion of the CO reduction, it was found necessary to outgas the germanium at the reduction temperature, since if the powders were cooled in the CO atmosphere there was a chemisorption of the monoxide. At the end of the reduction, while at the reduction temperature, there was no change in weight observed on pumping out the carbon monoxide.

The takeup of pure dry oxygen at average pressures of 75 mm. and at ten different temperatures ranging from 25 to 400° by the carbon monoxide reduced surface is shown in Fig. 2. The ordinate, weight of oxygen taken up by the surface, is the change of weight of the powder in oxygen from the vacuum condition. The layer coverages indicated are for the amorphous form of the oxide.

Some checks were made to see if any part of the oxygen uptake was desorbable from oxidations that had formed more than one layer of germanium dioxide. This was done by pumping out the oxygen from the oxidizing powder while maintaining the powder temperature. No weight loss to within  $1.23 \times 10^{-10}$  g./cm.<sup>2</sup> (1/300th of a monolayer as molecular oxygen) was observed in passing from 75 mm. of oxygen to a  $10^{-6}$  vacuum. Further



Fig. 1.—Total weight loss observed on reduction of GeO<sub>2</sub> on germanium by CO as a function of the amount of  $GeO_2$  on the surface.

no weight loss of this magnitude occurred in 15 minutes at  $360^{\circ}$  or in 30 minutes at  $310^{\circ}$ . Any sorbed oxygen might therefore be present to an extent less than this figure or the activation energy for desorption might be larger than 50 kcal./mole. This latter possibility is not too remote in view of the large activation energies (45 to 200 kcal./mole) for desorption which have been found for other systems.<sup>13</sup> However, if the same experiment were done before the oxygen taken up amounted to one layer of GeO<sub>2</sub>, most of the oxygen with the exception of about one-half of a monolayer could be removed by vacuum baking at temperatures of  $530^{\circ}$ .

#### Discussion

The oxygen takeup at 25° agrees in rate and magnitude with the vacuum crushed single crystal experiments of Green, Kafalas and Robinson<sup>6</sup> and with the argon bombarded germanium surfaces of Wolsky.<sup>7</sup> These rates are shown in Table I.

#### TABLE I

Slow oxygen uptake by germanium at room temperature

$$q = a \log t + o$$

where  $q = \text{oxygen atoms/cm.}^2$ ; t = minutes

(a) Present study: 
$$25^{\circ}$$
; 66 mm. of  $O_2$ . CO reduced

$$q = 1.09 \times 10^{14} \log t + 7.70 \times 10^{14}$$

(b) Green, Kačalas and Robinson<sup>6</sup>: 25°, 0.1 mm. of O<sub>2</sub>. Vacuum crushed.

 $q = 1.43 \times 10^{14} \log t \times 8.4 \times 10^{14}$ 

(c) Wolsky':  $25^{\circ}$ ; 3 mm. of  $O_2$ . Ion bombarded

$$q = 0.948 \times 10^{14} \log t + 8.88 \times 10^{1}$$

25°; 0.1 mm. of  $O_2$ . Ion bombarded

$$q = 1.31 \times 10^{14} \log t + 6.12 \times 10^{14}$$

A useful representation of the oxidation data is on a semilog plot with time on the logarithmic scale. Figure 3 shows the results of oxidation at 25, 150 and  $\pm 00^{\circ}$  on such a plot. The oxidation

(13) B. M. W. Trapnell, "Chemisorption," Academic Press. Inc., New York, N. Y., 1955, p. 79 ff.



Fig. 2.—The oxidation of Ge, from a carbon monoxide reduced surface, in pure oxygen at 10 different temperatures. The average oxygen pressure is 75 mm. The layer coverages as amorphous GeO<sub>2</sub> are indicated on the ordinate.

law is logarithmic in time between  $1.94 \times 10^{-8}$ and  $3.88 \times 10^{-8}$  g. of oxygen/cm.<sup>2</sup>. These numbers represent coverages of one and two oxygen atoms per surface germanium atom, respectively, in the [111] plane. After the oxygen uptake passes the latter value, the rate of uptake incre ses and is no longer logarithmic in time. Clearly after the state of two oxygen atoms per surface germanium atom has been reached, there is a profound change in the nature of the oxidation process.

The logarithmic rate can be derived by assuming a process with an activation energy that changes linearly with the extent of coverage, that is, as

$$\Delta E = \Delta E_0 + \frac{q - q_0}{q_0} \Delta E_1$$

In differential form this rate is

$$\dot{q} = A' \exp(-\Delta E_0/RT) \exp\left[-\frac{\Delta E_1}{q_0 RT} (q - q_0)\right]$$

Here

- $\dot{q}$  = rate of uptake in oxygen atoms/cm.<sup>2</sup>-min.
- $q = \text{amount of oxygen taken up in atoms/cm.}^2$
- $q_0 = 7.31 \times 10^{14}$  atoms/cm.<sup>2</sup>, the concn. of atoms in the [111] plane A' = a constant

 $\Delta E_0$  and  $\Delta E_1$  are the activation energies, the other symbols having their usual significance.

On admitting oxygen to the germanium, there is a fast takeup in time t' to form a layer of  $q_0$  oxygen atoms/cm.<sup>2</sup>. After this first stage is completed the logarithmic uptake begins. Using these boundary conditions, equation 1 integrates as

$$q = \frac{1}{a} \ln \left[ aA(t - t') + 1 \right] + q_0 \tag{1}$$

with  $A = A' \exp(-\Delta E_0/RT)$  and  $a = \Delta E_1/q_0RT$ . Defining  $t_0 = 1/aA$ 

$$q = \frac{1}{a} \ln \left[ (t - t') + t_0 \right] - \frac{1}{a} \ln t_0 + q_0 \qquad (2)$$

If t >> t' and  $t_0$ , equation 2 corresponds to the experimental result and on the semilog plot the

$$q = B \log t + C \tag{3}$$

intercept at t = 1 minute will be  $-2.303/a \log t_0 + q_0$  and the slope will be 2.303/a. Knowing the value of a the constant A in equation 1 can be found from the intercept C using the relationship  $t_0 = 1/aA$ . Since  $a = \Delta E_1/q_0RT$  a plot of  $aq_0$  against 1/T will yield a line whose slope is  $\Delta E_1/R$  if  $\Delta E_1$  is not a function of temperature. The other

activation energy  $\Delta E_0$  is obtained by plotting ln A against 1/T. The slope of this plot will be  $\Delta E_0/R$ and the intercept is  $\ln A'$ .

In general, equation 2 is not linear on the semilog plot when data are available for times smaller than  $t_0$ . For times greater than  $t_0$  the plots will be linear and equation 3 can be used directly.

Data on the logarithmic rate cast in terms of equation 3 are shown in Table II.

# TABLE II

PARAMETERS FOR THE LOGARITHMIC EQUATION AT DIFFER-ENT TEMPERATURES

( <i>t</i> >	1 min.); $q(\max.) = 14.62 \times 10^{14}$ atom $q = B \log t + C$	ns/cm.²
°C.	q (oxygen atoms/cm. <sup>2</sup> ), $t$ (min.)	Po₂ (mm.)
25	$1.09  imes 10^{14} \log t + 7.70  imes 10^{14}$	66
50	$1.23  imes 10^{14} \log t + 8.26  imes 10^{14}$	75
100	$1.46 \times 10^{14} \log t + 9.83 \times 10^{14}$	76
125	$1.49 \times 10^{14} \log t + 10.3 \times 10^{14}$	81
150	$1.58 \times 10^{14} \log t + 11.8 \times 10^{14}$	79
200	$1.78 \times 10^{14} \log t + 12.1 \times 10^{14}$	77

By applying the above analysis to the parameters of Table I the two activation energies in equation 1 can be found. The two activation energies and the constant A' are found to be

Further  $\Delta E_1/q_0 = 1.19 \times 10^{-11}$  cal.-cm.<sup>2</sup>/atom so that equation 1 becomes

$$\dot{q} = 3.67 \times 10^{21} \exp\left(-\frac{10,300}{RT}\right) \\ \exp\left[-\frac{1.19}{RT} \times \frac{10^{-11}}{R} (q - q_0)\right] \quad (4)$$

with  $q_0 = 7.31 \times 10^{14}$  atoms/cm.<sup>2</sup> and R is the gas constant 1.987 cal./°K./g.-mole.

Green, Kafalas and Robinson<sup>6</sup> report the result of an experiment at 60.5 mm. and  $25^{\circ}$ , the pressure changes being measured with a differential oil manometer. The over-all uptake was found to be 2.4 oxygen atoms/cm.<sup>2</sup> after 18 minutes of exposure with no further measurable takeup up to 2 days.

Similar results were obtained during the earlier stages of the present study before suitable precautions were taken to ensure the exposure of the powders to only dry pure oxygen. It is believed this type of takeup is real and catalyzed by moisture.

The logarithmic rate was obeyed at temperatures from 25 to 250°, up to a coverage of  $3.82 \times 10^{-8}$  g. of oxygen/cm.<sup>2</sup> ± 1% (two oxygen atoms per surface germanium atom in the [111] plane would weigh 3.88  $\times$  10<sup>-8</sup> g./cm.<sup>2</sup>) after which a new oxidation law is obeyed. This behavior is shown for one temperature, 150°, in Fig. 3. The transition appears to have associated with it a time-lag in the oxidation process. That is, when the state of two oxygen atoms per germanium surface atom has been reached, the oxygen uptake ceases for a time dependent on the temperature of the experiment. If this transition marks a change in the state of the surface germanium atoms and bound oxygen atoms, an event such as a time-lag in the oxidation rate is not too unlikely and would be



Fig. 3.-Germanium oxidation at 25, 150 and 300° on a semilog plot.

associated with some nucleation process for the formation of the first monolayer of the normal germanium dioxide. This time-lag could correspond to the time necessary to transform a layer of oxygen atoms chemisorbed to the germanium surface to a monolayer of germanium dioxide "molecules." The observed time-lags are 40 minutes, between 100 and 140 minutes at 125°; 15 minutes, between 40 and 55 minutes at 150°; 3 minutes, between 18.2 and 21.2 minutes at 200° and 0.7 minute, between 3.8 and 4.5 minutes at  $250^{\circ}$ . If the time-lag is taken as inversely proportional to a rate of nucleation, the process will have associated with it an activation energy of 13.4 kcal./mole.

The oxidation rates occurring after the formation of the first monolayer of oxide might be expected to be described by the equations of Mott and Cabrera<sup>5</sup> for very thin film metal oxidations. Since germanium is not a metal but a semiconductor, we should not expect their equations to hold in every detail.

Mott and Cabrera assumed the rate-controlling step in the thin film region at low temperatures to be a drift of ions in a high field rather than by the thermal diffusion of those ions. Electrons can tunnel through very thin films to form adsorbed oxygen ions at the oxide-gas interface. These electrons leave behind metal ions of charge Zeat the metal-exide interface. This separation of charges effects a potential difference V across the film which is assumed to be independent of temperature and oxide film thickness. The resultant field in the film of thickness X is V/X. The activation energy  $\Delta U$ , assumed to be a constant, for the pas-



Fig. 4.—A test of the Mott and Cabrera equation for thin film oxidations against the germanium oxidation data.



Fig. 5.—Dependency of the logarithm of the pre-exponential constant  $\omega$  of the Mott and Cabrera equation on the reciprocal of the absolute temperature for germanium oxidations. The slope of the plot is  $-\Delta U/4.58R$  where  $\Delta U$  is the activation energy term in the Mott and Cabrera equation.

sage of the metal ion from the metal-oxide interface into the first interstitial position for the ion in the oxide, is lowered by the high field according to  $\Delta U - ZeX_0V/X$  where  $X_0$  is one-half the jump distance for the ion. Because of this lowering, oxidations can proceed at relatively low temperatures. The probability per second that a metal ion will experience a jump is  $\nu \exp(-\Delta U/RT + ZeX_0V/XkT)$  where  $\nu$  is the frequency of vibration of a metal ion at the oxide-metal interface. Then the rate of growth of the film is

$$\frac{\mathrm{d}X}{\mathrm{d}t} = n\Omega\nu \exp(-\Delta U/RT) \exp(ZeX_0V/XkT) \quad (5)$$

.

or

$$\frac{\mathrm{d}X}{\mathrm{d}t} = \omega \exp(\lambda/X) =$$

$$\omega_0 \exp(-\Delta U/RT) \exp(\lambda/X) \quad (6)$$

where *n* is the concentration of ions at the metaloxide interface,  $\Omega$  is volume of oxide per metal ion and  $\lambda = ZeX_0V/kT$ .

Equations 5 and 6 cannot be integrated easily in closed form; the experimental data were therefore differentiated to compare experimental results with the Mott and Cabrera equation. This was done graphically from the semilog plots. Equation 6 can be recast as

$$X \log \frac{\mathrm{d}X}{\mathrm{d}t} = X \log \omega + \lambda/2.303 \tag{7}$$

If an experimental plot of  $X \log dX/divs$ . X is made the slope will be  $\log \omega$  and the intercept at X = x,  $\lambda/2.303$ . This is done in Fig. 4 for six temperatures. For the range of thickness available, the experimental points are linear in such a plot so that the Mott and Cabrera equation appears to hold.

The experimental parameters for equation 6 are given in Table III. It was assumed the oxidation creates the amorphous form of germanium dioxide. The "monolayer thickness" for this substance is  $(M/\rho N)^{1/3} = (104.6/3.637 \times 6.023 \times 10^{23})^{1/3} =$  $3.66 \times 10^{-8}$  cm./monolayer. The gravimetric factor to convert this figure to weight as oxygen is  $3.97 \times 10^{-8}$  g./cm.<sup>2</sup>/monolayer.

TABLE III

PARAMETERS FOR THE MOTT AND CABREBA EQUATION

Т, ⁰К.	$\omega$ , cm./min.	λ, cm.
673	$2.08 \times 10^{-11}$	$43.1 \times 10^{-8}$
623	$3.94  imes 10^{-12}$	$40.5 imes10^{-8}$
573	$2.10  imes 10^{-12}$	$31.8 \times 10^{-8}$
523	$5.65  imes 10^{-13}$	$26.3 imes10^{-8}$
473	$3.13  imes 10^{-13}$	$22.6 imes10^{-8}$
423	$1.72  imes 10^{-13}$	$20.5 \times 10^{-8}$

Since  $\lambda = ZeX_0V/kT$ , a value for V can be calculated from the values of  $\lambda$  and T given in Table II by taking Z = 4 and  $X_0 = 1.83 \times 10^{-8}$  cm. The results of this calculation are shown in Table IV.

TABLE	τv
INDDD	11

V OF THE MOTT AND CABRERA EQUATION AS A FUNCTION OF TEMPERATURE FOR GERMANIUM OXIDATIONS

<i>т</i> , °К.	V. v.	<i>T</i> , °K.	Γ, ν.
673	0.350	523	0.166
623	. 304	473	. 129
573	.220	423	. 105

Thus, V is found to exhibit a temperature dependency, the potential becoming larger as the temperature of the oxidation rises. There is, however, no dependency of the potential on the oxide film thickness in view of the linearity of the plots of Fig. 4.

A plot of  $\log \omega vs. 1/T$  is shown in Fig. 5. If  $\Delta U$  were a constant, this plot would be a straight line with a slope of  $\Delta U/R$ . The curvature in this plot means that the activation energy  $\Delta U$  is not a constant.  $\Delta U$  has a temperature dependency and its value increases as the temperature increases.

# RADIOLYSIS OF CHLOROFORM AND CARBON TETRACHLORIDE

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Irradiation of pure degassed CHCl<sub>3</sub> with cobalt-60 gammas results in the formation of HCl with  $G_{\text{HCl}} = 11.4 \pm 0.4$ . C<sub>2</sub>Cl<sub>6</sub> and a liquid which boiled at approximately 165° also are produced. No H<sub>2</sub> or Cl<sub>2</sub> was observed and these must be formed with efficiencies of  $G_{\text{H2}} < 0.003$  and  $G_{\text{Cl}_2} < 0.002$ . The irradiation of pure degassed CCl<sub>4</sub> results in the formation of Cl<sub>2</sub> with  $G_{\text{(Cl}_2)} = 0.66 \pm 0.4$ . A solid which is essentially pure C<sub>2</sub>Cl<sub>6</sub> is the only other observed product. No Cl<sub>2</sub> is produced in mixtures of CHCl<sub>4</sub> and CCl<sub>4</sub> in which  $N_{\text{CHCl}_3}$  is greater than  $\cong 0.008$  at a dose of  $1.06 \times 10^{21}$  e.v. per gram of mixture. HCl yields from CCl<sub>4</sub>-CHCl<sub>3</sub> mixtures indicate that an important part is played by energy transfer in this system.

Schulte, Suttle and Wilhelm<sup>1</sup> have studied the  $\gamma$ induced decomposition of CHCl<sub>3</sub> in the presence of O<sub>2</sub>. Cl<sub>2</sub>, HCl, COCl<sub>2</sub> and one or more peroxides were the major products. No definite conclusion regarding the mechanism of the reaction could be made. Their results, however, suggested the possible use of chloride production from this system as a dosimeter.

Hill<sup>2</sup> studied the gas phase decomposition of pure CHCl<sub>3</sub> in a flow system by light of 1935 to 2100 Å. He observed only HCl as a product, the yield corresponding to a quantum yield of 4. He proposed the series of reactions 1 through 4 to explain his results.

$$\begin{array}{c} \mathrm{CHCl}_{a} \longrightarrow \mathrm{CCl}_{a} + \mathrm{H} & (1) \\ \mathrm{CHCl}_{a} \longrightarrow \mathrm{CHCl}_{2} + \mathrm{Cl} & (2) \\ \mathrm{H} + \mathrm{CHCl}_{a} \longrightarrow \mathrm{CHCl}_{2} + \mathrm{HCl} & (3) \end{array}$$

$$Cl + CHCl_3 \longrightarrow CCl_3 + HCl$$
 (4)

Schulte<sup>3</sup> has studied the  $\gamma$ -induced decomposition of CCl<sub>4</sub> and the simultaneous exchange of Cl between Cl<sub>2</sub> and CCl<sub>4</sub>. Cl<sub>2</sub> was produced with  $G_{(Cl_2)} =$ 0.80 and C<sub>2</sub>Cl<sub>6</sub>, the only other observed product, was formed with essentially the same yield. The *G*value for the  $\gamma$ -induced exchange,  $G_{ex} = 3.5$ , was assumed to equal  $G_{(Cl)}$  and  $G_{(CCl_4)}$ . We have measured the HCl production from de-

We have measured the HCl production from degassed CHCl<sub>3</sub>, the Cl<sub>2</sub> production from degassed CCl<sub>4</sub>, and the HCl production from degassed  $CCl_4$ -CHCl<sub>3</sub> mixtures.

# Experimental

**Reagents.**—"Baker Analyzed" reagent grade CHCl<sub>3</sub> and CCl<sub>4</sub> were dried with anhydrous calcium chloride and distilled through a Widmer type fractionating column. A middle fraction comprising roughly 1/3 of the starting material was used for the sample preparations.

**Sample Preparation**.—Pyrex irradiation cells of approximately 20 cc. volume containing the samples of  $CHCl_{a}$ ,  $CCl_{4}$  and the  $CCl_{4}$ –CHCl<sub>3</sub> mixtures were degassed by several cycles of freezing, pumping and thaving on a vacuum line and sealed off. The amount of each sample (roughly 15 g.) was determined from the weight difference between the empty and filled cell.

HCl Analysis.—In order to determine the amount of HCl formed, the irradiated cell was broken under an excess of 0.1 N NaOH solution in a 100-ml. ground glass stoppered cylinder. The solution was well shaken for several minutes, transferred to a beaker, and the excess NaOH was back titrated with 0.1 N HCl to a pH of 6.6. Cl<sub>2</sub> Analysis.—For Cl<sub>2</sub> measurement, the irradiated cell

Cl<sub>2</sub> Analysis.—For Cl<sub>2</sub> measurement, the irradiated cell was broken under an acidie solution of KI in a 100-ml. ground glass stoppered cylinder. After shaking for several minutes, the solution was transferred to a 250-ml. flask and the  $l_2$  was titrated with a 0.01 N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution using starch as an indicator.

(1) J. W. Schulte, J. F. Suttle and R. Wilhelm, J. Am. Chem. Soc., **75**, 2222 (1953).

(2) D. G. Hill, ibid., 54, 32 (1932).

(3) S. W. Schulte, ibid., 79, 4643 (1957).

 $\rm H_2$  Analysis.—Attempts to measure  $\rm H_2$  produced in the reaction were made by the Saunders-Taylor technique.<sup>4</sup> Radiation Source.—Irradiations were carried out at 22  $\pm$ 

**Radiation Source.**—Irradiations were carried out at  $22 \pm 2^{\circ}$  in a cobalt-60 source of the type described by Burton, Ghormley and Hcchanadel.<sup>5</sup> This source contained chambers affording dose rates of 404, 240 and 170 kr./hr., as determined on March 1, 1959, on the basis of Fe<sup>+2</sup>-Fe<sup>+3</sup> dosimetry. The experiments were carried out during the period from December, 1956, to January, 1960, and appropriate corrections were made for intensity changes over this period. The source was so designed that the radiation field in the chamber of highest intensity was everywhere uniform to within 3%. The energy distribution was less uniform in the chambers of lower intensity.

### Results

Radiolysis of CHCl<sub>3</sub>.—Production of HCl from pure degassed CHCl<sub>3</sub> is directly proportional to the amount of energy absorbed to at least  $2 \times 10^{21}$  e.v. per gram of  $CHCl_3$  and is essentially independent of the intensity. The *G*-value for HCl production is  $G_{(HCl)} = 11.4 \pm 0.4$ . Evaporation of the CHCl<sub>3</sub> from a sample which had been subjected to a total dose of  $2.5 \times 10^{22}$  e.v. per gram left a solid and a liquid as a residue. The liquid phase (containing a small amount of the dissolved solid) boiled at 165°. The complexity of the infrared spectrum of the liquid phase prevented the definite characterization of any component. The spectrum and the boiling point, however, suggest the presence predominantly of 2-carbon compounds containing C-H and C-Cl linkages. The solid upon resublimation exhibited a sealed tube transition temperature of  $180.5^{\circ}$ . An infrared spectrum of the solid showed peaks identical to those characteristic of  $C_2Cl_6$ .

No H<sub>2</sub> or Cl<sub>2</sub> was observed by our analytical techniques. Upper limits for the production of these species were therefore set at  $G_{(H_2)} < 0.003$  and  $G_{(Cl_2)} < 0.002$ .

**Radiolysis of CCl<sub>1</sub>.**—The production of Cl<sub>2</sub> from pure, degassed CCl<sub>4</sub> is linear to at least  $3 \times 10^{21}$ e.v. per gram and is also independent of intensity. The *G*-value for Cl<sub>2</sub> production is  $0.66 \pm 0.04$ . A solid remaining upon evaporation of CCl<sub>4</sub> from a sample receiving a total dose of  $3.4 \times 10^{22}$  e.v. per gram exhibited a sealed tube transition point of  $179.5-181^{\circ}$ . After resublimation the transition temperature was  $184-185^{\circ}$ . The infrared spectrum of the resublimed material was identical with that for pure C<sub>2</sub>Cl<sub>6</sub>.

The Effect of Added CHCl<sub>2</sub> on  $G_{(Cl_2)}$  from CCl<sub>4</sub>.—A small concentration of CHCl<sub>3</sub> markedly decreases  $G_{(Cl_2)}$  from CCl<sub>4</sub>. Table I lists the results

(4) K. W. Saunders and H. H. Taylor, J. Chem. Phys., 9, 616 (1941).

 M. Burton, J. H. Ghormley and C. J. Hochanadel, Nucleonics, 13, No. 10, 74 (1955). of a series of experiments in which small quantities of CHCl<sub>3</sub> were added to CCl<sub>4</sub> prior to irradiation. The samples received  $1.06 \times 10^{21}$  e.v. per gram of mixture.

TABLE I

EFFECT OF ADDED CHCl <sub>3</sub>	ON $G_{(Cl_2)}$ from $CCl_4$
Mole fraction CHCla	$G_{(C)_2}$
0.0000	0.66
.0032	.36
.0064	.11
.0192	.00

The first three results of Table I were used to estimate the minimum mole fraction of CHCl<sub>3</sub> for which  $G_{(Cl_3)} = 0$ . This was found upon extrapolation to be  $N_{CHCl_1} = 0.0080$ . If no Cl<sub>2</sub> were formed until all of the CHCl<sub>3</sub> was consumed by reaction 4, the number of CHCl<sub>3</sub> molecules initially present per gram of mixture at this concentration could be equated to the number of chlorine atoms produced per gram of mixture at this dose. Such an assumption would permit an estimation of  $G_{(Cl)}$ the 100 e.v. yield for chlorine atoms which would not normally recombine with the parent radical. On this basis we obtain  $G_{(Cl)} \sim 3.0$ . Since this estimation assumes 100% efficiency for CHCl<sub>3</sub> as a scavenger, the value so obtained would be a maximum. This calculation is mentioned because of the qualitative agreement with the value  $G_{(Cl)} =$ 3.5 obtained by Schulte from exchange studies.

**Production of HCl from CCl<sub>4</sub>-CHCl<sub>3</sub> Mixtures.**— In Table II are summarized the results of a series of experiments in which the HCl produced from mixtures of CHCl<sub>3</sub> and CCl<sub>4</sub> was determined.

TABLE II

HCl PRODUCTION FROM CCl<sub>1</sub>-CHCl<sub>3</sub> MIXTURES

Weight % CHCla	E.v. absorbed per g. of mixture	Molecules of HCl per g. of mixture	Geneba	Genenceia
1.46	$7.18 imes10^{20}$	$3.65 imes10^{19}$	5.08	5.00
2.73	7.77	4.12	5.29	5.12
3.37	7.83	4.12	5.26	5.03
3.93	7.80	4.48	5.74	5.50
25.2	7.81	6.12	7.83	6.54
36.1	7.79	6.21	7.97	5.88
42.8	7.82	6.49	8.28	5.80
54.7	7.83	6.85	8.73	5.30
73.8	7.91	7.44	9.40	3.20
81.7	7.81	7.55	9.68	2.63
86.8	7.95	7.85	9.86	-1.50
93.2	7.77	7.89	10.15	-7.20

<sup>a</sup> Based upon total energy absorbed per gram of mixture. <sup>b</sup> Assuming that energy absorbed by CHCl<sub>1</sub> results in a production of HCl with  $G_{(\rm HCD)} = 11.4$  in all mixtures.

The  $G_{(\text{HCl})}$  values listed in column 4 are based upon the total energy absorbed per gram of mixture. The values in column 5 are apparent contributions to the total HCl production resulting from energy absorbed by CCl<sub>4</sub>. They were obtained by calculating from electron density ratios the fraction of the total energy absorbed per gram by CHCl<sub>3</sub>. The HCl produced from CHCl<sub>3</sub> was then obtained by assuming the value of  $G_{(\text{HCl})} = 11.4$  to apply in the mixtures as well. The difference between this and the total HCl was, on the basis of this assumption, the result of energy absorption by CCl<sub>4</sub>.

# Discussion

The observation that only HCl and a complex higher boiling residue comprised partially of  $C_2Cl_6$ are produced from the radiolysis of CHCl<sub>3</sub> is consistent with a mechanism involving reactions 1 through 4 followed by reactions of the type

$$2\text{CCl}_3 \longrightarrow \text{C}_2\text{Cl}_6 \tag{5-a}$$

$$2\text{CHCl}_2 \longrightarrow \text{CHCl}_2\text{CHCl}_2 \tag{5-b}$$

Our value for  $G_{(Cl_{2})}$  from the radiolysis of CCl<sub>4</sub> is significantly lower than that obtained by Schulte. We have no explanation for this difference. The occurrence of C<sub>2</sub>Cl<sub>6</sub> as the only other measurable product indicates, in agreement with Schulte, that the most important steps involved in the reaction are

$$\operatorname{CCL} \xrightarrow{\operatorname{w}} \operatorname{CCl}_3 + \operatorname{Cl} \tag{6}$$

$$2Cl \longrightarrow Cl_2 \tag{7}$$

$$2001_2 \longrightarrow 0_201_6 \tag{8}$$

It is interesting to note the marked difference in the values of  $G_{(HCl)}$  from CHCl<sub>3</sub> and  $G_{(Cl_7)}$  from CCl<sub>4</sub>. An inherently greater susceptibility of CHCl<sub>3</sub> to bond rupture as a result of energy absorption or ionization is an obvious possible reason for this difference. A more probable explanation, however, is that every H or Cl atom produced from CHCl<sub>3</sub> is formed in the immediate vicinity of a potential reactant partner, *i.e.*, another CHCl<sub>3</sub> molecule. By contrast, Cl<sub>2</sub> is most probably formed from CCl<sub>4</sub> by either of two mechanisms. One involves reaction 7 which requires the escape of a Cl atom from the parent radical and combination with other CCl<sub>3</sub> radicals until it combines with another Cl atom. The second involves the reaction 9, which

$$Cl + CCl_4 \longrightarrow Cl + CC._3$$
 (9)

because of a relatively high activation energy<sup>6</sup> is unlikely for Cl atoms with a normal energy distribution at this temperature but may be important if highly energetic chlorine atoms are produced. The activation energy for reaction 4 has been measured<sup>7</sup> as 8 kcal. per mole. An experimental value is not available for the activation energy of reaction 3.

Our results concerning the production of  $\text{Cl}_2$  from dilute solutions of  $\text{CHCl}_3$  in  $\text{CCl}_4$  and those of Schulte involving the radiation induced exchange of Cl between  $\text{Cl}_2$  and  $\text{CCl}_4$  indicate that the value for  $G_{(\text{Cl})}$  is within the range of 3–3.5. The HCl yields from mixtures of  $\text{CHCl}_3$  and  $\text{CCl}_4$  at high concentrations of the latter indicate a contribution by  $\text{CCl}_4$ somewhat greater than that expected from the above value for  $G_{(\text{Cl})}$ . This most probably is due to a reaction of Cl atoms which normally would recombine with the parent radicals with  $\text{CHCl}_3$  molecules since the latter are present in concentrations greater than 1.9 mole %.

The assumption that  $G_{(I|C|)}$  from CHCl<sub>3</sub> is 11.4 in the mixtures is made only for computational purposes. This value would be modified as a result of any interactions between excited or ionized CHCl<sub>3</sub> molecules and CCl<sub>4</sub>. That such interactions

<sup>(6)</sup> Unpublished results obtained by F. J. Johnston and J. E. Willard indicate a minimum activation energy for this process of 14 kcal. per mole.

<sup>(7)</sup> H. J. Schumacher and K. Wolff, Z. phys.k. Chem., 26B, 161 (1934).

occur is indicated by the observed decrease in  $[G_{(\text{HCD})}]_{\text{CCl}}$ , at lower CCl<sub>4</sub> concentrations. This quantity is less than the expected value for  $G_{(\text{CD})}$  at approximately 18% CCl<sub>4</sub> and becomes negative at lower concentrations. Our results were not extended to very low CCl<sub>4</sub> concentrations because of an increasing sensitivity of  $[G_{(\text{HCD})}]_{\text{CCl}}$  to small errors in HCl determination.

A concise discussion of such interactions has been given by Burton and Lipsky.<sup>8</sup> Our experimental

(8) M. Burton and S. Lipsky, THIS JOURNAL, 61, 1461 (1957).

results do not permit speculation concerning the nature of the energy transfer processes occurring in this particular system. They do, however, show a significant "protection" of  $CHCl_3$  by  $CCl_4$ . A mechanism is suggested in which excited or ionized  $CHCl_3$  molecules, which in the presence only of other  $CHCl_3$  molecules, may lose energy of excitation to  $CCl_4$ . The energized  $CCl_4$  molecules undergo energy dissipation without chemical change.

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# SHOCK TUBE EXPERIMENTS ON THE PYROLYSIS OF ETHANE

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The kinetics of ethane pyrolysis have been studied in the range 1057-1418 °K. in a single-pulse shock tube. Mixtures of methane, ethylene and hydrogen with ethane also have been studied, to determine their effect on the kinetics. These results and literature data at lower temperatures have been correlated by a modified Rice-Herzfeld free-radical mechanism, which accounts quite well for the observed effects.

#### Introduction

The kinetics of ethane pyrolysis have been studied previously in either tubular flow or static bulb reactors. The earlier work, in the temperature range 824–973°K., has been summarized by Steacie<sup>1</sup> who has also discussed current thinking on the mechanism of the reaction. An important paper by Davis and Williamson<sup>2</sup> recently has appeared, describing experiments with a flow reactor at 937–1044°K. Calculations based on a free-radical pyrolysis mechanism have recently been made by Snow, Peck and Von Fredersdorff.<sup>3</sup> The present paper deals with shock tube experiments in the range 1057–1418°K. With data available over this wide temperature range, more can now be said about the reaction mechanism.

## Experimental

The shock tube described in an earlier paper<sup>1</sup> was used, with identical techniques and methods of calculation. Experimental temperatures were corrected for variations in temperature due to minor pressure fluctuations during the runs, and for the heat effects due to chemical reaction. Vapor chromatographic analyses were made for CII<sub>4</sub>, I<sub>2</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>2</sub> in all experiments, and for propane, propylene, butane and 1,3-butadiene in several experiments.

Experiments were carried out with the gas mixtures listed in Table I. Total reaction pressures were five atmospheres, and dwell times about two milliseconds. Phillips reagent grade ethane, Matheson C.P. methane and ethylene, and Airco hydrogen and argon were used without further purification. The gas mixtures were always analyzed before reaction, and none of the products were ever found in the original mixtures.

	TABLE	I
REACTION	MIXTURE	COMPOSITIONS

Mixture	C2ll6	C2ll4	CH4	112	Ar
1	6	4.4			94
<b>2</b>	0.5				99.5
3	. 5			12	87.5
4	. 5		2.5		97
5	. 5		11.2		88.3
6	6		6		88
7	5.4	0.6		0.6	93.4
8	6	ն			88

# Results

As is the case at lower temperatures, the main products of ethane pyrolysis were found to be ethylene and hydrogen in equal molar amounts. Small amounts of methane were found in most of the runs with Mixture 1, the ethylene/methane ratio averaging 21, with no noticeable temperature dependence. For Mixtures 2 and 3 no methane was found since the original ethane concentration was too low, and for Mixtures 4-6 any methane formed was obscured by what was already present. For Mixture 7 the ethylene/methane ratio averaged 20, and for Mixture 8, the ratio was 10. Traces of *n*-butane were found in a few runs with Mixture 1, the ethylene/butane ratio averaging about 140. Some acetylene and 1,3-butadiene were found for Mixtures 7 and 8 at the higher temperatures, but these seemed to be primarily ethylene pyrolysis products.

Conversions were held to less than about 20% to minimize complications such as approach to equilibrium, decomposition of products, decrease of rate due to decreased reactant concentration, and excessive temperature drop due to heat of reaction. From the results for Mixtures 1 and 2 the reaction seemed to be first order, so the results were expressed as first-order rate constants in

<sup>(1)</sup> E. W. R. Steacie, "Atomic and Free Radical Reactions," 2nd ed., Reinhold Publ. Corp., New York, N. Y., 1954.

<sup>(2)</sup> H. G. Davis and K. D. Williamson, Fifth World Petroleum Congress, Section IV. Paper 4, 1959.

<sup>(3)</sup> R. H. Snow, R. E. Peck and C. G. Von Fredersdorff, A.I.Ch.E. J., 5, 304 (1959).

<sup>(4)</sup> G. B. Skinner and R. A. Ruchrwein, THIS JOURNAL, 63, 1736 (1959).

# TABLE II

RATE CONSTANTS IN ETHANE PYROLYSIS

Each pair of numbers gives first  $10^4/T$ , °K., and then k, sec. <sup>-1</sup>

Mixture 1: 9.46, 1.45; 9.38, 2.45; 9.33, 2.7; 9.15, 4.2; 8.99, 10.1; 8.76, 17.2; 8.50, 42; 8.25, 101; 8.20, 88

Mixture 2: 9.02, 10.1; 8.91, 14.0; 8.79, 20.0; 8.53, 39; 8.45, 64; 8.42, 61; 8.02, 185

Mixture 3: 9.32, 6.3; 9.31, 3.2; 9.31, 4.5; 9.12, 9.4; 8.99, 12.8; 8.95, 26; 8.94, 18; 8.90, 26; 8.68, 53; 8.55, 125; 8.51, 87

Mixture 4: 8.31, 9.4; 8.09, 18; 8.02, 27; 7.72, 52; 7.57, 74; 7.46, 124

Mixture 5: 8.19, 6.4; 7.97, 11.4; 7.74, 24; 7.30, 91; 7.27, 122; 7.05, 214

Mixture 6: 9.18, 2.6; 9.02, 4.6; 8.93, 11.1; 8.64, 20.6; 8.55, 20.6; 8.35, 41; 8.20, 54; 8.12, 72

Mixture 7: 8.89, 12.6; 8.73, 21.5; 8.58, 38; 8.42, 51; 8.27, 72

Mixture 8: 9, 15, 3, 7; 9, 01, 8, 4; 8, 90, 4, 6; 8, 66, 14, 1; 8, 63, 18, 6; 8, 40, 42; 8, 36, 45; 8, 18, 65; 8, 01, 83; 7, 91, 109; 7, 86, 134

(1

Table II. The results are corrected for the decrease in amount of reactant as the reaction proceeded (a small correction since the conversions were low) but not for any reverse reaction. The problem of approach to equilibrium is not nearly as serious at these high temperatures as it is at lower temperatures. For example, at  $1200^{\circ}$ K. a sample of ethane at 0.3 atmosphere initial pressure will be more than 98% decomposed at equilibrium, under constant pressure conditions.

Least-squares equations of the type

$$\log k = C + \frac{D}{T}$$

were calculated from the data of Table II. The values of C and D are given in Table III. Since it is difficult to visualize how the curves lie with differing values of both C and D, column 4 of Table III shows the value of C if the average D value (13,290) is used for all the curves. In this column, a change of 1 in C corresponds to a factor of 10 in rate. These curves, of course, apply over the range of temperatures given in Table II. Considering the scatter of the data and the limited temperature range covered, more weight should be given to the absolute values of the rate constants than to the activation energies derived from the temperature dependence.

# Table III

LEAST-SQUARES CONSTANTS FOR ETHANE PYROLYSIS

Mixture	C	D	$\begin{array}{c} C \text{ if} \\ D = 13,290 \end{array}$	IBM calc. C if D = 13,290
1	13.65	14,170	12.87	13.03
2	12.60	12,850	12.98	12.73
3	16.85	17,390	13.17	12.84
4	11.40	12,520	12.00	12.00
5	11.77	13,400	11.68	11.81
6	12.24	12,740	12.71	12.84
7	11.19	11,260	12.93	12.97
8	11.58	11,990	12.67	12.69

The standard deviation of the points from the curves of Table III, expressed in terms of log k, is 0.074, which corresponds to about 20% in k, or about 10° in temperature.

Table V summarizes results from runs with Mixture 2 at higher temperatures and conversions, times being 2 milliseconds as before. Actual product yields, uncorrected for the decrease in ethane concentration with time, are shown. Firstorder rate constants for ethane disappearance were calculated from the amounts of residual ethane in column 2.

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I ABLE I	V.		
FREE RADICAL REACTIONS 12	. Етнал	NE PYROL	YSIS
Reactions	Direc- tion	log A, sec. <sup>-1</sup> or mole <sup>-1</sup> cc. sec. <sup>-1</sup>	$\Delta H$ , cal.
) $C_2H_6 \rightarrow 2CH_3$	$k^a$	14.7	79,300
	r	12.5	-1,500

T 1 -

(2)	$\mathrm{CH}_{3} + \mathrm{C}_{2}\mathrm{H}_{6} \rightarrow \mathrm{CH}_{4} + \mathrm{C}_{2}\mathrm{H}_{6}$	ů	k	12.8	14,500
			r	11.7	18,000
(3)	$C_2H_5 \rightarrow C_2H_4 + H$		k	14.2	42,600
			r	12.3	3,900
(4)	$H + C_2H_6 \rightarrow H_2 + C_2H_5$		k	12.3	6,200
			r	12.4	12,200
(6)	$H + C_2 H_5 \rightarrow C_2 H_5 \qquad \langle$		k	13.6	0
	$\rightarrow$ H <sub>2</sub> + C <sub>2</sub> H <sub>4</sub> $\hat{)}$		r	14.4	97,800
(7)	$H + CH_3 \rightarrow CH_1$		r	14.4	101,000
(9)	$2C_2H_5 \rightarrow C_4H_{10}$		k	13.6	0
	$\rightarrow$ C <sub>2</sub> H <sub>4</sub> + C <sub>2</sub> H <sub>6</sub>				
(12)	$H + CH_4 \rightarrow H_2 + CH_3$		k	11.9	8,000
			r	11.2	10,000
(13)	$CH_3 + C_2H_3 \rightarrow C_3H_8$	1	k	13.6	0

$$\rightarrow CH_1 + C_2H_1$$

 $\ensuremath{^a}\xspace k$  represents the forward rate constant, r the reverse rate constant.

#### TABLE V

PRODUCT DISTRIBUTION IN RUNS WITH MIXTURE 2 AT HIGHER TEMPERATURES, 2 MSEC. TIME

$10^{4}/T$ ,	Moles pro	oduct/100	moles C2	He origin:	lly present	k,
7.54	37.4	54.5	3.6	4.5	64.5	490
7.31	19.1	62.8	9.6	8.3	84.6	830
7.13	12.4	60.1	16.4	11.6	86.7	1040
6.91	6.8	57.9	24.7	13.2	128.2	1340
6.39	3.4	40.6	44.5	20.6	129.7	1690
6.10	1.7	31.1	54.0	21.7	140.0	2040
5.74	1.3	9.2	76.2	21.3	165.5	2180

#### Discussion

The relative rates of ethane decomposition can be estimated from column 4 of Table III. The data for Mixtures 1 and 2 (ethane partial pressures 0.3 and 0.025 atmosphere) suggest a reaction order of one, or slightly less than one. Hydrogen increases the rate of ethane decomposition slightly, while methane and ethylene reduce the rate. These data, and the earlier data at lower temperatures, can be interpreted by a modified Rice-Herzfeld mechanism, as discussed by Steacie, Davis and Williamson, and Snow. The data of this paper permit more accurate calculations of the individual free radical reaction rates, partly because of the extended temperature range, and partly because the various compositions studied here emphasized certain reactions which were not important under previously studied conditions.

Qualitative evidence for the free-radical chain mechanism of ethane decomposition comes from Table V, which shows that the apparent activation energy falls off at high conversions. At the high-est temperature of Table V, the rate constants for ethane pyrolysis are only a few per cent. of those calculated by extrapolating the low-conversion rates of Table II or III. In a chain reaction the chain length would be expected to shorten as the ethane disappeared and was replaced by more stable product molecules, while for a molecular decomposition the first-order rate should hold to high conversions. The increase in methane yield at high conversions is evidence that the first step in ethane pyrolysis is breaking the C-C bond. It has been found in experiments to be described in another paper that the methane does not come from decomposition of the ethylene or acetylene.

The free radical reactions considered important are listed in Table IV. Certain other possible reactions have been neglected, for reasons discussed by Steacie and by Snow. We have determined best values of the rate constants for the reactions of Table IV, based on earlier work and our own. The rate constants have been expressed in the Arrhenius form

# $k = Ae^{\Delta H/RT}$

the values of A and  $\Delta H$  being given in Table IV. (Units of A are sec.<sup>-1</sup> for unimolecular reactions and mole<sup>-1</sup> cc. sec.<sup>-1</sup> for bimolecular;  $\Delta H$  in cal.)

There were, of course, many reasons for choosing the particular values of Table IV. With 15 reactions to consider, and many sets of experimental data, the approach was one of successive approximations. To correlate our shock tube data, a program was set up for the IBM 704 computer to make a direct numerical integration of the equations. Since our time intervals were only two milliseconds, there was some doubt that the free radical concentrations could be assumed to be at their steady-state values throughout the experiment. In our numerical integration the radicals were treated the same way as the molecules were, so the time dependence of their concentrations was determined. To do this required the use of very short time increments (0.1 or even 0.05 microsecond) so the calculations were quite time-consuming even on this high-speed computer. It turned out that the steady-state approximation was quite good (within 10%) for all sets of experiments except 2 and 3 (Table I). For these two cases, the ethane decomposition calculated by direct integration was about half that found by the steady-state approximation. IBM calculations were made for Mixtures 4 and 5 at 1300°K., and for the other mixtures at 1150°K. (that is, about in the middle of each experimental temperature range). The results are expressed as C values,

for D = 13,290, in column 5 of Table III. The standard deviation of the calculated C values from the observed is 0.175, corresponding to about 20° in temperature.

Many other conditions restrict the values which may be assigned to A and  $\Delta H$ . First, the  $\Delta H$ values must be consistent with the heats of formation of the substances involved. Heats of formation and thermal functions of C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, CH<sub>4</sub> and H are known accurately over our experimental temperature range,<sup>5</sup> but values for CH<sub>3</sub> and C<sub>2</sub>H<sub>5</sub> are not so well known. The  $\Delta H$  values of Table IV are consistent with heats of formation, at 1000°K., of +29,000 cal./mole for CH<sub>3</sub>, and +21,600 cal. for C<sub>2</sub>H<sub>5</sub>. The CH<sub>3</sub> value agrees with the generally given value of +32,000 cal. at 298°K.<sup>6,7</sup>

These heats of formation cannot be directly calculated from the  $\Delta II$  values of Table IV. because of the units of mole<sup>-1</sup> cc. sec.<sup>-1</sup> for bimolecular reactions. Since the number of moles per cc. decreases as the temperature is raised at constant pressure, the  $\Delta H$  for mole<sup>-1</sup> cc. sec.<sup>-1</sup> units is larger than it would be in  $atm.^{-1}$  sec.<sup>-1</sup> units, to which the thermodynamic  $\Delta H$  applies. In the neighborhood of 1000°K.. this corresponds to about 2,000 cal. For example, in reaction 3 of Table IV, the  $\Delta H$  of the reaction would be +42,600 – (3,900 - 2,000) = +40,700 cal. The point is that the  $\Delta H$ 's of Table IV include the temperaturedependent part of the frequency factor. In reactions such as 4 and 12, these cancel so that the  $\Delta H$ 's of Table IV give the thermodynamic heat of reaction.

To obtain  $k_1$ , it was assumed that the methane comes from reaction 2 ria reaction 1, at least in the early stages where we worked. Therefore,  $k_1$  is given by the rate of ethane pyrolysis divided by twice the  $C_2H_4/CH_4$  ratio. Our data for Mixture 1 give a  $k_1$  of 0.8 at 1170°K. Steacie and Shane<sup>8</sup> reported that 2 to 5 moles  $CH_4$  formed for each 100 of ethylene at an average temperature of 875°K., at which the over-all rate constant is about 0.00045, based on their data and those of Kuchler and Theile.9 Taking an average of 3.5 moles CH<sub>4</sub> for each 100 C<sub>2</sub>H<sub>4</sub>,  $k_1$  is 0.000008 at 875°K. From these two points the constants of Table IV were calculated. Both frequency factor and  $\Delta H$  are lower than the values used by Snow and by Davis, but the absolute values of  $k_1$  are not greatly different near 1000°K. The lower value of A agrees with an absolute rate calculation, assuming the activated complex is a normal molecule with 80,000 cal. extra energy in the C-C bond, but it does not agree with the value calculated from the reverse reaction rate by Trotman-Dickenson.10

The other constants of Table IV are essentially

<sup>(5)</sup> National Bureau of Standards, Selected Values of Chemical Thermodynamic Properties, Series III.

<sup>(6)</sup> G. Ribaud, Publ. sci. et tech. ministere air (France) 1952, No. 266, 169 pp.

<sup>(7)</sup> F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, U. S. Dept. of Commerce, Natl. Bur. of Standards, Circ. No. 500, 1952.

<sup>(8)</sup> E. W. R. Steacie and G. Shane, Can. J. Res., B18, 203 (1940).

<sup>(9)</sup> L. Kuchler and H. Theile, Z. physik. Chem., B42, 359 (1939).
(10) A. F. Trotman-Dickenson, J. Chem. Phys., 21, 211 (1953).



Fig. 1.—Initial rate of ethane pyrolysis: O, this research, 0.3 atm.;  $\Delta$ , Davis and Williamson, 1.0 atm.;  $\Diamond$ , Kuchler and Theile,  $\sim 0.5$  atm.;  $\times$ , Steacie and Shane,  $\sim 0.5$  atm.; -, calculated, 1.0 atm.

literature values, modified to fit the over-all thermodynamic and kinetic relationships. The negative temperature dependence of  $r_1$  has been established by Ingold and Lossing.<sup>11</sup> Trotman-Dickenson, Birchard and Steacie<sup>12</sup> studied the

(11) K. U. Ingold and F. P. Lossing, J. Chem. Phys., 21, 368, 1135 (1953).

relationship of  $k_2$  to  $r_1$  near 500°K., and this relationship is retained in our values. Similarly, our constants preserve the relation between  $r_{12}$ and  $r_1$  established by Majury and Steacie<sup>13</sup> near 500°K., and the value of  $k_{12}$  found by Berlie and Le Roy<sup>14</sup> near 400°K.

In addition to reproducing our own kinetic data, the constants of Table IV correlate with other data at lower temperatures, as shown in Fig. 1. The curve was calculated by the steady-state method. Also, the net rate of production of  $C_2H_4$  (but not of  $CH_4$ ) is zero when equilibrium concentrations of  $C_2H_6$ ,  $C_2H_4$  and  $H_2$  are used.

One notable discrepancy between theory and experiment remains. The free radical mechanism predicts that the over-all reaction order should be one-half at lower temperatures, while first-order kinetics actually have been found over the whole temperature range.

Acknowledgment.—The authors wish to thank Mr. Edward M. Sokoloski for his assistance with both experiments and calculations.

(12) A. F. Trotman-Dickenson, J. R. Birchard and E. W. R. Steacie, *ibid.*, **19**, 163 (1951).

(13) T. G. Majury and E. W. R. Steacie, Can. J. Chem., 30, 800 (1952).

(14) M. R. Berlie and D. J. Le Roy, ibid., 32, 650 (1954).

# SHOCK TUBE EXPERIMENTS ON THE PYROLYSIS OF ETHYLENE

By Gordon B. Skinner and Edward M. Sokoloski

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A single-pulse shock tube has been used to study the kinetics of ethylene pyrolysis in the range  $1300-1800^{\circ}$  K., where the chief products are acetylene, 1,3-butadiene and hydrogen. The reaction to form acetylene is essentially first order, and that to form butadiene is second order, with respect to ethylene partial pressure. The reactions seem to be molecular rather than free-radical in mechanism. The hydrogenation of acetylene to ethylene also was studied, and by relating the forward and reverse reactions by the equilibrium constant, it was shown that the shock tube temperature calculations were accurate within  $30-50^{\circ}$ .

#### Introduction

Pyrolysis of ethylene at relatively low temperatures and high pressures leads to a multitude of products,<sup>1</sup> but at higher temperatures and low pressures acetylene and hydrogen are the only main products.<sup>2</sup> This paper deals primarily with the kinetics of acetylene formation, but touches also on the condensation reaction to form butadiene.

#### Experimental

The shock tube described in an earlier paper<sup>3</sup> was used, with identical techniques and methods of calculation. Experimental temperatures were corrected for variations in temperature due to minor pressure fluctuations during the runs, and for the heat effects due to chemical reaction. Vapor chromatographic analyses were made for hydrogen, ethane, ethylene and acetylene in all experiments, and for methane, propane, propylene, butane, butenes and 1,3butadiene in most.

(2) F. Fischer and H. Pichler, Brennstoff-Chem., 13, 381, 406, 435 (1932).

(3) G. B. Skinner and R. A. Ruehrwein, THIS JOURNAL, 63, 1736 (1959).

Experiments were carried out with the gas mixtures listed in Table I. Total reaction pressures were five atmospheres, and dwell times two or ten milliseconds. Phillips reagent grade butadiene, Matheson C.r. ethylene and acetylene, and Airco hydrogen and argon were used without further purification, except that the acetylene was bubbled through concentrated sulfuric acid and then passed through an Ascarite-Drierite column. The gas mixtures were always analyzed before reaction, and none of the products were ever found in the original mixtures.

TABLE I

#### REACTION MIXTURE COMPOSITIONS

	-Mole % component					
Mixture	C2H4	C2H2	II2	Cells	Ar	
1	0.466				99.534	
$^{2}$	6.00				94.00	
3	6.00	6.00			88.00	
-1				0.265	99.735	
5		1.41	8.47		90.12	

## Results

With Mixture I the chief pyrolysis products of ethylene were hydrogen and acetylene, with minor amounts of 1,3-butadiene being produced at the lower temperatures, and of methane at the

<sup>(1)</sup> R. E. Burk, B. G. Baldwin and C. II. Whitacre, Ind. Eng. Chem., **29**, 326 (1937).

higher temperatures. Less than 2% of the decomposed ethylene went to methane, even for high conversions, and the carbon and hydrogen balances showed that no significant amounts of other materials were formed.

With Mixture 2, butadiene was a major product, more of it than of acetylene being produced at the lower temperatures. Up to 5% of the decomposed ethylene went to methane, and up to 15%(at the lowest temperatures) to propylene.

By comparison of the two sets of runs, it was concluded that acetylene formation is essentially first order in ethylene pressure, while butadiene formation is second order. The experimental results are expressed as rate constants in Table II, where the second-order constants are in terms of ethylene disappearance, which is of course twice the rate of butadiene appearance. The  $k_2$  values for Mixture 1 could be off by as much as 50%, since only small traces of butadiene were present to be analyzed for.

# TABLE II

RATE CONSTANTS FOR THE FORMATION OF ACETYLENE  $(k_a)$ and 1,3-Butadiene  $(k_b)$  from Ethylene

		1-1-
10י/ <i>T</i> , °K.	$k_{\rm A}$ , sec. <sup>-1</sup>	atm. " sec. "
	Mixture 1	
7.83	8.5	60
7.53	19.0	
7.53	19.5	60
7.29	29.0	60
6.93	68.5	40
6.78	85.5	4()
6.66	112	
6.52	142	
6.30	298	
6.16	364	
6.00	640	
5.75	1040	
5.61	1520	
	Mixture 2	
8.56	0.44	10
8.55	0.64	9
8.30	1.5	
8.24	1.6	12
8.06	3, 2	23
8.05	3.7	20
7.92	7.5	34
7 55	18.6	45
7.51	19.4	
7.43	21.7	53
7.03	82	59
7 01	88	

# TABLE III

RATE CONSTANTS FOR THE FROM AN ETHYLENE	Formation of 1,3-Butadiene -Acetylene Mixture
104/T, °K.	<i>k</i> b, atm. <sup>-1</sup> sec. <sup>-1</sup>
8.53	20
8,35	22
7.96	51
7.95	41
7.46	60
7.13	70

Rate constants for the conversion of ethylene to butadiene in Mixture 3 are given in Table III.

A brief study of butadiene decomposition was made with Mixture 4, at about ten milliseconds dwell time, with results shown in Table IV. Firstorder rate constants have been calculated for the disappearance of butadiene, although it is not certain that the kinetics are first order since only one pressure was used.

#### TABLE IV

KINETIC DATA FOR THE DECOMPOSITION OF 1,3-BUTADI-ENE-TIME 10 MSEC.

	Mole <b>s</b> p	product/10	0 moles bu	tadiene	
104/T	C.H.	C <sub>2</sub> H <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	I-I 2	k, sec1
8.28	91.9	6.4	6.7	2.4	8.5
8.05	87.4	7.0	7.8	2.2	13.5
7.76	67.0	23.6	21.7	7.9	40
7.50	51.2	36.2	29.3	12.7	67
7.24	28.1	57.6	36.3	19.7	127
7.08	19.2	76.5	37.0	34.1	165

Results of two series of experiments with Mixture 5, at two and ten milliseconds dwell time, are given in Table V. For comparison with the experimental ethylene yields, the amounts of ethylene in equilibrium with the original acetylenehydrogen mixture are tabulated in the last column.

TABLE V

KINETIC DAT	TA FOR T	не Ну	DROGENA	TION O	F ACETYLENE			
		(Міхт	ure 5)					
10¹/ <i>T</i> , °K.	←Moles pro C2H2	C2H4	00 moles C C4H6	C₂H₂ origi CII₄	nally present— C2H4 (equil.)			
	Series 1.	. Dwe	ell time 2	msec.				
8.42	§5.0	0.9	0.4	• •	660			
7.82	93.1	1.5	.6	• •	170			
7.23	94.3	2.7	.7	• •	47			
6.74	91.2	3.5	.8		15			
6.66	91.5	3.7	.8	• •	13			
6.12	91.0	3.5	1.5		3.9			
5.64	88.8	2.5	2.1	••	1.3			
Series 2. Dwell time 10 msec.								
8.48	91.4	4.4	1.4		750			
7.94	89.4	7.6		0.8	230			
7.34	87.2	9.0	1.3		60			
6.96	85.9	8.9		1.3	25			
6.54	88.2	7.2	1.3		10			
5.96	89.9	3.9		1.8	2.7			

Least-squares equations of the Arrhenius type (log k = A - B/T) have been calculated for several of the sets of experiments, the values of A and B being listed in Table VI.

## TABLE VI

CONSTANTS IN THE ARRHENIUS EQUATIONS							
Mixture	Rate	A	В	$\Delta H$ , cal.			
1	k.	8.87	10,150	46,400			
$^{2}$	ka	11.95	14,210	65,000			
	$k_{\mathbf{b}}$	6.49	6,440	29 , $500$			
3	ĸь	4.74	3,970	18,200			
4	k.	10.14	11,110	50 , $800$			

# Discussion

Our recent experiments on ethane pyrolysis<sup>4</sup> (4) G. B. Skinner and W. E. Ball, THIS JOURNAL, 64, 1025 (1960). have confirmed the generally held opinion that ethane decomposes by a free-radical chain mechanism. The present experiments, on the other hand, suggest that ethylene goes to acetylene by a molecular reaction in the classical sense, without the intermediate formation of free radicals.

The most direct evidence for this comes from the results for Mixture 1. The Arrhenius rate equation holds all the way from 2 to 95% ethylene decomposition, while for a chain reaction the rate should fall off at high conversions. Moreover, the product distribution (almost all hydrogen and acetylene) remained the same up to 95% decomposition. The activation energy for acetylene formation (46,400 cal.) is just slightly more than the heat of the reaction (43,900 cal. at  $1500^{\circ}$ K.).<sup>5</sup> Since this experimental activation energy is based on rate constants covering a considerable range, it is accurate to about 2,000 cal., though some of the other activation energies of Table VI are not so accurate.

At first glance, it seems easy to write free-radical reactions which will yield the observed products. For example, one could write

$$C_{2}H_{4} \longrightarrow C_{2}H_{3} + H \qquad (1)$$

$$H + C_{2}H_{4} \longrightarrow H_{2} + C_{2}H_{3} \qquad (2)$$

$$C_{2}H_{3} \longrightarrow H + C_{2}H_{2} \qquad (3)$$

$$2C_{2}H_{3} \longrightarrow C_{4}H_{6} \qquad (4)$$

This mechanism seems quite unreasonable when the energy relations are considered. The activation energy of (1) plus that of (3) is at least 150,000 cal., while that of (1) is about 100,000 cal. Activation energies of (2) and (4) will be low. For the low temperature runs with Mixture 2, where little acetylene formed, (3) can be neglected, and the rate of ethylene disappearance becomes simply twice the rate of (1). This has far too high an activation energy, and gives a first instead of second-order reaction. For the runs with Mixture 1, where acetylene is the main product and butadiene minor, then the rate of acetylene formation is half order, and the activation energy is  $(\frac{1}{2}E_1 + E_3 - \frac{1}{2}E_4)$ , that is, between 75,000 and 100,000 cal., again far too high.

The absence of methane as a pyrolysis product at high conversions argues against the breaking of the carbon-carbon bond as a source of free radicals, and calculated activation energies are high even if singlet state  $CH_2$  radicals are supposed to be formed. We have not been able to think of a free radical mechanism which would give activation energies close to those observed. The conclusion is that the reactions of ethylene to give acetylene and butadiene are molecular reactions, not involving free radicals.

It has been suggested<sup>1</sup> that ethylene first dimerizes to butene, which then loses hydrogen to form butadiene. Butenes are thermodynamically unstable with respect to butadiene under our experimental conditions, so, since they were not found in our samples, they must have been present as unstable intermediates, if at all. At lower temperatures, however, they would be stable.

It also seemed possible that butadiene forms by

(5) National Bureau of Standards, Selected Values of Chemical Thermodynamic Properties, Series III.

the reaction of ethylene with product acetylene. This seems unlikely, however, since runs with Mixture 3 produced little more butadiene than did those with Mixture 2.

The rate constants for acetylene formation from Mixtures 1 and 2 are equal at  $10^{4}/T$  of 7.5, which is one of the lower temperatures for Mixture 1, but one of the higher temperatures for Mixture 2. At lower temperatures with Mixture 2, the rate of formation of acetylene is less than that calculated by extrapolating the Mixture 1 curve. This first suggested that acetylene was reacting to form butadiene, but now another explanation must be found, since the effect seems real (see below). It may be that butadiene formation cuts down acetylene formation by removing partly activated molecules.

Decomposition of butadiene was studied to find whether much of the butadiene formed with Mixture I would decompose later in the same run. However, butadiene is stable enough that this effect is quite minor. The main reactions seem to be

$$C_4H_6 \longrightarrow C_2H_4 + C_2H_2$$

$$\Delta H(1300^{\circ} \text{K.}) = 39,100 \text{ cal.} (5)$$

 $C_4H_6 \longrightarrow 2C_2H_2 + H_2 \Delta H(1300^{\circ}K.) = 83.200 \text{ cal.}$  (6)

with (5) predominating at lower temperatures. The experimental activation energy, lying between those of the two reactions, again suggests that molecular reactions are involved. The material balance shows that significant amounts of materials not analyzed for are also produced.

Since the shock tube technique is new, it is important to take every opportunity to check on its operation. This has been done here by comparing forward and reverse reactions of ethylene pyrolysis. The forward reaction rates are obtained from the  $k_a$ 's for Mixtures 1 and 2, and the reverse rates from Table V.

It is seen from Table V that the ethylene yield goes through a maximum. At low temperatures the yield is restricted by kinetics, and at high temperatures by equilibrium. At the highest temperatures, yields of ethylene were greater than those calculated by the equilibrium, showing failure to quench the samples instantaneously. Kinetic comparisons, of course, had to be made at lower temperatures where kinetics control the reactions.

To make these comparisons most meaningful, it seemed best to compare the reaction rates for actual equilibrium pressures of the components. Since the ethylene pressure in Mixture 1 was  $(0.466 \times 100/1.41)$  33% of the acetylene pressure in Mixture 5, the last column of Table V suggests that the rates should be compared at about  $10^4/T =$ 7. Graphical interpolation gives  $10^4/T =$  7.07, or  $T = 1415^{\circ}$ K. A smooth curve through the points of Table V gives ethylene concentrations of 3.0% for Series 1 and 9.0% for Series 2, while the rate constant  $k_1$ , calculated from the constants of Table VI, Mixture 1, is 51 sec.<sup>-1</sup>. Thus we obtain

Forward rate:  $51 \times 0.00466 \times 5 = 1.19$  atm. sec.<sup>-1</sup>

Reverse rate (1):  $\frac{0.030 \times 0.0141 \times 5}{0.002} = 1.06$  atm. sec.<sup>-1</sup>
August, 1960

(2): 
$$\frac{0.090 \times 0.0141 \times 5}{0.010} = 0.64$$
 atm. sec.<sup>-1</sup>

The agreement between the first two values is as close as could be expected, while the second reverse rate is low because of approach to equilibrium.

In a similar way, the ethylene pressure in Mixture 2 is  $425^{\circ}c$  of the acetylene pressure in Mixture 5, so a comparison will be made at  $10^{4}/T =$ 8.23, or  $T = 1215^{\circ}$ K. Therefore, using Mixture 2 data for  $k_{1}$ , we obtain

Forward rate:  $1.75 \times 0.060 \times 5 = 0.52$  atm. sec.<sup>-1</sup> Reverse rate (1):  $\frac{0.0105 \times 0.0141 \times 5}{0.002} = 0.37$  atm. sec.<sup>-1</sup>

(2) 
$$\frac{0.060 \times 0.0141 \times 5}{0.010} = 0.42$$
 atm. sec.<sup>-1</sup>

This discrepancy between forward and reverse reaction rates can be accounted for by temperature errors in ethylene pyrolysis measurements of  $10-15^{\circ}$ , or in acetylene hydrogenation measurements of  $30-50^{\circ}$  (since the temperature dependence is smaller). The discrepancy would have been much greater if the Mixture 1 rate constant had been used instead of that for Mixture 2, which contained the correct equilibrium pressure of ethylene.

# SIMPLE EQUATIONS FOR CALCULATING BOND DISSOCIATION ENERGIES<sup>1</sup>

### By L. A. Errede

No. 170 from the Central Research Laboratories of the Minnesota Mining and Manufacturing Company, St. Paul, Minn. Received February 22, 1960

Simple equations for calculating bond dissociation energies were deduced empirically from the great number of experimentally determined bond dissociation energies now available in the literature. Thus, for the bond  $R_1$ - $R_2$  where  $R_1$  is CH<sub>3</sub>, CX<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>, RC=C-, R<sub>2</sub>C=CR-, RCO and CN, and  $R_2$  is  $R_1$ , H, X, CN, OH, OR, NR<sub>2</sub>, NO, NO<sub>2</sub> and SR, the bond dissociation energy (D) is given by  $D = 71\epsilon_1\epsilon_2$  where  $\epsilon_1$  is a constant characteristic of the group  $R_1$ . The  $\epsilon$  of a group  $R = \sqrt{A_2}$ 

 $A_1C \langle A_2 \\ A_3 \rangle$  is related to the three substituents on the carbon atom attached to the bond in question by  $\epsilon_g = 0.43 + 0.162 \Sigma \epsilon_i$ .

The calculated bond dissociation energies agree in most cases within 1-2 kcal, with the observed ones.

Several equations for calculating bond dissociation energies have been reported in the literature, but unfortunately they are either extremely complex and require the use of laborious calculations for the final computation, or their validity is so limited as to be of little value. The final results, even when the complex equations are used, remain only approximate despite the extraordinary effort required in computations. Hence, there is an obvious need for a simple and reliable equation for calculating bond dissociation energies.

A simple equation permitting calculation of bond dissociation energies with a remarkable degree of accuracy was deduced empirically from inspection of the great number of experimentally determined bond dissociation energies. Actually most of the observed values agree with the computed ones within 1–2 kcal./mole and the number of required constants is very small indeed.

Examination of the bond dissociation energy data compiled in many reviews on this subject,<sup>2-s</sup>

(1) Presented before the Physical Chemistry Division of the American Chemical Society at its 137th Meeting held in Cleveland, Ohio, April, 1960.

(2) M. Szwarc, Chem. Revs., 47, 75 (1950).

(3) A. H. Schon and M. Szware, Ann. Rev. Phys. Chem., 8, 439 (1957).

(4) T. L. Cottrell. "The Strengths of Chemical Bonds." 2nd Ed., Butterworth's Scientific Publications. London, 1958.

(5) E. W. R. Steacie, "Atomic and Free Radical Reactions." 2nd Ed., Vol. I, Reinhold Publ. Corp., New York, N. Y., 1958.

(6) N. N. Semencv, "Some Problems in Chemical Kinetics and Reactivity," Princeton U. Press, Princeton, N. J., 1958.

(7) G. Herzberg, "Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules," 2nd Ed., D. Van Nostrand Co., Inc., New York, N. Y., 1950. indicated a steady increase in bond dissociation energies for any series of compounds R–X, X being I, Br, Cl, H, F. Closer inspection of the data indicates that for any series of RX compounds the difference  $D(R-X_i) - D(R-X_j)$  decreases with the binding ability of R, but that this difference divided by the bond dissociation energy of a given member of the series is approximately constant and independent of R

$$\frac{D(R-X_i) - D(R-X_j)}{D(R-X_k)} = constant$$

Hence, a plot of  $D(R_1-X_i)$  as a function of  $D(R_2-X_i)$  where X is I. Br, Cl, H, F should be a straight line.

In view of the unavoidable errors in experimentally determined bond dissociation energies, it is convenient to introduce a parameter  $D(R_0-X_i)$ for each substituent  $X_i$  choosing its value in such a way that a plot of any  $D(R_n-X_i)$  series with respect to  $D(R_0-X_i)$  will give the least scatter of points for all available series of  $R_n$ . Those parameters  $D(R_i-X_i)$  could be considered as the respective bond dissociation energies for an ideal series  $R_0-X_i$ . The absolute values of  $D(R_0-X_i)$ are arbitrary and only their relative values are important. In the proposed scheme, they were chosen to be of the order of unity, and for the sake of brevity the parameter  $D(R_0-X_i)$  is denoted now by  $\epsilon_i$ .

The validity of this relationship can be seen readily in Figs. 1, 2 and 3 where the bond dissociation energies of few  $R-X_i$  series are plotted as (8) L. Pauling, "The Nature of the Chemical Bond," 2nd Ed., Cornell U. Press, Ithaca, N. Y., 1948.



Fig. 1.—Bond dissociation energy as a function of  $\epsilon$ .



Fig. 2.—Bond dissociation energy as a function of  $\epsilon$ .

a function of  $\epsilon_i$ . Obviously the slope of the line for a given series of  $R_n-X_i$  is characteristic of the group  $R_n$  and  $D(R_n-X_i)$  is given therefore by  $\alpha_{n}\epsilon_{i}$ . Let us now consider bond dissociation energies of

the type  $R_1-R_2$  where each R is a  $CA_1A_2A_3$  group ("A" being H, F, Cl, Br, I or group of atoms CX<sub>3</sub>). One can determine  $\epsilon_1$  using the line for the D- $(R_1-X_i)$  series and vice versa  $\epsilon_2$  can be deduced by



of the line representing the  $D(R_{2}-X_{i})$ means series. Hence

$$D(\mathbf{R}_1 - \mathbf{R}_2) = \alpha_1 \epsilon_2 = \alpha_2 \epsilon_1$$

and therefore

$$\frac{\alpha_1}{\epsilon_1} = \frac{\alpha_2}{\epsilon_2} = \lambda$$
 (a constant independent of R and X)

Thus

$$D(R_n - X_i) = \lambda \epsilon_1 \epsilon_2$$

In order to obtain the best value for  $\lambda$ ,  $\alpha_i$  were plotted as a function of its corresponding  $\epsilon_i$  for all available R and X and from the slope of the

line shown in Fig. 4 a value 71 was obtained for  $\lambda$ . In this way "n" constants for groups of the R type and "m" constants for groups of the X type, *i.e.*, a total of n + m + 1 constants determine



Fig. 6.—Comparison of calculated and observed bond dissociation energies for molecules of type R-X where: R is CX<sub>3</sub>-, CR<sub>3</sub>-, RCO-, CR<sub>2</sub> = CR-, CR<sub>2</sub> = CRCR<sub>2</sub>-, C<sub>6</sub>H<sub>5</sub>,C<sub>6</sub>H<sub>5</sub>CR<sub>2</sub>- and X is -H, -F, -Cl, -Br, -I.

 $n \times m$  bond dissociation energies. The number of constants can be reduced further to m + 3 since it was found empirically that a simple linear relationship exists between the  $\epsilon$  for groups of the R type and the  $\epsilon$  of its substituents, *i.e.*, of atoms or groups attached to the central carbon atom of the group R. This relation determines  $\epsilon_{\rm g} = a + b\Sigma\epsilon_{\rm i}$  and to what extent it is valid is seen in Fig. 5. The best line through the loci of available points is given by

### $\epsilon_{g} = 0.43 + 0.162\Sigma\epsilon_{i}$

This relationship, however, does not apply to groups such as  $C_6H_5$ , RCO—, CN, -HC—CH<sub>2</sub>, —C=CH, and perhaps NO<sub>2</sub> and NO. Hence, the  $\epsilon$  value for groups like  $C_6H_5CH_2$ -, CH=CH-CH<sub>2</sub>-, CH<sub>2</sub>=CHCH<sub>2</sub>-, and N=CCH<sub>2</sub>- must be determined from the experimental bond dissociation energy in conjunction with the relation  $D = \lambda \epsilon_1 \epsilon_2$ . Once this is done, however, the  $\epsilon$  can be used to calculate  $\epsilon$ -values of composite groups as explained previously. The  $\epsilon$ -values for numerous



Fig. 7.—Comparison of calculated and observed bond dissociation energies for molecules of type  $R_1$ - $R_2$  where:  $R_1$  is  $CX_{3-}$ ,  $CR_{3-}$ ,  $CR_2$ = $CRCR_2$ -, RC=C-, CN,  $C_6H_5-CR_2$ - and  $R_2$  is  $-CX_3$ , -CN, -OH,  $-NH_2$ - $NO_2$ -NO, -SR, -C=CR,  $-CR_2C_6H_5$ .



Fig. 8.—Comparison of calculated and observed bond dissociation energies for bond between two non-carbon atoms.

groups commonly found in organic molecules are listed in Table I.

The validity of the proposed equation  $D = \lambda \epsilon_{i\epsilon j}$  can be tested by comparing all the bond dissociation energies determined experimentally with the corresponding calculated values. The results are shown in Fig. 6 and 7, the straight line of unity slope represents the ideal relation. It is seen that the agreement is good. Actually about 4/5 of the data agree within 1-2 kcal, which is highly satisfactory in view of the fact that the best experimental data are only reliable to about 1-2 kcal.

It is interesting to note that the bond dissocia-

C	HARACTERIS	TIC E-VALUES	
Group	é	Group	e
-F	1.49	CH₂Cl−	1.04
-H	1.32	CH₂Br−	1.00
-Cl	1.04	$CHCl_{2}-$	0.97
-Br	0.86	CHBr <sub>2</sub> -	0.92
-I	0.68	$CH_{3}$ -	1.08
-CN	1,28	$CH_3CH_2-$	1.05
-OH	1.23	CH3CH2CH2-	1.03
$-NH_2$	1.05	CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> -	1.03
-OEt	$1.05^{a}$	$(CH_3)_2CH-$	1.01
$-OCH_3$	$1.04^{a}$	$(CH_3)_3C-$	0.95
-SH	0.98	CH=C-	1.44
$-SCH_3$	.94	CH <sub>2</sub> =CII-	1.42
-00H	. 93	$C_6H_{i}$	1.11
$-SCH_2CH_3$	. 92	CH <sub>3</sub> C()	$1.09^{n}$
$-\mathrm{NHC}_{6}\mathrm{H}_{5}$	$.85^{a}$	C <sub>6</sub> H <sub>5</sub> CO-	$1.04^{n}$
$-SCH_2C=CH$	. 69ª	$CH_2 = CBr -$	$1.03^{a}$
$-\mathrm{NO}_2$	. 57	HCO-	$1.01^{a}$
-NO	. 49	CH=CCH2-	0.94
$CF_3$	1.15	$C_6H_5CH_2-$	. 83
CCl <sub>3</sub> ~	0.94	CH_=CHCH2-	.78
CBr <sub>3</sub> -	0.85	$(C_6H_5)_2CH-$	.74"
CI <sub>4</sub> -	0.76	CH <sub>3</sub> CH=CHCH <sub>2</sub>	.74"
		CH <sub>2</sub> =CCH <sub>3</sub> CH <sub>2</sub> -	$.72^{a}$
		$(C_{6}H_{5})_{4}C-$	$.65^{a}$
<b>D</b>			

TABLE I

 $^{\rm a}$  Determined by only 1 or 2 values and may require revision at a later date.

TABLE II

Atom (X)	C	F	п	Cl	Br	I
Pauling's electronegativity (E)	2.5	4.0	2.1	3.0	2.8	2.4
C-X bond distance (r)		1.32	1.10	1.79	1.94	2.14
$\sqrt{E/r}$		1.52	1.33	0.98	0.86	0.73
é		1.49	1.32	1.04	0.86	0.68

tion energy for bonds between non-carbon atoms can also be calculated using analogous equations (*i.e.*,  $D = \lambda_{i\epsilon_1\epsilon_2}$ ) with a characteristic constant  $\lambda$ for each series. Thus the bond dissociation energies for the series H–A where A is I, Br, SH, NH<sub>2</sub>, Cl, OH, CN and F are given by  $D = 73\epsilon_1\epsilon_2$ . The bond dissociation energies of the disulfides (RSSR) are given by  $D = 84\epsilon_1\epsilon_2$ 

and

$$\epsilon_{\rm SR} = 0.73 + 0.21 \epsilon_{\rm F}$$

The bond dissociation energy equations for hydrazines ( $R_{2}N-NR_{2}$ ), and nitroso cr nitro compounds (ONX or  $O_{2}NX$ ) appear to be  $D = 54\epsilon_{1}\epsilon_{2}$ and  $D = 70\epsilon_{1}\epsilon_{2}$ , respectively. There is considerable uncertainty in these two series, however, because of the very limited number of reliable data and consequently the corresponding  $\lambda$  constants may require correction at a later date when more data become available. The validity of these equations can be seen from the examples shown in Fig. 8. The bond dissociation energies for the diatomic molecules H<sub>2</sub>, F<sub>2</sub>, Cl<sub>2</sub>, Br<sub>2</sub>, I<sub>2</sub> do not fall into a general series having a common  $\lambda$ . On the contrary, each has a  $\lambda$  characteristic of the element in question and its isotopes.

It is interesting to notice that the  $\epsilon$ -values for F, H, Cl, Br and I may be related to Pauling's electronegativity E.<sup>8</sup> The quantity  $\epsilon$  is given almost exactly by  $\sqrt{E}/r$  where r is the corresponding C-X bond length. (See Table II.) This is consistent with the observations of Glockler<sup>9</sup> who reported that the bond dissociation energy of R-X in the series, where X is F, Cl, Br and I (but not H) is inversely proportional to the C-X bond distance. The present correlation accounts for the earlier anomalous behavior of H.

It is also noted that the expression for calculating  $\epsilon_{g_1}$ , for the group  $R_1R_2R_3C$ , is very nearly equal to

$$\epsilon_{\rm g} = 1/6(E_{\rm c} + \Sigma\epsilon_{\rm i})$$

where  $E_c$  is Pauling's<sup>8</sup> electronegativity for carbon (equal to 2.5).

(9) G. Glockler, This Journal, **63**, 828 (1959); **62**, 1049 (1958); **61**, 31 (1957).

# THE THERMODYNAMICS OF BISMUTH-LEAD ALLOYS<sup>1</sup>

BY PRODVOT ROY, RAYMOND L. ORR AND RALPH HULTGREN

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Experimental determination has been made of heats of formation and heat contents of solid lead-bismuth alloys. These data have been correlated with previously known data in the liquid state and the phase diagram to give a complete self-consistent set of thermodynamic data for the system. Uncertainties in the phase diagram have been resolved.

### Introduction

The importance of having complete thermodynamic descriptions of metallic alloy systems has long been realized by metallurgists. Such descriptions permit the evaluation of phase diagram studies carried out by other methods and give direct knowledge of the relative bonding energies and stabilities of the alloys, which in turn govern their

(1) Based on a thesis by Prodyot Roy submitted in partial satisfaction for the requirements for the degree of Master of Science in Metallurgy, to the University of California. chemical and physical properties under various conditions. Unfortunately, however, sufficient data are available for only a few alloy systems.

The thermodynamic properties of liquid Bi-Pb alloys are fairly well known; but for the solid phases only a few data are available. Also, uncertainties still exist in the phase diagram, especially in the  $\beta$ - and  $\epsilon$ -phase boundaries. Shown in Fig. 1 is the phase diagram evaluated by Hansen<sup>2</sup>

(2) M. Hansen, "Constitution of Binary Alloys," 2nd Edition, Me-Graw-Hill Book Co., Inc., New York, N. Y., 1956.

from all work on the system prior to 1955. Two subsequent studies by Gershman<sup>3</sup> and Oelsen and Bennewitz,<sup>4</sup> however, are in considerable disagreement with Hansen's diagram with respect to the ranges of stability of the  $\beta$ - and  $\epsilon$ -phases.

The present work has been carried out in order to complete the thermodynamic description of the solid phases and to resolve the uncertainties in the phase diagram. This was accomplished with the aid of the heat of formation and high temperature heat content measurements for  $\beta^{-}$  and  $\epsilon$ -phase alloys reported in this paper.

### Experimental

Materials.—The lead used in this investigation was obtained from the Consolidated Mining and Smelting Co., Ltd., Canada, and the bismuth from the Fairmont Chemical Co., Newark, N.J. The purity of each was specified to be 99.999%.

Approximately 10-g. ingots of each of three  $\beta$ -phase alloys containing 85, 90 and 95 at. % Pb and three  $\epsilon$ -phase alloys containing 60, 65 and 70 at. % Pb were prepared by melting the pure metals together in sealed evacuated Vycor tubes at about 650°K. followed by quenching in cold water. Weight losses on fusion were 0.01% or less and were considered negligible. The resulting ingots were cold worked and homogenized in evacuated tubes for 15 days at 450 and 380°K. for the  $\beta$ - and  $\epsilon$ -phases, respectively.

Filings taken from both ends of each ingot were strain annealed under vacuum at 375°K, and quenched in icewater. The N-ray diffraction patterns showed the alloys to be homogeneous, except for the 60 and 65 at. % Pb alloys which precipitated  $\alpha$ -phase at room temperature. The measured lattice constants were in good agreement with those of Tyzack and Raynor<sup>5</sup> and also agreed fairly well with data of Hayasi<sup>6</sup> as tabulated by Pearson.<sup>7</sup>

Apparatus and Methods.—Heats of solution of pure Bi and the alloys in liquid Pb were measured using the calorimetric apparatus and methods described previously.<sup>8</sup> Spherical specimens weighing about 1 g. were used for the measurements. The liquid Pb bath containing about 400 g. of Pb was maintained at about 654°K. for all the runs. Measurements were made of the total heat effect for pure Bi and the alloys going from the solid states at a pre-drop temperature  $T_i$  about 400°K., to the dissolved states at the solution temperature  $T_i$  about 654°K. The  $\epsilon$ -phase alloys were kept in the pre-heat furnace for a sufficient length of time to ensure that single phase structures were obtained prior to dropping them into the Pb bath. The heats of formation at temperature  $T_i$  were determined from the measured heat effects and values of  $H_{T_i} - H_{T_i}$  for Pb taken from Stull and Sinke.<sup>9</sup>

The heat capacity of the calorimeter was determined by dropping room temperature specimens of pure Pb at intervals during the course of the runs. The concentration of Bi in the bath at the end of each series of runs was about 0.6 at. %. Concentration effects were found to be negligible as indicated by the good agreement of the measured heats of solution of Bi added at the beginning and end of each series.

Heat contents with respect to 298°K. for the three  $\beta$ alloys, the 70 at. %  $\epsilon$ -alloy, and pure Pb and Bi were measured in a drop calorimeter. This instrument, described elsewhere, <sup>10</sup> operates on the principle of the Bunsen

(3) R. B. Gershman, Zhur. Fiz. Khim., 37, 1973 (1957).

(4) W. Oelsen and R. Bennewitz, Arch. Eisenhuttenw., 29, 663 (1958).

(5) C. Tyzack and G. C. Raynor, Acta Cryst., 7, 505 (1954).

(6) M. Hayasi, Nippon Kink. Galk., 3, 123 (1939).

W. B. Pearson, "A Handbook of Lattice Spacings and Structures of Metals and Alloys," Pergamon Press, New York, N. Y., 1958.
 R. L. Ori, A. Goldberg and R. Hultgren, Rev. Sci. Instr., 28, 767

(1957). (9) D. R. Stull and G. C. Sinke, "Thermodynamic Properties of

the Elements," American Chemical Society, Washington, D. C., 1956.
(10) R. Hultgren, P. Newcomb, R. L. Orr and L. Warner, Proceed-

(10) R. Hultgren, P. Newcomb, R. L. Orr and L. Warner, Proceedings, Symposium No. 9, National Physical Laboratory: The Physical Chemistry of Metallic Solutions and Intermetallic Compounds, H.M.S.O., London, 1559, Paper 1H.



Fig. 1.—Phase diagram of the bismuth-lead system.



Fig. 2.—Heats of formation of  $\beta$ - and  $\epsilon$ -phase Bi–Pb alloys at  $400^{\circ}$ K.

ice calorimeter but uses diphenyl ether instead of water as the working medium.

### Results

The values of  $(H_T - H_{298})$  were determined for the  $\beta$ -alloys at 385 and 485°K. and for the 70 at. % Pb  $\epsilon$ -alloy at 385°K. The measured values indicated that heat contents were additive within a deviation of 0–5 cal./g.-atom, implying that the alloys obey Kopp's law ( $\Delta C_p = 0$ ) within the temperature range of present interest. This is in contrast with the results of Levi<sup>11</sup> who found a positive deviation from Kopp's law, undoubtedly due to precipitation at room temperature by many of his specimens.

The measured heats of solution for pure Bi and the alloys and the integral heats of formation evaluated at  $T_i$  are given in Table I. Also tabulated

(11) A. Levi, Atti reale ist. venuta eci. lettere ed arti, 75, 627 (1916).

are the values for the partial molar heat of solution of Bi(l) in Pb(l) at infinite dilution at 654°K. (av. = -885 cal./g.-atom) calculated from the data for pure Bi and values of  $H_{T_{t}} - H_{T_{i}}$  evaluated from published heat content data for Bi. Since  $\Delta C_{p} = 0$ , the heats of formation, shown plotted in Fig. 2, will be independent of temperature and thus apply to 400°K. or any other temperature of interest. Also shown are the data of Oelsen and Bennewitz,<sup>4</sup> who measured heats of formation by pouring the pure liquid metals into a calorimeter and allowing them to solidify, assuming that homogeneous solid phases were formed. Their data agree well with the present values in the  $\beta$ region but deviate considerably for the  $\epsilon$ -alloys, where a great deal of segregation during freezing would appear unavoidable. For this reason it is believed that the present values are to be preferred.

#### TABLE I

MEASURED HEATS OF SOLUTION AND HEATS OF FORMATION OF THE ALLOYS

Run no.	<b>x</b> Pb	Ti, °K.	<i>T</i> ₁, °K.	ΔH <sub>soln.</sub> , cal./ gatom	Δ <i>H</i> form., 400°K., cal./ gatom	
66-3	0.95, <i>β</i>	392.7	653.8	2857	113	
67-3	.95, <i>β</i>	395.3	653.6	2828	125	
66-4	.90, <i>B</i>	397.6	653.9	2831	139	
67-4	.90, <i>p</i>	395.8	653.6	2876	102	
66-5	.85,β	397.7	653.9	2754	244	
67-5	.85, β	396.0	653.7	2759	249	
66-7	.70, e	395.0	654.0	2591	516	
67-7	.70, e	394.6	653.7	2630	482	
66-8	.65, e	398.0	654.4	2539	584	
67-8	.65, e	396.4	653.7	2570	563	
66-9	.60, ε	393.0	654.4	2493	694	
67-9	.60, e	390.7	653.7	2522	679	
					( <i>H</i> — <i>H</i> <sup>4</sup> )ві.т <sub>f</sub>	
66-2	Pure Bi	392.9	653.9	3561	-879	
66-10	Pure Bi	393.0	654.5	3548	-896	
67-2	Pure Bi	404.4	653.7	3491	-876	
67-10	Pure Bi	405.1	653.7	3472	-888	

The curve drawn through the integral heats of formation of the  $\beta$ -phase is represented by the parabolic equations

$$\Delta H = 1950 x_{\rm Bi} x_{\rm Pb}$$

$$\Delta \vec{H}_{\rm Bi} = 1950 x^{2}_{\rm Pb}$$

$$\Delta \vec{H}_{\rm Pb} = 1950 x^{2}_{\rm Bi}$$
(1)

Within the  $\epsilon$ -phase the data are best fitted by a straight line

$$\Delta H = 1750 - 1790 x_{Pb}$$

$$\Delta \overline{H}_{Bi} = 1750$$

$$\Delta \overline{H}_{Pb} = -40$$

$$(2)$$

### Reconciliation of Thermodynamic Data

Liquid Alloys.—Heats of formation measured by Kleppa<sup>12</sup> at 623 and 723°K. and by Wittig and Huber<sup>13</sup> at 723 and 773°K. are in excellent agreement and are probably correct within  $\pm 15$  cal./g.-atom. These heats are about 200 cal./g.-atom less negative than the calorimetric values of Kawa-kami<sup>14</sup> and about 40 cal./g.-atom less negative

(13) F. E. Wittig and F. Huber. Z. Elektrochem., 60, 1181 (1956).

than the values derived from the temperature coefficients of e.m.f. determined by Strickler and Seltz.<sup>15</sup> The results of Kleppa and Wittig and Huber indicate that Kopp's law is obeyed by the liquid alloys, hence  $\Delta C_{\rm p} = 0$ .

The selected free energies of formation were taken from the e.m.f. measurements of Strickler and Seltz,<sup>15</sup> which are in agreement with the e.m.f. values of Wagner and Engelhardt<sup>16</sup> and the vapor pressure measurements of Gonser.<sup>17</sup>  $\Delta S$  values for the alloys were calculated from the selected values of  $\Delta H$  and  $\Delta F$ . The calculated partial and integral quantities for the liquid alloys at 700°K. are given in Table II.

TABLE	П	
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PROPERTIES OF LIQUID ALLOYS AT 700°K.

	$\Delta F$ ,	$\Delta H$ ,			
	cal./g	cal./g	Δ <i>S</i> ,		
хрь	atom	atom	e.u.	a Bi	арь
0.00	0	0	0	1.000	0.000
. 10	- 550	- 80	0.67	0.894	.051
. 20	- 880	160	1.03	.777	. 116
. 30	-1095	-215	1.26	.625	. 197
. 40	-1220	-250	1.38	. 531	. 289
. 50	-1260	-265	1.42	. 404	. 402
	$(\pm 75)$	$(\pm 15)$	$(\pm 0.1)$	$(\pm .022)$	$(\pm .022)$
. 60	-1220	-250	1.39	. 290	. 528
. 70	- 1095	-210	1.26	. 193	.058
. 80	- 880	-150	1.04	.114	.783
.90	- 550	- 80	0.67	.052	. 897
1.00	0	0	0	.000	1.000

Solid Alloys.—The values of  $\Delta \bar{F}_{Bi}$  along the  $\beta$ phase solidus have been calculated from the values in the liquid and the phase diagram. For changing the standard reference state from Bi(l) to Bi(s) a temperature independent value of 4.77 cal./deg. g.-atom for the entropy of fusion of Bi was assumed. I'rom these values of  $\Delta \bar{F}_{Bi}$  and the measured values of  $\Delta \bar{H}_{Bi}$  (eq. 1),  $\Delta \bar{S}_{Bi}$  has been evaluated along the solidus. Since  $\Delta \bar{H}_{Bi}$  could be evaluated at 400°K. and the values of  $\Delta \bar{F}_{Pb}$  obtained by Gibbs–Duhem integration. Thus the thermodynamic properties of the  $\beta$ -alloys could be evaluated at any composition or temperature within the phase.

The values of  $\Delta \bar{F}_{Bi}$  at 400°K. within the  $\epsilon$ phase from  $x_{Pb} = 0.58$  to the peritectic composition,  $x_{Pb} = 0.675$ , were calculated from the liquid data and the experimental  $\Delta \bar{H}_{Bi}$  values (eq. 2) in the same manner as for the  $\beta$ -phase. Using the same values for  $\Delta \bar{H}_{Bi}$ ,  $\Delta \bar{F}_{Bi}$  values at 400°K. also were calculated from the solid equilibria assuming  $\Delta \bar{F}_{Bi}$ = 0 along the phase boundary of  $\epsilon$  in equilibrium with almost pure Bi. The values of  $\alpha_{Bi} = \Delta \bar{F}_{Bi} x^{s}/x^{2}_{Pb}$  at 400°K. obtained from these two sets of calculations are in excellent agreement, confirming the consistency of the data with the phase boundaries employed in the calculations, and lie on a straight line when plotted vs. composition as shown in Fig. 3. From the extension of this line

(14) M. Kawakami, Z. anorg. allgem. Chem., 167, 345 (1927-1928).

(15) II. S. Strickler and H. Seltz, J. Am. Chem. Soc., 58, 2084 (1936).

(16) C. Wagner and G. E. Engelbardt, Z. physik. Chem. (Leipzig), 159, 241 (1932).

(17) U. Gonser, Z. physik. Chem. (Frankfurt), 1, 1 (1954).

<sup>(12)</sup> O. J. Kleppa, This JOURNAL, 59, 354 (1955).

n

and the measured  $\Delta \overline{H}_{\rm Bi}$  values, all the thermodynamic properties of the  $\epsilon$ -phase could be evaluated at 400°K. and at other desired temperatures. The calculated partial and integral quantities for the solid alloys at 400°K. are given in Table III.

TABLE III

10001-

PROPERTIES OF SOLID ALLOYS AT 400° K.					
∆F, cal./g atom	$\Delta H$ , cal./g atom	Δ <i>S</i> , e.u.	<b>a</b> Bi	գրե	
-392	712	2.76	0.961	0.440	
-401	676	2.69	.845	. 483	
-407	587	2.48	. 559	. 622	
<sup>a</sup> −390	495	2.21	. 309	.819	
$(\pm 75)$	$(\pm 30)$	$(\pm 0.2)$	$(\pm .630)$	$(\pm .030)$	
° −314	315	1.57	. 309	. 819	
-268	248	1.29	. 243	.863	
-211	176	0.97	.172	,905	
-134	93	. 57	.092	.950	
0	0	.00	.000	1.000	
	$\begin{array}{c} \Delta F, \\ \Delta F, \\ cnl./g \\ atom \\ -392 \\ -401 \\ -407 \\ a \\ -390 \\ (\pm 75) \\ a \\ -314 \\ -268 \\ -211 \\ -134 \\ 0 \end{array}$	$\begin{array}{c} \begin{array}{c} \Delta F, \\ \alpha I, /g, -\\ a tom \end{array} & \begin{array}{c} \Delta H, \\ cal, /g, -\\ a tom \end{array} & \begin{array}{c} \alpha I, /g, -\\ a tom \end{array} \\ -392 & 712 \\ -401 & 676 \\ -407 & 587 \\ a \end{array} \\ -390 & 495 \\ (\pm 75) & (\pm 30) \\ a \end{array} \\ \begin{array}{c} -314 & 315 \\ -268 & 248 \\ -211 & 176 \\ -134 & 93 \\ 0 & 0 \end{array} \end{array}$	$\begin{array}{c} \Delta F, & \Delta H, \\ \mathrm{cal}/g, - & \Delta H, \\ \mathrm{cal}/g, - & \mathrm{cal}/g, - & \mathrm{cal}/g, \\ \mathrm{atom} & \mathrm{atom} & \mathrm{e.u.} \\ -392 & 712 & 2.76 \\ -401 & 676 & 2.69 \\ -407 & 587 & 2.48 \\ \mathrm{a} & -390 & 495 & 2.21 \\ (\pm 75) & (\pm 30) & (\pm 0.2) \\ \mathrm{a} & -314 & 315 & 1.57 \\ -268 & 248 & 1.29 \\ -211 & 176 & 0.97 \\ -134 & 93 & .57 \\ 0 & 0 & .00 \end{array}$	$\begin{array}{c} \Delta F, & \Delta H, \\ \mathrm{cal}, g, - & \mathrm{cal}, g, - & \mathrm{cal}, c$	

<sup>a</sup> Phase boundary.

Values of  $\Delta \bar{F}_{Pb}$  evaluated at 398°K. from the selected data agree well with those measured at that temperature by Strickler and Seltz<sup>15</sup> in the  $\beta$ -phase and in the heterogeneous  $\epsilon + \alpha$  region. Their results are in error at intermediate compositions, however, probably due to the lack of equilibrium which they had suspected.

**Phase Diagram.**—The phase diagram given by Hansen<sup>2</sup> has been accepted in the present work in preference to the disagreeing diagrams of Gershman<sup>3</sup> and Oelsen and Bennewitz.<sup>4</sup> With Hansen's diagram it is possible to reconcile all the data for liquid and solid alloys; this is not possible for the other diagrams. From the liquid and solid data the  $\epsilon$ -peritectic point should be at  $x_{Pb} = 0.675$ , in agreement with Hansen.

However, the phase boundary between  $\epsilon$  and  $(\epsilon + \beta)$  is not very certain; Hansen represents it by a dashed line. By moving it slightly to smaller values of  $x_{Pb}$  as shown in Fig. 1, the thermody-



Fig. 3.— $\alpha_{Bi}$ -function for  $\epsilon$ -phase Bi-Pb alloys at 400°K.

namic functions for the  $\epsilon$ - and  $\beta$ -phases come into complete accord; that is, the values of  $\Delta \bar{F}_{Bi}$  and  $\Delta \bar{F}_{Pb}$  become equal at the phase boundaries. This is shown by the values of  $\alpha_{Bi}$  in the  $\epsilon$ -phase shown in Fig. 3 calculated from the  $\epsilon$ - $\beta$  equilibrium. All the thermodynamic functions presented in the tables are in accord with the corrected phase diagram.

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# ELECTROMOTIVE FORCE MEASUREMENTS IN THE SYSTEM AgNO<sub>3</sub>-NaCl-NaNO<sub>3</sub> AND THEIR COMPARISON WITH THE QUASI-LATTICE THEORY

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Measurements of the activity coefficients of AgNO<sub>3</sub>,  $\gamma_{AgNO3}$ , in dilute solutions of Ag<sup>+</sup> and Cl<sup>-</sup> ions in NaNO<sub>3</sub> have been made at 331, 364, 385, 402, 423, 438 and 500°. The concentration dependence of log  $\gamma_{AgNO3}$  is closer to the symmetric approximation based on the quasi-lattice model than to the asymmetric approximation. Average values of the relative energies of ion pair formation,  $\Delta E$ , as defined in the quasi-lattice model, were calculated by comparison of the symmetric approximation with the experimental results. For Z = 4, 5, and 6 the values of  $\Delta E$  averaged over all seven temperatures are -5.13, -4.83 and -4.59 kcal./mole, respectively. The values of  $\Delta E$  were constant, within experimental precision, at all seven temperatures. The conventional association constant for the formation of the ion pair A<sup>+</sup>-C<sup>-</sup>, K<sub>1</sub>, is equal to  $Z[\exp(-\Delta E/RT) - 1]$ . The constancy of  $\Delta E$  at all temperatures studied and for all reasonable values of Z means that from measurements of K<sub>1</sub> at one temperature, one may, in this system, correctly predict K<sub>1</sub> at all other temperatures by use of the lattice model.

### Introduction

Measurements of the activity coefficients of  $AgNO_3$  in dilute solutions of  $Ag^+$  and  $Cl^-$  ions in molten  $NaNO_3$  at several temperatures ranging from 331 to 500° are described in this paper. These measurements are part of a continuing study at this Laboratory of the thermodynamic properties of molten reciprocal salt systems.

In previous papers<sup>4,5</sup> measurements in the system AgNO<sub>3</sub>- KCl-KNO<sub>3</sub> were described and were compared to theoretical calculations based on a quasi-lattice model.<sup>6</sup> One of the results of the comparison was that the parameter  $\Delta E$ , which is the relative energy of ion pair formation as defined in the quasi-lattice model, did not vary with temperature, within the experimental error. This means that the quasi-lattice model, in its range of validity at low concentrations of Ag<sup>+</sup> and Cl<sup>-</sup> ions leads to a correct prediction of the temperature coefficient of the activity coefficients of AgNO<sub>3</sub>.

Two calculations based on the quasi-lattice model of molten reciprocal salt systems have been made. The *asymmetric* approximation<sup>6</sup> leads to the relation for the activity coefficient of the component AD in the system  $A^+$ ,  $B^+$ ,  $C^-$ ,  $D^-$  dilute in  $A^+$  ions

$$\gamma_{\rm AD} = \frac{(1-X)^Z}{N_{\rm D}} \left( 1 + \frac{X}{\beta(1-X)} \right)^{Z-1}$$
(1)

where Z is the quasi-lattice coördination number,  $\beta = \exp(-\Delta E/RT)$ ,  $\Delta E$  is the relative energy of formation of a mole of ion pairs,  $N_{\rm D}$ - is the ion fraction of D<sup>-</sup> ion and is  $n_{\rm D}$ -/( $n_{\rm C}$ - +  $n_{\rm D}$ -), and X is the fraction of positions adjacent to an A<sup>+</sup> ion that are occupied by C<sup>-</sup> ions and can be calculated from the equation

$$\frac{X}{1-X} = \left(\frac{N_{\rm C} - Z N_{\rm A} X}{1 - Z N_{\rm A} (1 - X) - N_{\rm C}}\right) \beta \quad (2)$$

The asymmetric approximation neglects groupings such as  $A_2C^+$  containing more than one  $A^+$  ion

- (4) M. Blander, F. F. Blankenship and R. F. Newton, This Journal, 63, 1259 (1959).
  - (5) J. Braunstein and M. Blander, ibid., 64, 10 (1960).
  - (6) M. Blander, ibid., 63, 1262 (1959).

and includes the groupings  $AC_n^{+(1-n)}$  where  $n \leq Z$ .

The symmetric approximation<sup>7</sup> is the quasichemical approximation<sup>8</sup> applied to the proposed model for a molten reciprocal salt system. It leads to the relation

$$\gamma_{\rm AD} = \left(\frac{1-Y}{1-Nc^2}\right)^Z \tag{3}$$

where Y, which corresponds to X in the asymmetric model, can be calculated from the relation

$$\frac{Y}{1-Y} = \left(\frac{N_{\rm C^-} - N_{\rm A^+}Y}{1-N_{\rm A^+}(1-Y) - N_{\rm C^-}}\right)\beta \qquad (4)$$

The symmetric approximation accounts for the groups  $A_m C_n^{+(m-n)}$  where at equal concentrations of  $A^+$  and  $C^-$  ions there is equal probability for  $A_i C_j^{+(i-j)}$  and  $A_j C_i^{+(j-i)}$ . The two approximations lead to different func-

The two approximations lead to different functional relationships for the concentration dependence of the deviations from ideality.

Preliminary measurements of the activities in the system  $AgNO_3$ -NaCl-NaNO<sub>3</sub> at 402° were reported previously.<sup>7</sup> The magnitude of the values of  $-\log \gamma_{AgNO}$ , in this system was about half as large as was observed in the AgNO<sub>3</sub>-KCl-KNO<sub>3</sub> system. The concentration dependence of the deviations from ideality for measurements in both the solvents  $NaNO_3$  and  $KNO_3$  was shown to be between the calculations based on the asymmetric and the symmetric approximations. The measurements in the  $NaNO_3$  solvent were somewhat closer to the calculations based on the symmetric approximation and those in the KNO<sub>3</sub> system were much closer to the calculations based on the asymmetric approximation. The difference between measurements in these two solvents was discussed in terms of the effect of the solvent cation on the interaction of Ag+ and Cl- ions.7

The purpose of this paper is to test the constancy of the parameter  $\Delta E$  as a function of temperature and to confirm further the usefulness of the quasilattice model in predicting the temperature coefficients of thermodynamic properties.

#### Experimental

- (7) M. Blander and J. Braunstein, Ann. N. Y. Acad. Sci., 79, 838 (1960).
- (8) E. A. Guggenheim, "Mixtures," Oxford University Press, 1952, p. 38.

<sup>(1)</sup> Duke University, Durham, North Carolina, Consultant, Reactor Chemistry Division, Oak Ridge National Laboratory, Summer, 1959.

<sup>(2)</sup> University of Maine, Orono, Maine, Summer Research Participant, Reactor Chemistry Division, Oak Ridge National Laboratory, 1958-1959.

<sup>(3)</sup> Operated for the United States Atomic Energy Commission by the Union Carbide Corporation.

Reagent grade NaNO<sub>4</sub> from Baker and Adamson and from J. T. Baker was used as solvent and reagent grade NaCl

from Mallinckrodt was used as a solute. The materials, apparatus and procedure were otherwise essentially the same as described previously.<sup>4,5</sup> Although NaNO<sub>3</sub> has a greater tendency to hold water than  $KNO_3$ , degassing the melts by sparging with dry helium seemed adequate to dry the melts.

### Results

Electromotive force measurements were made in the concentration cell

where  $R_i = n_i/n_{NaNO}$ , and is the mole ratio of the component i where the *n*'s are the number of moles of the component indicated.<sup>9</sup>

The left-hand or reference electrode was kept constant in any series of measurements as the concentration of solutes in the right-hand half cell was varied. The e.m.f. of the cell is given by

$$E = \frac{2.303RT}{F} \log \frac{a_{\Lambda g N O_3}}{a'_{\Lambda g N O_3}} \tag{5}$$

where a represents activity and the prime refers to the left-hand (reference) half cell. The liquid junction potential is negligible since most of the current is carried by the solvent NaNO<sub>3</sub>. As was shown in the solvent  $KNO_3$ , the Nernst equation

$$E = \frac{2.303RT}{F} \log \frac{R_{\text{AgNO}_3}}{R'_{\text{AgNO}_3}} \tag{6}$$

was shown to hold to less than 0.5 mv. in Na-NO<sub>3</sub> for  $R_{AgNO_3} < 0.003$  in the absence of chloride ions and at several temperatures. This means that the activity coefficients are constant in the range of concentrations studied. Adoption of a standard state such that the activity coefficient is unity at infinite dilution leads to the conclusion that the activity coefficient of AgNO<sub>3</sub> is unity in the absence of chloride ions over the concentration range of AgNO<sub>3</sub> studied. Increments of NaCl were added to the right-hand half cell at a constant concentration of AgNO<sub>3</sub>. The change of e.m.f. ( $\Delta E$ ) from the initial e.m.f. at concentrations of Ag<sup>+</sup> and Cl<sup>-</sup> too low to precipitate solid AgCl is a consequence of the change in the activity coefficient of AgNO<sub>3</sub>.

$$\Delta E = \frac{2.303RT}{F} \log \gamma_{\rm AgNO_3} \tag{7}$$

### TABLE I

E.M.F. CHANGE OF HALF-CELLS CONTAINING SOLUTIONS OF AgNO<sub>3</sub> in NaNO<sub>3</sub> upon Addition of NaCl Temperature = 331°

$R_{AgNOJ} = 0.$	$301 \times 10^{-3}$	$R_{\rm AgNO3} = 1.$	$033 \times 10^{-3}$
$R_{\rm NaCl} \times 10^3$	$-\Delta e.m.f.$	$R_{\rm NaCl} \times 10^3$	.c.m.f
0.461	0.0069	0.150	0.0023
0.660	. 0092	.335	.0047
1.037	. 0146	. 592	. 0080
1.338	. 0184		
1.565	. 0213		
1.935	.0264		
3.06	. 0405		
3.59	.0463		

(9) The cation fraction

$$N_{Ag^{+}} = \frac{n_{Ag^{+}}}{n_{Ag^{+}} + n_{Na^{+}}}$$

is smaller than the mole ratio  $R_{AgNO3}$  by the factor  $1/(1 + R_{AgNO3} + R_{NaC1})$ , which is close to unity in dilute solutions. The same relation holds between  $N_{C1}$ - and  $R_{NaC1}$ .

RASNOS	= 0.300 ×	$\frac{\text{Temperato}}{R_{\text{AgNO3}}} =$	$1.033 \times$	RAgNO3	= 1.033 ×
$R_{\rm NaCl}$	10 3	R <sub>NaCl</sub>	-3	$R_{\rm NaCl}$	0-3
0.149	- 2e.m.:. 0.0018	$\times 10^{3}$ 0.1092	$-\Delta e.m.r.$ 0.0013	$\times 10^{3}$ 0 1503	- \Delta m.r. 0 0015
. 580	0073	2664	0031	483	0053
. 887	0108	626	.0072	701	.0080
1.092	.0136	805	.0092	.970	.0108
1.368	.0169	.999	. 011.1	1.238	0138
1.670	.0202	1.186	. 0135		
1.843	0218	1.258	. 01.1.4		
2.423	0282				
3.300	.0372				
4.000	. 0439				
RARN	$n_3 = 0.300 \times 10^{-3}$	Temperatu R <sub>AgNO3</sub> ×	$re = 385^{\circ}$ = 1.032	RARNO;	= 2.20
$\frac{R_{NaCl}}{\times 10^3}$	$-\Delta e_{r}r_{1}f$	$\frac{R_{\rm NaCl}}{\times 10^3}$	$-\Delta e.m.f.$	$\frac{R_{\rm NaCl}}{\times 10^3}$	– Δe.m.f.
0.352	0.0039	0.500	0.0054	0 456	0.0014
0.793	0.0005	0.300	0.0034	0.450	0.00.0
1.257	0140	1 086	0114	1 273	0122
1.810	0197	1.572	0163	1.210	
2.361	0252	2.487	0253		
2.836	. 0292				
		Temperati	arc = $402^{\circ}$		
$R_{\rm AgNO}$	$3 = 10^{-3}$	$f_{AgNO3} =$	$R_{A_ENO3}$	$s = 10^{-3}$ 3	$R_{AgNO_2} = -50 \times 10^{-3}$
R <sub>NB</sub> CI	$-\Delta R_{Na}$	$c_1 - \Delta$	RNaCI	$-\Delta = R_{\rm c}$	$X_{BC} = \Delta$
$\times 10^{3}$	e.m.f. $\times$ 1	0 <sup>3</sup> c.m.f.	$\times 10^{3}$ c	e.m.f. ×	10 <sup>3</sup> c.m.f.
0.465 - 0	0.0048 0.43	71 0.0044	0.053 0	. 0007 0.	096 0.0006
1.021	.0101 1.1	13 . 0103	. 328	. 0029 .	443 . 0032
1.672	.0164 1.89	99 .0172	817	.0072 .	789 . 0058
2.448	. 0237 2. 60	08 . 0236	1.425	.0122 1.	135 . 0086
3.100	. 0293 3. 5.	55 0318	2.429	.0207 1.	535 0113
3.980	.0367 4.2	85 .0381			
4.380	.0401 5.2	45 .0434			
4.870	. 0439				
5.425	. 0483				
$R_{ m AgN}$	$0_3 = 0.30$	Temperatu RAgNO3	$re = 423^{\circ}$ = 1.033	RASNOS	= 2.20
RNACI	X 10-2	Rsuci	10-3	X Rs₀ci	10 *
$\times 10^{3}$	.e.m.f	$\times 10^{3}$	– 4e.m.t.	$\times 10^{3}$	.e.m.f
0.453	0.0046	0.305	0.0024	0.236	0.0021
0.715	.0071	0.785	.0069	. 524	. 0042
1.039	. 00§7	1.145	. 0101	. 809	.0061
1.393	. 0131	1.494	. 0136	1.162	. 0099
1.982	.0185	1.878	. 0168	1.553	. 0130
2.827	. 02 5 5	2.240	. 0201	1.952	0161
3.291	. 0288			2.770	.0225
RACE	$0_3 = 0.300$	Temperati	are = $438^{\circ}$ = 1.033	BARNO	= 2.20
BNO	X 10 -3	Ry Cl	10 - 1	RNO	10 - 3
$\times 10^{3}$	- Δe.m.f.	$\times 10^{3}$	$-\Delta e \cdot m \cdot f$ .	$\times 10^3$	$-\Delta e.m.f.$
0.424	0.0027	0.205	0.0017	0.301	0.0023
0.809	. 0071	. 473	. 0041	0.659	.0051
1.179	0102	. 928	.0075	1.063	. 0083
1.600	. 01 5 6	1.309	. 01 1 1	1.431	.0110
1.950	.0168	1.861	.0155	2.173	.0156
2,432	0201	2.308	. 0193	2.609	0197
2.805	. 0234	2.836	. 0235	3.019	. 0224
		Towner	.0208		
$R_{2}$	$v_{gNO3} = 0.299$	1  cmperat	$are = 500^{\circ}$ $R_{AgNO3}$	= 1.129 ×	10 *
$R_{ m Nac}$	n × 10°	.e.m.f	$R_{\rm NaCl}$ $\times$	$10^3 - 7$	e.m.f.
0	. 835	0.0063	0.200	о́. О.	0005
2	.247	.0162	0.691		0019
3	. 871	. 0263	1.115	<b>j</b> .	0061
5	.434	. 0358	1.453	3.	0084
7	256	0465	1.942	2	0110

where

$$\gamma_{\rm AgNO_3} \equiv \frac{a_{\rm AgNO_3}}{R_{\rm AgNO_3}}$$

 $\begin{array}{c} 2.417\\ 2.799 \end{array}$ 

0144

0164

In Table I are listed the measured changes of e.m.f. at several concentrations of  $AgNO_3$  and NaCl and at six temperatures ranging from 331 to 500°. The values of e.m.f. were somewhat less repro-



Fig. 1.—A comparison of the concentration dependence of  $-\log \gamma_{AgNO3}$  at 385° with the calculations based on the symmetric and asymmetric approximations.



Fig. 2.—A comparison of experimental values of  $-\log \gamma_{AgNO_3}$  at  $R_{AgNO_4} = 0.30 \times 10^{-3}$  at seven temperatures with calculations based on the symmetric theory.

ducible than those made in  $KNO_3$  as solvent, although the values of the e.m.f. were reproducible to about 0.5 mv. The measurements at 500° are uncertain since some decomposition occurred in the melt at this temperature. Two separate runs at  $R_{AgNO_2} = 1.13 \times 10^{-3}$  were within 0.5 mv. of each other and at 500°, the e.m.f. drifted about 1.0 mv. in one hour, apparently due to loss of AgNO<sub>3</sub>. The measurements at 500° were made in less than one hour. After 5 hr. a melt through which no gas had been bubbled turned yellow, presumably because of NO<sub>2</sub> formed in the decomposition of the melt, and the e.m.f. had drifted about 4 mv. A check was made of the effect of the possible decomposition reaction

$$NO_3^- \xrightarrow{} NO_2^- + \frac{1}{2}O_2$$

on the e.m.f. of the cell.  $NaNO_2$  was added to a melt of NaNO<sub>3</sub> containing  $0.30 \times 10^{-3}$  mole ratio of AgNO<sub>3</sub> at 385° until the concentration of NaNO<sub>2</sub> was  $0.95 \times 10^{-3}$  mole ratio. No change of e.m.f. was detected although the concentration of  $NO_2^$ ions was much larger than the concentration of Ag+ ions indicating that the effect of the decomposition of  $NO_3^-$  to  $NO_2^-$ , if it occurred, may be neglected. In Fig. 1 are plotted values of  $-\log \gamma_{AgNO_3}$  as a function of  $R_{\text{NaCl}}$  at two values of  $R_{\text{AgNO}_3}$  at 385°. The dashed lines are values of  $-\log \gamma$  calculated from the asymmetric and the symmetric approximations for the values of the parameters indicated. As was shown previously,<sup>7</sup> the experimental results are closer to the calculations based on the symmetric approximation and the symmetric approximation will be used to fit the data at the low concentrations of Ag<sup>+</sup> and Cl<sup>-</sup> ions. In Fig. 2 are plotted values of  $-\log \gamma_{AgNO_1}$  as a function of  $R_{\text{NaCl}}$  at the seven temperatures measured and at

a value of  $R_{AgNO_1} = 0.30 \times 10^{-3}$ . In columns 2, 3, and 4 of Table II are listed the values of  $\Delta E$  necessary to obtain a correspondence of the symmetric theory and the experimental results at the lowest concentration of Ag<sup>+</sup> and Cl<sup>-</sup> ions for values of Z (coördination numbers) of 4, 5 and 6, respectively. The dashed lines in Fig. 2 represent the theoretically calculated values of  $-\log \gamma_{AgNO_1}$  for values of the parameters given in Table II when Z = 6 at the temperatures and concentrations indicated. The calculated values of  $-\log \gamma$  in this range of concentrations are essentially independent of the value of  $Z(\beta - 1)$ .

TABLE II

Values of  $\Delta E$  and  $Z(\beta - 1)$  Obtained from the Comparison of the Data with the Theory

		$-\Delta E$ (kcal.)		$Z (\beta - 1)$
Т, °К.	Z = 4	Z = 5	Z = 6	$\times$ 10 <sup>2</sup>
604	5.10	4.83	4.62	2.77
637	5.12	4.84	4.62	2.26
658	5.17	4.88	4.65	2.05
675	5.10	1.81	4.57	1.76
696	5.13	4.83	4.59	1.60
711	5.12	4.81	4.56	1.46
773°	5.14	4.82	4.55	1.10

 $^a$  The results at 773  $^{\circ}{\rm K}.$  are less certain than those at the six lower temperatures.

Within the experimental reproducibility the values of  $\Delta E$  are constant over the entire temperature range studied. This means that from measurements at one temperature, one might have predicted the experimental results at all other

temperatures at the low concentrations of Ag<sup>+</sup> and Cl<sup>-</sup> ions where the theory is valid. The constancy of  $\Delta E$  is apparently independent of the choice of reasonable values of the coördination number in this case.

Relation of the Quasi-lattice Model to the "Chemical" Approach.<sup>10</sup>—The conventional approach to the description of the thermodynamics of the system studied is by the use of equilibrium quotients. In this "chemical" approach the assumption is made that the activity of  $AgNO_3$  is equal to the concentration of "free"  $Ag^+$  ion. The total stoichiometric concentration of silver ion  $N_{Ag}$  is set equal to the weighted sum of the concentrations of the species containing silver ions

$$N_{\mathrm{Ag}^{\star}} = N^{\mathrm{f}}_{\mathrm{Ag}^{\star}} + N_{\mathrm{AgCl}} + 2N_{\mathrm{AgcCl}^{\star}} + N_{\mathrm{AgCl}_{2}^{-}} + \dots$$
(8)

where the  $N_i$  are either ion fractions or mole fractions, depending on whether i is an ion or a neutral species, and superscript f denotes the free or uncomplexed species. The equilibria given below having the equilibrium constants  $K_1$ ,  $K_2$  and  $K_{12}$ , respectively, are postulated. Setting  $\gamma_{AgNO_4} =$ 

$$Ag^{+} + Cl^{-} \longrightarrow AgCl$$

$$AgCl + Cl^{-} \longrightarrow AgCl_{2}^{-}$$

$$AgCl + Ag^{+} \longrightarrow Ag_{2}Cl^{+}$$

$$K_{1} = \frac{N_{AgCl}}{N_{f_{Ag}^{+}}N_{f_{Cl}^{-}}}$$
(9)

$$K_2 = \frac{N_{AgC12^-}}{N_{AgC1}N'_{C1^-}}$$
(10)

$$K_{12} = \frac{N_{AgrC1^{*}}}{N_{Agc1}N'_{Ag^{*}}}$$
(11)

 $N_{Ag}^{*}/N_{Ag}^{*}$  and substituting into equation 8 from equations 9, 10 and 11 leads to

$$1 = \gamma_{AgNO_2} + K_1 \gamma_{AgNO_2} N'c_{1^-} + K_1 K_2 \gamma_{AgNO_2} (N'c_{1^-})^2 + 2K_1 K_{12} \gamma_{AgNO_2} N'c_{Ag^*} N'c_{1^-} + \dots$$
(12)

As 
$$N_{\mathbf{A}} \to 0$$
,  $N_{\mathbf{A}} \to 0$  and  $N_{\mathbf{Cl}} \to N_{\mathbf{Cl}}$ , so that

$$\lim \left(\frac{\partial \ln \gamma_{AgNO_3}}{\partial N_{C1^-}}\right)_{\substack{N_{Ag^*} \to 0 \\ N_{C1^-} \to 0}} = -K_1 \quad (13)$$

From both the symmetric and asymmetric calculations based on the quasi-lattice model<sup>11</sup>

$$\lim \left(\frac{\partial \ln \gamma_{AD}}{\partial N_{c}}\right)_{N_{c}} \rightarrow 0 = -Z(\beta - 1) \quad (14)$$

$$N_{c} \rightarrow 0$$

so that

$$K_1 = \mathbb{Z}(\beta - 1) \tag{15}$$

Values of  $Z(\beta - 1)$  are listed in column 5 of Table II.

The chemical approach leads to difficulties and needs to be qualified. For example, if the associated species behave non-ideally, the values of the equilibrium quotients defined by equations 9, 10 and 11 will not be constant. This difficulty

(10) The word "chemical" as used here implies the use of the massaction law only and is not meant to imply anything about the ionic binding.

(11) Appendix A.

can be avoided by defining  $K_1$  by equation  $13.^{12}$ In this definition,  $K_1$  is a true constant since there is only one limit of the continuous single valued function  $(\partial \ln \gamma_{AgNO_3}/\partial N_{C1})$ .  $K_2$  and  $K_{12}$  can be defined in terms of higher derivatives. The conclusions drawn from Table II in conventional "chemical" terms can be restated as follows:

The constancy of  $\Delta E$  at all temperatures studied and for all reasonable values of Z means that from measurements of the first association constant,  $K_1$ , at one temperature, one may correctly predict values of  $K_1$  in this system at all other temperatures by the use of equation 15. The lattice theory, in its present form, is not correct for the higher association constants. A more general theory which accounts for some of the higher association constants has been derived and will be submitted for publication, and measurements similar to those presented here in the mixed solvent NaNO<sub>3</sub>-KNO<sub>3</sub> will soon be completed.

Acknowledgment.—We wish to acknowledge the assistance given by Messrs. R. C. Bansal and R. M. Lindgren, of the University of Maine, in checking the data at 500° and valuable discussions with Dr. R. F. Newton, of the Oak Ridge National Laboratory, and Professor George Scatchard.

### Appendix A

Differentiating the logarithm of equation 1 with respect to  $N_{\rm C}$ -yields

$$\frac{\partial \ln \gamma_{AD}}{\partial N_{C^{-}}} = -\left(\frac{Z}{1-X}\right)\frac{\partial X}{\partial N_{C^{-}}} + 1 + \left[\frac{(Z-1)(1-\beta)}{X+\beta(1-X)}\right]\frac{\partial X}{\partial N_{C^{-}}} + \left(\frac{Z-1}{1-X}\right)\frac{\partial X}{\partial N_{C^{-}}}$$
(i)

Cross multiplying equation 2 and differentiating both sides with respect to  $N_{C}$ -

$$\frac{\partial X}{\partial N_{C^{-}}} (1 - ZN_{A^{*}} + ZN_{A^{*}}X - N_{C^{-}}) + X\left(ZN_{A^{*}} \frac{\partial X}{\partial N_{C^{-}}} - 1\right) = \left\{ (1 - X)\left(1 - ZN_{A^{*}} \frac{\partial X}{\partial N_{C^{-}}}\right)\beta + \left(-\frac{\partial X}{\partial N_{C^{-}}}\right)(N_{C^{-}} - ZXN_{A^{*}})\beta \right\}$$
(ii)

letting  $N_{C^+} \rightarrow 0$ , and  $N_{\Lambda^+} \rightarrow 0$  then  $X \rightarrow 0$  and

$$\lim_{\substack{\delta X \\ \delta X_{c^{-}}}} \left( \frac{\delta X}{\delta X_{c^{-}}} \right) = \beta$$
(iii)  
$$N_{\delta^{+}} \rightarrow 0$$

Substituting from equation iii into (i) and taking the limit

$$\lim_{N_{c^{+}} \to 0} \left( \frac{\partial \ln \gamma_{AD}}{\partial N_{c^{+}}} \right) = -Z(\beta - 1) \qquad (iv)$$
$$N_{c^{-}} \to 0$$
$$N_{A^{+}} \to 0$$

In a similar manner equation iv can be derived from equations 3 a.d 4.

<sup>(12)</sup> Any other method of extrapolating the *equilibrium quotient* to infinite dilution so as to obtain an *equilibrium constant* would be equivalent.

# THE SYSTEM IRIDIUM-TELLURIUM

BY E. F. HOCKINGS AND J. G. WHITE

RCA Laboratories, Princeton, New Jersey Received March 2, 1960

The system iridium-tellurium was examined by X-ray methods. Only two compounds  $IrTe_2$  and  $Ir_3Te_8$  were observed and their crystal structures have been determined.  $IrTe_2$  has the  $Cd(OH)_2$  type structure (C6) and  $Ir_3Te_8$  is a defect pyrite  $FeS_2$  structure (C2) with approximately one quarter of the cation sites vacant. The crystal structures formed by these compounds have been ascribed to the arrangement of the electronic energy levels of the metal atoms.

### Introduction

The tellurides of the platinum metals were prepared by Wohler, Ewald and Krall<sup>1</sup> who found that the reaction of iridium trichloride with excess tellurium gave a tritelluride  $IrTe_3$  and that this could be reduced by hydrogen at 600° to give a ditelluride IrTe<sub>2</sub>. The composition of the compound with the higher tellurium content was investigated experimentally by Biltz<sup>2</sup> and found to be IrTe<sub>2.89</sub>. Although he described this phase to be of the "pseudopyrite type," no details of the structure were reported. An X-ray study of two iridiumtellurium compositions was made by Groenveld Meijer.<sup>3</sup> He prepared the composition IrTe<sub>2.5</sub> and observed that it was a pyrite-type structure, in agreement with Biltz. The other composition was stated to be IrTe but as noted by Haraldsen<sup>4</sup> it was in fact the ditelluride, IrTe<sub>2</sub>. Hansen and Anderko<sup>5</sup> pointed out that the iridium-tellurium system had not been studied systematically, and as a consequence, the present work was undertaken.

### Experimental

Materials.—The iridium was in powder form, 200–300 mesh, and purity of at least 99.8%. The tellurium was of high purity 99.99%.

**Preparations.**—Weighed quantities of the elements were placed in fused silica ampules and scaled under vacuum. The ampules were heated to 950° for six hours, maintained at 600° for a further 18 hours and then cooled rapidly. There was on indication of any reaction with the ampules and it is assumed that the compositions remained unchanged during preparation. The resultant specimens were ground, rolled into thin cylindrical rods with Duco cement, and examined at room temperature by X-ray powder diffraction methods. The diffraction patterns were obtained in a 11.46 cm. diameter Straumanis type camera using Ni filtered Cu K $\alpha$  radiation at 35 kv. and 20 ma. The exposures were of four hours.

### Results

The qualitative results are given in Table I from which it is seen that only two compounds were found in the system and that their compositions are probably 66.7 and 73 at. % Te. X-Ray diffraction patterns were obtained from specimens prepared with these compositions and each was found to be a single phase.

The Crystal Structure of  $IrTe_2$ .—The X-ray powder photograph of  $IrTe_2$  could be indexed on the basis of a primitive hexagonal unit cell. A series of *a* values was obtained from *hk*0 reflections and *c* values from reflections with high *l* combined with

(1) L. Wohler, K. Ewald and H. G. Krall, Chem. Ber., 66, 1638 (1933).

- (3) W. O. J. Groenveld Meijer, Am. Min., 40, 646 (1955).
- (4) H. Haraldsen, Experientia Suppl., 7, 165 (1957).

TABLE I

PHASES OBSERVED	IN THE IRIDIUM-TELLURIUM SYSTEM
Composition at. 🎲 Te	Phases present
39.9	Iridium + lower telluride
51.4	Iridium + lower telluride
60.7	Iridium + lower telluzide
66.7	Lower telluride
68.0	Lower telluride + higher telluride
69.8	Lower telluride $+$ higher telluride
73.0	Higher telluride
80.4	Higher telluride + tellurium
89.9	Higher telluride + tellurium

### TABLE II

Crystallographic Data for  $IrTe_2$  and  $Ir_3Te_8$  at 25° ( $\lambda = 1.5405$  Å.)

	(n - 1.0100)	<b>1</b> •)
	IrTe <sub>2</sub>	IraTes
Crystal system	Trigonal	Cubie
$\pi_0$ (Å.)	$3.930 \pm 0.003$	$6.411 \pm 0.003$
$c_0$ (Å.)	$5.393 \pm 0.005$	
Absent spectra	None	Reflections of the form $\{0kl\}$ with 2 odd indices
Assumed space		
group	$D_{ad}^3 - P3ml$	T <sub>b</sub> <sup>6</sup> − Pa3
Z	1	$4 (Ir_{0.75}Te_2)$
X-Ray density	10.30	10.05
Measured density		9.87

the value of a appropriate to each reflection. The individual values of a and c were extrapolated<sup>6</sup> to  $\theta = 90^{\circ}$ , and these are the values given in Table II. The intensity distribution was strongly indicative of the Cd(OH)<sub>2</sub> structure type.<sup>7</sup> The calculated intensities given in Table III were obtained by assuming

Space group 
$$D_{3d}{}^3 - 1^{23}ml$$
 Ir in (a) 0,0,0  
2 Te in (d)  ${}^{1/_{3}}, {}^{2/_{3}}, u; {}^{-2/_{3}}, {}^{1/_{3}}, \bar{u}$ 

The structure factors F were calculated from the expressions given in the International Tables<sup>8</sup> for the space group  $P\overline{3}ml$ . The scattering factors for Ir and Te were those given in Internationale Tabellen<sup>9</sup> and were corrected for anomalous dispersion by the method of Dauben and Templeton.<sup>10</sup> Then calculated intensities were obtained from the expression

I calcd. = 
$$F^2 p \frac{(1 + \cos^2 2\theta) \times 10^{-5}}{\sin^2 \theta \cos \theta}$$

<sup>(2)</sup> W. Biltz, Z. anorg. Chem., 233, 282 (1937).

<sup>(5)</sup> M. Hansen and K. Anderko, "Constitution of Binary Alloys," McGraw-Hill Book Co., New York, N. Y., 1958, p. 874.

<sup>(6)</sup> J. B. Nelson and D. P. Riley, Proc. Phys. Soc., 57, 160 (1945).

<sup>(7)</sup> Strukturbericht, 1, 161 (1931).
(8) "International Tables for X-ray Crystallography," The Kynoch Press, Birmingham, 1952.

<sup>(9) &</sup>quot;Internationale Tabellen zur Bestimmung von Kristallstrukturen." Vol. II, Borntraeger, Berlin, 1935, p. 571.

<sup>(10)</sup> C. H. Dauben and D. H. Templeton, Acta Cryst., 8, 841 (1955).

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where p is the multiplicity of the reflecting planes. No absorption corrections were applied. The good agreement between the calculated and observed intensities supports the postulated structure although it is not established as definitively as would be the case with single crystal data.

TABLE III

LATTICE	SFACINGS AND I	NTENSITIES FO	r IrTe2
hkl	d obsil., Å.	I obsd.	I caled.
001	5.32	М	90
100			8
101	2.86	VS	284
002			$^{2}$
102	2.10	S	134
110	1 958	MS	108
111	1.840	W	30
003	1 791	vw	.1
200	1.101		-1
200	1 617	м	51
103	1.017	- 11	51
112	1.586	М	-18
202	1 436	M	38
004	1 348	W	10
113	1 292	VW	10
210	1.020		10
101	1.1.1		1
104	1.050		1
211	1.200		-+()
203	1.235	WM	19
212	1.160	M	38
300	1.133	W	18
$\begin{array}{c}114\\301\end{array}$	1.111	$\mathbf{MS}$	39
005			1
204			I
302)			
213	1.046	W M	27
105	1.029	WM	12
220	0.982	W	13
221 )			
303 }	. 958	VW	9
115	. 946	VW	6
310 J			
$\frac{214}{211}$	. 930	WM	25
311 J 999			
222			1
205	.911	w	12
006			0
312	.891	W M	29
106 304	. 869	MS	47
223	1241	10	6
400			0
401	.840	W	16
311	836	WM	32
215	826	M	34
116	. 020		1
402	812	w	•>:2
206	794	M.	31

The Crystal Structure of  $Ir_3Te_8$ .—The powder diffraction pattern of the higher telluride phase could be indexed on the basis of a cubic unit cell. The lattice parameter was obtained similarly to that for IrTe<sub>2</sub>. Integrated intensity measurements were made on a Norelco diffractometer. Some initial difficulty was experienced in obtaining reproducible data owing to the very high absorption of the sample. However, after very prolonged grinding the particle size was reduced to the range 0.5-5  $\mu$  as measured microscopically, and on this material reproducible results were obtained. The scanning rate was  $1/8^{\circ}$  per minute and the intensity measurements were made by graphical integration of the peak zreas above background as recorded on a chart. Two separately prepared samples showed a mean intensity deviation expressed as  $\Sigma I_1 - I_2/\Sigma I_1$  of seven per cent. and the mean values of these two intensity sets were used for  $I_{obsd}$ in Table IV.

The composition of the preparation was within experimental error of the formulation Ir<sub>3</sub>Te<sub>8</sub> and the density as measured by displacement of water by the powdered sample was 9.87 g. cm.<sup>-3</sup> indicating one  $Ir_3Te_8$  per unit cell. A survey of the simple cubic space groups which would allow three iridium atoms and eight tellurium atoms to be placed in ordered positions was made. Five space groups fulfill these conditions: P23, Pm3, P432, P43m and Pm-Within these space groups the atoms could 3m. be distributed in special positions in two general ways. The first may be exemplified by the space group P432 where the iridium atoms could be placed in the 3(c) or 3(d) positions and the tellurium atoms in the 8(g) positions. While reasonable interatomic distances could be obtained by such an arrangement the calculated intensities over the entire allowable range of the free parameter were incompatible with those actually observed. Another formal possibility, although one in which there would be crystallographically different sites for tellurium atoms, would be to place the tellurium atoms in the 1(a) and 1(b), and the 6(f), 6(g), 6(h), or 6(i) positions of the space group P23. There are corresponding positions in the other space groups listed above. However, no combination of these positions could give reasonable interatomic distances and Ir<sub>3</sub>Te<sub>8</sub> must have a disordered structure. The observed reflections were consistent with the space group  $T_{h}^{6}$  Pa3. The over-all intensity distribution was similar to that expected for a pyrite structure with space group Th<sup>6</sup> Pa3 having

4 M in (a) ), 0, 0; 
$$\frac{1}{2}, \frac{1}{2}, 0; \frac{1}{2}, 0, \frac{1}{2}; 0, \frac{1}{2}; 0, \frac{1}{2}, \frac{1}{2}$$
  
8 X in (c) u, u, u;  $u + \frac{1}{2}, \frac{1}{2} - u, \tilde{u};$   
 $\tilde{u}, u + \frac{1}{2}, \frac{1}{2} - u;$   
 $\frac{1}{2} - u, \tilde{u}, u + \frac{1}{2}$ 

despite the deviation in chemical composition from the MX<sub>2</sub> atomic ratio. The pyrite-type structure could be achieved by distributing three iridium atoms at random over the 4(a) positions. On this basis intensity calculations were made as for IrTe<sub>2</sub> above. It was found necessary to multiply the calculated intensities by a temperature factor  $\exp(-2B\sin^2\theta/\lambda^2)$  with 2B = 1.33. While ideally no absorption corrections are required with a diffractometer, in practice any surface roughness of the sample will affect the lower angle reflections more than those at high angle and the temperature factor deduced is probably a lower limit. A series of calculations with various u parameters showed the best agreement between calculated and observed intensities with u = 0.368, which is probably correct to  $\pm 0.005$ . This parameter has been used in obtaining the *I* calcd. values in Table IV.

<b><i>LABLE</i></b>	IV
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LATTICE	SPACINGS AND I	NTENSITIES FO	R Ir <sub>3</sub> Te <sub>8</sub>
hkl	d obsd., Å.	I obsd.	I calcd.
111	3.65	18	22
200	3.19	53	46
210	2.85	182	184
211	2.60	114	128
220	2.26	47	50
221	2.20		1
311	1 929	157	161
222	1.840	18	16
320	1.775	20	20
321	1.708	67	20 69
400	1.708	5	5
400	1.000	5	5
200			1
322 )			0
411		•••	0
331			2
420	1.421	27	27
421	1.397	30	32
332	1.366	13	13
422	1.306	16	14
430		••	0
431		••	1
511	1.233	41	37
333 )	1.200		0.
520	1 100		95
432 j	1.189	(،ک	23
521	1.169	17	16
440	1.132	33	33
522 )			0
441 ∫		••	0
433		· · ·	0
531			3
600 )	1.000	10	0
442∫	1.008	10	9
610	1.053	7	6
611 )	1.040	00	10
532 ∫	1.040	20	19
620	1.014	6	5
621			
540 }			3
443			
541			0
533	0.978	18	16
622	. 967	6	7
630 \	056	14	17
542∫	. 990	10	17
631	. 946	10	10
444			1
632			0
543			0
711 )			.,
551 ∫		••	ა
640			2
720	001	10	1.7
641 j	. 381	13	13
721			
633	.872	18	20
552		-0	
642	. 857	16	14
722 1			
544		••	1

$\left.\begin{array}{c}731\\553\end{array}\right\}$	.835	66	66		
$\left.\begin{array}{c}650\\643\end{array}\right\}$	.821	14	18		
$\left. \begin{array}{c} 651 \\ 732 \end{array} \right\}$	.814	26	27		
800	.802	17	18		
(Dente V					

	I ABL	IS V	
CLOSE IN:	FERATOMIC DISTA	NCES IN IrTe2	AND Ir3TCs
Atom	Neighbors	Interatomic IrTe2	distances, Å. IrsTes
Ir	6 Te	2.64	2.65
Te	3 Ir	2.64	2.65
$\mathbf{T}\mathbf{e}$	$\mathbf{T}\mathbf{e}$		2.93

Since a defect structure has been postulated there seems no reason why the ratio of iridium to tellurium should be *exactly* 3 to 8. An independent measure of the correctness of this ratio may be obtained from the X-ray intensity data. Reflections with mixed indices are dependent only on the tellurium atom positions while those of unmixed indices have contributions both from the iridium atoms and the tellurium atoms. Consequently, as the number of vacancies increases the average intensity of the reflections with unmixed indices is rapidly reduced with respect to that of the reflections with mixed indices. Since the two sets are interleaved in the experimental measurements, it is unlikely that any systematic error would be present. In the final intensity scales the ratio of  $\Sigma I_{\text{calcd}} / \Sigma I_{\text{obsd}}$  is 1.03 for the intensities of mixed indices reflections and 0.98 for those of unmixed indices. These ratios are within experimental error and again indicate close agreement with the Ir<sub>3</sub>Te<sub>8</sub> formulation.

### Discussion

The structures shown by the two iridium tellurides form a transition between osmium telluride OsTe<sub>2</sub> and platinum telluride PtTe<sub>2</sub>. The structure of OsTe<sub>2</sub> is the C2 type<sup>11</sup> and that of PtTe<sub>2</sub> is the C6  $type^{12}$  with the intermediate metal iridium showing both structural types. The compound  $RhTe_2$ shows two crystal structures, the low temperature modification being the C2 type and the high temperature modification the C6 type.<sup>13</sup> Both structures have certain characteristics in common as shown in Table V. In both arrangements each iridium atom has six tellurium atoms as nearest neighbors and each tellurium has three iridiums at the same distance (referred to the ideal structure with all cation sites occupied), but in the C2 structure there is an additional close approach of a tellurium atom. The Te-Te distance is 2.93 Å. Even though this distance is very sensitive to the u parameter ( $\pm 0.005$  in u is equivalent to  $\pm 0.11$  Å. in the Te-Te distance), these two atoms must be considered as forming a bond.

In the C6 structure each tellurium atom has three bonds to neighboring metal atoms, and it is likely that the electron octet is completed by a lone

(11) L. Thomassen, Z. physik. Chem., 2B, 349 (1929).

- (12) L. Thomassen, ibid., 2B, 364 (1929).
- (13) S. Geller, J. Am. Chem. Soc., 77, 2641 (1955).

pair. When Te-Te bonds are formed as in the C2 structure, fewer electrons from the metal atoms are required to complete the tellurium octets. Thus  $OsTe_2$ , having the fewest total electrons of the three tellurides, forms the C2 structure, while PtTe2 crystallizes in the C6 structure. IrTe<sub>2</sub> forms the C6 structure even though the total electron content is one fewer than that of  $PtTe_2$ . This structure may be stabilized by resonance so that the effective positive charge is shared by the tellurium atoms. This would permit the metal atoms in both PtTe<sub>2</sub> and IrTe<sub>2</sub> to have six electrons in non-bonding levels despite the difference in total number of electrons between the two compounds. The field resulting from a nearly octahedral arrangement of tellurium atoms around the metal atoms will give

rise to three low lying electronic energy levels in which six electrons can be spin-paired.

In  $OsTe_2$  the Te-Te bond permits the metal to retain six electrons and these would be expected to be spin-paired in the three low energy levels. Iridium telluride might be expected to form the C2 structure if the number of non-bonding electrons per metal atom can be reduced to six, and this is nearly achieved in the defect structure  $Ir_3Te_8$ . The vacancies on the iridium sites reduce the number of electrons for each metal atom to  $6^{1}/_{3}$  from the value of 7 in the case that the metal sites were fully occupied.

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# STUDIES ON FORMATION AND AGING OF PRECIPITATES. XLVII. MAXIMA IN PARTICLE SIZE OF LEAD SULFATE FORMED UNDER VARIOUS CONDITIONS<sup>1/2</sup>

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The critical supersaturation for maximum particle length was determined in precipitation of lead sulfate from aqueous solutions containing lead and sulfate in non-equimolar amounts (Pb/SO<sub>4</sub> varying from 46 to 0.2), from solutions in mixtures of ethanol and water, and from aqueous solutions at various temperatures. The activity product of lead and sulfate in a saturated solution in the same solvent at the same temperature.

In a previous paper it has been established that in precipitation of lead sulfate at  $25^{\circ}$  from equimolar solutions of lead and sulfate salts a sharp maximum in particle length occurs at a welldefined concentration of these ions.<sup>3</sup> In the present paper we present results of a similar study in which the solutions were not equimolar. In addition, the effect on particle size of solubility, ionic strength and temperature has been investigated.

### Experimental

Experimental procedures were the same as those described in the previous paper. A mixture was prepared by placing 50 ml. of a lead solution in a polyethylene beaker and adding with constant rapid stirring 50 ml of a sulfate solution from a graduate. The time of addition was less than one second. Stirring was continued for 5 minutes when precipitation was practically complete. On further standing a slow aging of the crystals occurred. The order of mixing had no effect on the habit and size of the crystals. The pH of the reactants was kept at 3.0 by addition of dilute perchloric acid.

Precipitation from Solutions Containing Excess of Lead or Sulfate.—In a given series of precipitations at 25° either the lead or sulfate concentration was kept constant, the concentration of the other reactant being varied. As an illustration, the initial lead perchlorate was kept constant at 0.100 M in the mixture and the sodium sulfate concentration was varied systematically. A well-defined maximum length of the crystals was observed within a narrow range of sulfate concentrations. At initial sulfate concentrations in the mixtures of 2.00, 2.10, 2.15, 2.20 and 2.25  $\times$  10<sup>-3</sup> M the length of the crystals was 24, 30, 35, 18 and 10 $\mu$ , respectively.

In mixtures more concentrated in sulfate than in lead, the lead concentration was varied at constant sulfate concentration. At relatively high sulfate concentrations the maximum length could not be determined accurately because the variation of particle length with change in concentration of lead became too small. The results are summarized in curve I of Fig. 1. Curve II in Fig. 1 illustrates the effect of an increase of ionic strength on critical concentrations for maxima in size by making the mixtures 0.100 M in sodium perchlorate.

Similar curves were obtained with lead nitrate instead of lead perchlorate, and with sulfuric acid instead of sodium sulfate as reactants.<sup>2</sup> Substitution of potassium sulfate for sodium sulfate caused the disappearance of a sharp maximum in length at lead perchlorate concentrations smaller than 0.0135 M at widely varied concentrations of potassium sulfate. The concentrations of various species in solutions of critical supersaturation for maxima are given in Tables I, II and III.

Effect of Ethanol.—In order to test the effect of solubility of lead sulfate on the critical supersaturation for maximum particle length, experiments were carried out in the presence of different concentrations of ethanol. Even at low concentrations of thanol the solubility of lead sulfate decreases markedly.<sup>4</sup> All experiments were carried out using equimolar solutions of lead perchlorate and sodium sulfate at 25°. The same techniques were used as in the previous paper,<sup>4</sup> except that the solutions contained a given percentage of alcohol.

At concentrations of  $4.0 \times 10^{-3} M$  lead perchlorate and sodium sulfate in the mixture the percentage of alcohol was varied from 0 to 10 volume %. The maximum length was observed at 4% ethanol. In the absence of alcohol maximum length was found at  $6.4 \times 10^{-3} M$  solutions of lead sulfate.

<sup>(1)</sup> This investigation was supported by a grant from the Office of Ordnance Research.

<sup>(2)</sup> From a Doctor's Thesis, submitted by Bartholomeus van't Riet to the Graduate School of the University of Minnesota, 1957.

<sup>(3) 1.</sup> M. Kolthoff and B. van't Riet, THIS JOURNAL, 63, 817 (1959).

<sup>(4)</sup> I. M. Kolthoff, R. W. Perlich and D. Weiblen, THIS JOURNAL, 46, 561 (1942).

### TABLE I

# CONCENTRATIONS AND ACTIVITY PRODUCTS IN CRITICAL MIXTURES OF LEAD PERCILORATE AND SODIUM SULFATE (pH3)

Pb(ClO <sub>4</sub> ) <sub>2</sub>	Na <sub>2</sub> SO <sub>4</sub>	<u> </u>	СРЬ++	CS04-	CHS04-	CP5504	CP6(SO4)2-	$a_{Pb-+} \times a_{S04-} \times 106$	Ionic
$\times$ 10°, M	$\times$ 104, M	γS04-	× 104, .1	X 104, 14	X 10 <sup>4</sup> , M	X 10°, .0	× 10°, 51	A 10 <sup>-</sup>	A 20
1000	21.5	0.24	985	6.3	0.15	15	0.06	3.6	0.30
500	24	.32	484	8.0	.25	16	. 09	3.8	.152
250	26.5	. 40	234	10.2	. 4	16	. 1 _	3.8	.077
200	27.5	. 43	184.5	11.3	. 5	16	.12	3.8	.063
150	31.0	. 46	133.5	13.9	. 6	16	. 15	3.9	.049
125	33.5	.48	108	16.1	.7	16	.18	4.0	.042
100	38.0	. 50	83	19.8	1.0	17	.22	4.1	.035
87.5	43.5	.52	69.4	23.8	1.2	18	. 27	4.4	.033
80	50	.52	60.5	28.8	1.4	19	.37	4.6	.033
64	64	.52	43.4	40.8	2.0	20	. 6	4.8	. 031
61	80	.51	38.4	54.6	2.0	22	. 8	5.3	.034
52	100	. 50	29.1	73	3	22	1.1	5.3	.036
47	110	. 49	25.3	83	4	21	1.2	5.0	. 039
44	120	.49	22.4	94	4	20	1.3	4.9	. 040
41.5	140	.47	19.6	114	4	20	1.6	4.9	.045
41	150	.46	19.3	119	5	20	1.7	4.9	.048
39	200	43	16.2	168	6	20	2.6	4.9	.061

TABLE II

CONCENTRATIONS AND ACTIVITY PRODUCTS IN CRITICAL MIXTURES CONTAINING 0.1 M SODIUM PERCHIORATE

Pb(ClO <sub>4</sub> ) <sub>2</sub> $\times$ 10 <sup>4</sup> , M	$Na_2SO_4 \times 10^4$ , M	$\frac{\gamma P_{b} + +}{\gamma S 0_4 -}$	$\times 10^{4}$ , M	$\times$ 104, M	снзо4- × 104, М	срьзо <sub>4</sub> Х 104, М	$\times^{CPb(SO_4)_2-}$ X 10 <sup>4</sup> , M	$a_{Pb++} \times a_{SO_4-} \times 10^6$	Ionic strength
1000	27	0.22	982	9.1	0.2	17	0.1	4.2	0.40
500	30	. 26	483	12.8	.3	17	.15	4.0	. 265
250	39	. 29	233	20.6	.7	17	.25	4.1	.180
200	44.5	. 30	182	25.6	. 8	18	.3	4.3	. 167
150	55	.31	131	34.5	1.1	18	.4	4.4	. 153
125	68.5	.32	105	46.2	1.4	20	. 6	4.8	. 149
87.5	100	.32	66	75	2.4	21	1.1	5.0	. 148
64	150	.31	43.5	123	3.0	21	1.8	5.0	. 155
52	200	. 30	30.3	172	4	19	2.3	4.7	. 167
36	375	. 28	15.5	344	7	16	4.0	4.0	. 215

TABLE III

CONCENTRATIONS AND ACTIVITY PRODUCTS IN CRITICAL MIXTURES OF POTASSIUM SULFATE AND LEAD PERCHLORATE (25°)

Pb(ClO <sub>4</sub> ) <sub>3</sub> × 10 <sup>4</sup> , M	$ ext{K}_2 \text{SO}_4 \\  imes 10^4, M$	<u>γΡb++</u> γ=04=	$\times 10^{4}, M$	$\times 10^4$ , M	сизо4- × 104, М	× 104, M	CPb(504)2= × 104, M	арь++ X азол- X 106	Ionic strength
500	25	0.32	484	8.3	0.2	16	0.1	4.0	0.151
200	35	. 42	180	14.8	. 6	19	. 2	4.7	.064
150	40	.46	129	18.4	. 8	20	. 25	5.0	. 050
135 <b>°</b>	50	. 47	110	24.0	1.1	24	. 4	5.9	.045

<sup>a</sup> Sharp maxima in particle length could not be observed at lead perchlorate concentrations below  $135 \times 10^{-4} M$  at varying potassium sulfate concentration.

The concentration of alcohol was kept constant at 10 volume % in a different set of precipitations and the concentrations of lead perchlorate and sodium sulfate were varied systematically. The maximum particle length was found at a concentration of  $1.9 \times 10^{-3} M$  lead sulfate in the mixture. Thus alcohol markedly lowers the critical concentration for maximum particle size, the relative decrease being of the same order of magnitude as that of the solubility.

Effect of the Temperature.—Equimolar solutions of lead perchlorate and of sodium sulfate were brought to a given temperature and mixed at this temperature. Particles of maximum length were precipitated from mixtures  $5.3 \times 10^{-3}$  M in lead sulfate at  $0.5^{\circ}$ ;  $6.4 \times 10^{-3}$  M at  $25^{\circ}$ ; and  $7.2 \times 10^{-3}$  M at  $50^{\circ}$ .

In mixtures which were 0.05 M lead perchlorate, maximum size was found at sodium sulfate concentrations of  $1.85 \times 10^{-3} M$  at 0°,  $2.4 \times 10^{-3} M$  at 25° and  $3.3 \times 10^{-3} M$  at 50°. At a concentration of 0.025 M of lead perchlorate the sodium sulfate concentrations at maxima were  $2.0 \times 10^{-3} M$  at 0°,  $2.65 \times 10^{-2} M$  at 25° and  $3.7 \times 10^{-3} M$  at 50°.

The Activity Product of Lead and Sulfate Ions.—Be cause aqueous solutions of 2-2 electrolytes generally show appreciable ion association, calculation of the actual concentrations of lead and sulfate ions should consider ion pair formation and complex formation between lead sulfate and sulfate ions. From solubility data of lead sulfate in solutions of sodium sulfate<sup>4,5</sup> and of sulfuric acid<sup>6</sup> at various temperatures complex constants can be calculated. Also, the concentration of undissociated lead sulfate (ion pair) has been estimated. A factor to be considered in these calculations is the hydrolysis of lead ions in sclutions which do not contain an excess of acid.

The solubility data were evaluated using the Debye-Hückel equation with an effective radius of 4.5 Å, for lead and sulfate ions. Various  $K_{sp}$  values were assumed and the difference between total lead found and the calculated lead ion concentration was plotted as a function of the sulfate

<sup>(5)</sup> M. Huybrechts and N. A. Delangeron. Bull. soc. chim. Belg., 39, 43 (1930).

<sup>(6)</sup> D. N. Craig and G. W. Vinal, d: Research Natl, Rur. Standarde, 22, 55 (1939).

concentration in the saturated solution. The closest correlation between solubility data in sulfuric acid and in sodium sulfate solutions was obtained using the following constants at  $25^{\circ}$  in aqueous solutions

$$\begin{split} K_{s\nu} \text{PbSO}_{4} &= 1.65 \times 10^{-8} \\ \text{cpbSO}_{4} (\text{ion pair}) &= 6.8 \times 10^{-6} M \\ \text{PbSO}_{4aq} + \text{SO}_{4}^{-} &= \text{Pb}(\text{SO}_{4})_{2}^{-}, K_{1} = 7 \\ \text{PbSO}_{4aq} + \text{HSO}_{4}^{-} &= \text{HPb}(\text{SO}_{4})_{2}^{-}, K_{2} = 1.4 \\ K_{2}(\text{H}_{2}\text{SO}_{4}) &= 1.04 \times 10^{-2} \end{split}$$

In view of the uncertainty in the solubility measurements the estimated accuracy of the various values is of the order of 10%. The value of  $K_2$  is a maximum value because possible formation of  $H_2SO_4$ . PbSO<sub>4</sub> was ignored in the calculations. This seems justified because it is evident that even HPb- $(SO_4)_2^-$  formation can be ignored in solutions of low acidity. The dissociation constant of monomeric lead sulfate (ion pair) is found to be  $1.65 \times 10^{-8}/6.8 \times 10^{-6} = 2.4 \times 10^{-3}$ .

Measurement of the concentration of undissociated lead sulfate in supersaturated solutions by determination of the conductivity is possible only in such solutions which have a sufficiently long induction period. Measurements of conductivity have been made in mixtures of concentrations up to  $3.5 \times 10^{-3}$  M lead perchlorate and sodium sulfate (pH 3.0). The effect of association on conductivity could be accounted for quantitatively by using the above constants derived for saturated solutions. For details reference is made to the thesis of the junior author.<sup>2</sup>

Highly supersaturated solutions may contain other species in addition to those discussed, but the formulas and formation constants are unknown. Using the above association constants, an attempt was made to calculate the concentrations of various species in mixtures which form crystals of maximum size. The ionic strength was corrected for ion association. Activity coefficients ( $\gamma$ ) were calculated at the corrected ionic strength using the Debye–Hückel equation assuming the radius of all divalent ions to be 4.5 Å.

#### Discussion

From Tables I and II it is seen that in critical mixtures of sodium sulfate and lead perchlorate the calculated activity product of lead and sulfate ions is reasonably constant and equal to  $4.5 (\pm 0.5) \times 10^{-6}$ . This constancy is significant, considering the various assumptions which have been made and the wide variations of ionic strength, lead and sulfate concentrations in the mixtures. It also has been assumed that the activity coefficient of the ion pair Pb<sup>++</sup>·SO<sub>4</sub><sup>=</sup> is equal to unity at varying ionic strength. Even with this approximation the concentration of PbSO<sub>4</sub> in the critical mixtures is found reasonably constant and equal to  $1.9 (\pm 0.3) \times 10^{-3} M$ .

The data with potassium sulfate as reagent (Table III) were obtained in a much more narrow range of lead and sulfate concentrations than those with sodium sulfate. Double salt formation between potassium and lead sulfate<sup>7</sup> has not been considered in the calculations. Still the activity product of lead and sulfate ions and the concentration of  $PbSO_4$  in the critical mixtures was calculated to be of the same order of magnitude with potassium as with sodium sulfate.

(7) J. N. Brønsted, Z. physik. Chem., 77, 315 (1911).



Fig. 1.—Combinations of concentrations of lead perchlorate and of sodium sulfate in mixtures which produce crystals of maximum length; temperature  $25^{\circ}$ ; pH 3.0: I, without sodium perchlorate; II, 0.1 *M* sodium perchlorate mixtures.

The effect of sodium perchlorate on the critical supersaturation as illustrated in Fig. 1 is accounted for quantitatively in Table II by its effect on the activity coefficients of the various species.

The dissociation constant of lead sulfate and the various complex constants at temperatures different from 25° and in dilute alcohol are not known. By making reasonable assumptions<sup>2</sup> it is concluded that the ratio  $K_{ss}/K_{sp}$ , in which  $K_{ss} = a_{Pb} + \times a_{so_4}$  at critical supersaturation for maximum particle size, is constant in a temperature range between 0 and 50° and up to an ethanol concentration of 10% at 25°. The value of the ratio  $K_{ss}/K_{sp}$  is calculated to be 2.6 (± 0.4) × 10<sup>2</sup>.

The ratio  $K_{ss}/K_{sp}$  is the same as the ratio of the lead sulfate monomer concentration in solutions of critical supersaturation and in saturated solutions. Thus the difference in free energy between critical supersaturation and saturation for this monomer is  $PT \log 2.6 \times 10^2 = 3.3 \text{ kcal./mole.}$ This value is close to the heat of solution of lead sulfate (3.6 kcal./mole from solubility data,<sup>2</sup> 3.0 kcal./mole from thermodynamic constants<sup>8</sup>) and it may be concluded that the crystallization of lead sulfate from critically supersaturated solutions takes place without change of entropy of lead sulfate. Crystallization from solutions less supersaturated than the critical one occurs with decrease of entropy of lead sulfate. The drastic change in kinetics of precipitation at the critical supersaturation<sup>4</sup> may very well be due to this entropy effect.

(8) W. M. Latimer, "Oxidation Potentials," 2nd Ed., Prentice-Hall, Inc., New York, N. Y., 1952.

# ELECTROLYTE UPTAKE BY ION-EXCHANGE RESINS<sup>1</sup>

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The measurement of electrolyte uptake by ion-exchange resins is shown to be subject to consistent experimental error and to imperfections within ion-exchange resins. A treatment is presented for handling the imperfections analytically so as to remove their effect upon the measured electrolyte distribution. The logarithm of the invacing species activity coefficient, defined to exclude these imperfections, is thus found to vary linearly with co-ion concentration over a wide range. It is shown that this result is required by a simplified theoretical treatment of invading ion interactions.

The distribution of strong electrolyte between aqueous solution and ion-exchange resin containing a common ion is observed to be regular at moderate concentrations but at low concentrations, uncommonly large amounts of electrolyte appear to enter the exchanger phase. As a result the activity coefficients of the invading species vary smoothly except in dilute solutions where extremely low values are measured and these decrease suddenly and markedly with decreasing concentration. The complete description of uptake measurements in dilute solutions, however, must include a special consideration of two possibly small, but highly influential, perturbations. In particular, the customary analysis of electrolyte and water in the exchanger phase tends to include small quantities of external electrolyte solution. At low concentrations this causes an enormous error in the measured invading species concentration. A second factor causes even greater difficulty at low concentrations; this arises with certain systems where impurities within the exchanger sorb small and nearly constant quantities of electrolyte. The purpose of the present work is to propose and justify a treatment of electrolyte uptake measurements so that the invading species may be studied in the absence of effects due to these imperfections.

A mechanical separation of equilibrated ionexchange material from aqueous solution is, in general, incomplete. A subsequent analysis for electrolyte and water in the exchanger phase will thus include quantities corresponding to the amount of external solution which is retained by imperfectly separated exchanger phase. A convenient de-scription of the resultant error is made by the consideration of the weight of water G' in the retained solution which corresponds to the weight of water G imbibed by the separated exchanger material. The relative weights of retained and imbibed water are chosen for convenience in the following where we shall be concerned with the molal (moles per kg. of water) concentrations of species in both phases. If  $m'_{i(r)}$  is the measured molal concentration of species i inside the exchanger,  $m^*_{i(r)}$  the true, and  $m_i$  the concentration of i in the external solution, these quantities will be related as <sup>3</sup>

$$m'_{i(r)} = \frac{Gm^{*}_{i(r)} + G'm_{i}}{G + G'}$$
(1)

As will be shown later, impurities exist in various ion-exchange materials which are responsible for an approximately constant and reversible sorption of distributing electrolyte. We may consider the concentration  $Q_i$  of impurity-bound species separately so that

$$m^*_{i(r)} = m_{i(r)} + Q_i$$
 (2)

where  $m_{i(r)}$  is the concentration of internal species which, by definition, is independent of retention and sorption effects. If we define the ratio G'/Gto be the fractional retention, e, and substitute for eq. 2, eq. 1 becomes

$$m'_{i(r)} = (m_{i(r)} + Q_i + em_i) \frac{1}{1+e}$$
 (3a)

While eq. 3a may apply to any diffusible species within an ion exchanger, it is useful to consider the distribution of the electrolyte component J which has the formula  $A_{*A}B_{*B}$ . If we choose A to refer to the co-ion, *i.e.*, that ion whose electrical charge has the same sign as the functional group of the exchanger, then the following is valid for uptake by either anion or cation exchanger systems. We assume, with Kraus and Nelson,<sup>4</sup> that J has the same standard state in the external and internal phases, in which case the equilibrium activities of J arc also equal in the two phases. It follows that

$$(m_{\rm J(r)})^{\nu_{\rm A}}(m_{\rm J(r)} + m_{\rm R}/\nu_{\rm A}\nu_{\rm B})^{\nu_{\rm B}} \gamma^{\nu}_{\pm (r)} = (m_{\rm J}\gamma_{\pm})^{\nu} \quad (4)$$

where  $m_{\rm R}$  is the functional group molality and  $(m_{\rm J(r)} + m_{\rm R}/\nu_{\rm A}\nu_{\rm B})$  is the gegenion concentration. By setting i = J in eq. 3a, dividing each side by  $m_{\rm J}$ , and using eq. 4, we obtain an expression for the measured distribution coefficient

$$D' \equiv \frac{m'_{J(r)}}{m_J} = \left(\phi m_{J}^{\mu_{\rm B}/\mu_{\rm A}} + e + \frac{Q}{m_J}\right) \frac{1}{1+e} \quad (5)$$

where  $\phi$  is given by

$$\phi = (m_{J(r)} + m_R / \nu_A \nu_B)^{-\nu_B / \nu_A} \left( \frac{\gamma_{\pm}}{\gamma_{\pm}(r)} \right)^{\nu/\nu_A}$$
(6)

At very low external concentrations we know that each term in  $\phi$  with the exception of  $\gamma_{\pm(r)}$  has a finite limit. Further, since the ionic strength of the internal solution does not change a great deal at the low concentrations, we expect the value of  $\gamma_{\pm(r)}$ to reach a finite limit. For the present we assume that  $\gamma_{\pm(r)}$  does reach a limiting value, in which case the first term in eq. 5 varies directly with  $m_{\rm J}$ , the second term is independent of it, and the third

(4) K. A. Kraus and F. Nelson, J. Am. Chem. Soc., 80, 4154 (1958).

<sup>(1)</sup> Taken in part from D. H. Freeman, Ph.D. Thesis, Massachusetts Institute of Technology, 1958.

<sup>(2)</sup> Department of Chemistry, Washington University, Pullman, Washington.

<sup>(3)</sup> With indirect measurements of electrolyte uptake, *i.e.*, by using column elution techniques, or by analyzing only the external phase, the quantity  $G'm_i^*$  can be eliminated from eq. 1. The problem of making an exact measurement of imbibed water, which would eliminate G' in the denominator, is as yet an unsolved problem.

term varies inversely. It follows that the presence of impurities which sorb electrolyte requires that D' pass through a minimum; if this occurs at a sufficiently dilute concentration where the variations in gegenion concentration,  $\gamma_{\pm(r)}$ , e, and Qare negligible, we obtain relation (7) by differentiating eq. 5 with respect to  $m_{\rm d}$ 

$$\frac{Q}{m_{\rm J(r)}} = \frac{\nu_{\rm B}}{\nu_{\rm A}} \left( 1 + \frac{\nu}{\nu_{\rm B}} \frac{\mathrm{d}\,\ln\,\gamma_{\pm}}{\mathrm{d}\,\ln\,m_{\rm J}} \right) \tag{7}$$

Although distribution coefficient minima are found to occur under conditions which should make eq. 7 valid, the usefulness of the equation for determining Q may be hampered by the practical difficulty in locating the exact value of  $m_J$  which corresponds to the minimum. If impurities are absent, *i.e.*, if Q = 0, then eq. 5 shows that D' should reach the limiting value e/(1 + e) in very dilute solution. If both e and Q are zero, a condition which is rather difficult to find experimentally, the distribution coefficient is obtained directly from eq. 4 and it must vanish with vanishing external concentration. Using measurements to be discussed later, the characteristic distribution coefficient variations resulting from the effects of sorption plus retention, and of retention effects alone, are shown by the upper and lower curves, respectively, in Fig. 1.

Although it is possible to assign values of e and Q from the variation of D' with  $m_J$  at very low concentrations, an iterative method which uses measurements at higher concentrations is found to give greater accuracy. As a first approximation, log  $\gamma_{\pm(r)}$  values are calculated without correction for retention or sorption by applying eq. 4 directly to the measured quantities. For well-behaved systems, *i.e.*, those in which e and Q are relatively small and electrolyte is largely dissociated in both phases, the values of log  $\gamma_{\pm(r)}$  are reasonably accurate at the higher concentrations and taken as a function of  $m_{J(r)}$ , they are found to define a nearly linear trend from which a fairly sharp break occurs at a lower concentration. Since the imperfections can be shown to dominate only at the lower concentrations the variation of log  $\gamma_{\pm(r)}$ before the break may be extrapolated to zero concentration as a first approximation. Whether this procedure is valid will be determined by finding values of e and Q which will cause the corrected measurements to behave the same as the extrapolation. To find such values, it is convenient to calculate values of  $m_{J(r)}$  which correspond to the extrapolated values of  $\gamma_{\pm(r)}$  by using eq. 4. Then, by using eq. 3a in a more convenient form

$$m'_{J(r)} - m_{J(r)} = (m_J - m'_{J(r)})e + Q$$
 (3b)

the newly calculated values of  $m_{J(r)}$  are used with the apparent quantities to obtain e as the slope and Q as the intercept of eq. 3b. Since the imperfections will cause a slight difference between the measured and corrected invasion at high concentrations, at least one more iteration is necessary. The result of following this procedure is shown by Fig. 2 where the measurements reported by Davies and Yeoman<sup>5</sup> of HCl uptake by cation exchanger (5.5% cross-linked) were used for the iterative

(5) C. W. Davies and G. D. Yeoman, Trans. Faraday Soc., 49, 968 (1953).



Fig. 1.—Curve A gives the measured distribution coefficients of HCl for anion exchanger, as calculated from the measurements of Kraus and Moore.<sup>6</sup> In dilute solutions, the effect of impurity dominates the measured uptake. Curve B gives the distribution of KCl with the same type of exchanger, as measured by the author. In dilute solutions, these measurements are dominated by retention error.

computation of the corrected invading species activity coefficient variation given in Table I. At the lowest five concentrations studied, the iterated constants in eq. 3b are determined quite precisely. Since these measurements were not carried out below 0.05 molal HCl the distribution coefficient variation gives only a qualitative indication that sorption effects are present. For each of the systems to be discussed later, the iterative correction of measured uptake leads to invading species activity coefficients which are found to vary according to the general equation

$$\log \gamma_{\pm(r)} = a + bm_{J(r)} \tag{8}$$

where a and b are constants which depend upon the electrolyte and type of ion exchanger.

### Discussion

It is found that small quantities of HCl are sorbed by impurities within each ion-exchange resin for which measurements are reported. The study of HCl uptake by anion-exchange resin (Dowex 1) reported by Kraus and Moore<sup>6</sup> has been used for the computation of the upper curve in Fig. 1. A detailed analysis of these measurements shows that they must be affected by retention error in addition to the immediately recognized influence of impurities. Since the procedure used for this study includes a correction based upon the measured (6) K. A. Kraus and G. E. Moore, J. Am. Chem. Soc., **76**, 1457 (1953).

### TABLE I

### CORRECTED UPTAKE MEASUREMENTS

Elec-		Cross-			πιj	In per	fections	
trolyte	Ion exchanger	linking	Gegenion co-ion relation	$\log \gamma \pm (\mathbf{r})$	range	e	Q	Ref.
HCl	Anion (Dowex 1)	10	$m_{\rm Cl(r)} = 6.1 + 1.31 m_{\rm H(r)}$	$-0.43 \pm 0.12 m_{\rm H(r)}$	0.1-10	0.013	0.012	6
LiCl	Anion (Dowex 1)	10	$m_{\rm CI(r)} = 6.4 + 1.16 m_{\rm Li(r)}$	$-30 + .12m_{\rm Livr}$	2 - 13	а		4
NaCl	Anion (Dowex 1)	10	$m_{\rm Cl(r)} = 6.7 \pm 1.9 m_{\rm Na(r)}$	$10 + .06m_{Na(r)}$	0.2 - 6	.045*	c	4
KCl	Anion (Dowex 1)	$7^{1/2}$	$m_{\rm Cl(r)} = 6.4 + 1.0 m_{\rm K(r)}$	$21 \pm01$	1 -4	. 09	c	1
HCl	Cation	$5^{1}/_{2}$	$m_{\rm H(r)} = 3.8 + 2.9 m_{\rm Cl(r)}$	$017 + .39m_{Cl(r)}$	0.1-4.4	. 036	0.0010	<b>5</b>
KCl	Cation	$5^{1}/_{2}$	$m_{\rm K(r)} = 5.7 \pm 3.7 m_{\rm Cl(r)}$	$29 +05m_{Cl(r)}$	0.2 - 2	.087	с	<b>5</b>
- 711			1		· .• •	11	4 1 4 1	

<sup>a</sup> The uptake of LiCl is not measured at dilute concentrations which prevents the determination of e directly. Although the retention could be estimated from measurements in the same paper on NaCl uptake, the correction does not lead to a substantial difference. <sup>b</sup> This result may be somewhat in error since useful measurements are available at only four concentrations. <sup>c</sup> No sorption effects are apparent.

retention of external solution after centrifugal filtration of glass beads, we conclude that the cor-rection is insufficient. The measurements also show that the value of Q is relatively constant above 0.01 molal HCl, but that it decreases with decreasing concentration to a value of 0.0087 at 0.0022 molal HCl. The uptake measured for this region of concentration may be further analyzed according to the interaction between acid (H) and base impurity (B) suggested by Kraus and Moore. The stoichiometric constant for the reaction,  $H + B \rightleftharpoons HB$ , may be obtained from analyzing the measured uptake below 0.03 molal HCl. The concentration of impurity-bound hydrogen  $q_{\rm H}$ is available after correction only for retention; the corresponding internal concentrations of hydrogen ion not sorbed by impurity may be calculated from eq. 4 using  $\gamma_{\pm(r)} = 0.371$ . The stoichiometric constant is given by  $K = q_{\rm H}/[m_{\rm H(r)}(Q - q_{\rm H})]$ where Q is the upper limit of impurity-bound hydrogen. From the resulting linear variation of  $q_{\rm H}$  with  $q_{\rm H}/m_{\rm H(r)}$ , the intercept (Q) and slope -1/K give the values Q = 0.012 and  $K = 5 \times$ 10<sup>5</sup>. Thus, the enormous effect upon the distribution coefficient curve A shown in Fig. 1 is found to be caused by impurity-bound hydrogen whose maximum concentration is only 0.2% of the functional group concentration.

Using the same type of anion exchanger as that in the preceding discussion, Kraus and Nelson measured the uptake of NaCl at sufficiently dilute concentrations to establish negligible sorption of the salt by impurities within the exchanger. Since the sorption of HCl is plausibly explained by an acidbase equilibrium, it is not at all surprising to find the apparent absence of neutral salt sorption by the same exchanger. There are other examples where impurities cause pronounced sorption of strong acid while the sorption of neutral salt occurs to a much lesser extent, if at all. The measurements of Davies and Yeoman<sup>5</sup> reported in Table I show this to be the case for HCl and KCl uptakes by 5.5% cross-linked cation-exchange resin. In the work of Scatchard, Anderson and Schödel<sup>\*</sup> the uptake of HCl and NaCl was studied with Dowex 50W, and HCl uptake by Dowex 1, using a method which avoids external retention effects. In these measurements there is clear evidence for the sorption of HCl by impurities within both types of exchanger. The sorption of NaCl in Dowex 50W is at least one-fourth to one-six-h the

HCl sorption according to measurements carried down to  $2 \times 10^{-4}$  molal.

The behavior of another anion exchanger (Dowex 2) at dilute electrolyte concentrations is more erratic. From calculations based upon the graphed measurements of Gottlieb and Gregor,<sup>8</sup> it is apparent that HCl as well as a number of potassium salts are each affected by impurities within this exchanger. We repeated and extended measurements on this material and on Dowex 1 using essentially the same techniques as other workers.<sup>5,9</sup> Some of the important differences are described below.

**Experimental.**—Resin and solution were equilibrated in single batches for at least four hours. Resin samples were pre-treated as suggested by Kraus and Moore.<sup>6</sup> The separation of resin from solution was carried out by blotting with filter paper that was slightly moistened with water vapor to improve the effectiveness of the blotting. Invading potassium ion concentrations were determined to  $10C_c$ .ccuracy using potassium-42 as an indicator and well-type scintillation<sup>10</sup> counting of constant geometry samples of resin or solution. The water content of separated resin was determined by weight difference after drying to constant weight over P<sub>2</sub>O<sub>5</sub> at 75°. Chloride was determined after cisplacement elution with LM NaClO<sub>4</sub> (chloride free) by potentiometric titration with 0.1 M AgNO<sub>3</sub> using Ag-AgCl electrode, and NaNO<sub>3</sub>-agar salt bridge to a calomel cell.

The variation in KCl uptake for two different batches of Dowex 2 indicated impurities (Q) of 0.0004 and 0.0014 molal. With two other batches of this resin, however, and with two batches of Dowex 1, no impurities were evident at external concentrations as low as  $10^{-6}$  molal. The measurements for one batch of Dowex 1 are plotted in Fig. 1 and listed in Table I; these measurements are typical of those obtained with each resin for which sorption effects were found to be absent. These measurements, however, are clearly dominated by retention effects at all concentrations below  $10^{-3}$  molal. After an examination of the manufacturer's production records<sup>11</sup> for the series of anion exchangers we used in these studies, the two batches of Dowex 2 containing impurities were found to have been processed at substantially higher temperatures than those used for the others. One possible explanation is the formation of a small

(8) M. H. Gottlieb and H. P. Gregor, J. Am. Chem. Soc., 76, 4639 (1454).

(9) K. W. Pepper, D. Reichenberg and D. Hale, J. Chem. Soc., 3129 (1952).

(10) J. W. Irvine, Jr., Nucleonics, 12, No. 10, 62-63 (1954).

(7) Personal comm., G. Scatchard.

<sup>(11)</sup> We are grateful to R. W. Wheaton, Dir. of Ion Exchange Research, Dow Chemical Company, Midland. Michigan, for his cooperation in providing this information.

capacity for cation exchange at the higher processing temperatures. This explanation was tested by acetylating one batch of Dowex 2 (Q = 0.0014) with acetyl chloride in acetic anhydride. Repeated uptake measurements at  $10^{-4}$  molal KCl showed a subsequent reduction of KCl sorption by at least a factor of four. Whatever basic groups existed before acetylation appear to have become coupled with acetyl groups and thereby blocked from the sorption of salt. While this experiment does not prove the explanation, it does make it seem likely.

Further results of applying the foregoing treatment are given in Table I for the various aqueous electrolytes listed in the first column and the ion exchange resins described in the second and third columns. The measured uptake reported by the authors referenced in the last column is affected by and cerrected for the effects of retention and impurities according to the parameters in columns seven and eight. For each system, the gegenion molality and the logarithm of the invading species activity coefficient are each found to vary linearly with co-ion concentration; these dependencies are given in the fourth and fifth columns. Column six defines the range of external concentration over which both of the preceding variations are maintained to within a few (2 or 3) per cent. At external concentrations above one molal, the log of the activity coefficients with or without correlation tend to vary linearly with co-ion concentration. Below one molal, however, negative deviations from linearity become increasingly large without correction; after correction they follow the linear variation to substantially lower concentrations. The lower limit of concentration where measurements cease to be significant is determined primarily by the limit of experimental precision. The foregoing is illustrated by the calculations plotted in Fig. 2.

To help explain the corrected invading species activity coefficient variations which are reported herein, Scatchard<sup>7</sup> has suggested that the simplest possible dependence of ion activity coefficient upon internal concentration would be given by the theory of specific ion interactions<sup>12</sup> in the form

$$\log \gamma_{i(r)} = \Sigma_{j} \beta_{ij} m_{j(r)}$$
(9)

This equation is obtained from a much more detailed expression<sup>13</sup> after dropping the Debye-Hückel and higher order interaction terms which should be small at the high ionic strength of the internal solution. For a 1:1 electrolyte, with subscripts (1) referring to co-ion, (2) to gegenion, and (3) to functional group, the expansion and collection of terms gives

$$\log \gamma_{i}\gamma_{j} = 2 \log \gamma_{\pm(r)} = (\beta_{11} + \beta_{12})m_{1(r)} + (\beta_{12} + \beta_{22})m_{2(r)} + (\beta_{13} + \beta_{23})m_{3(r)}$$
(10)

and from the condition for electroneutrality

$$m_{2(\mathbf{r})} = m_{1(\mathbf{r})} + m_{3(\mathbf{r})} \tag{11}$$



Fig. 2.—The values of log  $\gamma_{\pm(r)}$  in the upper and lower curves, respectively, are obtained from the measurements of Davies and Yecman<sup>s</sup> with and without correction for the imperfections listed in Table I.

$$\log \gamma_{\pm(r)} = \frac{1}{2} \left(\beta_{11} + \beta_{12} - \beta_{13} - \beta_{23}\right) m_{1(r)} + \frac{1}{2} \left(\beta_{12} + \beta_{22} + \beta_{13} + \beta_{23}\right) m_{2(r)} \quad (12)$$

where the  $\beta_{ij}$  values are independent of concentration (but not of temperature). Under the restriction that gegenion concentration varies linearly with co-ion concentration, eq. 8 reduces to the very simple relation

$$\log \gamma_{\pm(\mathbf{r})} = a + bm_{1(\mathbf{r})} \tag{13}$$

where a and b are constants. This agrees with eq. 8 which is found experimentally.

### Conclusions

The uptake of strong electrolyte from aqueous solution by ion-exchange resin may be completely described by three considerations: (a) the dependence of invading species activity upon co-ion concentration; (b) the variation of gegenion concentration with that of the co-ion, and (c) the extent to which electrolyte is sorbed by impurities in the exchanger material. The measurement of electrolyte uptake is found in several instances to be affected by a consistent experimental error due to retention. When uptake is measured at very dilute concentrations, evidence is provided for or against the effect of possible impurities. If the latter effect is absent, the measurements provide a direct and sensitive test for experimental consistency.

The simple linear correlations of log  $\gamma_{\pm}(z)$  with co-ion concentration are found to be valid over a wide range of concentration. The form of this variation is in good agreement with the behavior of mixtures of strong electrolytes in aqueous solution,<sup>14</sup> and with the simplified ion interaction treatment presented here.

Acknowledgments.—The author wishes to thank Professor George Scatchard for his helpful suggestions and valuable discussions, and Professor Charles D. Coryell for his friendly interest and support. Financial assistance for this work was received from the United States Atomic Energy Commission.

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# STUDY OF THE CHANGE IN SPECIFIC HEAT OF MONOMERIC AND POLYMERIC GLASSES DURING THE GLASS TRANSITION

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An analysis of specific heat data of 41 glasses shows that if glasses are looked upon as being built up of "beads" their rise in specific heat during the glass transition measured by calorimetric methods is 2.7 = 0.5 cal./mole of "beads" (rule of constant  $\Delta C_p$ ). Using Eyring's hole theory of liquids, expressions for the molar hole energy and molar hole volume are derived. Calculations are made for 34 monomeric and polymeric glasses, using specific heat data, specific volume determinations and cohesive energy estimations.

### A. Introduction

Some of the earliest measurements of the specific heat at constant pressure,  $c_p$ , of a glass are those by Regnault<sup>1</sup> on selenium. His measurements already show the features of the specific heat of glasses and their variation with temperature: at low temperature there is not much difference between the specific heat of the crystalline and glassy material, at temperatures above a certain value<sup>2</sup> the glass has the higher specific heat. This temperature at which the specific heat changes is called the glass transition temperature  $T_g$ . The use of  $T_g$  throughout this article will be such that the numerical values give the abscissa of the point of inflection of the particular measured  $C_p$ -curve. This is comparable with the definition by Kauzmann.<sup>3</sup>

Figure 1 shows the  $C_p$ -curves for an 80/20 mole ratio poly-(ethylene terephthalate-sebacate) copolymer<sup>52</sup> as an example of a typical glass-forming high polymeric material.

Many specific heat measurements in the glass transition region (see references 6-41 in Table I) have been made during the last 50 years. It will be attempted in this article to correlate all available data of the increase of the specific heat in the transition temperature range. As theoretical basis the hole theory of liquids will be used. In particular the formulations developed by Hirai and Eyring in their "Theory of Bulk Viscosity"<sup>4,5</sup> will be applied.

### B. Theory of Hirai and Eyring

Hirai and Eyring describe the equilibrium between holes and the phonons associated with the liquid lattice as characteristic of the liquid state. Each hole is characterized by its molar  $v_{\rm h}$ and the molar excess energy over the "no hole" situation  $\epsilon_{\rm h}$ . The process of disappearance of a hole creates elastic strain, which propagates with the velocity of elastic waves. The excess energy is taken up by the changed liquid lattice.

On a molecular basis a rearrangement of neighboring molecules or molecule segments is necessary

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to allow the creation or disappearance of a hole. This molecular rearrangement is a slow process and has been treated by Hirai and Eyring using the transition state theory.

The heat capacity can be assumed to be separable on this assumption

$$C_{\rm p \ total} = C_{\rm p_b} + C_{\rm po} \tag{1}$$

One part,  $C_{pb}$  being due to the creation of new holes and the other,  $C_{po}$ , being due to the lattice vibrations. The part of interest here is the one due to the change in number of holes with temperature which can be written

$$C_{\mathbf{p}_{\mathbf{h}}} = \epsilon_{\mathbf{h}} \times \left(\frac{\partial N_{\mathbf{h}}}{\partial T}\right)_{\mathbf{p}} \tag{2}$$

where  $\epsilon_h$  is the above defined difference in energy.  $N_h$  is the number of moles of holes present. Using the equilibrium value for  $N_h^{5a}$  Hirai and Eyring arrive at an expression for  $C_{ph}$ 

$$C_{\rm ph}' = \frac{Rv_0}{v_{\rm h}} \left(\frac{\epsilon_{\rm h}}{RT}\right)^2 e^{-\epsilon_{\rm h}/RT}$$
(3)

(for one mole of liquid molecules,  $N_0 = 1$ )

where  $v_0$  is the volume of one mole of liquid molecules.

On cooling a liquid the mechanism decreasing the number of holes is freezing-in at the glass transition temperature, so that at lower temperatures the number of holes is constant and corresponds to the equilibrium value at the transition interval. For rapidly cooled samples this equilibrium value will be higher than for slowly cooled samples. The frozen-in state, the glass, will only be unchanged over long periods of time if the temperature is far enough below  $T_g$ . The heat capacity is then largely dependent upon the liquid lattice vibrations and is often similar to the heat capacity of the crystalline lattice. At and above  $T_g$  the additional term  $C_{\rm ph}$ , due to the increase in hole concentration, has to be added. This term should solely account for the rise in heat capacity at  $T_g$ 

$$\Delta C_{\rm p}' = R \times \frac{v_0}{v_{\rm h}} \left(\frac{\epsilon_{\rm h}}{RT_{\rm g}}\right)^2 e^{-\epsilon_{\rm h}/RT_{\rm g}} \tag{4}$$

## C. Discussion

(1) Rule of Constant Heat Capacity Increment. —Table I summarizes all available specific heat data to date. For a comparison heat capacities have to be calculated on the basis of one mole of fundamental units of the substances. The simplest

(5a)  $N_h/N_0 = (v_0/v_h)e^{-(\epsilon_h + p_{\nu_h})/RT}$  see ref. 4, appendix I at ordinary pressures the  $p \cdot v_h/RT$  term is negligible. See ref. 4 also for additional assumptions.

SI	PECIFIC HEAT AND VO	lume Data at t	HE GLASS TRANSI	TION $T_{g}^{a}$		
Substance	Mol. wt.	c at $T_{\mathbf{g}}$ glass, cal. g. <sup>-1</sup> deg. <sup>-1</sup>	$c_p$ at $T_g$ liquid, cal. g. <sup>-1</sup> deg. <sup>-1</sup>	cal. g. $^{\Delta c_{p}}$ deg. $^{-1}$ deg. $^{-1}$	$^{T_{g},}_{^{\circ}\mathrm{K}.}$	$ml. g.^{-1}$
Selenium	78.96	0.08157.37	0.12637	0.0445	304	$0.242^{43}$
Boron trioxide	69.64	. 0635 36 - 38	. 087 38	.0238	521	0.54644
H <sub>2</sub> SO <sub>4</sub> ·3H <sub>2</sub> O	152.13	. 20721	. 48221	.275	158	
Ethyl alcohol	46.07	.27823	.41423	.136		
2211291 11101		.27432	$(.444)^{32}$	(.170)	95	$1.035^{45}$
<i>n</i> -Propyl alc.	60.09	2732.33	. 4332.33	.16	95	0.91545
Prop. glycol	76.09	. 25332	. 46432	.211	160	.95432
F. 8-3.00-	1.000			. 2125		
Glycerol	92.09	. 23627.32.19	. 44827, 32, 19	.212	183	.76245
1-Butene	56.10	.2198	. 5008.39	.281	60	1.17546
d.l-Lactic ac.	90.08	. 26030	. 498 30	.238	204	0.7847
Isobutyl alc.	74.12			. 1422	115	1.04245
sec-Butyl alc	74 12	27030	39830	.128	115	1.0447
2-Methylpentane	86.17	21613	40013	.184	80	1.14346
3-Methylpentane	86.17	20913	39513	186	77	1.1594
Cyclohevanol	100 16	.200	.000	.07428	150	0.94845
Clucose	180.16	29827-29	48027-29	182	282	
3-Mathylheyane	100.20	224 20, 30	394 20 - 30	170	88	1.15946
2 3-Dimethylnentane	100.20	21420	37320	159	85	1.14246
4-Methylbentanol-2	130.23	2712	3912	12	148	1.0547
4 Mothylhoptanol-3	130.23	$(26)^{12}$	4112	(15)	138	1.0447
4-Methylheptanol-4	130.23	2912	4212	.13	167	1.0847
5-Methylheptanol-1	130 23	2712	3912	.12	138	1.0447
5-Methylheptanol-2	130.23	2712	4112	.14	140	1.0447
3-Methylhentenol-2	130.23	2712	4212	.15	120	1.0247
2-Methylheptanol-4	130.23	2912	.4112	.12	167	1.0847
6-Methylheptanol-2	130 23	.3012	.4112	.11	160	1.0647
4-Methylnonane	142 28	.25231	43831	.186	118	1.15048
Distyrene	208.29	. 16741	. 249541	.0825	209	0.9248
Polystyrenes:						
$(a) \mathbf{M} \mathbf{W} 2200$	104 14*	25440	41040	056	341	$0.959^{49}$
(a) $MW 2270$	104.14*	34441	40441	.060	344	.96549
(b) $M W 3650$	104.14*	37040	42240	.052	356	.96249
	104.14 54.00*	.010	. 122	14915	100	1 02550
Polybutadiene	$54.09^{+}$		97010	.148**	100	1 0389,42
~ ! !	00 11*	.270%	.378**	. 108	199 969)	1.000
Rubber	68.11*	01111	45011	( .098	202)	1 011
Hycar O.R.	• • • •	.311**	. 400**	. 139	200	1.0
Poly-(butadiene-styrene):						1 0101
(a) 8.58% styrene	56.5*	$.275^{16}$	. 39715	.122	193	1.01051
(b) 22.61% styrene	60.7*	. 28216	. 39916	.117	213	1.005
(c) 25.5% styrene	61.5*	. 28434	. 39734	.113	212	0.99951
(d) 42.98% styrene	68.2*	$.285^{16}$	. 39316	.108	237	. 98751
Poly-(ethylene terephthala	te) 192.16*	. 3235	. 40 35	.0807	342	.7753
Poly-(ethylene terephthala	te-					
sebacate) 80-20 mole rat	io 199.38*	.31652	.416 <sup>52</sup>	. 100	296	.77852
Polyisobutylene	56.10*	. 27417	. 36917	.095	199	
and an		.28414	.36914	.085	197	$1.048^{14}$
PVC	62.50*	. 2756.18	. 3436	.068	353	0.7547
Rosin		. 321 37	.38837	.067	301	0.93543

TABLE I

<sup>a</sup> All values of polymeric substances are derived from measurements on completely amorphous polymers. \* M.W. of the repeating unit.

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11:

11

11



1054

 $\mathbf{c}_{\mathbf{p}}$ 

Fig. 1.—Specific heat of a typical glass forming high polymer: 80/20 mole ratio poly-(ethylene terephthalatesebacate) copolymer. Based on data of ref. 52. Solid line, completely amorphous polymer  $T_v = 23^\circ$ ; broken line, partially crystalline polymer (maximum crystallinity  $25\ell_o$  by weight). The only crystallizing units are ethylene (terephthalate) units.  $\Delta c_p$  is lowered and shifted to 0°. Dotted line, expected curve for all ethylene (terephthalate) units crystallized. Not realizable by experiment.

molecular unit which fits the hole theory is a "bead" of the polymer chain like  $-CH_2$ - or  $-CH_2$ -CH<sub>3</sub>- or a similar unit of the monomeric materials. Oxygens are best counted as separate beads because it is probable that they form bonds in the glass and may be looked upon as -O- beads with no reference to the actual situation. This model implies that the "beads" are the smallest molecular units whose movements may change the "hole-equilibrium." Table II contains the "average

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Specific Volume References (42) to (53):

bead molecular weight"  $\overline{M}$  and the heat capacity in cal. deg.<sup>-1</sup> (mole of beads)<sup>-1</sup>. The average value and standard deviation of 39 measurements are

$$\Delta C_{\rm p} = 2.7 \pm 0.5 \, {\rm cal. \, deg.^{-1} \, mole^{-1}}$$
 (5)

showing a remarkable constancy for all carbon containing substances.

Formula 4 should thus give as a first approximation a constant value also. Hirai and Eyring's assumption that

$$\frac{v_0}{v_1} \approx \frac{\epsilon_0}{\epsilon_1} = 5-6 \qquad (\text{Ref. 4})$$

and the assumption that at the glass transition the free volume reaches an approximately constant value of  $2\%^{5.54-56}$  which leads to

$$\left(\frac{\epsilon_{\rm h}}{RT_{\rm g}}\right)^2 \times e^{-\epsilon_{\rm h}/RT_{\rm g}} \approx 0.2 \text{ to } 0.4 \quad (\text{Ref. 5})$$

for a respective free volume fraction of 0.01 to 0.03 are the only two assumptions necessary to give equation 4 the value

$$\Delta C_{\rm p}' = \bar{M} \Delta c_{\rm p} = 2.97 \text{ cal. deg.}^{-1} \text{ mole}^{-1} \qquad (6)$$

$$\left(\text{using } \frac{v_0}{v_{\rm b}} = 5 \text{ and a free volume of } 2\%\right)$$

In view of the rather crude estimation of the fundamental unit or "bead" this is a reasonable agreement. The three inorganic glasses measured fit less well indicating that one or more of the assumptions made (subdivision into beads,  $v_0/v_h = 5$ and free volume = 2%) do not apply.

(2) Calculation of  $\epsilon_h$ .—If more detailed information is wanted, it is necessary to make use of more than one experimental quantity. Equation 4 contains four variables:  $v_0, v_h, \epsilon_h$  and  $T_g$ . But

$$\frac{\epsilon_0}{v_h} \approx \frac{\epsilon_0}{\epsilon_h}$$
 (Ref. 4) (7)

and  $n \cdot \epsilon_0 = E_g$  where  $E_g$  is the internal latent heat of vaporization at the glass transition per mole of molecules (or mole of repeating units) and n is the number of fundamental units per molecule or per repeating unit. Making use of the relations 7, equation 4 can be rewritten

$$\Delta C_{\rm p} = M \Delta c_{\rm p} = \frac{E_{\rm g}}{T_{\rm g}} \left( \frac{\epsilon_{\rm h}}{R T_{\rm g}} \right) c^{-\epsilon_{\rm h}/R T_{\rm g}}$$
(8)  
$$\left( M = n \cdot \overline{M} \right)$$

thus eliminating one unknown quantity.  $T_g$  has been determined (see Table I) by plotting published

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				Ec.	€h,	¢h.	۲b.	€h
Substance	$\overline{M}$	$\overline{M} \cdot \Delta c_{\rm P}$	$\Delta C_{\rm P}$	cal.	RTg	cal.	cm.3	υь
Selenium	78.96	3.51	3.51					
Boron trioxide	23.21	(0.55)	1.66					
$H_2SO_4-3H_2O$	21.73	(5.97)	41.9					
Ethyl alcohol		2.09	6.27		4.6	880	3.2	
	15.36	2.61	7.83	13200	4.3	820	3.0	270
<i>n</i> -Propyl alc.	15.02	2.40	9.61	17500	4.4	840	2.6	320
Prop. glycol	15.22	3.21	16.05	20500	3.3	1060	3.8	280
Glycerol	15.35	3.24	19.52	33200	3.5	1270	2.7	470
1-Butene	14.02	3.94	15.76	7900	3.4	410	3.4	120
d,l-Lactic ac.	15.01	3.57	21.44	20000	2.4	980	3.4	290
Isobutyl alc.	18.53	2.59	10.38	15900	4.0	920	4.5	200
sec-Butyl alc.	18.53	2.37	9.49	15600	4.1	940	4.6	200
2-Methylpcntane	17.23	3.17	15.86	10800	3.4	540	4.9	110
3-Methylpentane	17.23	3.20	16.03	10600	3.4	520	4.9	110
Cyclohexanol	25.04	1.86	7.41	15400	4.0	1200	7.4	160
Glucose	15.01	2.73	32.79					
3-Methylhexane	16.70	2.84	17.03	11600	3.2	560	5.6	100
2,3-Dimethylpentane	20.04	3.24	15.93	11800	3.4	580	<b>5</b> .6	100
4-Methylheptanol-2	17.28	2.1	15.63	20600	3.4	1000	6.6	150
4-Methylheptanol-3	17.28	2.6	19.53	20900	3.2	880	5.7	150
4-Methylheptanol-4	17.28	$2_{-2}$	16.93	19800	3.1	1040	7.4	140
5-Methylheptanol-1	17.28	2.1	15.63	21600	3.6	990	6.2	160
5-Methylheptanol-2	17.28	2.4	18.23	20900	3.3	920	6.0	150
3-Methylheptanol-2	17.28	<b>2</b> . 6	19.53	21400	3.5	840	5.2	160
2-Methylheptanol-4	17.28	2.1	15.63	19800	3.2	1070	7.6	140
6-Methylheptanol-2	17.28	<b>2</b> . 0	14.33	20300	3.4	1090	7.4	150
4-Methylnonane	15.81	2.94	26.46	14900	2.5	590	6.5	91
Distyrene	34.71	2.86	17.18	20700	2.8	1200	11.1	110
Polystyrenes:								
(a) M.W. 2300	$52.07^{a}$	2.92	5.83	7370	2.0	1400	19.0	74
(b) $M.W. 3370$	$52.07^{a}$	3.12	6.25	7270	1.8	1200	16.6	72
(c) $M.W. 3650$	$52.07^{a}$	2.71	5.42	7320	2.1	1500	20.5	73
Polybutadiono	$18 01^{a}$	2 68	8.01	.1000	1 7	650	7 )	90
Bubber	$222 - 70^{a}$	2.08	7 35	6200		0.50	10.5	88
Hycar O.R.	22.10	2.40	1.00	0200	2.0	020		
Poly-(hutadiene-styrone).								
( ) $( )$	10 0%		(° 90	5050	0.1	810	0.9	00
(a) $8.58\%$ styrene	19.2*	2.34	0.89	5050	2.1	810	9.2	00
(b) $22.61\%$ styrene	21.2	2.48	7.10	5300	1.9	810	0.0	01
(c) $25.5\%$ styrene	21.6	2.44	0.95	5400	2.0	850	9.7	00
(d) $42.98\%$ styrene	25.15	2.71	1.31	5700	1.4	810	9.0	04
Poly-(ethylene terephthalate)	$38.34^{a}$	3.10	15.51					
Poly-(ethylene terephthalate-	_							
sebacate) 80–20 mole ratio	$29.25^{a}$	2.92	19.94					
Polyisobutylene	$28.05^{a}$		5.32					
		2.50	4.77	4750	2.5	1000	12.4	81
PVC	$31.25^{a}$	2.13	4.25	-1440	1.5	1100	11.6	95

TABLE II Derived Results Using Table I Data

Rosin

• The number of "beads" assumed coincides with Bunn's number of "chain Units," see ref. 57.

data and finding the point of inflection of the  $c_{\rm p}$ curve.  $E_{\rm g}$  may be estimated from known values of the molar cohesion energy. Table II gives values which are based on Bunn's list of cohesion energies,<sup>57</sup> E. The cohesion energies are corrected for the different specific volume at the glass transition. The correction was made using Bunn's volumes  $v^{57}$ at the boiling point and measured or estimated volumes at the glass transition  $v_{\rm g}$  (Table I, refs. 42– 53).  $\frac{E_{\rm Tg} - E}{E} = 1.73 \frac{v - v_{\rm g}}{v_{\rm g}} \quad ({\rm Ref.}\ 57) \quad (9)$ 

The empirical formula (above) was used for the extrapolation. The knowledge of  $\Delta C_{\rm p}$ , the molar heat capacity jump at  $T_{\rm g}$  allows then a calculation of  $\epsilon_{\rm h}$ , the excess in energy of 1 mole of holes over the nohole situation.

**3.** Calculation of  $v_{\rm h}$ .—The volume of one mole of holes  $v_{\rm h}$  can be estimated also. From equation 7

(57) C. W. Bunn, J. Polymer Sci., 16, 323 (1955).

$$\frac{v_0}{v_{\rm h}}\approx\frac{E_{\rm g}}{n\epsilon_{\rm h}}$$

$$v_{\rm h} \approx \frac{v_0 n \epsilon_{\rm h}}{E_{\rm g}}$$

By substitution of  $Mv_g$  for  $nv_0$  which introduces only a small error, a value of  $v_h$  can be found without knowledge of n.

$$v_{\rm h} \approx \frac{v_{\rm g} M \epsilon_{\rm h}}{E_{\rm g}} \tag{10}$$

The  $v_h$  column in Table II lists the volume in cm.<sup>3</sup> per mole of holes calculated using equation 10.

4. Comparison of the Results.—Before comparing the results it is of value to recall the specific assumptions on which the calculations are based:

a. A Boltzmann type distribution for the total hole volume  $N_h v_h$  (free volume) emerged from the specific model of the hole-phonon equilibrium

$$\frac{N_{\rm h}v_{\rm h}}{N_{\rm 0}v_{\rm 0}} = e^{-\epsilon_{\rm h}/RT}$$

b. Equation 7 implies that the internal latent heat of vaporization per unit volume of molecules and the hole energy per unit volume of holes are equal

$$\epsilon_0/v_0 = \epsilon_h/v_h$$

c.  $E_g$ , the molar cohesion energy at  $T_g$  is obtained from the knowledge of E of monomeric particles at their boiling point by empirical extrapolation over a rather large distance (equation 9).

In particular assumptions b and c indicate that absolute accuracy may be limited, but on a comparative basis of similar substances errors should be similar and valuable conclusions can be drawn.

TABLE III

COMPARISON OF CARBON BACKBONE POLYMERS

	€h, cal.	$\frac{(r_0^2/r_0^2)}{(r_0^2)^{1/2}}$	$\epsilon_2 - \epsilon_1,$ cal.	εh/υh, cal./cm. <sup>3</sup>	<sup>υ</sup> հ, Cm. <sup>3</sup>
Polybutadiene	650			90	7.2
Rubber	930	1.7158		88	10.5
Polyisobutylene	1000	1.9358	76059	81	12.4
PVC	1100		116059	95	11.6
Polystyrene	12 - 1500	$2.44^{58}$	143059	72 - 74	17 - 20

Table III shows carbon backbone polymers arranged as to increasing  $\epsilon_{\rm b}$ . The second column contains values for the ratio of the unperturbed end-to-end distance calculated from viscosity measurements to the end-to-end distance calculated assuming free rotation around all bonds of the polymer molecule. These values indicate clearly that stiffer chains (chains with a larger end-to-end dis-

(58) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 618.

tance) have a higher energy requirement for a hole creation.

The third column in Table III shows values calculated by Gibbs and DiMarzio<sup>59-62</sup> for the average difference between the low energy orientation of a bond and all other orientations. The almost identical numerical values for PVC and polystyrene are accidental because there is no obvious relationship between  $\epsilon_2 - \epsilon_1$  and  $\epsilon_h$ , but a high value of ( $\epsilon_2 - \epsilon_1$ ) will indicate a less flexible polymer than a low value. Inspection of the hole volume and hole energy per unit volume column shows that for polystyrene steric reasons alone account for the high hole energy.

Increasing length of chain molecules increases both the hole energy and volume as can be seen from Table IV.

TABLE IV

COMPARISON OF COMPOUNDS WITH INCREASING CHAIN

	DENOTI		
Compound	eh, cal.	<i>v</i> <sub>h</sub> , cm. <sup>3</sup>	€h∕ľh
(1-Butene)	410	3.4	120
Hexanes	<b>5</b> 30	4.9	110
Heptanes	<b>5</b> 70	5.6	100
Decanes	<b>59</b> 0	6.5	91
Ethanol	820	3.0	270
Propanol	840	2.6	320
Butanols	930	4.5	200
Cyclohexanol	1200	7.4	160
Heptanols	1000	6.5	150

Besides steric reasons strong secondary forces may bring about a high hole energy as demonstrated in the compounds with increasing amounts of OH-groups

Propanol	$\epsilon_{\rm h} = 840  {\rm cal.}$
Propylene glycol	$\epsilon_{\rm h} = 1060  {\rm cal.}$
Glycerol	$\epsilon_{\rm h} = 1270  {\rm cal.}$

The molar hole volume for all three compounds is only about 3 cm.<sup>3</sup>.

(59) J. H. Gibbs and E. A. DiMarzio, J. Chem. Phys., 28, 373 (1958).

(60) E. A. DiMarzio and J. H. Gibbs, ibid., 28, 807 (1958).

(61) E. A. DiMarzio and J. H. Gibbs, J. Polymer Sci., 39, 121 (1959).

(62) Gibbs and DiMarzio used their theory of the glassy state for these calculations. This theory treats the glass transition as the point where the number of possible configurations of the amorphous phase decreases sharply toward one. The theory should with appropriate substitutions lead to similar expressions as are discussed here. The main difference is the line of attack on the problem, the start from the molecular configuration instead of the hole configuration. If Gibbs and DiMarzio's equation for  $C_p$  can be solved, it should give more information about the structure of the glass than the formulas here discussed. The theory has only been applied to polymers.

# THE THERMODYNAMIC FUNCTIONS FOR THE SOLUTION OF CALCIUM HYDROXIDE IN WATER

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The solubility products for calcium hydroxide were evaluated from the solubility as a function of ionic strength, pH and temperature. From these data the standard thermodynamic functions were derived:  $\Delta F^0 = -17.67RT$  in T + 0.078.  $RT^2 + 89.0RT$ ,  $\Delta H^0 = 17.67RT - 0.078RT^2$ , and  $\Delta S^0 = 17.67R$  in T - 0.156RT - 71.3R. The lattice energy of calcium hydroxide is -562 kcal./mole when calculated by means of the Born expression. A Born-Haber cycle gave a value of 77 kcal./mole for the electron affinity of the hydroxyl ion and a heat of hydration of 98 kcal./mole for the gaseous hydroxyl ion. At 25° the solubility product  $K_{\rm sp}$  is  $9.10 \times 10^{-6}$ .

### Introduction

Although the chemistry of calcium hydroxide is involved in many industrial processes and is especially important for an understanding of the nature of fresh concrete, relatively little quantitative information on this subject is available. In this survey an attempt is made to use the literature solubility data to obtain the solubility products. With these data the thermodynamic functions for solution were derived. The lattice energy of the solid calcium hydroxide was evaluated from theoretical considerations.

### Discussion

Lattice Energy.—Two methods are available for calculating the lattice energy  $U_{0}$ . One is from experimental data and the second from theoretical considerations as developed by Born, Haber and Madelung.<sup>1</sup>

The lattice energy of -562 kcal./mole was found with the theoretical Born expression.<sup>2,3</sup>

$$U_0 = \frac{NA_{\delta}e^2}{\delta} \left(1 - \frac{1}{n}\right) \tag{1}$$

where N is Avogadro's number,  $6.0228 \times 10^{23}$ ;  $A_{\delta}$  is the Madelung constant,  $6.21^{4,5}$ ;  $\delta$  is the cube root of the molecular volume  $(74.10/2.241)^{1/3}$ ; *e* is the charge,  $4.802 \times 10^{-10}$  e.s.u.; and *n* is the Born constant which is 8 for calcium hydroxide according to the Pauling approximation.<sup>6,7</sup> In this calculation second-order effects such as the van der Waals attractive forces and the zero-point energy are neglected. Justification for this procedure has been discussed by Sherman<sup>3</sup> who demonstrated that the error involved in most cases is not more than two or three per cent. Also an error of plus or minus one in the constant *n* will result in an error of about 2%in the lattice energy value.

It is possible to write the Born–Haber<sup>2,8</sup> thermochemical cycle for calcium hydroxide in this form

(1) M. Born, "Atom Theories des festen Zustandes," B. G. Teubner, Leipzig, 1923; "Handbuch der Physik," Vol. 24, J. Springer, Berlin, 1927.

(2) M. Born, Verhandl. deut. physik. Ges., 21, 13 (1919).

(3) J. Sherman, Chem. Revs., 11, 93 (1932).

(4) F. Hund, Z. Physik, 34, 833 (1925)

- (5) R. G. Bates, V. E. Bower, R. G. Canham and J. E. Prue, *Trans. Faraday Soc.*, **55**, 2062 (1959).
  - (6) L. Pauling, J. Am. Chem. Soc., 49, 772 (1927).
- (7) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940.

(8) F. Haber, Verhandl. deut. physik. Ges., 21, 750 (1919).

$$Ca(s) \xrightarrow{S} Ca(g) \xrightarrow{I} Ca^{++}(g) \xrightarrow{U_0} U_0$$
$$O_2(g) + H_2(g) \xrightarrow{\Delta H_f} 2OH(g) \xrightarrow{-2F} 2OH^-(g) \xrightarrow{Ca(OH)_0(s)} U_0$$

where the sublimation energy S is 47.5 kcal./mole<sup>3,9</sup>; the ionization energy I is 412.9 kcal./mole<sup>3,9</sup>; and the heat of formation of two OH radicals is 20.12 kcal./mole.<sup>10</sup> The value for the electron affinity F for OH groups has been estimated to be between -48 and -88 kcal./mole.<sup>11,12</sup> For the equation

$$Ca(s) + O_2(g) + H_2(g) = Ca(OH)_2(s)$$
 (2)

the heat of reaction Q is -235.8 kcal./mole according to the National Bureau of Standards value for the heat of formation of calcium hydroxide.<sup>10</sup> The relationship between the terms in the Born-Haber cycle is

$$Q = S + I + \Delta H_f - 2F + U_0 \tag{3}$$

When it is assumed that  $U_0$  is -562 and S, I and  $\Delta H_{\rm f}$  have the values given above, then F is found to be 77 kcal./mcle, which is reasonably close to the 88  $\pm$  1 value estimated by Lederle<sup>11</sup> and the 76 value originally set by Goubeau.<sup>12</sup> It was later reported by Goubeau and Klemm<sup>13</sup> to be 48.

It is interesting to calculate the Ca–OH distance in calcium hydroxide. The ratio of the  $A_r$  Madelung constant  $\neg$ o the equilibrium cation-anion distance r is equal<sup>3</sup> to the ratio of the  $A_{\delta}$  to  $\delta$ . Since  $A_r$  is 4.71 for the cadmium iodide structure, which calcium hydroxide resembles, then r is 2.43 Å. This is reasonably close to the 2.37 Å. Ca–O interatomic distance in calcium hydroxide as reported by Busing and Levy.<sup>14</sup>

Thermodynamic Solubility Products  $K_{sp.}$ —The equation for the solution reaction of calcium hydroxide is

$$Ca(OH)_2(s) + nH_2O(1) = Ca^{++}aq + 2OH^{-}aq \quad (4)$$

For this reaction the equilibrium constant  $K_{sp}$  may be written

$$K_{\rm sp} = a_{\rm Ca}^{++} a_{\rm OH}^{-2} \tag{5}$$

where a refers to the activities of the ions. For con-

(9) J. E. Mayer and M. McC. Malthie, Physik. Z., 75, 748 (1932).

 (10) F. D. Rossini, et al., "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500, U. S. Govt. Printing Office, Washington, D. C.

(13) J. Goubeau, ibid., B34, 432 (1936).

(14) W. B. Busing and H. A. Levy, J. Chem. P ys., 26, 563 (1957).

<sup>(11)</sup> J. Goubeau and W. Kleinm, Z. physik. Chem., B36, 362 (1937).
(12) E. Lederle, *ibid.*, 17B, 368 (1932).

venience this equation may be expressed in the form

$$K_{\rm sp} = m_{\rm Ca^{++}} m^2_{\rm OH^-} f^{\pm 3} \tag{6}$$

where *m* is the concentration in moles per 1000 g. of solvent or per liter of solution if the solubility is small, and  $f^{\pm}$  is the mean activity coefficient.

The dissociation constant of the CaOH<sup>+</sup> ion has been reported<sup>5</sup> to be 0.071 mole kg.<sup>--</sup> at  $25^{\circ}$ . This constant should not substantially affect the conclusions discussed in the present study.

Three sets of reported data were used to evaluate  $K_{sp}$ : (1) solubility as a function of the concentrations in sodium chloride solutions<sup>15,16</sup>; (2) solubility as a function of the hydroxyl ion concentration<sup>17</sup>; (3) solubility as a function of temperature.<sup>17-21</sup>

For the first set of data the concentration of calcium hydroxide is m and therefore by substitution in the previous equation we obtain

$$\frac{1}{3}\log\frac{K_{\rm sp}}{4} = \log m + \log f^{\pm} \tag{7}$$

Hitchcock<sup>22</sup> has reported that a good empirical equation for  $f^{\pm}$  in not too concentrated solution is

$$-\log f^{\pm} = Z_{+}Z_{-}A\mu^{1/2} - B'\mu$$
 (8)

where A and B' are constants,  $Z_+$  and  $Z_-$  are absolute values of the valences of the calcium and hydroxyl ions, and  $\mu$  is the ionic strength. By substituting this expression for log  $f^{\pm}$  in eq. 7, it is possible to derive the relationship

$$\log m - 2.4 \mu^{1/2} = \frac{1}{3} \log \frac{K_{\rm sp}}{4} - B' \mu \qquad (9)$$

This equation was applied to the solubility of calcium hydroxide in sodium chloride solutions at 25° as reported by Johnson and Grove<sup>15</sup> and to the 20° data of Dschorbenadse, Mosebach and Naken.<sup>16</sup> By plotting the left-hand side of eq. 9 as a function of ionic strength, a curve may be drawn through the points which gives  $\frac{1}{3} \log K_{sp}/4$  as the intercept at zero ionic strength. The  $pK_{sp}$  values at 20 and  $25^{\circ}$  evaluated in this way are listed in Table I (column 2).

## TABLE I

$pK_{sp}$ Values				
<i>t</i> , <sup>1</sup> °C.	2 Set 1 data	3 Set 2 data	4 Set 3 data	5 A∵erage
20	4.83	5.12	4.99	$\div.98$
25	5.10		5.04	5.07
40		5.30	5.18	5.24

It follows from eq. 6 and 8 that

$$\log K_{\rm sp}^* - 6.4\mu^{1/2} = \log K_{\rm sp} - 3B'\mu \qquad (10)$$

where  $K_{sp}^*$  is the concentration solubility product,  $m_{Ca}^{*+m^2_{OH}-}$ . Equation 10 may be applied to the

(15) J. Johnson and C. Grove, J. Am. Chem. Soc., 53, 3976 (1931).
(16) D. Dschorbenadse, R. Mosebach and R. Naken, Zement, 31, 513 (1942).

(17) S. Fratini, Ann. Chem. Applicata, 39, 616 (1949).

(18) R. G. Bates, V. E. Bower and E. R. Smith, J. Research Natl. Bur. Standards, 56, 305 (1956).

(19) H. Bassett, J. Chem. Soc., 1270 (1934).

(20) R. T. Haslan, G. Calingaert and C. M. Taylor, J. Am. Chem. Soc., 46, 308 (1924).
(21) J. Mellor, "A Comprehensive Treatise on Inorganic and California Comprehensive Treatise on Inorganic and California Comprehensive Treatise Treatise Comprehensive Treatise Comprehensive Treatise Comprehensive Treatise Comprehensive Treatise Comprehensive Treatise Comprehensive Treatise Tre

(21) J. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. III, Longmans, Green and Co., New York, N. Y., 1923, p. 623.

(22) D. I. Hitchcock, J. Am. Chem. Soc., 50, 2076 (1928).

data reported by Fratini<sup>17</sup> for the solubility of calcium hydroxide in sodium and potassium hydroxide solutions at 20 and 40°. The left-hand side of eq. 10 may then be plotted as a function of ionic strength and log  $K_{\rm sp}$  is obtained as the intercept at zero ionic strength. In Table I (column 3) the 20 and 40°  $pK_{\rm sp}$  values are given.

In the third procedure for obtaining  $K_{sp}$  values all the reported solubility data<sup>15-21</sup> for calcium oxide and hydroxide were first plotted versus temperature. It was obvious immediately that there are not large differences in the solubilities reported by the many different research workers who used samples of various degrees of purity and of crystallinity. This indicated that at equilibrium for calcium oxide and hydroxide samples in contact with water only one form of crystalline Ca(OH)<sub>2</sub> was present. By weighting heavily the carefully determined data of Bates, et al.,<sup>18</sup> a line was drawn through the points from 20 to 100°. In Table II the data taken from the curve are listed.

It is possible to evaluate the  $K_{\rm sp}$  values from these solubility data by calculating the  $f^{\pm}$  values by means of the Debye-Hückel<sup>23</sup> equation useful in the concentration range prescribed by the solubilities of the hydroxide. According to the general form of the Debye-Hückel expression

$$-\log f_{\pm} = \frac{Z_{\pm} Z_{-} A \mu^{1/2}}{1 + B a_{i} \mu^{1/2}}$$
(11)

where  $a_i$  is the mean ionic diameter in angström units. It was estimated to be approximately four. By means of eq. 11  $f^{\pm}$  values were evaluated and  $K_{\rm sp}$  values at temperatures up to 100° were obtained. In Table II the results are summarized. As Table I (column 4) illustrates, the  $pK_{\rm sp}$  values calculated by this method agree fairly well with the values derived from the other two sets of data by methods in which extrapolations to infinite dilutions were performed.

The average  $pK_{sp}$  values are thus 4.98, 5.07, 5.24 at 20, 25 and 40°, respectively (column 5, Table I).

Evaluation of the Thermodynamic Functions for Solution.—By the least squares method the relationship between  $\ln K_{sp}$  and temperature was computed to be

$$\ln K_{\rm sp} = 17.67 \ln T - 0.078T - 89.0 \tag{12}$$

From this equation the standard free energy  $\Delta F^0$ , enthalpy  $\Delta H^0$  and entropy  $\Delta S^0$  changes for the solution of calcium hydroxide were evaluated

$$\Delta F^{0} = -17.67RT \ln T + 0.078RT^{2} + 89.0RT \quad (13)$$
  
$$\Delta H^{0} = 17.67RT - 0.078RT^{2} \quad (14)$$

$$\Delta S^0 = 17.67R \ln T - 0.156RT - 71.3R \quad (15)$$

At 298°K. the thermodynamic functions are:  $\Delta F^0 = 6.81 \text{ kcal./mole}; \quad \Delta H^0 = -3.29 \text{ kcal./mole}; \quad \Delta S^0 = -34.0 \text{ c.u./mole}.$  These values agree fairly well with those at 25° estimated by Latimer, Schutz and Hicks<sup>24</sup> ( $\Delta H^0 = -3,385 \text{ cal.}; \quad \Delta F^0 = 6,960 \text{ cal.};$  and  $\Delta S^c = -34.7 \text{ e.u.}$  per mole). It is interesting to note the large decrease in entropy which the system undergoes when the calcium and

(23) P. Debye and E. Huckel, Physik. Z., 24, 185 (1923).

(24) W. M. Latimer, P. W. Schutz and J. F. G. Hicks, Jr., J. Am. Chem. Soc., 55, 971 (1933).

TABLE 11	Π	TABLE
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EVALUATION OF  $pK_{sp}$  from Solubility Data<sup>21-28</sup> and Mean Activity Coefficients  $f \pm$  (Eq. 6 and 11)

								. ,
<i>t</i> , °C.	G./l.	lity, CaO Moles, 1.	μ	A	В	<i>f</i> =	$rac{K_{ m sp}  imes 10^{+6}}{ m (exptl.)}$	$K_{\rm sp} \times 10^{-6}$ (calcd. $\epsilon$ q. 12)
20		0.0211	0.0633	0.5046	0.3276	0.647	10.2	9.98
25		. 0203	. 0609	. 5092	.3286	. 647	9.04	9.10
30		.0195	.0585	.5141	.3297	. 647	8.00	8.25
35	1.06	.0189	.0567	. 5190	. 3307	. 647	7.28	7.46
40	1.022	.0183	.0549	.5241	.3318	. 648	6.64	6.70
45	0.984	.0176	.0528	.5296	. 3330	. 651	6.00	6.00
50	.947	.0169	.0507	.5351	. 3341	. 653	5.52	5.35
55	. 910	.0163	. 0489	. 5410	. 3353	. 654	4.84	4.74
60	. 870	.0155	. 0465	.5471	. 3366	. 659	4.24	4. <u>1</u> 9
65	. 837	.0150	.0450	5534	.3379	.659	3.84	3.69
70	. 796	.0142	.0426	.5599	.3392	. 659	3.24	3.23
75	.758	.0136	.0408	. 5668	. 3406	. 661	2.88	2.82
80	.717	.0128	.0384	.5739	.3420	664	2.44	2.46
85	.678	.0121	. 0363	. 5814	. 3434	. 667	2.08	2.13
90	. 640	.0114	.0342	. 5891	. 3450	. 670	1.76	1.84
95	. 600	.0107	.0321	.5972	. 3466	. 673	1.48	1.58
100	. 562	. 0100	. 0300	. 6056	3482	. 678	1.24	1.36

hydroxide species dissolve. This reduction is probably due to the decrease in randomness of the water in the environment of the ions.

**Born-Haber Cycle for Solution.**—The energy changes for the solution of calcium hydroxide may be represented by a Born-Haber cycle<sup>25</sup>

$$\begin{array}{ccc} Ca(OH)_{2}(s) & \stackrel{-U_{0}}{\longrightarrow} & Ca^{++}(g) + 2OH^{-}(g) \\ L & & \\ L & & \\ \hline & & \\ L^{++} & + 2L^{-} \\ \hline & & \\ Ca^{++}aq + 2OH^{-}aq \xleftarrow{-} & (16) \end{array}$$

The heat of solution L at 25° is equal to the difference between the heat evolved on hydration of the ions  $L^{++}$  for Ca<sup>++</sup> and  $L^{-}$  for OH<sup>-</sup> and the lattice energy

$$L = L^{++} + 2L^{-} - U_0 \tag{17}$$

Since the heat of solution at  $25^{\circ}$  is equal to -3.29 kcal./mole and  $U_0$  is -562 kcal./mole, then the sum of the heats of solutions of the ions is -565 kcal./mole. The value given by Rice<sup>25</sup> for the reaction

$$Ca^{++}(g) + nH_2O(1) = Ca^{++}aq$$
 (18)

is -369 kcal./mole which leaves approximately -98 kcal./mole for the hydration of the gaseous

(25) For good discussion see O. K. Rice, "Electronic Structure and Chemical Binding," McGraw-Hill Book Co., New York, N. Y., 1940. hydroxyl ions. This is reasonably close to the value of -105 kcal./mole offered by Bernal and Fowler.<sup>26</sup>

The Heat of Neutralization.—The heat of solution of calcium hydroxide in hydrochloric acid solution at 20° is -30.85 kcal./mole according to Thorvaldson and Brown.<sup>27</sup> By means of eq. 14,  $\Delta H^{0}_{293}$  is found to be -3.02 kcal./mole. Therefore we can assume that the heat of neutralization is approximately -13.92 kcal./equiv. wt. This value agrees very well with the -13.98 kcal./equiv. wt given by Berthelot<sup>28</sup> for the heat of neutralization at 16° and with the -13.924 kcal./mole value obtained for the heat of neutralization at 20° of sodium hydroxide by hydrochloric acid.<sup>29</sup> It is thus possible to conclude that calcium hydroxide is a very strong base. Because calcium hydroxide forms solutions of only pH 12.5 at room temperature, some chemists regard it as a weak base. The low pH is, of course, due to the relatively low solubility of calcium hydroxide.

(26) J. D. Bernal and R. H. Fowler, J. Chem. Phys., 1, 515 (1933).

(27) T. Thorvaldson and W. G. Brown, J. Am. Chem. Soc., 52, 80 (1930).

(28) M. Berthelot, Ann. Chim., 4, 531 (1875).

(29) T. W. Richards and L. P. Hall, J. Am. Chem. Soc., 51, 731 (1929).

# THE EFFECT OF OXYGEN ON THE RADIOLYSIS OF SILICONES<sup>1</sup>

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The effect of high pressures of oxygen on the radiolysis of hexamethyldisiloxane has been studied. Hexamethyldisiloxane was held under an oxygen pressure of ten atmospheres and irradiated with 800 kvp. electrons from a resonance transformer unit. Qualitative and quantitative analyses were carried out chemically, by gas chromatography and by infrared spectroscopy. The over-all effect of oxygen, at 10 atmospheres, was the diminution of the vacuum irradiation products and the formation of three major oxygenated products. A marked increase in the total product yield, relative to the vacuum irradiation, was observed with the oxygenated products accounting for approximately 70% of the total yield. The oxygenated products were concluded to be a carboxylic acid (CH<sub>3</sub>)<sub>2</sub>Si-O-Si(CH<sub>3</sub>)<sub>2</sub>CO<sub>2</sub>H and two Si-OOC- peroxides, namely (CH<sub>3</sub>)<sub>3</sub>Si-O-Si(CH<sub>3</sub>)<sub>2</sub>CO<sub>2</sub>H and two Si-OOC- peroxides, namely (CH<sub>3</sub>)<sub>3</sub>Si-O-Si(CH<sub>3</sub>)<sub>2</sub>CO<sub>2</sub>H and two Si discussed from the point of view of their effect on polymer crosslinking reactions.

#### Introduction

The effect of oxygen on the radiation chemistry of polymers has been the subject of a number of recent publications.<sup>2</sup> Usually the role of oxygen can be rationalized as that of a radical trapping agent with a resultant diminution in the yield of vacuum irradiation products. Indeed in the case of polyethylene it has been possible to inhibit totally the formation of carbon-carbon crosslinks by the introduction of sufficient oxygen.<sup>3</sup> The radiationoxidation chemistry of the polydimethylsiloxanes has proven to be a somewhat more complex study than those on hydrocarbon polymers for a number of reasons. First the simple correlation between oxygen concentration and crosslinking inhibition has not been sustained<sup>4</sup> and secondly the fund of knowledge available on the radiation and radiationoxidation chemistry of the dimethylsiloxanes is very small.

The detailed investigation of the vacuum irradiation of hexamethyldisiloxane given in the previous paper<sup>5</sup> has afforded a base for a similar study of the radiation-oxidation chemistry of the same molecule. The present paper presents the results of this investigation and discusses the implication of the results to the radiation-oxidation of polydimethylsiloxanes.

### Experimental

Hexamethyldisiloxane samples were irradiated to a total dose of  $2.9 \times 10^{21}$  e.v./g. under an oxygen pressure of 10 atmospheres. The radiation source, dose rates and hexamethyldisiloxane used were described previously as was the container used for the high pressure oxygen irradiations.<sup>6</sup>

In conjunction with the infrared spectroscopy, gas chromatography and mass spectrometry methods reported in the previous paper<sup>6</sup> certain chemical techniques also were used. These consisted of treatment of the irradiated samples with four reagents: powdered sodium carbonate, powdered KOH, anhydrous alumina and acidic silica gel. Liquid phases remaining after shaking irradiated samples with

(5) H. A. Dewhurst and L. E. St. Pierre, THIS JOURNAL, 64, 1063 (1960).

(6) H. A. Dewhurst, ibid., 63, 813 (1959).

these solid reagents were analyzed by the previously mentioned physical techniques. Semi-quantitative iodometric analyses<sup>7</sup> for peroxides also were performed on certain fractions.

### **Results and Discussion**

The experimental conditions under which the oxygen irradiations were carried out severely limited the extent to which we were able to analyze the reaction products. Specifically, a gas analysis which is vital to a determination of the stoichiometry of a reaction was not obtained due to the difficulties in isolating small yields of product gases from large quantities of reagent oxygen. The discussion which follows is therefore limited to products exhibiting gas chromatographic retention times greater than those of the starting material. Furthermore in an analysis of this type one is faced with the question as to whether peaks observed on the oxygen product analysis represent the same products they did in the case of the vacuum products. We have arbitrarily settled this question by assigning the vacuum peak identities to all products exhibiting the identical retention times shown by the vacuum product on both the didecyl phthalate and the silicone columns.

Table I shows the relative yields of products for vacuum and oxygen irradiations. For the sake of simplicity the methyl groups have been removed from the structural formulas. The product yields are listed in terms of area percentages relative to the parent area rather than as G-values. This terminology is necessary since calibrations based on the behavior of known products were impossible due to the inaccessibility of the oxygenated compounds. It is to be expected however that the relative area percentages will be a nearly direct measure of the weight percentages of the products, and consequently the numbers in Table I can be interpreted as a measure of the actual product vields. The product times cited are the retention times at  $100^{\circ}$  on the didecyl phthalate column (2 meters) while the product assignments are those previously arrived at.<sup>5</sup> As in our previous publication<sup>a</sup> the discussion assumes, in all cases, one radiation event per molecule.

Comparison of the total product yields, shown in Table I, at the same total dose indicated a marked increase when the irradiation was carried out in the presence of oxygen. Most of the increased product

(7) V. R. Kokatnur and M. Jelling, J. Am. Chem. Soc., 63, 1432 (1941).

<sup>(1)</sup> Presented at the 136th meeting of the American Chemical Society, Atlantic City, September 1959.

<sup>(2) (</sup>a) F. A. Bovey, "Effects of Ionizing Radiation on Natural and Synthetic High Polymers," Interscience, New York, N. Y., 1958; (b) N. Bakh, "International Conference on Peaceful Uses of Atomic Energy," United Nations, New York, 1956, Vol. 7, p. 538.

<sup>(3)</sup> L. E. St. Pierre and H. A. Dewhurst, J. Chem. Phys., 29, 241 (1958).

<sup>(4)</sup> Unpublished experiments by L. E. St. Pierre, H. A. Dewhurst and A. M. Bueche, showed a decrease in the *G* crosslinking in (MD<sub>2</sub>M) from a value of  $2.5 \pm 0.4$  in nitrogen to a value of  $1.1 \pm 0.5$  in presence of 10 atmospheres of oxygen.

TABLE I

Effect of Oxygen on Product Formation
Energy absorbed = $2.9 \times 10^{21}$ e.v./g.; oxygen pressure
10 atmospheres

Product, min.	Assignment	Relative : Vacuum	area % O2
4.9	CH <sub>3</sub> CH <sub>2</sub> SiOSi	1.2	0.9
7.6	SiOSiOSi	0.65	0.4
9.5	Oxidation product		2.4
11.5	Oxidation product		4.7
23.7	SiOCH <sub>2</sub> SiOSi	.3	1.5
31.6	SiOSi-SiOSi	.7	0
35.5	Oxidation product		0.6
65	SiOSiCH <sub>2</sub> SiOSi	1.5	.3
79.5	SiOSiCH <sub>2</sub> CH <sub>2</sub> SiOSi	0.4	0

yield, however, can be accounted for by the presence of three new products which comprise approximately 70% of the total yield.

With the singular exception of the 23.7 minute product all of the vacuum yields are diminished in the oxygen irradiation. No definite pattern is discernible however as the 5.0 and 7.0 minute products are only moderately affected while the 65 minute dimer is greatly diminished and the other dimers entirely eliminated. It is noteworthy however that in the very low temperature irradiations the 23.7 and 79.5 minute products were the only ones unaffected. The (pentamethyldisiloxanyl)-methyl radical is present in both, and with the acquisition of a good product balance in the future, some firm correlation based on this fact may be possible. The oxygen effect on the remainder of the products is quite similar to that observed during low temperature irradiation.<sup>5</sup>

The simple "known compound" analytical technique used in the vacuum irradiation analyses was not possible in the present study due to the vast number of oxygen products possible. For this reason a combination of chemical and physical techniques was used.

The liquid products were treated with several solid reagents as described in the experimental section. The roles of these solid reagents were: Na<sub>2</sub>CO<sub>3</sub>—remove strong acids; KOH—remove weak acids and react with base sensitive components;  $Al_2O_3$ —remove active hydrogen components;  $al_2O_3$ —remove active hydrogen components;  $al_2O_3$ —remove active hydrogen components.

nents, e.g., -SiOH; acidic  $SiO_2$ -react with acid

sensitive components.

Table II shows the effect of these reagents on the amounts of the oxygen products remaining after an irradiation sample had been treated with each of them. Infrared absorptions and relative iodometric peroxide titers are also listed. The chemical behavior of the individual products and the conclusions to be drawn are discussed below.

9.5 Minute Product.—The 9.5 minute product can be seen to have reacted with the weak base, with the strong base, and was removed by alumina and silica. The infrared absorptions at 5.8 and 8.35  $\mu$  characteristic of carboxylic acids<sup>3</sup> were greatly decreased when only this peak was markedly decreased. A marked decrease in this peak could not be related to the change in the peroxide

(8) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958.

TABLE II

Chemical Behavior of Oxygen Irradiated Hexamethyl-	-
DISILOXANE	

Energy absorbed	$= 29 \times$	10 <sup>2</sup> : e v /	/	vgen nr	essure =
Zinerg, andornea	10	) atm.	ь, о.,	, sen 1/	0.000.0
		Relat	ive area	%	
Product, min.	Un- treated	Na2CO1, 10 min.	кон	Al <sub>2</sub> O <sub>2</sub>	Acidic SiO2
9.5	2.4	0.7	0.0	0	0
11.5	6.0	5.8	. 0	2.76	. 25
35.5	0.6	0.5	0	0.4	0
IR: A5.8µ	.37	0.08	0.04	0.07	0.06
A8-35µ	.15	0	0	0	0
Relative peroxide					
titer	1.00	0.70	0	0.40	0

titer. These results suggested that the 9.5 minute product was a carboxylic acid. This inference was substantiated by the observation that pyrolysis of the products yielded carbon monoxide. Benkeser and Severson<sup>9</sup> have observed carbon monoxide as a decomposition product from the pyrolysis of triphenylsilylcarboxylic acid.

The position of the peak on the chromatogram suggested the product to be a molecule containing not more than two silicon atoms. The only product meeting all of these requirements was  $(CH_3)_3$ -SiOSi $(CH_3)_2$ COOH.

11.5 and 35.5 Minute Products.—The 11.5 and 35.5 minute products exhibit exactly the same chemical properties; hence they are discussed together.

The following facts, contained in Table II, support the conclusion that these products are peroxides: (1) their presence or absence can be related to the change in peroxide titer.

(2) They are removed by strong base as would be predicted from the observations of Buncel and Davies<sup>10</sup> on the chemical reactions of silicon per-oxides.

(3) They are partially removed by weakly acidic aluminum oxide but are completely removed by strongly acidic silica gel. Such acid sensitivity is characteristic of peroxides.<sup>11</sup> Five types of peroxides are possible as radio-oxidation products from

hexamethyldisiloxane.

They are -SiOOH,

-COOH, -COOC-, -SiOOSi-, and -SiOOC-. Selection from among these possibilities was made in the following way: (a) The 11.5 and 35.5 minute

products were not entirely removed by the active hydrogen scavenger aluminum oxide. Therefore

the hydroperoxides -SiOOH and -COOH were

eliminated. (b) Hexamethyldisilyl peroxide was synthesized and a dilute solution in hexamethyldisiloxane prepared. Treatment of this solution with acidic silica gel resulted in only a 20% decrease in peroxide concentration. Since the 11.5 and 35.5 minute products were almost completely removed

(11) A. V. Tobolsky and R. B. Mesrobian, "Organic Peroxides," Interscience Publishers, New York, N. Y., 1954.

<sup>(9)</sup> R. A. Benkeser and R. G. Severson, J. Am. Chem. Soc., 73, 1424 (1951).

<sup>(10)</sup> E. Buncel and A. G. Davies, J. Chem. Soc., 1556 (1958).

by the identical treatment, the possibility of it being a disilyl peroxide, -SiOOSi-, was discounted.

-COOC-. The latter was not considered a likely

choice since marked base sensitivity to this type of peroxide is rare.<sup>11</sup> However exclusion cannot be made on this basis. The positions of these two products on the gas chromatogram make possible the differentiation we seek. Based on the product retention times the 11.5 minute product is concluded to contain two silicon atoms and the 35.5 minute product three silicon atoms. Consideration of all the possible peroxides containing two silicon atoms shows that both types under consideration are possible for the 11.5 minute product. The same condition does not hold for the three silicon

35.5 minute products, where only the -Si-O-O-C-

type product is possible. Since the two products exhibited identical chemical behavior, we conclude they are both of this type. Only two peroxides meet all requirements, namely,  $(CH_3)_3SiOSi(CH_3)_2$ -OOCH<sub>3</sub> which must be the 11.5 minute product and  $(CH_3)_3SiOSi(CH_3)_2CH_2OOSi(CH_3)_3$  which must be the 35.5 minute product.

### Conclusions

The mechanism of formation of two of the three main oxidation products can be explained on the basis of the trapping of primary radicals by oxygen.

The primary radicals possible from a single event per molecule are

$$(CH_{a})_{3}SiOSi(CH_{a})_{3} \longrightarrow (CH_{a})_{3}SiOSi(CH_{a})_{2} + CH_{3} \cdot (a) \quad (b)$$

$$(CH_{a})_{3}SiOSi(CH_{a})_{2}CH_{2} + H \cdot (c) \quad (d)$$

$$(CH_{a})_{3}SiOSi(CH_{a})_{2}CH_{2} + H \cdot (c) \quad (d)$$

$$(CH_{a})_{3}SiO + (CH_{a})_{3}Si \cdot (c) \quad (f)$$

The formation of the 11.5 minute product can take place by the trapping of a methyl radical (b) and a pentamethyldisiloxanyl radical (a) by an oxygen molecule to give  $(CH_3)_3SiOSi(CH_3)_2$ -OOCH<sub>3</sub>. The 35.5 minute product can be formed by the trapping of a trimethylsilyl radical (f) and a (pentamethyldisiloxanyl)-methyl radical (c) by oxygen to give  $(CH_3)_3SiOSi(CH_3)_2CH_2OOSi(CH_3)_3$ . The formation of the 9.5 minute product probably proceeds by the sequence

$$(CH_3)_3SiOSi(CH_3)_2CH_2 + O_2 \longrightarrow$$

$$(CH_3)_3SiOSi(CH_5)_2CH_2O_2, \longrightarrow (CH_3)_3SiOSi(CH_5)_2CH_2O_2, (CH_3)_3SiOSi(CH_3)_2CHO + OH (U)$$

The aldehyde, I, or its precursor is then rapidly oxidized to the acid product. In any event, the formation of the acid from the simple radical requires more than one oxidation event. The possibility that the acid is formed by some other radical or ionic mechanism cannot be excluded. Support for the radical mechanism, however, is found in the fact that the proposed participating radical is generated in high yield (G = 2.8) in the vacuum irradiation. Similarly the hypothesis that the pentamethyldisiloxanyl radical is an intermediate in the formation of the 11.5 minute product is supported by the observation that this radical also is generated in high yield in the vacuum irradiation.

That some dimer should form, even under the strenuous oxidative conditions employed, is possibly indicated by our previous findings<sup>4</sup> and by those of Miller<sup>12</sup> who was unable to reduce the G crosslinking in polydimethylsiloxanes below 25% of the nitrogen value under similar conditions. The small yield of residual dimer observed is, however, insufficient to account for all of the crosslinking observed by Miller. It is probable that decomposition or rearrangement of the oxidation products accounts for the remainder of the crosslinking. Indeed one very probable contributor is the acid (the 9.5 minute product) which, according to the observations of Benkeser and Severson<sup>9</sup> could decompose to form a cross-link.

$$(CH_3)_3 SiOSi(CH_3)_2 CO_2 H \longrightarrow (CH_3)_3 SiOSi(CH_3)_2 OH + CO$$

$$2(CH_3)_3SiOSi(CH_3)_3OH \longrightarrow (CH_3)_3SiOSi(CH_3)_2OSi(CH_3)_2OSi(CH_3)_3 + H_2O$$

Certain oxygen effects, such as inhibition to recombination reactions, invite comment at this time but require a more detailed quantitative study before they can be properly handled.

Acknowledgment.—We are indebted to J. S. Balwit for performing the irradiations and to A. A. Miller and S. W. Kantor for many helpful discussions.

(12) A. A. Miller, A.A.A.S. Symposium on Chemical Effects of High Energy Radiation (Washington, 1958).

# RADIATION CHEMISTRY OF HEXAMETHYLDISILOXANE, A POLYDIMETHYLSILOXANE MODEL<sup>1</sup>

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A detailed analysis has been made of the products from the 800 kvp. electron radiolysis of hexamethyldisiloxane. The yields of volatile products were established as  $G(H_2) = 0.7$ ,  $G(CH_4) = 1.4$  and  $G(C_2H_6) = 0.4$ . These yields were decreased by only 50% in the presence of high iodine concentrations indicating a significant contribution by molecular-like processes. The non-volatile liquid products were examined by gas chromatography, and classified into low molecular weight, intermediate molecular weight and dimer with the yields, 0.5, 1.8 and 1.8 molecules/100 e.v., respectively. The results are discussed in terms of free radical and molecular-like reactions and their pertinence to radiation effects in polydimethylsiloxanes indicated.

### Introduction

It has been shown by a number of workers that the organopolysiloxanes are crosslinked on exposure to high energy radiations.<sup>2-4</sup> Recently a precise determination of the crosslinking efficiency has been reported.<sup>5</sup> The nature of the crosslinks have been only partially elucidated by studying the radiolysis of hexamethyldisiloxane and octamethylcyclotetrasiloxane.<sup>6</sup> To obtain a more complete understanding of the radiation chemical processes occurring in polydimethylsiloxanes, it was necessary to determine the total chemistry which occurred in a model system. We chose hexamethyldisiloxane as a model compound for the polydimethyl system and were able to study the nature of the products formed by gas chromatography and mass spectrometry. The pertinence of these results to the polymer system are discussed.

### Experimental

Degassed or nitrogen purged samples were irradiated with 800 kvp. electrons from the General Electric Research Laboratory resonant transformer unit. A specially designed high pressure cell' was used which enabled irradiations to be made up to 10 atmospheres pressure of nitrogen. To establish the effect of product gases, experiments were carried out separately under 10 atmospheres pressure of hydrogen and of methane. Dosimetry was based on ionization chamber measurements and checked independently by chemical methods.

The hexamethyldisiloxane used had been purified by distillation and shown by gas chromatography to be of high purity.

Product identification and analyses were based on a combination of gas chromatography, infrared and mass spectrometry. Identification of products by gas chromatography was based on retention time studies of known compounds on two different columns, namely, didecyl phthalate and a silicone column. For quantitative determination of products a calibrated two meter didecyl phthalate column was used. Gas analyses were performed as previously described.<sup>7</sup> The formation of Si–II bonds was determined by infrared measurements at a wave length of 2150 cm.<sup>-1</sup> as described by Bueche.<sup>4</sup>

### **Results and Discussion**

**Gas Products.**—The volatile products (at  $-120^{\circ}$ )

(1) Presented at the 136th meeting of the American Chemical Society, Atlantic City, September, 1959.

(2) (a) E. J. Lawton, A. M. Bueche and J. S. Balwit, Nature, 172, 76
 (1953); (b) A. Charlesby, Proc. Roy. Soc. (London), A230, 120 (1955).

(3) E. L. Warrick, Ind. Eng. Chem., 47, 2388 (1955).

(4) A. M. Bueche, J. Polymer Sci., 19, 292 (1956).

(5) W. Barnes, H. A. Dewhurst, R. W. Kilb and L. E. St. Pierre, *ibid.*, **36**, 525 (1959).

(6) S. W. Kantor, Abstract No. 55-0, Am. Chem. Soc. Meeting, September, 1956.

(7) H. A. Dewhurst, THIS JOURNAL, 63, 813 (1959).

from vacuum irradiated samples were hydrogen, methane and ethane with the following yields,  $G(H_2) = 0.7$ ,  $G(CH_4) = 1.4$  and  $G(C_2H_6) = 0.4$ molecules/100 e.v. The relatively high yield of methane is of interest since the mass spectral fragmentation pattern of hexamethyldisiloxane shows that the most abundant positive ion results from loss of a methyl group. The ratio of hydrogen to methane is in fair agreement with Warrick's results with octamethylcyclotetrasiloxane; however the ratio of ethane to methane is about four times that reported by Warrick.<sup>3</sup> It is conceivable that the discrepancy in the ethane-methane ratio could be due partly to the fact that different starting materials were used and partly to a dose rate effect since the dose rate in the electron beam experiments was approximately 2000 times that in Warrick's  $\gamma$ -ray experiments.

In the presence of iodine  $(\sim 10^{-2} M)$  the total gas yield was decreased by approximately one-half; the yield of hydrogen and methane was 0.4 and 0.70 molecules/100 e.v., respectively. These results are similar to those observed with liquid alkanes<sup>8</sup> where it was concluded that a significant fraction (0.60) of the hydrogen yield is formed by molecular processes.

Liquid Products.—A gas chromatogram, obtained at 100° on a 2-meter didecyl phthalate column, of the non-volatile products is shown in Fig. 1. The product assignments shown in Fig. 1 were in general based on a comparison of the retention times of the observed peaks with the retention times of known compounds. The assignments were further checked by determinations of the retention times at different temperatures. Since a standard sample for the 23.7 min. product ( $\alpha$ -trimethylsiloxyhexamethyldisiloxane), was not available, its identity was established indirectly. The position of this product peak on the chromatogram established it as a 3-silicon atom compound of which only four possibilities can be derived from hexamethyldisiloxane. Two of these possibilities are present and identifiable as the 7.6 (octamethyltrisiloxane) and 21.5[(trimethylsilylmethyl)-pentamethyldisiloxane] minute products. A third possibility would require a product containing an Si-Si bond. This possibility was ruled out since treatment with bromine did not affect the 23.7 minute product whereas the 31.6 minute, which had been established as the Si-Si dimer [1,2-bis-(trimethylsiloxy)-tetramethyldi-

(8) H: A: Dewhurst, ibid., 62, 15 (1958).







Fig. 2.—Formation of products from radiolysis of hexamethyldisiloxane.



Fig. 3.—Formation of dimer products from radiolysis of hexamethyldisiloxane.

silane], was completely removed. The only remaining possibility,  $\alpha$ -trimethylsiloxyhexamethyldisiloxane, was assigned the 23.7 minute product as shown in Fig. 1. In addition to the products shown in Fig. 1, gas chromatograms obtained at 50° showed small amounts of tetramethylsilane and pentamethyldisiloxane.

The formation of the more abundant products was studied as a function of the energy absorbed and the results are shown in Figs. 2 and 3. The relative area per cent. was obtained by planimeter integration of the peak areas on the gas chromatogram. In all cases shown in Figs. 2 and 3, it was found that the amount of product formed was linear with total energy absorbed up to approximately  $6 \times 10^{21}$  e.v./g. By suitable calibration with known samples, the relative area per cent. was readily converted to weight per cent. Thus from the initial slopes of such curves the initial *G*-values were obtained and are given in Table I. For the sake of simplicity the methyl groups have been removed from the structural formulas.

### TABLE I

YIELDS OF NON-VOLATILE PRODUCTS FROM RADIOLYSIS OF HEXAMETHYLDISILOXANE

	11 DAMETHINDIOL		
	Vacuum (nitrogen)	irradiated	
Peak, min.	Assignment	G (25°), molecules,	G (-195°) /100 e.v.
	Low molecular weigh	t products	
1.0	Si-CH <sub>3</sub>	0.2	0.4
2.0	SiOSi-H	0.3	0.1
	Intermediate molecular w	eight produ	cts
4.0	Si-Si	Trace	Trace
	SiO-H	Absent	0.1
4.9	SiOSiCH2-CH3	1.1	0.5
7.6	SiOSi-OSi	0.5	0.3
21.5	$SiOSiCH_2$ -Si	Trace	Trace
23.7	SiOSiCH <sub>2</sub> -OSi	0.2	0.2
	Dimer produ	ets	
31.6	SiOSi-SiOSi	0.5	Absent
65	SiOSiCH <sub>2</sub> -SiOSi	1.0	0.4
79.5	SiOSiCH <sub>2</sub> -CH <sub>2</sub> SiOSi	0.3	0.3

The liquid products have been classified into low molecular weight, intermediate molecular weight and dimer products. The yield of low molecular weight liquid products was approximately 0.5 molecules/100 e.v. and consisted of about equal amounts of tetramethylsilane and pentamethyldisiloxane. The intermediate molecular weight products were mainly ethylpentamethyldisiloxane (G = 1.1), octamethyltrisiloxane (G = 0.5) and  $\alpha$ -trimethylsiloxyhexamethyldisiloxane (G = 0.5), ctrimethylsiloxy)-tetramethyldisilane (G = 0.5), bis-(pentamethyldisiloxanyl)-methane (G = 1.0) and 1,2-bis-(pentamethyldisiloxanyl)-ethane (G = 0.3). Infrared analysis of the irradiated liquid established the formation of Si-H bonds with an initial yield of about G = 0.3. This yield correlates fairly well with the small amount of pentamethyldisiloxane shown in Table I. Similar yields of Si-H bonds have been observed with polydimethylsiloxanes.<sup>4</sup>

On the basis of the gas yields and the data in Table I, material balances for hydrogen and methyl groups have been derived. These results are summarized in Table II. It is of interest to note that in both the hydrogen and methyl balances more gas has been evolved than can be accounted for from the observed products. The major contribution to these small differences can be attributed to the formation of post-dimer products which were not observed by the gas chromatography analysis. The amount of postdimer product was obtained by simple residue determinations corrected for the dimer content of the residue by gas chromatography. The nature of the residue is unknown; it may result from rearrangement of difunctional products. An attempt to account for all the products which result from ultimate cleavage of the Si-O bond have not been successful. There are more (CH<sub>3</sub>)<sub>3</sub>SiO fragments than  $Si(CH_3)_3$  fragments in the observed products. The reason for this is not clear; however, part of the explanation may be the formation of postdimer products.

### TABLE II

MATERIAL BALANCE FOR RADIOLYSIS OF HEXAMETHYLDI-SILOXANE

Hydrogen balance	Methyl balance
G(H-release) = 2.8	$G(CH_3-release) = 2.8$
G(H-uptake) = 3.1	$G(CH_{3}uptake) = 3.3$

To determine the effect of product gases, samples of hexamethyldisiloxane were irradiated in the presence of ten atmospheres of hydrogen (electrolytic grade) and methane (Matheson). No significant change in the yields of the non-volatile products was observed.

Effect of Temperature.-The product yields obtained on irradiation at liquid nitrogen temperature (crystalline solid) are shown in Table I. Comparison of these yields with those obtained at room temperature shows some very interesting differences. In most cases the product yields decreased on irradiation at liquid nitrogen temperature; however, the yield of tetramethylsilane actually doubled. It is of interest that the total yield of low molecular weight product was unchanged whereas the total yield of intermediate and dimer products was essentially decreased by one-half at liquid nitrogen temperature. These results are in striking contrast with the alkane system where it was found that the intermediate product was eliminated on irradiation at liquid nitrogen temperature.8 It is also of interest to note that the two major intermediate products (4.9 and 7.6 minutes) were decreased by only 30% even in the presence of ten atmospheres of oxygen.<sup>9</sup> The 65 minute dimer product was suppressed by low temperature irra-

(9) L. E. St. Pierre and H. A. Dewburst, THIS JOURNAL, 64, 1063 (1960).

diation to about the same extent observed in the presence of oxygen.<sup>9</sup> The 31.6 minute dimer product is absent both at low temperatures and in the presence of oxygen<sup>9</sup> whereas the 79.5 minute dimer product is eliminated by oxygen<sup>9</sup> but unaffected by low temperatures. Another important difference was the formation of a small yield of trimethylsilanol by low temperature irradiation, a product which was not observed at room temperature. These results suggest that both radical and molecular-like reactions are important in the radiolysis of hexamethyldisiloxane.

### Conclusion

The observed products can be accounted for on the basis of the following simplified reaction scheme. In this scheme it is assumed that only one radiation event can occur per molecule. Primary cleavage of the three different bonds in hexamethyldisiloxane lead to the processes

$$(CH_{3})_{3}SiOSi(CH_{3})_{3}$$

$$(CH_{3})_{3}SiOSi(CH_{3})_{2} + CH_{3} \cdot (1)$$

$$(CH_{3})_{3}SiOSi(CH_{3})_{2} \cdot CH_{2} + H \cdot (2)$$

$$(CH_{3})_{3}SiOSi(CH_{3})_{2} \cdot CH_{2} + H \cdot (2)$$

$$(CH_{3})_{3}SiO \cdot + \cdot Si(CH_{3})_{3} \quad (3)$$

Although subsequent recombination reactions of the various fragments can qualitatively account for the observed products, it is evident from the results that a consideration of only random recombination of radical fragments cannot explain all the observa-The results indicate that the 4.9 and 7.6 tions. minute products are to a large extent formed by molecular-like processes. These products cannot be formed by a simple bimolecular process involving excited molecules because of the non-equivalence of the conjugate product in each reaction; that is the 4.9 and 2.0 minute products should be formed with the same yield, similarly the 7.6 and 1.0 minute products should be formed with the same yield. It is conceivable that ion-molecule reactions could explain some of these observations.

On the basis of the present results with a model compound it is concluded that the cross-links formed in the radiolysis of polydimethylsiloxanes are of the type Si–CH<sub>2</sub>–Si, Si–Si and SiCH<sub>2</sub>CH<sub>2</sub>Si in the ratio of 2/1/0.6. The ratio of SiCH<sub>2</sub>Si to Si-Si type cross-links is in good agreement with the results of Kantor<sup>6</sup> and of Bueche<sup>4</sup>; however, these authors did not observe the formation of SiCH<sub>2</sub>CH<sub>2</sub>-Si type cross-lir.ks. The results of the model compound study show that silethylene cross-links make an important contribution to the total cross-linking efficiency. The results of the model study also indicate that an appreciable amount of main chain scission and branching can occur in siloxanes. The small amount of siloxane cleavage observed in the model study is in accord with the recent results of Kilb.10

Acknowledgment.—The authors are indebted to Dr. S. W. Kantor for the purified hexamethyldisiloxane and the dimer calibration samples, to J. S. Balwit for the irradiations and to Drs. A. A. Miller and S. W. Kantor for valuable discussions.

(10) R. W. Kilb, ibid., 63, 1838 (1959).

## HEATS OF SOLUTION IN LIQUID AMMONIA AT 25°1

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Heats of solution at 25° of water, methylamine and several salts in ammonia, and of potassium iodide in methylamine have been measured, mostly at mole ratios of 200 to 16,000. Heats of dilution of the salts in ammonia are very large, some ten times the calculated limiting Debye-Hückel slope for 1-1 electrolytes, and are nearly independent of valence type and ionic size. Heats of dilution of non-electrolytes are not detectable.

### Introduction

Many measurements of heats of solution in liquid ammonia have been reported.<sup>2-14</sup> With the single exception of the measurements of Chall and Doepke<sup>14</sup> with NaCl at 20° these measurements have been performed at the normal boiling point of ammonia,  $-33^{\circ}$ , using vaporization calorimeters wherein the major portion of the heat effect is measured by observing the amount of ammonia vaporized at constant temperature. The inherent difficulties of this method limit the attainable precision.

In particular, the increasing uncertainty associated with measurements of heats of solution at low concentrations has resulted in few heats being measured at mole ratios (ammonia/solute) greater than 1000, and none are sufficiently accurate to permit detection of heat effects due to dilution at mole ratios greater than 500. Using the dielectricconstant data of Grubb, Chittum and Hunt<sup>15</sup> and the Debye-Hückel theory the limiting slope of the relative apparent molal heat content of a 1-1 electrolyte at  $25^{\circ}$  is calculated to be

$$\frac{\mathrm{d}\theta_{\mathrm{L}}}{\mathrm{d}\sqrt{c}} = 2.3 \text{ kcal./mole}^{-2/2} \text{ liter}^{1/2}$$

The uncertainty of this number is fairly large, perhaps of the order of 20%, but it may be compared with a corresponding value of 0.47 kcal. mole<sup>-3/2</sup> liter'<sup>1/2</sup> for water. Although measurement of heats of dilution at the extreme concentrations that have been attained in work with aqueous solutions would be extremely difficult, it seemed possible to make measurements of reasonable precision at moderate dilutions in order to achieve a better understanding of ionic solutions in this "water-like" solvent.

- $\left( I\right)$  This work was performed under the auspices of the U. S. Atomic Energy Commission.
- (2) C. A. Kraus and J. A. Ridderhof, J. Am. Chem. Soc., 56, 79 (1934).
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- (6) F. C. Schmidt, F. J. Studer and J. Sottysiak, *ibid.*, **60**, 2780 (1938).
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  - (13) L. V. Coulter, THIS JOURNAL, 57, 553 (1953).
- (14) P. Chall and O. Doepke, Z. Elektrochem., 37, 357 (1931).
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Because of the large and uniform dilution heats which we observed in ammonia for several salts, one series of measurements of the heat of solution of potassium iodide in monomethylamine was performed. Dielectric constant data for this solvent are not adequate to estimate the Debye-Hückel limiting slope. The heats of solution of the nonelectrolytes water and methylamine in ammonia also were measured.

### Experimental

With the use of the sealed-bomb calorimeter previously described<sup>16</sup> it is possible to measure reaction heats at  $25^{\circ}$  in ammonia nearly as easily and precisely as in water. Two bombs, IB<sup>16</sup> and ID, were used in this work. Bomb ID is similar to IA<sup>16</sup> but is made of coinage gold instead of gold-plated copper for greater corrosion resistance. The free internal volumes of the bombs were 628 and 648 ml., respectively. Bomb IB was loaded with about 400 ml. of ammonia and ID with about 540 ml.; the magnitude and uncertainty of one of the heat-correction terms described below is decreased by decreasing the vapor space.

Auxiliary equipment was essentially as previously described; a platinum resistance thermometer was used for most measurements. The accuracy of the measurement of integral heats of solution at high dilutions was limited by the useful thermometric sensitivity of about  $\pm 1 \times 10^{-40}$ , which corresponds to about 50 cal. mole<sup>-1</sup> at a mole ratio ratio of 16,000. In one series of runs a thermistor was used with calorimeter ID to permit measurements at lower concentrations; the instrumental combination is designated IDT. The thermistor, a glass-enveloped bead with a resistance of about 2000 ohms, was used as a two-lead differential thermometer with the G-2 Mueller bridge, an auxiliary decade box being inserted in the adjacent arm. Unbalance was detected with a Liston-Becker breaker-amplifier and a recorder, as before; the combination proved to have a useful sensitivity of about  $2 \times 10^{-50}$ .

The solute samples were enclosed in thin-walled spherical bulbs blown on Pyrex tubing. Adequate thinness of wall was judged by listening to the sound produced by gently bouncing the bulbs on a bench top. The bulbs were then sealed off and tested at an external pressure of 15 atmospheres for a few seconds before being opened, cleaned, filled and sealed under vacuum. Of the bulbs thus selected few if any failed upon exposure to the vapor pressure of ammonia at 25° (10 atmospheres) for several hours, and only about 20% failed to break under the action of the springloaded hammer. The external volumes of the filled and sealed bulbs were measured with a pycnometer and the internal volumes calculated from the gross weight, sample weight, and density of Pyrex. All weighings were corrected to vacuum.

The valve on the bomb was replaced by a Pyrex tube terminating in a flange sealed to the bomb with a gasket and retaining nut. After being assembled with sample, the bomb was attached to a vacuum line and evacuated to about  $10^{-5}$  mm. overnight. Ammonia (Matheson, anhydrous grade, claimed minimum purity 99.99%) was treated with a small amount of sodium and distilled into the bomb, a Dry Ice-acetone-bath being used around the bomb and the ammonia pot being warmed as required to maintain a pressure of about 2 atmospheres; the pressure was lowered briefly to slightly below one atmosphere while the Pyrex tube was sealed off close to the bomb. Monomethylamine

<sup>(16)</sup> S. R. Gunn, Rev. Sci. Instr., 29, 377 (1958).
(Matheson, claimed minimum purity 96.5%, principal impurities di- and trimethylamine and ammonia) was dried with lithium and loaded in the same manner. The amount of solvent used was determined to about  $\pm 0.5$ ° after the run by weighing the bomb before and after removal of the solvent.

NaCl, KI and Ba(NO<sub>3</sub>) were reagent grade, oven-dried at 120° and cooled in a desiccator; NH<sub>4</sub>Cl, NH<sub>4</sub>I and HgI<sub>2</sub> were reagent grade, dried under vacuum at 90°; CsI was Harshaw crystal containing 0.04% Tl. Methylamine was treated as above and distilled into sample bulbs; water was deaerated by repeated freezing and pumping of the bulbs before sealing off.

Lanthanum iodide was prepared by treating 10.4 g. of La<sub>2</sub>O<sub>3</sub> with 130 g. of NH<sub>4</sub>I in a helium atmosphere at about 350° for 65 hours. The system then was evacuated and the excess NH<sub>4</sub>I sublimed away. The material was about 99% soluble in water, indicating a low oxide or oxyiodide content. An attempt was made to purify the salt by dissolution in ammonia and filtration; however, when ammonia was condensed on the solid, it expanded prodigiously with a large evolution of heat and was still solid after about 30 moles of ammonia per mole of LaI<sub>3</sub> had been added. Ammonia was then pumped off the material for several days at room temperature; at the end it exhibited an ammonia pressure of about 15  $\mu$ . Analysis by ignition to La<sub>2</sub>O<sub>3</sub>, precipitation of AgI, and Kjeldahl approximated closely the formula LaI<sub>3</sub>-6NH<sub>3</sub>: La, 22.47% (theo. 16.43%). This material was more satisfactory for heat of dilution studies than LaI<sub>3</sub>, since the total heat of solution of the latter would be much larger.

The corrections necessary to calculate the molar heat of solution,  $\Delta H$ , from the observed heat of reaction,  $q_{obs}$ , are indicated in the equation

$$-\Delta H = \frac{q_{\rm obs} - q_{\rm ham} + q_{\rm vap} - q_{\rm cond}}{n}$$
(1)

where *n* represents the moles of solute.

The term  $q_{\rm ham}$  is the energy released by the hammer spring in the bulb-breaking operation. From the force constant of the spring and its change of length, this is calculated to be 0.007 cal., which is barely significant only for runs in calorimeter IDT.

The term  $q_{\rm vap}$  is the absorption of heat associated with volatilization of the amount of solvent required to saturate the increased volume of the vapor phase when the evacuated sample bulb is broken. With the use of data from the International Critical Tables, it may be calculated that when a bulb of  $V_{\rm b}$  ml. internal volume is broken the vapor volume increases by  $1.013 V_{\rm b}$ , the liquid volume decreases by  $0.013 V_{\rm b}$ , and  $0.00789 V_{\rm b}$  g. of ammonia are vaporized with the absorption of  $2.200 V_{\rm b}$  cal. However, there is also a PV thermal effect due to expansion of gas into the initially vacant space as noted, for example, by Guderjahn, *et al.*<sup>17</sup>; this results in the production of  $0.240 V_{\rm b}$  cal. Hence, for

$$q_{\rm vap} = 1.960 V_{\rm b} \, {\rm cal.}$$
 (2)

Experimental checks of this quantity, by breaking empty bulbs of 2.94, 2.90, 3.59 and 12.01 mL, gave, respectively, 1.98, 1.94, 1.96 and 1.955 cal. mL<sup>-1</sup>. A similar calculation for monomethylamine gives  $0.757 V_b$  cal. for  $q_{\rm vap}$ ; checks with bulbs of 6.73 and 11.60 mL gave results of 0.780 and 0.778 cal. mL<sup>-1</sup>.

The volume used in calculating  $q_{vap}$  for runs with salts is the total internal volume of the sample bulb; the volume of the salt is neglected since it is assumed that the volume of the solution is the same as that of the pure solvent. The data of Ritchey and Hunt<sup>18</sup> indicate that this is nearly true for ammonium chloride solutions. In the runs with water and methylamine in ammonia, it is assumed that the volumes are additive; hence the free internal volume of the bulb, exclusive of the sample volume, is used for  $V_{\rm b}$ . With these volatile solutes, a correction is also applied to reduce the vapor in the bulb to the liquid state.

The value of the constant in equation 2 is well established and the error associated with this correction term is negligible. Sample bulb volumes were usually about 3 ml., except where larger ones were needed to contain the 1067

larger samples, and in the case of calorimeter IDT where bulbs of about 0.5 ml. were used.

The term  $q_{\text{cons}}$  represents the heat produced by condensation of ammonia due to the reduced vapor pressure of the solution. Its value for ammonia solutions is given by the expression

$$t_{\text{cond}} = 0.00289 \Delta p V_{\text{v}} \tag{(3)}$$

where  $q_{\text{cond}}$  is in calories,  $\Delta p$  is the vapor pressure depression in cm., and  $V_{\psi}$  is the volume of the vapor phase in the bomb.

Accurate experimental data for vapor-pressure lowerings in dilute solutions in ammonia are available only for  $NH_4$ -Cl solutions<sup>18</sup>; accordingly, these were used for all salt solutions. Under the conditions used in calorimeter IB, the correction is roughly 50 cal. mole<sup>-1</sup> at a mole ratio 500 and 80 cal. mole<sup>-1</sup> at a mole ratio of 16,000. The value of the correction on a mole basis is directly proportional to the volume of the vapor space and inversely proportional to the liquid volume (since an increase in liquid volume involves use of a larger amount of solute at a given mole ratio); the corrections necessary to the runs in ID were somewhat less than half as large as with IB. The uncertainty associated with this correction term is one of the largest sources of error in the measurements. The term was not applied to runs with water and methylamine in ammonia and with potassium iodide in methylamine.

It was also necessary to establish that the heat of breakage of an empty bulb (release of strain energy) is negligible. Experiments were performed with calorimeter IDT, wherein  $\pm 2 \times 10^{-6^\circ}$  corresponds to  $\pm 0.010$  cal., and are listed in Table I.

TABLE I

HEAT OF BREAKAGE OF EVACUATED BULBS

Vb.	$q_{\rm obs} + 1.950  V_{\rm b} - 0.007$	
ml.	cal.	Annealing
0.771	-0.006	No
.411	+ .047	No
.388	+ .055	No
. 673	+ .002	Yes
. 598	003	Yes
. 401	+ .032	Yes
. 445	001	Yes

The results suggest, with limited statistical confidence, that annealing of the bulbs is generally effective in reducing the heat of breakage to a negligible quantity. All bulbs used with calorimeter IDT were annealed; the others were not.

#### Results

Results of the measurements are listed in Table II.

The data are plotted in Fig. 1, normalized at a mole ratio of 1000. The remarkable similarity of the curves for the salts may be noted; except for  $LaI_3$ , the differences at concentrations lower than mole ratio 1000 are barely significant while at higher concentrations the differences, although real, are small. LaI<sub>3</sub> in the mole ratio 4,000-16,000 range shows a slope similar to the other curves; in the 1000-4000 range it is about twice as This slope is based solely on the one run at great. mole ratio 1220, but on the basis of a less consistent series of runs in another bomb, it appears that this difference is real. The heats of solution of water and methylamine in ammonia are independent of concentration within experimental error; as expected, methylamine shows the more nearly ideal behavior.

The measurements of potassium iodide at the lowest concentrations are shown in Fig 2. The points at the three lowest concentrations are fitted, within the rather large experimental error, by a

<sup>(17)</sup> C. A. Guderjahn, et al., J. Chem. Phys., 28, 520 (1958).

<sup>(18)</sup> H. W. Ritchey and H. Hunt, THIS JOURNAL, 43, 407 (1939).



Fig. 1.-Heat of solution in ammonia.

straight line with a slope of 27 kcal. mole  $-^{3/2}$  liter'/<sup>2</sup>, some twelve times the calculated Debye-Hückel limiting slope.

It is remarkable that all of the salts, over a considerable range of ionic sizes and valence types, should show such similar heat-of-dilution curves. The Debye-Hückel limiting slope for 2-1 electrolytes is 5.2 times greater than that of 1-1 electrolytes, and for 3-1, 14.7 times. In aqueous solutions, heats of dilution of 1-1 salts are generally in good agreement with Debye-Hückel theory, and the same is true, with less precision, for 2-1 electrolytes. However, for 2-2 electrolytes the slopes at the lowest concentrations exceed the theoretical by a factor of two or three; this is attributed to the incomplete dissociation of these salts. As the dielectric constant of the solvent is lowered, ionic association increases; it is probable that in these ammonia solutions the principal thermal effects are due to dissociation of ion pairs and solvation of the resulting ions.

There have been very few measurements of heats of solution of salts in non-aqueous solvents at low concentrations. Wallace, Mason and Robinson<sup>19</sup> used a twin dilution calorimeter to measure sodium chloride in ethylene glycol (dielectric constant 37.7) and obtained a result in agreement with the theoretical limiting slope, which is some four times greater than that of water. Jackson, et al.,20 worked with several systems, most extensively in methyl alcohol (dielectric constant 31.5), down to concentrations of  $3 \times 10^{-3}$  molar, and found slopes considerably exceeding the theoretical, which for methyl alcohol is about six times that of water. Lange and Robinson performed measurements with potassium chloride in aqueous solutions of sucrose and urea and found reasonable agreement with theory, but the concentration of added non-electrolyte was such as to decrease the dielectric constant only slightly.

For non-electrolytes in water, the most extensive data are for succose.<sup>21</sup> Here the relative apparent molal heat content is a linear function of concentration up to about 0.2 M, with a slope of about 130 cal. mole<sup>-1</sup> (kg. H<sub>2</sub>O); the slope decreased

<sup>(19)</sup> W. E. Wallace, L. S. Mason and A. L. Robinson, J. Am. Chem. Soc., 56, 362 (1944).

<sup>(20)</sup> N. S. Jackson, A. E. C. Smith, O. Galtz and J. H. Wolfenden, J. Chem. Soc., 1376 (1934).

<sup>(21)</sup> H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd ed., Reinhold Pub. Corp., New York, N. Y., 1958, pp. 345-346.

		IAI						
	HEATS OF SOLUTION							
Mole		A 17	Mola					
solvent/	Calorim-	kcal.	solver.t/	Calorim-	$-\Delta H$ kcal.			
N	aCl in N	H <sub>2</sub>	solute	eter KI in NH	mole -			
192	IR	6 410	201	TR	0.016			
176	IB	6 726	189		0 402			
405		6 749	402 510	ID	0 452			
514	IB	6 764	1 020		0.796			
000	ID	6.067	2 080		9.720 10.27			
1 015	IB	6.074	3,080		10.07			
3 970	ID	7 50	15,100		11.10			
3,870		7.08	17,100	IDT	11.00			
4,000		7.59	30,330		11.49			
4,100		1.52	31,300		11.43			
15,500		8.30	60,500		11.70			
15,800	ID	8.42	65,300	IDI	11.69			
$\operatorname{Ba}(\mathbf{I})$	NO3)2 in 2	NH3	(	CsI in NH	3			
94.3	5 IB	14.704	475	ID	5.252			
213	IB	15.046	9:0	$\mathbf{ID}$	5.544			
970	IB	15.536	3,880	ID	6.138			
1,010	IB	15.554	14,900	ID	6.76			
4,070	IB	16.11	15,200	ID	6.79			
15,700	IB	17.03						
15,800	IB	16.98			_			
NT			Н	lgl₂ in NH	[ <sub>3</sub>			
NE	I₄Cl in N	113	4,100	IB	21.61			
198	ID	7.884	15,400	IB	22.62			
479	ID	8.202						
958	IB	8.461		H <sub>4</sub> I in NF	1.			
972	ID	8.450	194	ID	15.641			
986	IB	8.438	488	ID	16.090			
3,820	IB	8.96	933	ID	16.406			
3,880	ID	8.95	3,990	ID	17.016			
15,920	ID	9.70	11,510	ID	17.56			
16,525	ID	9.68	15,840	ID	17.72			
LaI <sub>3</sub> .	6NH <sub>3</sub> in	$NH_3$	E	I₂O in NH	3			
1,220	ID	41.20	195	ID	3.314			
4,130	ID	42.19	814	ID	3.322			
4,530	ID	42.31	3,830	ID	3.32			
13,000	ID	42.92	13,200	ID	3.37			
16,300	ID	43.05						
18,500	ID	42.67						
KI	in CH <sub>3</sub> N	$H_2$	CH	<sub>3</sub> NH <sub>2</sub> in N	TH <sub>3</sub>			
215	IB	6.635	192	ID	-0.497			
490	IB	6.754	940	ID	-0.499			
984	IB	6.84	3,860	ĪD	-0.51			
3.865	IB	6.98	0,000		V . V .			
15.680	IB	7.31						
15.830	IB	7.18						

TABLE H

somewhat at higher concentrations. Such a slope would not be outside the precision of our measurements of methylamine and water in ammonia, which extended only to about 0.25 M.

In Table III are listed the values for heats of solution at a mole ratio of 500 in ammonia at 25 and  $-33^{\circ}$  and in water at 25°. Heats of solution of salts in ammonia are much more negative than in water. Heats for salts in ammonia at 25° are



Fig. 2.—Heat of solution of potassium iodide in ammonia.

TABLE III

Н	EATS	$\mathbf{OF}$	SOLUTION	AТ	M	OLE	R	ATIO	500
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Solute	H:O, 25°22	Solvent NH2, 25°	NH1 -33°
$H_2O(l)$	0	- 3.32	- 2.81
CH <sub>3</sub> NH <sub>2</sub> (l)	-5.0	+ 0.50	
HgI2		(-20.8)	-20.15
NaCl	+1.02	- 6.75	$-1.5^{7}$
KI	+4.95	- 9.44	$-7.8^{9}$
CsI	+7.9	- 5.27	<i></i>
NH₄Cl	+3.71	- 8.23	-6.95
NH₄I	+3.3	-16.10	$-13.3^{7}$
$Ba(NO_3)_2$	+9.96	-15.31	

more negative than at  $-33^{\circ}$ . Our results for NaCl are in very poor agreement with those of Chall and Doepke<sup>14</sup> who reported values of  $\Delta H$ ranging randomly from -2.2 to -3.0 kcal. mole<sup>-1</sup> at six mole ratios from 57 to 340. Hunt<sup>23</sup> has reported the solubility limit of NaCl in ammonia at 25° to be at mole ratio 114. We found the dissolution of NaCl in the more concentrated runs to be quite slow, 20 minutes being required for termination of heat evolution in the case of the run at mole ratio 192. It is possible that the exceptionally large difference between the  $+25^{\circ}$  and  $-33^{\circ}$  values for NaCl is due to incomplete dissolution in the  $-33^{\circ}$  measurements.

(22) F. D. Rossini, et al., Circular of the National Bureau of Standards, 500 (1952).

(23) H. Hunt, J Am. Chem. Soc., 54, 3509 (1932).

# A SPECTROPHOTOMETRIC STUDY OF THE BLEACHING OF FERRIC CYSTEINATE

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The bleaching of ammonia-ammonium chloride solutions of ferric cysteinate was studied in the pH range 8.80 to 10.10.

The election follows the paths  $2\text{FeOH}(cy)_2^- \rightleftharpoons k_1$  dimer  $\stackrel{K_1}{\longrightarrow} 2\text{Fe}(11) + \text{cystine}$ ,  $\text{FeOH}(cy)_2^- \oiint \text{FeOH}(cy)_2^- \bigcap \text$ 

Ferric iron reacts with cysteine in ammoniacal solutions to form a violet complex.<sup>2</sup> A moderately rapid oxidation-reduction reaction takes place in which the iron is reduced to a less highly colored ferrous complex and the cysteine is oxidized to cystine.<sup>2-5</sup> The rate of reoxidation of the ferrous complex to one of ferric by oxygen is very rapid. Since the rates of both of these reactions is faster than the oxidation of cysteine alone by oxygen a catalytic effect results in the presence of small amounts of iron salts.

A similar catalytic effect occurs with mercapto-acetate.<sup>4,5</sup> The kinetics of the bleaching have been investigated in ammoniacal buffers where it has been found that the reaction proceeds along paths in which a molecule of the predominant complex,  $FeOH(RS)_2^=$ , reacts with a molecule of either  $FeOH(RS)_2^=$ ,  $Fe(OH)_2(RS)^-$  or  $FeOHRS.^6$  The mechanism and rate constants found in ammoniacal solutions were found to hold in phosphate and acetate buffers at least down to pH 4.6.7 The rate of oxidation of the ferrous complex by oxygen was also studied.7

Tanaka, Kolthoff and Stricks<sup>8</sup> have investigated the composition of the ferrous and ferric cysteinate complexes in alkaline solutions. For iron(III) they report that the principal species are  $FeOH(cy)_2^{=}$ and  $Fe(cy)_{3}$  and that the constant of the reaction  $FeOH(cy)_2^{=} + cy^{=} \rightarrow Fe(cy)_3^{=} + OH^{-}$  has a value of 0.065. These authors also have made a brief investigation of the kinetics of bleaching of the ferric cysteinate complexes and have found that the rate is second order with regard to total iron and is approximately inversely proportional to the concentration of cysteine. The rates are much faster than those observed with mercaptoacetate under comparable conditions.

In the present investigation we have undertaken a more detailed study of the bleaching of ferric cysteinate with the hope of further elucidating the

general features of the iron(III)-mercaptide reactions.

#### Experimental

Eastman White Label cysteine hydrochloride was used without purification. Titration of the reagent in an alcoholic solution with a standard iodine solution gave a purity of  $98 \pm 1\%$  calculated on the basis of the mono-hydrate. Titration of the carboxyl in aqueous solution with standard potassium hydroxide indicated a purity of Stock solutions 0.10 to 0.20 M in strength  $100.0 \pm 0.5\%$ were prepared by dissolving a weighed amount of the reagent in de-acrated water. The stock solutions were maintained under a positive nitrogen pressure to reduce contamination by air.

Ferric ammonium sulfate solution, 0.0493 M, was prepared from the reagent grade chemical and was standardized using the dichromate titration. This solution was also made 0.025 M in sulfuric acid to reduce hydrolysis.

Ammonia stock solutions were prepared from the freshly Twice distilled water was used in all redistilled reagent. experiments.

A Beckman Model G pH meter was used to determine the pH of the reaction solutions. The electrodes were standardized against a 0.025 M KH<sub>2</sub>PO<sub>4</sub>, 0.025 M Na<sub>2</sub>HPO<sub>4</sub>, buffer pH 6.86; and a 0.010 M borax buffer pH 9.18 at 25°. National Bureau of Standards reagents were used to prepare the buffers.

The bleaching reactions were followed in air-free ammoniaammonium chloride buffers using essentially the same techniques employing sealed bottles and syringes as were used in the mercaptoacetate study.<sup>6</sup> The amount of ammonium chloride was adjusted so that the ionic strength was maintained at 0.10 M in each experiment. In making this adjustment the contributions of  $cy^{=}$  and  $cyH^{-9}$  were taken into account using values of  $K_{2a}$  and  $K_{3a}$  for cysteine equal to  $5.6 \times 10^{-9}$  and  $4.0 \times 10^{-11}$  as determined in solutions at an ionic strength of  $0.10 \ \mu$ ,  $25^{\circ,10}$  The bleaching reaction was followed by measuring the absorbance at 580 m $\mu$  using a Cary Model 14 Spectrophotometer. Some of the rates were sufficiently fast that the reactions were completed in a few minutes. These were followed continuously. The starting time of all runs was taken at the moment when the iron solution was injected into the cysteine solution.

Preliminary runs (about 60 in all) were made at ambient room temperature over a pH range 8.1 to 10.7 and a range of total cysteine from 0.0050 to 0.040 M. From these it was found that the second-order rate constant for the bleaching is independent of the initial concentration of iron(III) (at least at 0.00030 and 0.00060 M iron) all other factors being the same. The presence of ferrous iron initially (2.0  $\times$  10<sup>-4</sup> M) also was observed to have no effect. Deviations from a simple second-order dependence on iron-(III) were observed for the bleaching reaction when the cysteine concentration was less than 0.010 M. These results

<sup>(1)</sup> Financial assistance for this work was provided by a grant from the National Science Foundation.

<sup>(2)</sup> L. J. Harris, Biochem. J., 16, 739 (1922).

<sup>(3)</sup> L. Michaelis and E. S. G. Barron, J. Biol. Chem., 83, 191 (1929). (4) B. K. Cannon and G. W. Richardson, Biochem. J., 23, 1242 (1929).

<sup>(5)</sup> M. Schubert, J. Am. Chem. Soc., 54, 4077 (1932).

<sup>(6)</sup> D. L. Leussing and L. Newman, ibid., 78, 552 (1956).

<sup>(7)</sup> H. Lamfrom and S. O. Nielsen, ibid., 79, 1966 (1957).

<sup>(8)</sup> N. Tanaka, I. M. Kolthoff and W. Stricks, ibid., 77, 1996 (1955).

<sup>(9)</sup> The total concentration of cysteine is designated as  $cy_t$ . The variously ionized forms will be designated as cyH2, cyH - and cy No attempt is made to distinguish between the tautomeric forms of CyH -. The symbol RS shall refer to mercaptoacetate.

<sup>(10)</sup> R. C. Hansen, unpublished experiments.

are essentially the same as those observed with mercapto-acetate. $^{6}$ 

Several runs were made in an all glass reaction flask equipped with an optical cell. The solutions were made up and transferred using only glass equipment. The purpose of these runs was to determine whether any catalysis occurs from trace metals which might be introduced when the hypodermic needles are used. No differences were obtained between these runs and the others, indicating that such effects, if any, are much less than that of the iron.

From the results of these preliminary runs points were selected for a more accurate determination of the rate constants. In these latter runs all solutions were thermostated in a water-bath before and after mixing. Solutions were removed from the water-bath for only the time required to measure the absorbance. Most of these experiments were conducted at  $25^{\circ}$  but one series was run at  $10^{\circ}$ . The experimental details are given in Table I.

#### TABLE I

#### THE RATE CONSTANTS FOR THE REACTION

ŀ

$2[Fe(III) complex] \longrightarrow 2[Fe(II) complex]$	+ cystine
Ionic strength $= 0.10 M$	

Cysteine, moles/l. × 10+2	NH₄Cl, <sup>a</sup> moles/l, × 10+	NH1, a moles/l. × 10 <sup>+1</sup>	n]]	k, 1. mole <sup>-1</sup>
// 10	~ •••	25°	pn	
1.00	7.48	6.22	10.09	28.8
1.00	7.64	3.12	9.80	56.0
1.00	7.82	1.88	9.56	83.0
1.00	7.88	1.13	9.30	158.0
1 50	6.96	5.68	10.05	20.6
1.50	6.48	3.30	9.82	37.6
1.50	6.76	1.90	9.55	63.2
1.50	6.80	1.13	9.31	112.0
1.50	7.16	0.550	8.80	315.0
1.50	7.40	0.410	8.45	500.0
3.00	2.32	5.55	10, 10	12.3
3.00	3.76	3.67	9.83	16.9
3.00	3.50	2.27	9.57	30.2
3.00	3.82	1.52	9.30	50.3
3.00	4.18	1.09	9.04	89.4
3.00	4.58	0.830	8.72	169
4.00		5.75	10.03	11.1
4.00	0.60	3.63	9.82	14.8
4.00	1.32	2.38	9.53	25.6
4.00	1.82	1.71	9.29	37.4
4.00	2.24	1.28	9.01	75.3
4.00	2.84	1.08	8.80	124
		0°		
1.00	7.23	5.76		78.0
1.50	6.09	5.72		61.2
2.00	4.69	5.76		43.7
2.50	3.58	5.89		34.4
3.00	2.12	5.98		27.2
3.50	0.82	5.86		28.8

<sup>*a*</sup> Initial concentrations, not corrected for the neutralization of the cysteine hydrochloride.

Also given in Table I are the values of the constant, k, for the rate expression

$$\frac{-\mathrm{d}\mathbf{Fe}(\mathbf{III})}{\mathrm{d}t} = k \left[ \mathrm{Fe}(\mathbf{III}) \right]$$

These constants were calculated using the relationship  $k = \epsilon l(\text{slope})$  where  $\epsilon$  is the extinction coefficient based on total iron, l is the optical path length (here 1.00 cm.) and the slope is that obtained from a plot of the reciprocal of the absorbance versus time. From the extrapolation of such plots for the more alkaline solutions to zero time a value of  $\epsilon$  is calculated to be  $3.05 \times 10^{+3}$  l. mole<sup>-1</sup> cm.<sup>-1</sup> at 580 m $\mu$ . This is in excellent agreement with the value obtained by Tanaka, Kolthoff and Stricks.<sup>5</sup> In the more



Fig. 1.—The over-all rate constant for the bleaching of ferric cysteinate as a function of the uncombined cysteinate concentration: •,  $cy_t = 0.0100 \ M$ ;  $\bigcirc$ ,  $cy_t = 0.0150 \ M$ ;  $\square$ ,  $cy_t = 0.030 \ M$ ;  $\triangle$ ,  $cy_t = 0.040 \ M$ .

acid solutions the zero time absorbance gives lower values of the extinction coefficient. This latter effect is likely due to a mixing reaction such as was observed with mercaptoacetate.<sup>6</sup> A rapid reduction of some of the iron(III) occurs when acid ferric solutions come in contact with those mercaptide solutions which are less alkaline. However, this reaction merely causes some decrease in the initial iron(III) concentration and does not invalidate the calculation of k as described above. Another possibility which involves the formation of a lower complex with significantly lower extinction coefficient at 580 m $\mu$  is ruled out according to the conclusions discussed below.

#### **Results and Discussion**

The values of k in Table I are seen to depend on the pH and cy. These variables, however, affect the values of k only to the extent that they determine the cy<sup>=</sup> concentration. This is seen in Fig. 1 where a plot of k vs.  $1/(cy^=)$  shows that the points fall along one curve. At low values of  $1/(cy^=)$  the plot indicates a linear relationship which is described by the equation  $k = k' + k'' - (cy^=)$ . The data at 25° yield a value of k' which is approximately equal to 2.1. mole<sup>-1</sup> sec.<sup>-1</sup> and a value of k'' which is equal to 0.105 sec.<sup>-1</sup>. The data at 10° give a value of k' which is also about 2.1 mole<sup>-1</sup> sec.<sup>-1</sup> but the value of k'' was not evaluated at this lower temperature because the proton dissociation constants of cysteine are not known.

According to calculations which can be made from the conclusions of ref. 8 both  $Fe(cy)_3^{=}$  and  $FeOH(cy)_2^{=}$  are present to an appreciable degree in those experiments which give rate constants lying in the linear region of Fig. 1. Except for a peculiar set of circumstances it is expected then that kshould be a function not only of the  $cy^{=}$  concentration but also should be a function of the  $CH^{-}$  concentration since the relative amounts of the two complexes is determined by both of these quantities. Furthermore, in the calculations of the formation constant of  $Fe(cy)_3^{=}$  in ref. 8, Table VI, the tacit assumption has been made that  $FeOH(cy)_2^{=}$  is colorless. Considering the intense color of the analogous complex with mercaptoacetate<sup>6</sup> this assumption is not expected to be valid and the data of Table IV in reference 8 show that the assumption does indeed fail. There the extinction coefficients, which have been calculated on the basis of total iron(III), are seen to be constant although the ratio of  $Fe(cy)_3 \equiv$  to  $FeOH(cy)_2 \equiv$  is calculated to vary throughout the region investigated. We conclude therefore that the interpretation is not correct regarding the existence of two principal iron(III) complexes under the experimental conditions which were investigated in ref. 8 and which are similar to the experimental conditions of the more alkaline solutions in the present work. These conclusions support the evidence of Table V in ref. 8 where it is strongly indicated that the only principal complex is  $FeOH(cy)_2^{=}$ .

With this view the mechanism of the ferric cysteinate bleaching then can be explained easily using reaction paths which are similar to those proposed for the bleaching of ferric mercaptoacetate. The present observations can be accounted for by the reaction sequence

$$2\text{FeOH}(\text{cy})_{2} \xrightarrow{} \text{Fe}_{2}(\text{OH})_{2}(\text{cy})_{4} \xrightarrow{} \frac{}{k_{1}} 2\text{Fe}(\text{II}) + \text{cystine}$$

$$\text{FeOH}(\text{cy})_{2} \xrightarrow{} \frac{}{K_{2}} \text{FeOH}(\text{cy} + \text{cy}^{-})$$

$$\text{FeOH}(\text{cy})_{2} \xrightarrow{} \frac{}{K_{3}} \text{Fe}_{2}(\text{OH})_{2}(\text{cy})_{3} \xrightarrow{} \frac{}{k_{2}}$$

$$2\text{Fe}(\text{II}) + \text{cystine}$$

According to this set of reactions, k' is equal to the product of  $k_1K_1$  and k'' is equal to the product  $k_2K_2K_3$ . This reaction sequence gives a rate equation which is linear in  $1/(cy)^{=}$  when the concentration of FeOH(cy)<sub>2</sub><sup>=</sup> is considerably greater than the concentrations of the other complexes.

The curvature in Fig. 1 at higher values of  $1/(cy^{=})$  can be explained without invoking additional steps by assuming that the concentration of FeOHcy increases to the point where an appreciable fraction of the iron(III) is present as this lower complex and that two molecules of this species do not react. Taking these features into account it can then be shown that

$$k = \frac{k_t K_1 + \frac{k_2 K_2 K_3}{(\text{ey}^{-})}}{\left(1 + \frac{K_2}{(\text{ey}^{-})}\right) \left(1 + \frac{\epsilon_1}{\epsilon_2} \times \frac{K_2}{(\text{ey}^{-})}\right)}$$

where  $\epsilon_1$  and  $\epsilon_2$  are the extinction coefficients of FeOHey and FeOH(cy)<sub>2</sub><sup>=</sup>, respectively. For the case where the ratio  $\epsilon_1/\epsilon_2$  is close to unity the denominator can be approximated as  $(1 + K_2'/(cy^{-}))^2$ . Using the values given above for the products  $k_1K_1$  and  $k_2K_2K_3$ , a value of  $K_2'$  was calculated to be  $4.1 \times 10^{-5}$  moles  $1.^{-2}$  from the value of k observed to be 500 l. mole<sup>-1</sup> sec.<sup>-1</sup> in a solution 0.015 M in cy<sub>1</sub> at pH 8.45. The solid line in Fig. 1 has been calculated using this value of  $K_2'$  and those given for the other constants. It is seen, by the good agreement which is obtained that the above model, for the case where the extinction coefficients of the two complexes are nearly the same, satisfactorily explains the results. In the mercaptoacetate study,<sup>6</sup> the hypothesis was proposed that the oxidation of two mercaptide groups to disulfide takes place most readily when both of the mercaptide groups are bound to the same metal ion. This hypothesis is strongly supported by the present results since it is observed that, although FeOHcy is present in relatively high concentration, two molecules do not appear to react with each other to give disulfide whereas a molecule of FeOHcy readily reacts with one of FeOH(cy)<sub>2</sub><sup>=</sup>.

The constant,  $k_1K_1$ , for the limiting rate at high ligand concentration is not accurately obtained with the cysteinate system but qualitatively it appears to be about 100 times greater than that for the limiting rate with the mercaptoacetate system. The energy of activation for this limiting path is about 20 kcal. with mercaptoacetate but is apparently much less with cysteinate. The greater ease of electron transfer from cysteinate sulfur to iron-(III) than from mercaptoacetate sulfur to iron(III) can be observed by comparing the absorption spectra of the two complexes. The maximum of the charge transfer absorption band lies at 537 m $\mu$  with  $FeOH(RS)_2$  and at 580 mµ with  $FeOH(cy)_2$ . This difference amounts to only about 3 kcal. in the energy of electron transfer, however. Both of these absorption bands drop off at the same rate on the long wave length side of the maximum so the difference in energy is the same at a given wave length in the near infrared as at the maxima. From these considerations it appears that other factors are more important in bringing about the differences in reaction rates than the ease of charge transfer. The bimolecular reaction kinetics also give evidence for this, as a reaction depending simply on charge transfer would be first order with regard to the complex.

A possible explanation for the observed differences in the limiting rates might be had by considering the nature of the groups with the different ligands that are coordinated to the central iron(III) atom. With mercaptoacetate, mercaptide and carboxylate are coordinated, whereas with cysteinate, more likely mercaptide and amine are coordinate to form a five-membered ring than are mercaptide and carboxylate which would form a sixmembered ring. Thus, while the bis complexes in both systems have a net charge of minus two, the charge is located on, or near, the central iron(III) atom with mercaptoacetate but is located at a greater distance from it with cysteine. In bringing two such complexes together to form a dimer, less charge repulsion need be overcome in the cysteinate complexes than with the mercaptoacetate complexes. This would cause  $K_1$  to be larger with cysteine, thereby producing an increased rate even if the  $k_1$  values are not much different.

Another interesting feature is that the reaction path in which the mono complex takes part is proportionately much greater with cysteine than with mercaptoacetate. At least part of this difference must be attributed to the higher concentration of FeOHcy than FeOHRS which is produced under comparable conditions. The mercaptoacetate data show no evidence for the formation of appreciable quantities of the lower complex as is found with cysteine.

While the two paths discussed above are much faster with cysteine it is interesting to note that no path involving a dihydroxy complex is observed in the cysteine reactions. With mercaptoacetate, evidence is given for a path involving  $Fe(OH)_2RS^-$ . Apparently, the aquo FeOHcy molecule is less acidic than is aquo FeOHRS molecule. This again may be a consequence of the coördination to the iron(III) ion of the more basic amino group in cysteine compared to the coördination of the carboxylate in mercaptoacetate.

# NOTES

# THE EXTREME SENSITIVITY OF PARAMAGNETIC SITES TO POISONING BY DESORBED GASES EVALUATED BY THE LOW TEMPERATURE ORTHO-PARAHYDROGEN CONVERSION

By Douglas S. Chapin, C. Dick Park and Myron L. Corrin

#### The Department of Chemistry, University of Arizona, Tucson, Arizona Received September 8, 1959

Catalytic studies invariably involve questions of surface cleanliness and of the maintenance of the surface in a given state of cleanliness between the time of the cleaning process and the time of the catalytic rate determination. In the case of ortho-parahydrogen conversion at 77°K. on silica gel supported neodymia the question arose as to whether an observed decrease in rate constant with time of standing at room temperature should be attributed to further diffusion of water from the silica gel or to poisoning of the catalysts from gases desorbed from the Pyrex glass walls. Results show that minute quantities of gas, probably CO<sub>2</sub> and  $H_2O_1$ , drastically poison the catalysis of the orthoparahydrogen conversion at 77°K. Extreme precautions to exclude the poisoning gases from reaching a catalytic surface which is being studied are advisable. Gases desorbed from the Pyrex walls of the vacuum system or stopcock grease following bake out of the catalyst are sufficient to cause a fourfold reduction in the rate constant. Liquid nitrogen trapping was effective, but solid  $CO_2$ trapping was ineffective in preventing the poisoning effect on a silica gel supported neodymium oxide catalyst.

#### Experimental

Davison No. 923 silica gel was washed with hot aqua regia, hot concentrated nitric acid, hot concentrated hydrochlorie acid and exhaustively washed with demineralized water. The gel then was dried at 110° and 8 g. was impregnated with 25 cc. of 0.26 M NdCl<sub>3</sub> in 0.1 N HCl by tumbling overnight in a thermostated water-bath in a polyethylene bottle. The catalyst was sucked free of gross solution on a sintered glass funnel, rinsed with one volume of water and dried in an air oven at 90°. Ten-mg. samples were weighed into approximately 20-cc, bulbs and sealed on to 2 mm. i.d. capillary Pyrex tubes connected to a stopcock on the vacuum system in the case of the first three reactors and through a U-tube trap to a stopcock in the case of the remaining reactors. A two-stage mercury diffusion pump was used to evacuate the catalysts while heating them to temperatures and for times indicated in Fig. 1A. The pump was capable of evacuation of the system to  $10^{-6}$  mm. or better. Pressure measurements with a type GIC-001 ionization gage attached to a typical reaction vessel showed a pressure of  $7 \times 10^{-7}$  mm. after an outgassing of the reaction vessel for 24 hours above 450° followed by 24 hours at 300°.

Samples of hydrogen were analyzed for their orthoparahydrogen content by the Farkas microthermal conductivity method.<sup>1,2</sup>



Fig. 1. Effect of trap temperature on the poisoning of a silica gel-neodymia catalyst toward the ortho-parahydrogen conversion measured at 77°K. and a pressure of 27 mm. Fig. 1A shows the pretreatment time-temperature history given all reactors. Fig. 1B shows the time-temperature history for the traps. Fig. 1C gives the average rate constants found after the pretreatment indicated in Figs. 1A and 1B. The solid lines refer to reactors 1-3 and the dotted lines refer to reactors 4-7 throughout.

#### **Results and Discussion**

Rate data taken for the seven reactors at iour different times are given in Table I. Averages are

(1) A. Farkas, "Orthohydrogen, Parahydrogen and Heavy Hydrogen," Cambridge University Press, 1935, p. 25.

(2) Douglas S. Chapin, Dissertation, Ohio State University, 1954.

#### NOTES

TOWARD THE ORTHO-PARAHY	drogen Conversion M	IEASURED AT 77°K	. AND A PRESSURE	с ог 27 Мм.
Pretreatment <sup>a</sup>	A	В	С	D
Rate constant $(\min.^{-1})^b k \times 10^2$				
Reactor 1	9.42	2.62	12.4	3.26
Reactor 2	10.9	1.73	13.1	3.36
Reactor 3	9.99	2.64	15.9	3.09
Av. rate constants 1–3	$10.1\pm0.53$	$2.33 \pm 0.39$	$13.8 \pm 1.40$	$3.24 \pm 0.10$
Reactor 4	9.89	11.6	15.7	5.77
Reactor 5	12.8	12.5	21.1	4.89
Reactor 6	14.0	15.1	19.9	4.81
Reactor 7	11.2	12.9	19.5	4.25
Av. rate constants 4–7	$\frac{12.0 \pm 1.43}{12.0 \pm 1.43}$	$13.0 \pm 1.03$	$19.1 \pm 1.65$	$4.93 \pm 0.42$

TABLE I

RATE DATA SHOWING THE EFFECT OF TRAP TEMPERATURE ON THE POISONING OF A SILICA GEL-NEODYMIA CATALYST

<sup>a</sup> Pretreatment A: Samples were heated and pumped 51 hours at 450°, 21 hours at 525° and 29 hours at 300°, all with room temperature traps; liquid nitrogen traps were used after 100 hours of heating on reactors 4 through 7. All reactors were exposed twice to 4 cm. pressure of He for one minute and pumped off at 300°; the reactors were cooled to 77°K., and exposed twice to 4 cm. pressure of H<sub>2</sub> for one minute and pumped off. Pretreatment B: All reactors were warmed to room temperature with liquid nitrogen traps on reactors 4 through 7 and pumped for 54 hours; then all reactors were cooled to 77°K., exposed twice to 4 cm. pressure of H<sub>2</sub> and pumped. Pretreatment C: All reactors were warmed to 300° and pumped at that temperature for 122 hours with liquid nitrogen traps on reactors 4 through 7. All reactors were exposed twice to 4 cm. pressure of He at 300°, cooled to 77°K., and exposed twice to 4 cm. pressure H<sub>2</sub> for one minute and pumped. Pretreat-ment D: All reactors were warmed to room temperature with traps on reactors 4 through 7 cooled with Dry Ice-methanol ment D: All reactors were warmed to room temperature with traps on reactors 4 through 7 cooled with Dry Ice-methanol (195°K.) and pumped for 120 hours. Reactors 4 through 7 were given two exposures of one minute each with 4 cm. pressure of He with pumping; all reactors were cooled to 77°K. and given two exposures to 4 cm. pressure of H<sub>2</sub> with pumping.  $^{b}$  10-mg. samples and 25 ml. reactor volumes.

plotted in Fig. 1. The pretreatment time-temperature history for the reactors is given in Fig. 1A. Trap temperature for the first three reactors was room temperature, while that for the remaining reactors was varied between room temperature and liquid nitrogen temperature as indicated by the dotted line in Fig. 1B. To aid in the clean-up of surfaces the first and third rate determinations were preceded by exposure to He at  $300^{\circ}$  and to H<sub>2</sub> at 77°K. It is apparent that allowing the catalyst to stand at room temperature with no trapping results in a drastic poisoning of the catalyst surface; while allowing the catalyst to stand at room temperature with liquid nitrogen trapping results in a slight further cleaning of the catalyst surface. Heating of the poisoned catalyst surface with no (room temperature) trapping results in a cleaning of the surface. Trapping with Dry Ice and methanol fails to prevent poisoning of the surface.

Pressure determinations with the ionization gage conducted on one of the reactor stations showed that the pressure was  $1.2 \times 10^{-7}$ mm, with liquid nitrogen in a trap located between the stopcock and the reactor plus ionization gage. With the stopcock closed, the dewar of liquid nitrogen suddenly was lowered and the pressures noted. The pressure rose to about  $7 \times 10^{-4}$  and remained for about 2 minutes, then suddenly rose to greater than  $10^{-3}$ mm. On cooling the trap to liquid nitrogen temperatures, the pressure slowly decreased. The pressure in the system which had been cut off from the vacuum system for 4 days was  $6 \times 10^{-6}$  mm. On replacing the liquid nitrogen with Dry Ice- $CCl_4$ , the pressure increased to greater than  $10^{-3}$ mm. and remained. It appears that the gas responsible for poisoning is one which has an ap-

preciable vapor pressure at 195°K. but a negligible vapor pressure at 77°K. Two possibilities appear reasonable: (1) carbon dioxide and (2) water. Carbon dioxide and water both are known to be evolved from Pyrex glass on heating.<sup>3</sup> The vapor pressures of solid  $CO_2$  and  $H_2O$  at 195°K. are of the order of  $10^3$  and  $10^{-4}$ mm., respectively; while at  $77^{\circ}$ K. they are of the order of  $10^{-8}$  and 10<sup>-20</sup>mm., respectively.<sup>4</sup>

#### Conclusion

It therefore appears that trapping close to the catalyst surface in the vicinity of 77°K. serves to minimize  $CO_2$  or  $H_2O$  from poisoning the catalyst surface; and further, that supported paramagnetic catalysts such as neodymia are extremely sensitive to small quantities of gases which probably desorb from the glass surfaces and adsorb on active paramagnetic sites of the catalyst.

Though water in mono- and multilayer quantities is sometimes purposely employed to produce a surface which is non-catalytic toward the paramagnetic ortho-parahydrogen conversion,<sup>5</sup> it should be emphasized that such extremely small quantities of water or carbon dioxide have been found to poison paramagnetic surfaces and that careful attention to rigorous exclusion of these gases is mandatory for quantitative conversion results.

Acknowledgments.—Ortho-parahydrogen analyses were performed by Mr. Stanley Grenda. Financial support for this work which was performed under contract AT (11-1)-367 with the AEC is gratefully acknowledged.

- (4) S. Dushman, ref. 3, Chapter 11.
- (5) Y. L. Sandler, THIS JOURNAL, 58, 54 (1954).

<sup>(3)</sup> S. Dushman, "Vacuum Technique," John Wiley and Sons, Inc., New York, N. Y., 1949, Chapter 8.

# A RADIOTRACER STUDY OF AN OPTICAL METHOD FOR MEASURING ADSORPTION<sup>1</sup>

#### BY L. S. BARTELL AND J. F. BETTS

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It was discovered many years ago by Drude<sup>2</sup> that the ellipticity of polarized light reflected from metal surfaces is an exceedingly sensitive gauge of the thickness of films on metals, sufficiently sensitive for the measurement of films of molecular thickness. A particularly simple and useful modi-fication of Drude's method was developed by Rothen,<sup>3</sup> who showed for Langmuir-Blodgett multilayers of barium stearate, that the optical readings become a linear function of the number of molecular layers as the film thickness approaches zero. At surface coverages below a complete monolayer, the orientation and packing of molecules may be different from those in close-packed molecular layers, and the index of refraction and optical thickness may cease to become clearly defined quantities. Furthermore, unpublished studies<sup>4</sup> have suggested that the optical difference between monolayer coverage and bare substrate is a more sensitive function of surface roughness than the difference between multilayer and monolayer coverage. Accordingly, except for the most idealized models, it is not clear whether optical readings can be expected to be a linear function of the amount of material adsorbed in the case of fractional coverages.

Experimental studies by Feachem and Tronstad<sup>5</sup> on liquid-expanded and expanded monolayers of lauric acid on mercury (smooth liquid) have indicated that optical readings are at least roughly linear functions of surface concentration in the region of fractional coverage. In studies of the wetting of incomplete condensed solid,<sup>6</sup> and liquidlike<sup>7</sup> monolayers of long-chain amines on solid surfaces, linearity has been explicitly assumed in the interpretation of results. The object of the present investigation was to test optical readings as a function of coverage by a direct radiotracer study, for complete and depleted monolayers of long-chain polar molecules. Circumstances beyond our control required the termination of research before the accuracy achieved attained the limit of accuracy of the techniques used. Nevertheless, the results obtained appear to be definitive and offer useful checks of assumptions made in earlier studies.

#### Experimental

**Radioactive Measurement**.—The amount of radioactive material in the films was measured with a Q-gas flow counter connected to a conventional scaler. To ensure an accurate

knowledge of the area being counted, a mask with a hole 1/2'' in diameter was placed over the specimen.

**Optical Measurement.**—The instrument used to measure optical thicknesses of films was similar in design to Rothen's ellipsometer,<sup>3</sup> except for its improved collimating system and half-shade device. Half fields, with extinctions separated by 5°, were obtained by means of a thin sheet of mica placed near the specimen. Filtered illumination from a sodium vapor lamp was used at an angle of incidence of approximately 69°. The quarter wave plate was adjusted to give nearly equal extinctions for both fields at a film thickness of one-half of a monolayer. The setting was then fixed, and the analyzer reading. The optical readings,  $\Delta E$ , plotted in Fig. 1, represent the differences between analyzer readings before and after the deposition of a film. The numbers plotted are averages of readings made at five reproducible positions which sample the area counted in radioactive measurements.

**Materials**.—*n*-Octadecylamine and stearic acid, both tagged with carbon-14, were used as obtained from the New England Nuclear Corporation and Nuclear Chicago, respectively. The solvents benzene and *n*-hexadecane were carefully freed of adsorbable impurities.

Chromium plated slides, cut from commercial ferretype plates, were prepared by polishing with levigated alumina in soap solution, rinsing with distilled water, drying with soft tissue, flushing with pure benzene, and flaming over a Meker burner for a few seconds. Monolayers were formed on the slides variously by adsorption from 0.1°, solutions in *n*-hexadecane, by the Langmuir-Blodgett technique,<sup>8</sup> and by the polishing down of bulk (1000 Å.) films left by evaporation of benzene solutions.

#### Results

A comparison between optical readings and radiotracer measurements is shown in Fig. 1 for depleted monolayers of *n*-octadecylamine as a function of depletion by benzene. The scatter of points is due as much, perhaps, to inhomogeneities arising during depletion as to the uncertainties in experimental measurements. The optical method samples a much smaller area than the radiotracer method, and, as a result, the readings for the two methods do not represent precisely the same surface. Similar results were obtained for films of tagged stearic acid, although the experimental readings, taken before the technique was fully developed, were somewhat more erratic. Plots for films depleted by polishing with soft tissue resembled plots for films depleted by the solvent benzene.

The data in Fig. 1 fall into two distinct lines corresponding to depletion of Langmuir-Blodgett (L. B.) monolayers (open points) and monolayers adsorbed from *n*-hexadecane solutions (solid points). The simplest interpretation of the results is that (a) films formed by adsorption from n-hexadecane contain appreciable amounts of the solvent molecules (approximately 20%) dispersed among the structurally similar, vertically oriented hydrocarbon chains of the amine, and (b) the total number of molecules in the adsorbed films is essentially the same as that in the L. B. films. The optical readings do not discriminate between amine and nhexadecane and measure the total material which is apparently the same in adsorbed and L.B. films. The radiotracer method measures only the tagged molecules of amine, and, accordingly, detects a smaller activity for the adsorbed films. The difference between the two curves in Fig. 1,

(8) I. Langmuir, J. Franklin Inst., 218, 143 (1934); K. E. Blodgett J. Am. Chem. Soc., 56, 495 (1934); 57, 1007 (1935).

<sup>(1)</sup> This research was supported by a grant-in-aid from the American Petroleum Institute.

<sup>(2)</sup> P. Drude, Ann. physik, Chem., 36, 532 (1889); 36, 865 (1889); 39, 481 (1890).

<sup>(3)</sup> A. Rothen, Rev. Sci. Instr., 16, 26 (1945).

<sup>(4)</sup> C. L. Sutula and L. S. Bartell (unpublished research).

<sup>(5)</sup> C. G. P. Feachem and L. Tronstad, Proc. Roy. Soc. (London), A145, 127 (1934).

<sup>(6)</sup> L. S. Bartell and R. J. Ruch, THIS JOURNAL, 60, 1231 (1956); 63, 1045 (1959).

<sup>(7)</sup> R. J. Ruch and L. S. Bartell, ibid., 64, 513 (1960).



Fig. 1.—Optical readings compared with radioactivity of monolayers of *n*-octadecylamine depleted with benzene: solid points, films adsorbed from *n*-hexadecane; open points, Langmuir-Blodgett films; star, film obtained by polishing bulk film. Different runs are indicated by different shapes of points.

then, presumably represents the solvent remaining in the film during depletion. Films obtained by the polishing down of bulk amine resemble more closely the L. B. films than the adsorbed films.

This interpretation is in accord with earlier reports of mixed films by Bartell and Ruch<sup>6</sup> and by Cook and Ries.<sup>9</sup> Levine and Zisman also have inferred the presence of mixed films from studies of friction.<sup>10</sup> The latter authors claimed that mixed films, which are formed initially upon adsorption, transform spontaneously into films free of solvent as equilibrium is attained. This result has been interpreted as being general by some authors, but a kinetic study indicated that it does not apply to the present system. The adsorption of amine was found to be virtually as complete after five minutes as after several days. The maximum adsorption of amine, however, was only 80% of the amount deposited by the L. B. method, although the optical readings of adsorbed films were the same as for L. B. films.

Electron micrographs of the slides indicate that the surfaces were smooth and free of conspicuous fissures and cracks. Accordingly, it is probable that all of the radioactive material deposited was accessible for radioactive measurement. The close correlation between optical and radiotracer measurements for films applied in widely different manners, extending from compact to molecularly dilute films, makes it tempting to conclude that all of the material is optically accessible, also. This would be difficult to understand if the roughness factor were greatly different from unity. The apparent equality between numbers of adsorbed molecules and L. B. molecules, where, for the latter, the geometric rather than total surface area determines the number deposited, is another argument favoring a roughness factor near unity. Whether the roughness factor would be as low for adsorption of small gas molecules is an interesting point which deserves investigation.

Finally, it is to be noted that the optical readings

(9) H. C. Cook and H. E. Ries, Jr., THIS JOURNAL, 63, 226 (1959).
(10) O. Levine and W. A. Zisman, *ibid.*, 61, 1188 (1957).

do indeed appear to be proportional to the amount of material adsorbed, to within experimental error, even for films only a fraction of a monolayer thick.

# CHEMICAL EFFECTS OF THE (n,γ) ACTIVATION OF BROMINE IN THE ALKYL BROMIDES: ISOMERIZATION IN THE BROMOBUTANES<sup>1</sup>

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Study of the hot atom chemistry of bromine by irradiation of bromoalkanes with neutrons has shown that the radiobromine produced by the  $(n,\gamma)$  reaction may be found in inorganic form and in **a** variety of organic compounds. Among the many radioactive organic bromides which have been identified are isomers of the original molecule formed by a shift of the bromine atom. However, it has not been demonstrated conclusively whether isomers can be formed as a result of carbon skeletal rearrangement in hot atom chemistry.

In studies of the organic products obtained from the neutron irradiation of the two isomeric bromopropanes, Willard and co-workers<sup>3,4</sup> observed isomerization for both these molecules which involved only a shift of the bromine atom. From a similar study with 1- and 2-iodobutanes, McCauley, et al.,5 have shown that simple positional isomerization occurs for both these molecules but whether carbon skeletal rearrangement occurs or not was not determined. In a related study on the  $\gamma$ -radiolysis of liquid *n*-butane with radio-iodine scavenger, McCauley and Schuler<sup>6</sup> state that 1-iodo-2methylpropane and 2-iodo-2-methylpropane were not expected to occur because their formation involves complicated rearrangements. Similarly, in the  $\gamma$ -radiolysis of bromobutanes, Wilcox<sup>7</sup> found no isomerization of the carbon skeletal type but it was not apparent whether 2-bromobutane was separated from 1-bromo-2-methylpropane.

As a result of the above and similar studies, it was generally assumed that no appreciable amount of carbon chain isomerization occurs during the  $(n,\gamma)$  activation of bromine in the bromoalkanes. The results obtained in this work from the neutron irradiation of the four bromobutanes show that such isomerization does occur for these compounds and furthermore that it may be as extensive as the simple isomerization involving only shift of the bromine atom. A related phenomenon has been observed by Keenan,  $\epsilon t al.$ ,<sup>8</sup> from the electron bom-

- (3) G. Levey and J. E. Willard, J. Am. Chem. Soc., 78, 2351 (1956).
  (4) J. C. W. Chien and J. E. Willard, *ibid.*, 79, 4872 (1957).
- (5) C. E. McCauley, G. J. Hilsdorf, P. R. Geissler and R. H. Schuler, *ibid.*, **78**, 3246 (1956).
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  - (7) W. S. Wilcox, Radiation Research, 10, 112 (1959).
- (8) V. J. Keenan, R. M. Lincoln, R. L. Rogers and H. Burwasser, J. Am. Chem. Soc., 79, 5125 (1957).

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bardment of the two isomeric butanes. Although no isomerization of the parent compounds was detected, octanes formed by dimerization were obtained whose structures indicated carbon rearrangement.

#### Experimental

Most of the details of the experimental techniques used in this study have been described in other papers.<sup>9,10</sup> Briefly samples of about 0.1 to 0.2 ml. were purified by gas chromatography and sealed in blackened glass ampoules. They were irradiated at ambient temperature, about 25°, in a special low  $\gamma$ -flux facility of the NRX reactor which gave a neutron flux of about 10<sup>8</sup> neutrons per sec. per cm.<sup>2</sup>. The  $\gamma$ -flux was about 11 r. per hour and the usual irradiation time was about 16 hours so that the total  $\gamma$  dosage was less than 200 r. The radioactive organic reducts were separated by gas chromatography. The organic retention was measured by a technique in which inorganic radiobromine was absorbed from a gas stream on solid potassium ferrocyanide and the organic radiobromine-80 and -82 activity of the samples was carried out by  $\gamma$ -counting using a well-type scintillation crystal and conventional counting equipment.

To determine whether carbon skeletal rearrangement takes place, it was necessary to separate each of the four bromobutanes from its isomers and from the other products of the hot atom reactions. Because 1-bromo-2-methylpropane and 2-bromobutane have nearly identical separation coefficients for a wide variety of chromatographic substrates they cannot be separated by the usual gas chromatographic techniques.<sup>11</sup> However, the radiobromine activity of these two can be resolved readily through the use of selective reactivity with silver nitrate.<sup>12</sup> Reaction of gaseous 2bromobutane with a small quantity of solid silver nitrate is rapid and complete at room temperature but 1-bromo-2methypropane is not affected. This reaction with silver nitrate occurs with all secondary and tertiary bromoalkanes and with allyl type bromoalkenes.

In this study charcoal collector tubes were used for collection and assay of the organic radiobromides as they were eluted from the gas-liquid chromatographic column.<sup>10</sup> When a mixture of radioactive 2-bromobutane and 1-bromo-2-methylpropane was being eluted, the charcoal collector tube was preceded by two tubes of similar dimensions containing silver nitrate on firebrick. The radiobromine from 2-bromobutane was retained on the first silver nitrate tube and the second silver nitrate tube served only as a precaution to ensure that the separations had proceeded as expected and generally showed no activity. 1-Bromo-2-methylpropane passed through both silver nitrate tubes and was collected on the charcoal. The silver nitrate and charcoal tubes were disconnected for separate radioassay by  $\gamma$ -counting and a correction applied to allow for the higher  $\gamma$ -ray absorption of the silver nitrate relative to that of charcoal.

High vacuum silicone stopcock grease was used as the stationary liquid for most separations and the sample was injected without the addition of carrier compounds.<sup>13</sup> Unfortunately, the following important groups were not adequately resolved by this substrate: dibromomethane, 2bromobutane and 1-bromo-2-methylpropane; 1-bromopropane and 2-bromo-2-methylpropane; 1-bromobutane and 1,1-dibromoethane. The activity due to 2-bromobutane and to 2-bromo-2-methylpropane was obtained by the use of silver nitrate as described above. The activity due to the traces of dibromomethane and 1,1-dibromoethane was obtained from a separate sample in which Tween 30 was used as the stationary liquid in the gas chromatography column. This column satisfactorily separated these compounds from the isomeric butanes and from themselves.<sup>14</sup> The results obtained were used to make small corrections to the results of the analyses obtained from the silicone stopcock grease column.

The analyses in this work separated all of the lower molecular weight products but no attempt was made to resolve substances with poiling points above that for 1,2-dibromoethane. These high boiling point products were largely dibromobutanes and were collected as a single fraction and their total activity measured.

#### **Experimental Results and Discussion**

The results from the irradiation of the four bromobutanes are summarized in Table I. In most respects the results obtained were similar to those that have been found for other bromoalkanes. All four isomers undergo fragmentation yielding radioactive bromomethanes, bromoethanes and bromopropanes to the extent of 4.5 to 6%. All isomers yield 10 to 20% of high boiling point organic bromides which are mostly dibromobutanes. For three of the bromobutanes the organic retention was in the expected range of 30 to 40%. The data show that all four isomers undergo the expected simple isomerization involving only a change of the position of the bromine atom. The extent of this kind of isomerization was between 1 to 4%and was comparable in extent to the results reported for the bromopropanes.<sup>3,4</sup> The above aspects of the data would seem to require no further comment. In view of the objective of this study attention should be drawn to the results as they relate to carbon chain isomerization. This type of isomerization involving rearrangement of the carbon skeletal structure was also observed and the results for 2-bromo-2-methylpropane were especially noteworthy. The large proportion of isomerization for this compound, along with its organic yield of nearly 100%, would seem to warrant some additional comment and possible interpretations for the observations should be examined.

High organic yields up to about 80%, are nor-mally ascribed to the effects of impurities in the irradiated materials or to a high  $\gamma$ -radiation field. In this work the  $\gamma$ -field was extremely low<sup>9</sup> and so the high organic yield cannot be due to this cause. To obtain correct organic yields it is necessary to rigorously process the materials to exceedingly high purities. In the present work the materials were purified by gas chromatography.<sup>9</sup> This technique was found to be adequate for the purification of other organic bromides for this type of study. Further, it should be noted (Table I) that the distribution of organic products from the irradiation of 2bromo-2-methylpropane was in no way unusual, except for the amounts of radioactive parent material and 2-bromobutane. It therefore seems unreasonable to attribute the retention of nearly 100% solely to reaction of the radiobromine with impurities. Reaction of the inorganic bromine with unsaturated products resulting from the reactions induced by the recoil radiobromine are not normally encountered and should also not be considered as an important contribution to the high organic yield observed here.

(14) W. H. McFadden, Anal. Chem., 30, 479 (1958).

<sup>(9)</sup> W. E. Harris, W. H. McFadden and R. G. McIntosh, This Journal, 63, 1784 (1959).

<sup>(10)</sup> W. E. Harris and W. H. McFadden, Can. J. Chem., in preparation.

<sup>(11)</sup> Application of the recently developed technique of capillary gas chromatography to this separation indicates a separation of these two isomers is possible. The authors acknowledge that Dr. Roy Teranishi of the Western Regional Research Laboratories, demonstrated a practical separation of these two using a 200 ft. polypropylene glycol capillary column. Retention time was 15 min. at 50°, at a flow rate of 1 ml./min.

<sup>(12)</sup> W. E. Harris and W. H. McFadden, Anal. Chem., 31, 114 (1959).

<sup>(13)</sup> J. B. Evans and J. E. Willard, J. Am. Chem. Soc., 78, 2908 (1956).

RADIOBROMINE	Products	Obtained	FROM	THE	NEUTRON
IRRADIATION	OF THE FO	UR ISOMER	ic Bro	MOBU	TANES

		-Material	irradiated-	
Product	1-Bromo- butane % of	2-Bromo- butane total radio	1-Bromo- 2-methyl- propane bromine ac	2-Bromo- 2-methyl- propane tivity
1-Bromobutane	13.7	1.0	0.8	0.0
2-Bromobutane	1.1	13.5	2.7	13.6
1-Bromo-2-methyl-				
propane	0.5	0.9	14.7	1.3
2-Bromo-2-methyl-				
propane	0.3	0.3	3.7	66
Bromomethane	2.3	3.2	4.7	2.9
Bromoethane	0.9	0.5	0.3	0.1
2-Bromopropane	. 1	. 1	.3	. 4
1-Bromopropane	.2	.0	.0	.0
Dibromomethane	.4	.7	. 3	1.7
1,1-Dibromoethane	.1	. 5	.2	0.2
1,2-Dibromoethane	. 3	.2	. 1	. 3
Other low boiling point				
materials	. 1	.3	. 4	. 0
High boiling point or-				
ganic bromides <sup>b</sup>	10	19	15	11
Inorganic yield	70	60	57	2.6

<sup>a</sup> Unidentified materials with boiling points between those of bromoethane and 2-bromobutane, probably unsaturated organic bromides. <sup>b</sup> Unidentified but mostly dibromobutanes.

It seems most reasonable to attribute the high organic yield to a scavenging type reaction of the radiobromine by either a high concentration of organic ions (or radicals) or by the 2-bromo-2-methylpropane itself to give the unusually large proportions of 2-bromobutane and 2-bromo-2-methylpropane observed. Some experiments in which inactive bromine or hydrogen bromide were mixed with 2-bromo-2-methylpropane resulted in no isomerization to 2-bromobutane and so scavenging by 2bromo-2-methylpropane may not be an important reaction in this system. Due to their ease of formation, ions or radicals of the type  $(CH_3)_3C^+$  or  $(CH_3)_3C^0$  from 2-bromo-2-methylpropane may be present in an exceptionally high concentration in the radiobromine recoil zone. Furthermore, the carbonium ions are<sup>15</sup> self propagating due to a simple chain reaction of the type

$$(CH_3)_3C^+ + (CH_3)_3CBr \longrightarrow (CH_3)_3CBr + (CH_3)_3C^+$$

so that the radiobromine has a high probability of encountering a butyl ion. Rearrangement of tertiary butyl ions occurs rapidly<sup>15</sup> so that the secondary butyl ions would also be present in a reasonable concentration to yield straight chain isomers. The ratio of 0.2 of radioactive 2-bromobutane to 2bromo-2-methylpropane observed in this work is notably close to the value 0.23 determined for the equilibrium ratio of *n*-butane to 2-methylpropane in the presence of aluminum bromide at  $25^{\circ}$ .<sup>16</sup> In addition, if the assumption were made that equilibrium was established among all four possible butyl carbonium ion structures, the data of Table I would indicate that the structures leading to 1-bromobu-

(15) P. D. Bartlett, F. E. Condon and A. Schneider, J. Am. Chem. Soc., 66, 1531 (1944).

(16) H. Pines, B. Kvetinskas, L. S. Kassel and V. N. Ipatieff, *ibid.*, **67**, 631 (1945).

tane and 1-bromo-2-methylpropane are virtually absent.

The data of Table I indicate that chain isomerizations occurred with the other three bromobutanes to a much smaller extent. While extended discussion of these results is unwarranted, it would seem relevant to point out that the proportion of chain isomerization was 0.8, 1.2, 3.7 and 13.6% for 1-bromobutane, 2-bromobutane, 1-bromo-2-methylpropane and 2-bromo-2-methylpropane. The fact that chain isomerization was much more extensive with 2-bromo-2-methylpropane than with the other three bromobutanes may be additional indication that chain isomerization occurs by way of butyl ions since it forms a carbonium ion most readily.

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# THE IONIZATION CONSTANTS OF 2-CHLORO-4-NITROPHENOL AND 2-NITRO-4-CHLOROPHENOL

#### BY V. E. BOWER AND R. A. ROBINSON

#### National Bureau of Standards, Washington, D. C. Received February 3, 1960

In the course of a search for an indicator with  $pK \approx 6.2$  and a suitable absorption spectrum, we made measurements on 2-chloro-4-nitrophenol and 2-nitro-4-chlorophenol in aqueous solution at 25° and we can report pK = 5.45 and 6.46, respectively. The phenols were recrystallized from commercially available material; m.p. of the recrystallized material for the former, 110.5-111.2°; for the latter, 87.0-87.8°. 2-Chloro-4-nitrophenol is characterized by maxima at 400 mu (molar absorbance index,  $\epsilon$  16,600) and 265 m $\mu$  ( $\epsilon$  4,000) in alkaline solution and at 315 m $\mu$  ( $\epsilon$  8,700) in acid solution with isosbestic points at 347 m $\mu$  ( $\epsilon$  5,000), 273 m $\mu$  ( $\epsilon$  3,500) and 248 m $\mu$  ( $\epsilon = .,100$ ). 2-Nitro-4-chlorophenol has maxima at 427 m $\mu$  ( $\epsilon = 4.460$ ) in alkaline solution and at 363 m $\mu$  (é 2,700) and 275 m $\mu$  (é 5,400) in acid solution with isosbestic points at 383 m $\mu$  $(\epsilon 2,300)$  and 260 m $\mu$  ( $\epsilon 4,500$ ).

Measurements were made on a Beckman Model DU Spectrophotometer. The spectrophotometric method employed has been outlined elsewhere<sup>1</sup> and it only needs to be added that in the pK determination of 2-chloro-4-nitrophenol, we used the succinate buffers of Bates, Pinching and Smith.<sup>2</sup> The relation

$$pK = pH - \log \frac{D - D_1}{D_2 - D} - \log \gamma$$

was used to calculate pK. The pK thus calculated was further corrected for the contribution of the chloronitrophenol to the acidity of the solution.<sup>3</sup>

The experimental results are given in Tables I and II. All measurements were made using 1 cm. absorbance cells. In the tables  $D_1$  and  $D_2$  represent

(1) R. A. Robinson and A. I. Biggs, Trans. Faraday Soc., **51**, 901 (1955).

(2) R. G. Bates, G. D. Pinching and E. R. Smith, J. Research Natl. Bur. Standards, 45, 418 (1950).

(3) R. A. Robinson and A. K. Kinng, Trans. Faraday Sec., 51, 1398 (1955).

the optical densities of the solutions containing the phenol at pH 2 and 12, respectively, and D the optical density of the buffer solutions with the phenol. The resultant pK values 5.45 and 6.46 may be compared with those calculated on the assumption that chloro and nitro substituents have additive effects on the pK of phenol; from the data of Judson and Kilpatrick<sup>4</sup> on monosubstituted phenols we calculate pK 5.67 and 6.66, respectively.

TABLE I

IONIZATION CONSTANTS OF 2-NITRO-4-CHLOROPHENOL<sup>a</sup> AT 25°

		20		
Buffer	D	$\log \frac{D-D_1}{D_2-D}$	pK	pK(cor.)
	Series I	: 410 m $\mu$ , $D_1 = 0.20$	$02, D_2 =$	0.924
a	0.732	0.441	6.45	6.45
b	.749	. 495	6.47	6.46
с	.755	.515	6.47	6.46
d	.767	.556	6.48	6.46
е	.775	. 585	6.49	6.46
	Series II	: 420 m $\mu$ , $D_1 = 0.1$	21, $D_2 =$	= 1.004
a	0.767	0.436	6.45	6.45
b	. 790	. 495	6.47	6.46
е	.798	.517	6.47	6.46
d	. 810	. 550	6.49	6.47
е	. 821	. 583	6.49	6.46
	Series III	I: 430 m $\mu$ , $D_1 = 0.0$	$D70, D_2 =$	= 1.020
a	0.769	0.445	6.44	6.44
b	. 789	.488	6.48	6.47
е	. 793	. 503	6.48	6.47
d	.807	. 539	6.50	6.48
e	. 824	.585	6.49	6.46
	Series IV	: 440 m $\mu$ , $D_1 = 0.0$	)39, D <sub>?</sub> =	= 0.964
a	0.721	0.448	6.44	6.44
b	.738	. 490	6.47	6.47
с	.749	.519	6.46	6.46
d	.764	.559	6.48	6.46
e	.772	. 582	6.50	6.46
		A	17 9	1= × 10-7

Avg. pK 6.46,  $K = 3.47 \times 10^{-7}$ "The molarity of 2-nitro-4-chlorophenol was 2.33 ×  $10^{-4}$  throughout. Buffers a, b, c, d and e were mixtures of  $rMKH_2PO_1$  and  $rMNa_2HPO_4$  where x = 0.05, 0.025, 0.02, 0.01 and 0.005, pH 6.77, 6.80, 6.89, 6.96 and 7.02 and  $-\log \gamma = 0.12$ , 0.10, 0.10, 0.08 and 0.06, respectively.

TABLE II

IONIZAT	non Cons	TANT OF 2-CHLOR	o-4-nitropi	$ienol^a$ at $25^{\circ}$
Buffer	D	$\log rac{D-D_1}{D_2-D}$	pK	pK(cor.)
	Series I:	400 m $\mu$ , $D_1 = 0$	$.005, D_2 = 0$	0.865
f	0.493	0.015	5.45	5.45
ß	. 514	.053	5.45	5.45
h	. 543	. 106	5.44	5.44
	Series 2	II: 410 m $\mu$ , $D_1 =$	$0, D_2 = 0.5$	919
f	0.463	0.007	5.45	5.45
g	. 488	.054	5.45	5.45
h	. 513	. 102	5.45	5.45
		Av. pK 5.	45, K = 3.	$56 imes10^{-6}$

<sup>a</sup> The molarity of 2-chloro-4-nitrophenol was  $0.58 \times 10^{-4}$  throughout. Buffers f, g and h were mixtures of xM sodium hydrogen succinate and xM sodium succinate where x = 0.05, 0.025 and 0.01, pH 5.343, 5.403 and 5.474 and  $-\log \gamma = 0.118, 0.103$  and 0.077, respectively.

(4) C. M. Judson and M. Kilpatrick, J. Am. Chem. Soc., 71, 3110 (1949).

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# KINETICS OF A cis-trans ISOMERIZATION IN A HEAVY-ATOM SOLVENT

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Magee, Shand and Evring<sup>1</sup> proposed that certain cis-trans isomerizations proceed via a half-twisted intermediate of triplet multiplicity. The very low frequency factors characteristically shown by reactions of this class are then attributed to the low probability of crossing between the singlet and triplet potential energy surfaces. This in turn has suggested that it might be possible to catalyze the reaction by intense magnetic or electric fields of molecular origin, since these are known, $^{2-4}$  in the context of spectroscopy, to enhance the probabilities of transitions between states of unlike multiplicity. Paramagnetic catalysts already have been examined, but it now appears that they are either ineffective<sup>5</sup> or else that they affect the activation energy as well, and thus act chemically.<sup>6</sup>

Intense electric fields exist near the nuclei of atoms of high atomic number, and again by analogy with spectroscopic observations, such heavy atoms might be expected to be effective either as substituents in the reactive molecule, or as constituents of a solvent. Thus intramolecular heavy-atom catalysis might be expected in such substances as diiodoethylene, but this substance is unstable and the rate of its thermal isomerization is overwhelmingly regulated by the iodine produced by decomposition.<sup>7</sup> Other compounds of a similar type are probably equally unsuitable. We have therefore sought to effect catalysis using a heavy-atom solvent.

Even here, systems suitable for study are rather few, since the reagents must be relatively highboiling and stable (the reactions mostly require temperatures around 200°). Stability is crucial, since this isomerization is notoriously susceptible to impurity catalysis. We chose dimethyl maleate in iodobenzene, the former because its kinetics are cleanly first order and have been studied in a light atom solvent (anisole)<sup>8</sup>; the latter because of its thermal stability and boiling point (188°).

In the event, no significant catalysis was found (Fig. 1).

The triplet-intermediate theory is not without its critics<sup>9</sup> and is certainly far from proven; never-

(1) J. L. Magee, W. Shand and H. Eyring J. Am. Chem. Soc., 63, 677 (1941).

(2) D. F. Evans, J. Chem. Soc., 1351, 3885 (1957).

(3) M. Kasha, Disc. Faraday Soc., 9, 14 (1950); D. S. McClure, J. Chem. Phys., 7, 905 (1949).

(4) M. Kasha, *ibid.*, 20, 71 (1952); M. Kasha and S. P. McGlynn, Ann. Rev. Phys. Chem., 7, 403 (1956).

(5) E. Gelles and K. S. Pitzer, J. Am. Chem. Soc., 77, 1974 (1955).

(6) H. McConnell, J. Chem. Phys., 20, 1043 (1952).

(7) R. M. Noyes, R. G. Dickinson and V. Schomaker, J. Am. Chem. Soc., 67, 1319 (1945).

(8) M. Davies and F. P. Evens, Trans. Faraday Soc., 51, 1506 (1955).

(9) D. Schulte-Frohlinde, Ann., 612, 138 (1958).



Fig. 1.—Arrhenius plots of the rates of isomerization of dimethyl maleate: +, anisole solution (Davies and Evans); •, iodobenzene solution (present work); ×, pure ester (Davies and Evans).

theless, we do not consider that the present result negates the mechanism. Our reasons are two. (i) The spectroscopic experiments previously referred to involved either direct transitions, by absorption or emission, between singlet and triplet states, or else crossovers between excited singlet and triplet states whose potential energy surfaces are presumed to intersect. The latter process is the more relevant to the kinetic experiments, but quantitative information is available only for the former. In the first case certainly, and probably also in the second, the heavy atom perturbation operates by mixing of the triplet state with some higher, particularly effective, perturbing singlet. In our view, this is probably a chargetransfer level. For perturbation by iodine, this level may lie around 30,000 cm.<sup>-1</sup>, and is far removed from the energy of the singlet-triplet intersection (8000 cm. $^{-1}$ ) in the kinetic experiment. The triplet upper states of the spectroscopic experiments, however, typically lie around 20-25,000 cm.<sup>-1</sup>, and must be much more accessible to perturbation. (ii) The perturbation by the heavy atom is probably most effective when it is in intimate contact with the perturbed molecule (though how sensitive it is to intermolecular distance is still an unresolved question.<sup>10</sup>) However, the reaction process of minimum energy requires that a colliding solvent molecule should first recede, permitting the energy of the momentary compression to concentrate in the torsional mode of the olefin, which may then just reach the singlettriplet crossing point. Stating this another way, the singlet-triplet intersection in a compressed solute-solvent pair must lie at higher energy than it does in the same pair of molecules while separated, and thus offers a reaction path whose higher energy offsets a presumably enhanced frequency factor. Radiative spectral transitions on the other hand can take place at any instant during a collision, while intersystem crossing between excited

(10) W. W. Robertson and R. E. Reynolds, J. Chem. Phys., 29, 138 (1958).

states occurs in the course of collisional degradation of the excitation energy, and its rate is not restricted by an activation requirement.

#### Experimental

Dimethyl maleate was dried over  $CaCl_2$  and vacuum distilled, and filtered just above its freezing point to remove the fumaric ester. Iodobenzene, dried over  $CaH_2$ , was repeatedly passed through alumina and vacuum distilled. It was shaken with, and stored over, mercury and  $CaH_2$ .

Reactions were carried out in sealed Pyrex glass tubes; the reaction mixtures were scrupulously outgassed before sealing, while frozen, under  $10^{-4}$  mm. of purified nitrogen. The sensitivity to the impurity catalysis which these precautions circumvented was evidenced by the fact that improving reproducibility was accompanied by a fifty-fold decrease in rate relative to runs which, early in the investigation, were considered fairly good.

The reaction was accessible to study only over a narrow temperature range; above  $235^{\circ}$  iodobenzene itself discolors on long heating; below  $215^{\circ}$  the long runs, of over a week, gave unsatisfactory results. In all cases mixtures became yellowish after 20-30% reaction, and measurements were therefore confined to the earlier stages of reaction, within which at least 30 tubes were examined at each temperature. Rates were satisfactorily first order, and quantitative infrared measurements disclosed no obvious side-reactions.

Approximately 10% solutions of ester in iodobenzene were used. The analytical method made use of the very low solubility of dimethyl fumarate in the chilled solvent. Reaction mixtures were equilibrated at 0°, whereupon most of the fumarate was precipitated; the refractive index of the mother liquor measured the extent of reaction.

First-order rate constants (including a small correction for the back reaction) were:  $10^{7}k$  (sec.<sup>-1</sup>) = 5.0 (217.2°), 6.6 (223.3°), 8.7 (227.5°), 12.4 (232.8°). Temperatures are all  $\pm 0.3^{\circ}$ . The Arrhenius parameters were  $A = 6 \times 10^{6}$  sec.<sup>-1</sup>,  $E = 28.5 \pm 3$  kcal./mole.

We are indebted to Mr. R. H. Roper for the infrared measurements. We also thank Dr. Mansel Davies for supplying us with some further details of his published work incorporated in Fig. 1.

### PHYSICO-CHEMICAL STUDIES ON OVALBUMIN. II. THE EFFECT OF CHARGE ON DIFFUSION

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#### Received March 5, 1960

Procedures for the determination of heterogeneity from diffusion measurements on mixed solute systems have been shown to be valid for dilute solutions of simple substances such as sucrose and urea and have been applied to a few protein systems.<sup>1-7</sup> Deviations from "ideal" diffusion behavior in a manner indicative of heterogeneity have been observed in all protein systems studied, the deviations generally being represented in terms of fringe deviation diagrams.<sup>2,4</sup> However, analysis by these procedures assumes independence of flow of each solute component: in a previous com-

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(2) D. F. Akeley and L. J. Gosting, J. Am. Chem. Soc., 75, 5685 (1953).

(3) J. M. Creeth and L. J. Gosting, THIS JOURNAL, 62, 58 (1958).

(4) J. M. Creeth, *ibid.*, **62**, 66 (1958).

(5) R. L. Baldwin, L. J. Gosting, J. W. Williams and R. A. Alberty, *Disc. Faraday Soc.*, 20, 13 (1955).
(6) I. J. O'Donnell, R. L. Baldwin and J. W. Williams, *Biochim.*

(b) 1. J. O Donnell, R. L. Baldwin and J. W. Williams, Biochim. Biophys. Acta, 28, 294 (1958).

(7) J. M. Creeth, L. W. Nichol and D. J. Winzor, This Journal, 62, 1546 (1958).

#### Notes

		SOLUTI	UTION DATA AND DIFFUSION RESULTS ON OVALBUMIN						
Expt. no.	Buffer compn., ª M	рНь	Relative viscosity of buffer, 7rel	Apparent valence «	Total no. of fringesd	∆1 °	${\mathfrak D}_{\rm A} f \ {\mathfrak a}^{-1.00^{\circ}}, {\rm cm.}^2 \ {\rm sec.}^{-1} \times 10^7$	$\frac{\Omega R^{e}}{\max}$	ΩR max cor. × 104
1	0.15 NaCl .01 NaAc .01 HAc	4.59	1.011	0	68.53	140	3.895	37	37
2	.09 NaCl .07 NaAc .01 HAc	5.40	1.034	- 5.1	111.42	260	3.872	32	42
3	. 15 NaCl .01 NaV .02 HV	7.51	1.022	- 10.0	113.36	150	3.954	19	48
4	. 12 NaCl .04 NaV .01 HV	8.42	1.040	-10.5	110,59	60	3.902	26	51

 TABLE I

 DUCTION DATA AND DIFFUSION RESULTS ON OVALBUMIN

<sup>a</sup> Ac = acetate, V = diethyl barbiturate. <sup>b</sup> Measured with a Doran Universal pH meter. <sup>c</sup> Calculated on the basis of the method given by Abramson, Moyer and Gorin<sup>10</sup> using the mobility data of Longsworth.<sup>11</sup> <sup>d</sup> In this apparatus, J = 100 corresponds to a concentration increment of 0.582 g./100 ml. for ovalbumin, based on Perlmann and Longsworth's value<sup>12</sup> for the specific refractive increment. <sup>c</sup> The significance of these quantities is discussed in a previous paper.<sup>2</sup> <sup>J</sup> Values corrected to water basis (by multiplying by  $\eta_{rel}$ ).

munication<sup>7</sup> evidence indicative that this assumption is not satisfied has been obtained in a study of the diffusion of crystalline ovalbumin and also the leading electrophoretic component,  $A_1$ , at a pH value close to the isoelectric point. The resultant fringe deviation diagrams were generally of the same form as that obtained in the presence of a fast diffusing impurity, and it therefore appears that detailed information on the heterogeneity of protein samples cannot be gained from diffusion measurements until the effect of heterogeneity can be separated from that due to flow interaction. Although the exact nature of the latter phenomenon is unknown, if the suggestion that interaction of solute flows results in part from electrostatic coupling of ion flows<sup>6,8</sup> is correct, then the deviation from ideal behavior observed with  $A_1$  at its isoelectric point presumably represents the minimum effect of flow interaction. The diffusion experiments on ovalbumin reported in this work have been performed at several pH values specifically to determine the effect of charge on the diffusion coefficient and on the fringe deviation diagram.

(1

#### Experimental

Materials and Methods.—The ovalbumin was from "sample 3" previously described<sup>7</sup>: at the time of use it had been stored for approximately 18 months. Its electrophoretic analysis was unchanged. The buffer solutions were prepared from analytical reagent grade materials, and were all made up to a nominal ionic strength of 0.16; all the relevant details of composition, etc., are given in Table I.

The diffusion experiments were performed in a Spinco Model H electrophoresis-diffusion apparatus, employing a slightly modified' Rayleigh optical system. The general procedures for the conduct of experiments and the measurement of records were identical with those previously described.<sup>4,7</sup> It should perhaps be emphasized that these procedures give a rigorously defined quantity, which has been called<sup>8</sup> the "reduced height-area ratio" and given the symbol  $\mathfrak{D}_A$ ; in the absence of flow interaction and secondorder concentration dependence effects  $\mathfrak{D}_A$  reduces to the "height-area average" diffusion coefficient,<sup>9</sup>  $\mathfrak{D}_A$ .

#### **Results and Discussion**

All the relevant information relating to the diffusion experiments is summarized in Table I, which is largely self-explanatory. The values of  $\mathfrak{D}_A$  in the table agree closely with previously reported<sup>7</sup> values (which extended over a range of protein concentration) and it is at once clear that they do not show any significant dependence on the net charge of the protein (within the range 0 to -10.5). The insensitivity of  $\mathfrak{D}_A$  is in some respects an important finding, for if it were a general property of protein-buffer systems, it would imply that no additional error would be introduced into molecular weight calculations by employing the results of diffusion experiments performed at pHvalues removed from the isoelectric point: these conditions are frequently necessary because of solubility and stability limitations. However, little precise information on other systems is yet available (Charlwood's results<sup>13</sup> on human albumin could not be analyzed for deviations from Gaussian form, while O'Donnell, et al.,6 observed pH dependent  $\mathfrak{D}_A$  values for bovine albumin) and in any case, it must be borne in mind that the Drequired in the Svedberg equation will generally differ from  $D_A$ .

In column 9 of Table I the maximum values of the relative fringe deviation,  $\Omega_R$ , are reported; the deviation graphs themselves, which give the  $\Omega_R$  values over the whole boundaries, are given in Fig. 1, the crosses representing the mean observed deviations. The following points require comment. Experiment 1, performed under conditions where the protein is essentially uncharged,<sup>14</sup> gives a deviation graph of the same general shape and magnitude as obtained previously<sup>7</sup>: the experimental conditions differ only in that sodium salts

(10) H. A. Abramson, L. S. Moyer and M. H. Gorin "Electrophoresis of Proteins," Reinhold Publ. Corp., New York, N. Y., 1942, p. 153.

<sup>(8)</sup> P. J. Dunlop and L. J. Gosting, J. Am. Chem. Soc., 77, 5238 (1955).

<sup>(9)</sup> O. Quensel, Dissertation, Uppsala, 1942.

<sup>(11)</sup> L. G. Lorgsworth, Ann. N. Y. Acad. Sci., 41, 267 (1941).

<sup>(12)</sup> G. E. Perlmann and L. G. Longsworth, J. Am. Chein. Soc., 70, 2719 (1948).

<sup>(13)</sup> P. A. Churlwood, Biochem. J., 56, 259 (1954).



Fig. 1.—Fringe deviation diagrams of ovalbumin, the experiment number referring to Table I. The crosses represent mean experimentally observed deviations, the solid line represents the deviation due to the buffer gradient consequent on dialysis and the dashed line is a summation of the two.

have been used instead of potassium salts. Inspection of the deviation graphs of experiments 2, 3 and 4, where the protein bears a generally increasing net negative charge, shows a trend in which the maximum becomes shifted from the extreme right and, furthermore, the value of  $\Omega_{\rm R}$ max. is decreased. This implies that diffusion is more nearly "ideal" and appears at first sight contrary to the postulate that flow interaction results in part from electrostatic coupling of ion flows, since greater deviations would be expected in the case of charged systems. However, the diffusion experiment is conducted with dialyzed solutions and accordingly the initial conditions require close examination (cf. ref. 6). Should the protein bear no net charge, the salt redistribution on dialysis is a measure of preferential "binding" of the buffer constituents by the protein: depending on specific effects, this may lead to a greater or less buffer salt concentration within the dialyzed protein solution. When the protein is charged, the Donnan effect, considered above, must-always result in a lowered buffer salt concentration within the dialyzed solution. If the Donnan effect is predominant, the conditions at the start of the experiment must involve a small negative concentration increment of salt superimposed on the positive concentration increment of protein. Qualitatively it is then clear that, in diffusion, salt will only be transported in those regions where there is a protein concentration gradient,<sup>15</sup> for elsewhere its chemical potential is constant. The general solution for this type of problem is known,<sup>16</sup> but its application is not yet possible with protein systems; accordingly we cannot present here a precise interpretation of the results. Nevertheless it is of some interest to see how much of the observed deviations can be accounted for in the assumption that the flow of salt (due to the Donnan concentration gradient) proceeds independently of the other diffusion processes. From the data of Table I, and taking the molecular weight of oval-bumin to be 45,000,<sup>17</sup> it is possible to calculate, following established procedures, a value for the initial concentration increment of salt. On the assumption that this consists of NaCl alone, a value for the refractive index proportion  $\alpha_2$  and diffusion coefficient ratio  $r_2$  ( $r_2 = D(albumin)/D$ -(NaCl)  $\simeq 1/18$ ) may be found, using the results of Vitagliano and Lyons<sup>18</sup> for NaCl. This is sufficient to calculate a first approximation to the expected fringe deviation, as we have, from equation 17a of ref. 3,  $\Omega_{\rm R} = \alpha_2 F(z^*, \sqrt{r_2}) + \ldots$  This function is shown in each case as the solid line in the graphs of Fig. 1: it is of course zero for experiment 1. From the nature of the calculations, it is obvious that these lines can only be approximately defined. If the observed deviations are regarded as the sum of the effects of flow interaction and of an independently diffusing salt gradient, then the magnitude of the former effect may be obtained by subtracting the (negative) value of the latter from the observed deviation at a given value of  $z^*$ . By this means the dashed curves in the figure have been computed.

From the general appearance of these curves,

<sup>(14)</sup> At this pH, 4.59, some 15-20% of the protein would bear a net positive charge of approximately +1 per molecule. This, therefore, does not represent the limiting case of a completely uncharged species, but should serve as a valid standard for comparison with markedly charged species.

<sup>(15)</sup> Strictly, the protein concentration gradient only reaches zero at infinite distance from the initial boundary, but the limits of optical resolution allow precise definition of regions of effectively zero gradient.

<sup>(16)</sup> H. Fujita and L. J. Gosting, J. Am. Chem. Soc., 78, 1099 (1956).

<sup>(17)</sup> M. Halwer, G. C. Nutting and B. A. Brice, ibid., 73, 2786 (1951).

<sup>(18)</sup> V. Vitagliano and P. A. Lyons, ibid., 76, 1549 (1956).

it is clear that the assumption stated above leads to a rational qualitative interpretation of the diffusion results: the general trend shown by the measured deviations in experiments 2-4 is what would be expected on the basis of increasing negative increments of NaCl combined with increasing *positive* deviations due to "flow interaction." The former would be expected on the basis of increasing negative charge on the protein, and the latter on the supposition that interaction (being due to coupled ion-flows) will also increase with the charge on the protein ion. The maximum values of the dashed curves (reported as " $\Omega_{\rm R}$  corrected" in column 10 of Table I) show a fairly smooth pH-dependence, while there is a marked similarity in the general shapes of these curves and resemblance to the experimental curve obtained at the isoelectric point.

It is hoped that these experiments and the attempted interpretation given will prove useful in developing a more exact theory for this important field.

Acknowledgments.—We are grateful to Professor L. J. Gosting, of the University of Wisconsin, for discussions on the subject of flow-interaction; we also wish to thank the Commonwealth Scientific and Industrial Research Organization for a studentship held by D. J. W. and General Motors-Holden's Ltd. for a Postgraduate Research Fellowship held by L.W.N.

# DISSOCIATION OF THE PROTON COMPLEXES OF $\beta_{,\beta}{}'_{,\beta}{}''_{-}$ TRIAMINOTRIETHYLAMINE

#### BY THERALD MOELLER AND RICARDO FERRÚS

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#### Received March 5, 1960

The formation constants of a number of complexes are conveniently evaluated by procedures involving the auxiliary complexing agent  $\beta_i \beta'_i \beta''$ -triaminotriethylamine (tren).<sup>1</sup> Procedures of this type require accurate values for the dissociation constants of the proton complexes of tren

$$H_{3} \operatorname{tren}^{3+} \xrightarrow{\longrightarrow} H_{2} \operatorname{tren}^{2+} + H^{+} \qquad pK_{1}$$

$$\begin{array}{ccc} H_2 \text{tren}^{2+} & \swarrow & H \text{tren}^{+} + H^{+} & pK_2 \\ H \text{tren}^{+} & \swarrow & \text{tren}^{+} + H^{+} & pK_3 \end{array}$$

Although Schwarzenbach and co-workers<sup>2,3</sup> report for 0.1 *M* KCl and 0.5 *M* KCl solutions, respectively, at 20°,  $pK_1$ , 8.56 and 8.79;  $pK_2$ , 9.59 and 9.84;  $pK_3$ , 10.29 and 10.29; data for other temperatures are not available.

In this communication, values for these constants, as determined by the potentiometric method of Ackermann and Schwarzenbach,<sup>2</sup> are given for six temperatures, and these data are employed to calculate the enthalpy changes for the three equilibria.

#### Experimental

**Materials and Apparatus**.—A sample of  $\beta_{\beta}\beta'_{\beta}\beta''$ -triaminotriethylamine trihydrochloride was obtained by the procedure of Jonassen and Strickland.<sup>4</sup> Only the first material to crystallize was employed.

Anal. Caled. for  $\dot{C}_6\dot{H}_{18}N_4$  3HCl: C, 28.19; H, 8.28; N, 21.92. Found: C, 28.30; H, 8.21; N, 21.80.

Mercurimetric analysis for chlorine<sup>s</sup> indicated the sample to be 99.4% tren:3HCl.

All pH measurements were made with a Beckman-Model G pH-Meter, which was standardized against pH 4 and 9 Leeds and Northrup standard buffers. The titration cell was a 200-ml. Berzelius beaker fitted with a rubber stopper with suitable holes to accommodate electrodes from the meter, nitrogen inlet and outlet tubes, and the tip of a 10-ml. microburet. Titrations were carried out with samples thermostated to within  $\pm 0.05^{\circ}$  of the stated temperature.

**Procedure.**—Titration of  $5 \times 10^{-3}$  M amine trihydrochloride solutions was carried out with 0.1 M carbon dioxide-free potassium hydroxide. Stirring was effected with nitrogen that had been bubbled previously through a solution of the same ionic strength and temperature. The ionic strength was maintained at 0.09–0.11 by addition of potassium nitrate. Each pH reading was converted to hydrogen ion concentration by use of an additive factor calculated from the pH value recorded for a  $10^{-3}$  M nitric acid solution in 0.1 M potassium nitrate.

#### **Results and Discussion**

Experimental pK values calculated from the titration data by the method of Ackermann and Schwarzenbach<sup>2</sup> are summarized in Table I. The excellent agreement between the values at 20° and those cited above<sup>2</sup> for solutions maintained at ionic strength 0.1 by addition of potassium chloride indicates no substantial difference between chloride and nitrate ions as the inert electrolyte.

TABLE I

pK Values for Dissociation of Proton Complexes of  $\beta_i\beta'_j\beta''$ -Triaminotriethylamine at Ionic Strength 0.1

Temp., °C.	$pK_1$	$pK_2$	$pK_{1}$
15.0	8.74	9.77	10.44
20.0	8.58	9.59	10.29
25.0	8.42	9.44	10.13
30.0	8.27	9.28	9.99
35.0	8.11	9.12	9.85
40.0	7.95	8.98	9.71

Plots of pK vs. the reciprocal of the absolute temperature yield straight lines from which individual pK values deviate by no more than 0.01 unit. From the slopes of these lines and the expression

$$-\log K = \frac{\Delta H}{2.303 RT} + \text{constant}$$
(1)

 $\Delta H_1$ ,  $\Delta H_2$  and  $\Delta H_3$  values of 13.1  $\pm$  0.2, 13.1  $\pm$  0.2, and 12.1  $\pm$  0.2 kcal./mole, respectively, were calculated. The smallness in deviation among the *pK* values rendered use of the least-squares approach unnecessary. Although equilibrium constants given in eq. 1 are thermodynamic values, concentration constants were employed in these calculations. However, the activ-

(4) H. B. Jonassen and G. T. Strickland, J. Am. Chem. Soc., 80, 312 (1958). See also H. B. Jonassen, R. B. LeBlanc, A. W. Meibohm and R. M. Rogan, *ibid.*, 72, 2431 (1950).

(5) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1948, p. 576.

<sup>(1)</sup> G. Schwarzenbach and E. Freitag, Helv. Chim. Acta, 34, 1503 (1951).

<sup>(2)</sup> H. Ackermann and G. Schwarzenbach, *ibid.*, **32**, 1543 (1949).
(3) J. E. Prue and G. Schwarzenbach, *ibid.*, **33**, 963 (1950).

ity coefficient factor essential to correcting the latter can be included in the constant term in eq. 1 and is probably not highly significant since the solutions used were dilute, the ionic strength was kept constant, and the activity coefficients have only a small temperature dependence.

The essential constancy among these  $\Delta H$  values indicates chemical similarity among the three primary amine nitrogen atoms. The  $\Delta H$  values for the three dissociation steps of the trihydrochloride of diethylenetriamine are, respectively, 11.1, 12.25 and 7.6 kcal./mole.<sup>6</sup> If the first two are assigned to the  $-NH_3^+$  groups at the end of the chain, agreement with values for the structurally analogous groups in the hydrochloride of  $\beta_i \beta'_i \beta''_$ triaminotriethylamine is quite satisfactory.

(6) G. H. McIntyre, Jr., B. P. Block and W. C. Fernelius, J. Am. Chem. Soc., 81, 529 (1959).

# THE EFFECTS OF TEMPERATURE ON THE DISSOCIATION CONSTANTS OF SOME COMPLEXES OF THE TYPE R<sub>2</sub>Se·I<sub>2</sub><sup>1</sup>

#### By J. D. McCullough and Irmela C. Zimmermann

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#### Received March 8, 1960

Dissociation constants in carbon tetrachloride solution at 25° for eleven complexes of the type  $R_2Se \cdot I_2$  have been reported in previous communications from these laboratories.<sup>2</sup> The present communication reports a study of the dissociation constants of four representative complexes from this group over a range of temperatures in order to permit calculation of values for  $\Delta H_c^0$  and  $\Delta S_c^0$ for the dissociations.

#### Experimental

The preparation and purification of materials and the experimental procedures have been described in the earlier communications. For each complex some eight to ten solutions were prepared covering a wide range of ratios of selenide to iodine. Several spectrophotometric recordings were made of each sample at each temperature. The data for each complex at each temperature and at each of several wave lengths were fit to the equation

$$SHl/A_{c} = (S + H - C)/\epsilon + K_{c}/\epsilon$$
 (1)

This equation is a modification of that suggested by Scott.<sup>3</sup> In Equation 1 the symbols have the meanings noted: S and H are the formal or total concentrations (in moles per liter) of the sclenide and iodine, respectively, C is the molar concentration of the complex at equilibrium,  $A_c$  is the absorbance of the solution, corrected for absorbance due to uncombined iodine and uncombined selenide, l is the optical path length in cm.,  $\epsilon$  is the molar absorptivity (extinction coefficient) of the complex and  $K_c$  is the dissociation constant in moles per liter. In the above form, the equation is not restricted to the condition S>>H as it is in the form given by Scott.

Equation 1 represents a straight line if  $SHl/A_c$  is plotted against (S + H - C). The slope of this line is  $1/\epsilon$  and the intercept is  $K_c/\epsilon$ . The experimental data for each complex at a given temperature and wave length are fit to the straight line represented by equation 1 by a cyclic least-squares routine on the IBM 709. In each cycle the observed absorbance is corrected for the absorbance due to uncombined selenide and iodine and the least-squares line is obtained.

(1) This research was sponsored by the National Science Foundation under Research Grant NSF-G5922.

(2) J. D. McCullough and Denise Mulvey, THIS JOURNAL, 64, 264 (1960). References to earlier work are given in this paper.

(3) R. L. Scott, Rec. trav. chim., 75, 787 (1956).

In the first cycle, the absorbance corrections are made on the assumption that all of the selenide and iodine are uncombined, *i.e.*,  $K_c = \infty$ . This leads to tentative values for  $\epsilon$  and  $K_c$ . In subsequent cycles the concentrations of uncombined selenide and iodine are computed on the basis of the  $K_c$  from the previous cycle. The computing routine continues these least-squares cycles until the change in  $K_c$  is inappreciable. All significant quantities from each cycle are printed out so that the progress of the calculation can be followed. Three or four cycles are normally sufficient. The equilibrium constants obtained in this way are given in Table I.

TABLE I

VALUES OF	K. FOR	$R_2Se^-I_2$ at	VARIOUS	TEMPERATURES	AND
		WAVE I	ENOTHS		

λ(mµ)	(a) $R = n$	nethyl (Ke 15.3°	$\times 10^{3}$ ) 35.8°	48.4°
420	2,500	1.1	3.1	5.6
430	2,790	1.1	3.2	5.6
440	2,850	1.1	3.2	5.3
450	2,660	1.2	3.0	5.2
	Av.	1.12	3.17	5.43
λ(mµ)	(b) $R = p$ -meth	oxyphenyl 15.8°	$(K_{c} \times 10^{2}) = 35.8^{\circ}$	47.2°
370	16,500	0.93	2.3	3.6
380	16,700	0.95	2.0	3.6
390	14,900	0.96	2.3	3.6
	Av.	0.947	2.20	3.60
	(c) $\mathbf{R} = \mathbf{v}$	-toly! (Ke )	× 10 <sup>2</sup> )	
λ(mµ)		16.0°	36.4°	45.0°
350	18,100	1.5	3.3	<b>5</b> .0
360	20,100	1.6	3.4	5.1
370	19,400	1.7	3.5	5.2
380	16,900	1.7	3.5	5.3
	Av.	1.63	3.43	5.15
) (m))	(d) $R = p - c$	hloropheny	$1 (K_{c} \times 10)$	46.50
λ(mμ)	<b>د</b> ۱۵ ۵۵۵	15.7-	30.4	40.0
350	16,200	1.00	1.0	2.2
360	13,100	0.86	1.4	1.8
370	10,400	0.81	1.3	1.7
	Av.	0.89	1.43	1.90

Values for  $\Delta H_c^0$ ,  $K_c$  and  $\Delta F_c^0$  for each compound at 25° were obtained by use of equation 2

$$\Delta H_{\rm c}^{0} = -R[\mathrm{d} \ln K_{\rm c}/\mathrm{d}(1/T) + \alpha T^{2}] \qquad (2)$$

In this equation,  $\alpha$  is the coefficient of thermal expansion of carbon tetrachloride in the temperature range covered. Finally, values for  $\Delta S_c^0$  at 25° were computed. A summary of the  $\Delta F_c^0$ ,  $\Delta H_c^0$  and  $\Delta S_c^0$  values is given in Table II, which also includes values of these quantities for some other halogen complexes for comparison purposes.

halogen complexes for comparison purposes. The data in Table II show the interesting trends pointed out by Keefer and Andrews' for alkylbenzene, dioxane and *t*-butyl alcohol complexes with iodine. It was later observed by Ogimachi, Andrews and Keefer<sup>4</sup> that the ICl complexes of eight donors also fit the same linear plots. It is quite probable that the data in Table II would also fit these plots if converted to a mole fraction-formation basis from the concentration-dissociation basis used by the present authors.

Apparently the linear relationships between  $\Delta F$  and  $\Delta H$ and between  $\Delta H$  and  $\Delta S$  are of wide application to equilibria of the type  $DX_2 = D + X_2$ . The relationships appear to hold even for the compounds  $R_2SeBr_2$  in which the bonding is Br-Se-Br, in contrast to that in the iodine complexes in which the bonding Se—I-I has been found.<sup>6</sup> However, it should be noted that the structural studies were made on

(4) R. M. Keefer and L. J. Andrews, J. Am. Chem. Soc., 77, 2164 (1955).

(5) N. Ogimachi, L. J. Andrews and R. M. Keefer, *ibid.*, 77, 4202 (1955).

(6) J. D. McCullough, G. Y. Chao and D. E. Zuccaro, Acta Cryst., 12, 815 (1959).

#### TABLE II

MOLAR FREE ENERGIES, ENTHALPIES AND ENTROPIES OF Dissociation in Carbon Tetrachloride Solution of Some Halogen Complexes at 25°

Ref.	Donor	Halo- gen	∆ <i>Fe</i> °. kcal.	∆ <i>H</i> c⁰. kcal.	Δ.Se". cal./ deg.
7	4-Methoxydiphenylselenium	$Br_2$	5.74	14.4	29
7	3-Methoxydiphenyl-				
	selenium	$Br_2$	4.98	11.3	<b>21</b>
7	Diphenylselenium	Br <sub>2</sub>	4.69	9.7	17
7	4-Chlorodiphenylselenium	Br <sub>2</sub>	4.15	13.1	30
a	Dimethyl selenide	$I_2$	3.68	8.6	16.4
a	4,4'-Dimethoxydiphenyl-				
	selenium	$I_2$	2.48	7.6	17.1
a	4,4'-Dimethyldiphenyl-				
	selenium	$I_2$	2.19	6.9	16.4
8	Diphenylselenium	$I_2$	1.97		
a	4,4'-Dichlorodiphenyl-				
	selenium	$I_2$	1.26	4.2	10.0
n ]	Present study.				

crystalline solids while the equilibria were studied in dilute solution. The structures of the complexes in solution are accordingly subject to some uncertainty. The reported values of  $\Delta H_c^0$  and  $\Delta S_c^0$  for 4-chlorodiphenylselenium dibromide suggest that these are too high and that they should be redetermined.

Acknowledgments.—The authors gratefully acknowledge the financial assistance of the National Science Foundation under Research Grant NSF-G5922 and the kindness of the Western Data Processing Center, U.C.L.A., in providing free access to the IBM 709.

(7) J. D. McCullough and M. K. Barsh, ibid., 71, 3029 (1949).

(8) J. D. McCullough, *ibid.*, **64**, 2672 (1942).

# THE AUTOXIDATION OF METHOXYPHENYLALKANES

#### BY A. MERTWOY, M. TRACHTMAN AND H. GISSER

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In the autoxidation of branched chain amyl adipates<sup>1</sup> it was observed that the distance of the tertiary carbon atom from the ester group exerts a considerable effect on the oxidation rate, the rate decreasing as the distance is decreased. The difference in the oxidation rate was attributed to resonance at the ester group which made electrons less available to the tertiary carbon atom as it moves progressively closer to the ester group. In the oxidation of two isomeric octyl sebacates<sup>2</sup> it was found that bis-(2-ethylhexyl) sebacate oxidized at a faster rate than bis-(1-methylheptyl) sebacate. This difference in oxidation rates was attributed to the shielding effect of the ester group, the effect decreasing with distance and having little if any effect beyond two carbon atoms.

In the oxidation of aralkyl hydrocarbons<sup>3</sup> it has been reported that the rate of reaction of a peroxy radical with *para*-substituted cumenes or toluenes shows a pronounced polar effect. Electron with-

M. W. Rigg and H. Gisser, J. Am. Chem. Soc., 75, 1415 (1953).
 C. M. Murphy and H. Ravner, Ind. Eng. Chem., 44, 1607 (1952).

(3) G. A. Russel, J. Am. Chem. Soc., 78, 1046 (1956).

drawing groups decrease and electron supplying groups increase the reactivity of the  $\alpha$ -hydrogen atoms of cumene or toluene toward a peroxy radical. It has also been shown<sup>4</sup> that electron-withdrawing groups decrease the rate of reaction of benzaldehyde with peroxy radicals. The above work would seem to confirm the work of Rigg and Gisser<sup>1</sup> wherein they state that the rate of oxidation is due to the proximity of the oxidation site to areas of high or low electron density.

If the oxidation rate is dependent on the proximity of tertary carbons to centers of electron density as suggested by Rigg and Gisser,<sup>1</sup> the effect of distance observed by them with esters should be reversed in the oxidation of compounds having an electron releasing group instead of the ester group. To accomplish this, several methyl-1-*p*methoxyphenylalkanes (which have a high electron density at the carbon atom adjacent to the benzene ring) were prepared in which the distance of the tertiary carbon atom from the ring was varied, and their autoxidation rates studied.

#### Experimental

1-Methyl-1-*p*-methoxyphenylbutane was prepared by the method of Tsukervanik and Nazarova<sup>7</sup> from anisole and pentanol-2 with anhydrous aluminum chloride. The distilled material was collected at  $81-82^{\circ}$  at 3.5 mm. The yield was 120 g. (25%),  $n^{20}$  observed 1.49865, reported 1.499. Anal. Calcd. for  $C_{12}H_{18}O$ : C, 80.85; H, 10.18. Found: C, 80.35; H, 10.16.

2-Methyl-1-*p*-methoxyphenylbutane was prepared from *p*-methoxybenzyl bromide and *se*-butylmagnesium bromide. The distilled material was collected at  $82-84^{\circ}$  at 2 mm. The yield was 84 g. (25%),  $n^{\infty}$ p observed 1.49982. Anal. Calcd. for C<sub>12</sub>H<sub>18</sub>O: C, 80.85; H, 10.18. Found: C, 81.43; H, 9.74.

3-Methyl-1-*p*-methoxyphenylbutane was prepared in a manner similar to 1-methyl-1-*p*-methoxyphenylbutane<sup>8</sup> from anisole and isoamyl chloride. The distilled material was collected at  $78-79^{\circ}$  at 1.25 mm. The yield was 70 g. (10%),  $n^{\alpha}p$  observed 1.50752, reported 1.5112. Anal. Calcd. for  $C_{12}H_{19}O$ : C, 80.85; II, 10.18. Found: C, 81.23; H, 9.95.

4-Methyl-1-*p*-methoxyphenylpentane was prepared in a manner similar to 2-methyl-1-*p*-methoxyphenylbutane from isoamylmagnesium bromide and *p*-methoxybenzyl bromide. The distilled material was collected at  $125-127^{\circ}$  at 9.0 mm. The yield was 91 g. (50%),  $n^{20}$  observed 1.49524. Anal. Calcd. for C<sub>13</sub>H<sub>21</sub>O: C, 81.25; 11, 10.42. Found: C, 81.23; H, 10.39.

**Bis-(1,3-dimethylbutyl) adipate** was prepared by esterification of 1,3-dimethylbutyl alcohol and adipic acid with a catalytic quantity of *p*-toluenesulfonic acid monohydrate.

**Oxidation** —Oxidation rates were determined by measuring the rate of oxygen consumption using the apparatus and technicue previously described.<sup>1</sup> The rates of oxidation of the methyl-*p*-methoxyphenylalkanes were determined at 120°, using 5.36  $\times$  10<sup>-5</sup> *M* copper 2-ethyl hexoate as catalyst per mole of alkane. The oxidation rates of bis-(1,3dimethylbutyl) adipate and its mixture with 1-methyl-1*p*-methoxyphenylbutane were determined at 110° without catalyst.

#### **Results and Discussion**

The oxidation data obtained show that for 2methyl-1-*p*-methoxyphenylbutane, 3-methyl-1-*p*methoxyphenylbutane and 4-methyl-1-*p*-methoxyphenylpentane the oxidation rate decreases as the distance of the tertiary carbons from the center of high electron density increases. (Relative oxi-

<sup>(4)</sup> C. Walling and E. A. McElhill, ibid., 73, 2927 (1951).

<sup>(7)</sup> J. P. Tsukervanik and Z. N. Nazarova, C. A., **31**, 5778 (1937).
(8) I. P. Tsukervanik and V. D. Tambovtseva, *ibid.*, **34**, 4729 (1940).

dation rates are 1.00, 0.548 and 0.211, respectively.) However, 1-methyl-1-*p*-methoxyphenylbutane oxidized at the lowest rate (relative rate 0.199). This may be explained by noting that 1-methyl-1*p*-methoxyphenylbutane-1-hydroperoxide may decompose in the same manner as cumene hydroperoxide<sup>5</sup> yielding *p*-methoxyphenol which is an inhibitor.<sup>6</sup> (It may be noted that *p*-methoxytoluene and anisole appear to be good retarders in the oxidation of cumene.<sup>3</sup>)

(5) Hock and Lange, Ber., 77, 257 (1914).

(6) G. E. Penketh, J. Appl. Chem., 7, 512 (1957).

If the slow oxidation of 1-methyl-1-*p*-methoxyphenylbutane is due to the inhibition by *p*-methoxyphenol formed during the oxidation, then the former compound should have an oxidation inhibiting effect on other compounds. Earlier work<sup>1</sup> has shown that bis-(1,3-dimethylbutyl) adipate autoxidizes rapidly. However, when mixed with 25 mole % of 1-methyl-1-*p*-methoxyphenylbutane the oxidation rate is reduced by a factor of 10<sup>3</sup>. It is apparent that 1-methyl-1-*p*-methoxyphenylbutane has a strong inhibiting effect.

# COMMUNICATION TO THE EDITOR

# THE FREE-RADICAL CLEAVAGE OF PEROXYBENZOIC ACID

Sir:

We have found evidence that peroxybenzoic acid in benzene solutions can decompose into free radicals, a type of reaction which had not been known for peroxycarboxylic acids. Solutions of this peroxyacid in benzene were studied using a small amount of  $\alpha, \alpha$ -diphenyl- $\beta$ -picrylhydrazyl as a free-radical scavenger, as described by Bawn and Mellish. The decrease in optical density at 520 m $\mu$  was followed with a Beckman Model DU spectrophotometer until most of the hydrazyl had been consumed, thus giving measurements over a wide range of hydrazyl concentration. The data follow the rate law

#### $-\mathrm{d}\mathfrak{D}/\mathrm{d}t = k[\mathrm{P}]$

where  $\mathfrak{D}$  is the optical density, and [P] is the concentration of peroxy acid. This rate law with a large excess of peroxybenzoic acid is best explained by a first order cleavage of peroxide molecules into two free radicals (1), presumably by rupture of the O-O bond. Results of a number of experiments are listed in the table. The rate constant, k, is for the first order, free-radical decomposition of the peroxide. The activation energy for this process is approximately 30 kcal., about the same as the activation energy for the corresponding freeradical cleavage of benzoyl peroxide. The specific rate constants, however, are only one-tenth as large.

In 1-butanol solutions the rate of decrease of optical density is very much less than in benzene solution, and, depending on the history of the peroxybenzoic acid, the reaction is first to second order in diphenylpicrylhydrazyl. Any free-radical cleavage at a rate comparable to the rate in benzene would have given an over-all zero or fractional order reaction with hydrazyl. These results indicate that free-radical cleavage does not occur to any significant extent in this solvent.

(1) C. E. H. Bawn and S. F. Mellish, Trans. Faraday Soc., 47, 1216 (1951).

		Тав	BLE I	
<b>Results in Benzene</b>				
D	Temp.,	Initial conen. hydrazyl,	Conen, PBA, [?]	
Run	°U.	mole/l.	mole/l.	K X Sec.
23	60	$4.0 \times 10^{-6}$	$0.959 \times 10^{-2}$	$1.21 \times 10^{-i}$
<b>26</b>	60	4.0	1.918	1.12
27	60	4.0	0.959	1.01
28	60	4.0	1.341	0.95
29	60	-1.0	0.575	1.05
30	60	4.0	1.918	0.96
31	60	4.0	1.918	1.05
32	60	8.0	1.918	1.31
			Average	1.08
33	65	8.0	0.959	2.07
34	65	8.0	0.575	2.14
35	65	8.0	0.1916	2.18
36	65	8.0	1.342	1.94
37	65	8.0	0.384	2.35
			Average	2.14

This difference in behavior may be due to the difference in structure of peroxybenzoic acid in these two solvents. In benzene, peroxybenzoic acid exists in the internally hydrogen bonded form  $(I)^2$ ; in 1-butanol the ring presumably is opened and the acid is hydrogen bonded to the solvent (II). In the open form (II) the electrons in the O–O bond are displaced toward the oxygen at-



tached to carbon. This polarization may prevent appreciable free-radical cleavage of the peroxide bond. In the cyclic form (I) the electron withdrawing benzoyl group also acts through the hydrogen bond to draw electrons toward the hy-

(2) D. Swern, L. P. Witnauer, C. R. Eddy and W. E. Parker, J. Am. Chem. Soc., 77, 5537 (1955).

drogen in the O-OH bond, in addition to drawing electrons toward the oxygen attached to carbon, thus decreasing the polarization of the O-O bond enough to permit the observed slow free-radical cleavage of peroxybenzoic acid.

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# ON THE USE OF TANTALUM KNUDSEN **CELLS IN HIGH TEMPERATURE** THERMODYNAMIC STUDIES OF OXIDES

Sir:

It has been shown by several investigators<sup>1-5</sup> that the volatility of oxides is greatly enhanced in the presence of tantalum. Chupka, et al.,<sup>4</sup> have shown that this is due to the formation of gaseous TaO and TaO<sub>2</sub>. Inasmuch as heats of formation of these species have been reported,6 it might appear that tantalum cells would still be useful for oxide studies provided the presence of gaseous tantalum oxides in the effusing vapors is taken into account. The purpose of this note to point out that such corrections will not necessarily lead to meaningful equilibrium constants for reactions because of the manner in which TaO(g)and  $TaO_2(g)$  are formed and escape the Knudsen cell.

For some time we have been studying the vaporization of rare earth oxides by the Knudsen effusion technique. These oxides vaporize much more readily from tantalum than from tungsten crucibles.<sup>5</sup> Figure 1 shows the isothermal rate of weight loss of a tantalum Knudsen cell<sup>7</sup> containing  $La_2O_3$  as a function of the ratio of the total weight of material vaporized to the weight of the initial charge of La<sub>2</sub>O<sub>3</sub>. It should be noted that the steady rate of vaporization persists beyond the point where the weight of material vaporized exceeds the weight of  $La_2O_3$  originally in the crucible. This was assumed to result from the escape of TaO(g) and  $TaO_2(g)$  through the orifice in equilibrium with the LaO(g) arising from  $La_2O_{3.5}$ Subsequent mass spectroscopic experiments, using a Bendix time-of-flight instrument, under identical conditions, have shown that this assumption was erroncous.

In these experiments, the *only* vapor observed effusing from the Knudsen orifice was LaO. The intensity of La<sup>2+</sup> varied with amount vaporized in a manner identical to that shown in Fig. 1.

(2) R. J. Ackermann and R. J. Thorn, ibid., 78, 4169 (1956).

(4) W. A. Chupka, J. Berkowitz and M. G. Inghram, J. Chem. Phys., 26, 1207 (1957).

(5) P. N. Walsh, H. W. Goldstein and D. White, J. Am. Ceram. Soc., 43, 229 (1960).

(6) M. G. Inghram, W. A. Chupka and J. Berkowitz, J. Chem. Phys., 27, 569 (1957).

(7) The empty tantalum crucible was thoroughly degassed at 2400° in vacuo just prior to this set of runs.



No tantalum oxides were observed<sup>8</sup> until beyond the flat in the isotherm and then only when the temperature was increased 100° or more. It is therefore concluded that most of the oxygen from La<sub>2</sub>O<sub>3</sub> is absorbed in the wall of the cell, through which it diffuses with subsequent evolution of TaO(g) and  $TaO_2(\mathbf{g})$  from the exterior surface of the crucible.<sup>9</sup> We do not believe that any equilibrium involving gaseous tantalum oxides is established on the cell.

There is further evidence to support the conclusion reached here. Tantalum Knudsen cells containing  $T\epsilon_2O_5$  lose weight at a rate of 30 to 50 times that predicted from the reported thermodynamic properties of TaO(g) and  $TaO_2(g)^6$ , become heavily etched on the *outside* at the sample level. A  $1/_{16}$  crucible wall has been eroded completely in less than one hour at 2050°K.

Tungsten crucibles may exhibit similar behavior, but to a lesser extent. For example, Drowart, et al.,<sup>10</sup> mass spectrometrically observed that the effusate from a tungsten cell containing Al<sub>2</sub>O<sub>3</sub> showed a lower W/Al ratio than observed in total weight loss measurements.<sup>2,11</sup>

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(8) The upper limit of these was 1/500 of the LaO + intensity.

(9) Gases formed in this manner would be prevented from reaching the ionization chan ber by the collimating system.

(10) J. Drowart G. De Maria, R. P. Burns and M. G. Inghram, J. Chem. Phys., 32, 1366 (1960).

(11) R. J. Ackermann and R. J. Thorn, Argonne National Laboratory Report ANL-5824, January, 1958.

# RADIOLYSIS OF FERROUS ION SOLUTIONS IN HEAVY WATER WITH ALPHA PARTICLES AND GAMMA RADIATION

Sir:

A previous communication<sup>1</sup> reported ferric ion vields,  $G(Fe^{+3})$ , for the radiolysis of heavy water solutions of ferrous sulfate by cobalt-60 gammaradiation. These experiments have been repeated

(1) C. N. Trumbore and A. H. W. Aten, Jr., J. Am. Chem. Soc., 78, 4179 (1956).

<sup>(1)</sup> L. Brewer and A. Searcy, J. Am. Chem. Soc., 73, 5308 (1951).

<sup>(3)</sup> L. Navias, Am. Ceramic Soc. Bull., 38, 256 (1959).

and the results of these and other experiments using low energy alpha particles are reported.

Solutions irradiated were 1 mM in ferrous sulfate, 1 mM in sodium chloride and 0.4 M in sulfuric acid. The heavy water was purified in a manner previously described<sup>2</sup> and was found to contain 99 atom % deuterium in the solvent hydrogen. Measurements of the heavy water ferric sulfate complex were made on a Beckman DU spectrophotometer at 3020 Å. using the value of 2350 as the molar extinction coefficient for solutions containing 99% and 50% deuterium in the solvent hydrogen. The corresponding value for light water solutions was taken as 2250. Radiation sources were a cobalt-60 source previously described<sup>3</sup> and a collimated polonium-210 alpha particle source.<sup>4</sup> The energy of the alpha particles absorbed by the ferrous sulfate solutions was 3.4  $\pm$  0.2 Mev.

 $G(\text{Fe}^{+3})$  for the ferrous sulfate solutions for cobalt-60 gamma-radiation are found to be: 17.1  $\pm$  0.3 for solutions 99% D in solvent hydrogen and 16.1  $\pm$  0.2 for solutions containing 50% D. These values are based on a  $G(\text{Fe}^{+3})$  of 15.6 for light water solutions.<sup>5</sup> The ferric ion yield for heavy water solutions (99%) agrees with several other reported values.<sup>67</sup>

 $G(Fe^{+3})$  for 99% D solutions identical with those described above irradiated with 3.4 Mev. alpha particles is found to be 5.3 for air saturated solutions and 3.9 for air free solutions,  $G(Fe^{+3})_{air}$  and  $G(Fe^{+3})_{vac}$ , respectively. These values may be compared with yields for identical light water solutions established by N. Miller<sup>8</sup> using the same

(2) E. J. Hart, J. Am. Chem. Soc., 73, 68 (1951).

(3) R. A. Blomgren, E. J. Hart and L. S. Markheim, Rev. Sci. Instr., 24, 298 (1958).

(4) E. J. Hart and J. Terandy, ibid., 29, 962 (1958).

(5) C. J. Hochanadel and J. A. Ghormley, J. Chem. Phys., 21, 880 (1953).

(6) T. J. Hardwick, ibid., 31, 226 (1959).

(7) H. A. Mahlman and J. Boyle, J. Am. Chem. Soc., 80, 773 (1958).
(8) N. Miller, private communication. See also Radiation Research.

9, 633 (1958), for yields with 10 mM FeSO4.

alpha source:  $G(Fe^{+3})_{air} = 4.7$  and  $G(Fe^{+3})_{vac} = 3.4.9$ 

As with cobalt gamma radiation, the ferric ion yields with alpha particles are about 10% higher in heavy water solutions than in light water. If the normal mechanism for the oxidation of ferrous sulfate by ionizing radiation is assumed,<sup>10</sup> the ratio G(H)/G(D) can be calculated from the equation

$$\frac{G(Fe^{+3})_{\text{air. H2O}} - G(Fe^{+3})_{\text{vnc. H2O}}}{G(Fe^{+3})_{\text{air. D2O}} - G(Fe^{+3})_{\text{vac. D2O}}} = \frac{G(H)}{G(D)}$$

since:

 $G(Fe^{+3})_{air} = 3G(H) + G(OH) + 2G(H_2O_2) + 3G(HO_2)$ and:

 $G(Fe^{+3})_{vac} = G(H) + G(OH) + 2G(H_2O_2) + 3G(HO_2)$ 

For 3.4 Mev. alpha particle radiation, the ratio G(H)/G(D) is found to be 0.93. This figure is identical, within experimental error, to the same ratio of radical yields calculated from data reported by other investigators for cobalt gamma-radiation<sup>6,7,11</sup> and for 220 kvp. X-rays.<sup>12</sup>

If the preceding reasoning is correct, any explanation of the isotope effect in water radiolysis must take into account this constant ratio of hydrogen atom yields despite the large change in linear energy transfer of the radiations employed.

This work was performed under the auspices of the United States Atomic Energy Commission at the Argonne National Laboratory.

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(10) A. O. Allen, Int. Conf. on Peaceful Uses of Atomic Energy, Vol. 7, 513, United Nations, New York, 1956.

(11) D. A. Armstrong, E. Collinson and F. S. Dainton, Trans. Faraday Soc., 55, 1375 (1959).

(12) K. Coatsworth, E. Collinson and F. S. Dainton, *ibid.*, 56 1008 (1960).

<sup>(9)</sup> All reported values for 3.4 Mev. alpha-particles are related to  $G(\text{Fe}^{+3})_{air} = 4.80$  for solutions 10 mM in FeSO<sub>4</sub>, 0.4 M in H<sub>2</sub>SO<sub>4</sub> and 1 mM in NaCl.<sup>8</sup>

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