## THE JOURNAL OF

# PHYSICAL CHEMISTRY

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## CONTENTS

M. Mirnik, F. Flajsman, K. F. Schulz and B. Teżak: The Negative Activity Limit of Stability and the Coagulation Values of the Silver Halides	1473
G. Nareimhan: On the Equation of Motion of a Particle in a Centrifugal Field	1476
C. N. Spalaris: The Micropore Structure of Artificial Graphite	1480
Jih-Heng Hu and George E. MacWood: The Solubility of Hydrogen in Diborane	1483
Ell S. Freeman: The Kinetics of the Thermal Decomposition of Sodium Nitrate and of the Reaction between Sodium Nitrite and Oxygen	1487
G. W. Leonard, Maynard E. Smith and David N. Hume: Thiocyanate Complexes of Lead and Thallium in Solution.	1493
Naokazu Kolzumi and Tetsuya Hanai: Dielectric Properties of Lower-membered Polyethylene Glycols at Low Frequencies	1496
S. G. Hindin and S. W. Weller: The Effect of Pretreatment on the Activity of Gamma-Alumina, L. Ethylene Hydrogenation	1501
S. W. Weller and S. G. Hindin: The Effect of Pretreatment on the Activity of Gamma-Alumina, II. Hydrogen-Deuterium Exchange	1508
Joseph Yudelson and Bernard Rabinovitch: The Light Scattering Behavior of Three Dimensional Network Gela	1512
F. I. Shipko and David L. Douglas: Stability of Ferrous Hydroxide Precipitates	1519
Harold F. John and Henry E. Bent: Separation of Organic Solutions by Thermal Diffusion	1524
S. H. Bauer and R. E. McCoy: Energetics of the Boranes. III. The Enthalpy and Heat Capacity of Trimethylamine-Trifluoroborane as Determined by the Drop Method.	1529
Hurley D. Cook and Herman E. Ries, Jr.: Effects of the Spreading Solvent on Monolayers as Determined by Pressure-Area and Radio- activity-Area Isotherms.	1533
Frances E. Helders and John D. Ferry: Non-Newtonian Flow in Concentrated Solutions of Sodium Desoxyribonucleate	1536
J. W. S. Jamieson and C. A. Winkler: The Reactions of Ethylenimine and N-Methylethylenimine with Atomic Hydrogen and their Re- lation to Complexes in Active Nitrogen Reactions.	1542
Alfred A. Schilt and G. Frederick Smith: Acid Dissociation Constants of Substituted 1.10-Phenanthrolines	1546
Robert B. Anderson, W. Keith Hall, James A. Lecky and Karl C. Stein: Sorption Studies on American Coals	1548
Gunnar O. Assarsson: Hydrothermal Reactions between Calcium Hydroxide and Amorphous Silica in Atmospheres of Unsaturated Steam	1550
I. M. Kolthoff and A. M. Shams El Din: Reduction of Hexavalent Chromium at the Rotated Platinum Electrode. Permeability of the Film Formed	1564
K. H. Gaver and Leo Woontner: The Solubility of Ferrous Hydroxide and Ferric Hydroxide in Acidic and Basic Media at 25°	1569
G. H. Cartledge: The Passivation of Iron by Osmium(VIII) Oxide and the Origin of the Flade Potential	1571
Frances E. Helders, John D. Ferry, Hershel Markowitz and L. J. Zapas: Dynamic Mechanical Properties of Concentrated Solutions of Sodium Desorvribonucleate.	1575
NOTES: Ralph A. Hovermale and Paul G. Sears: Dipolar Ions in Non-aqueous Solvents. I. Dielectric Increments as Supporting Evidence for the Dipolar Structure of Sulfamic Acid	1570
Denie W Schmidt Ian Kroch-Moe and Herold D Rele · Smell Angle X-Ray Scattering by Aluminum Hydroxide Cal	1580
ran w. Schmudt, jan Aloga-Mod and Halou D. Date. Date. The Analy Scattering of Arbumum Aydronic Sci	1500
Einer J. Huber, Jr., Barl J. How and Chaines J. Honey, Jr The Heat of Combusion of Hubins	1502
Danis waits claim - The Dialectic Properties of Solid Nitrodichlarowavilance	1594
Rebuen B, wood and Carl Boynes. The Delectric Hopeneo, both information of systems and the South Constant of the South Constant of Could be and the South Could	1595
R. M. Dell, D. F. Klemperer and F. S. Stone: Thermal Effects in the Chemisorption of Oxygen on Nickel: A Comparative Investi-	1594
gaun deing fores and seponted and seponted and the second se	1588
m. Construct and a location source of the start Study of the Photolysis of Pentaborane Vanor	1580
Toman Durants of Wards and William L. Korst: Solutions of Flynbium and Ytterhuim Metals in Liquid Ammonia	1590
R I. Rush, D. C. Ames, R. W. Horst and I. R. MacKayi, Some Properties of the Systems Diogane-Butyl Alcohols.	1591
Terrell L. Hill: Swelling of Protein Molecules in Solution. II.	1593
M. Garcia Morin. Grover Paulett and Marcus E. Hobbas - Nuclear Magnetic-Resonance Chemical Shift Determinations by Means of a	
Concentric Cylinder Sample Cell.	1594

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Robert W. Rosenthal, Reuben Proper and Joseph Egstein: The Distribution of Some Rhosphonosuoridates between Organic and Water.	Solvents 1596
COMMUNICATIONS TO THE EDITOR: Simon Larach and John Turkevich: Magnetic Properties of Zinc Sulfide Phosp Manganese Activator	hors with 1598
C. T. O'Konski and W. I. Higuchi: The Kinetics of Nucleation in Turbulent Jets	
James D. Ray and Richard A. Ogg. Jr.: The Anomalous Entropy of Potassium Nitrite	

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# THE JOURNAL OF PHYSICAL CHEMISTRY

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# THE NEGATIVE ACTIVITY LIMIT OF STABILITY AND THE COAGULATION VALUES OF THE SILVER HALIDES

BY M. MIRNIK, F. FLAJŠMAN, K. F. SCHULZ AND B. TEŽAK

Contribution No. 55 from the Laboratory of Physical Chemistry of the University of Zagreb, Croatia, Yugoslavia Received December 12, 1955

The negative activity limit of stability was determined for the AgCl and AgBr precipitating systems at various concentrations of neutral electrolytes (NaNO<sub>3</sub>, Ba(NO<sub>3</sub>)<sub>2</sub>) and amounts when the concentration of neutral electrolyte is  $<10^{-3}$  N to a value of pAg 6.2 which is equal to the value in the AgI system. The activity limits of the three halides are practically the same in the region of NaNO<sub>3</sub> 0.1 to 0.0001 N. The activity limit shifts toward higher pAg values with the increasing concentration of the neutral electrolyte and no continuous change into the coagulation values can be observed. The coagulation values are practically independent of pAg. The points  $-\log_{10}$  [Na<sup>+</sup>] = 1, pAg = 8;  $-\log_{10}$  [Ba<sup>++</sup>] = 2.6, pAg = 7.2 and  $-\log_{10}$  [La<sup>3+</sup>] = 4.1, pAg = 6.2 can be considered as the intersections of the coagulation value lines with the lines of activity limits.

The isoelectric or equivalency coagulation can be characterized quantitatively by the negative<sup>1</sup> and positive<sup>2</sup> activity limits of stability as shown previously for the AgI system. To elucidate the influence of the halide component the negative limit was determined for all three halides with various concentrations of NaNO<sub>3</sub>. To elucidate the influence of the valency of the neutral electrolyte upon stability the negative limit was determined for the AgI system with various concentrations of Ba-(NO<sub>3</sub>)<sub>2</sub>, and the coagulation values were determined for Na<sup>+</sup>, Ba<sup>2+</sup> and La<sup>3+</sup> in the negative stability region from pI 1 to the negative activity limit of stability.

By following the intensity of scattered light through longer periods of time various precipitation processes characteristic for the Ag halides were observed.

The purpose of this investigation was to gather new experimental facts necessary for the development of the theories of stability and of the electrical double layer, and also as an experimental check of the existing ones.

#### Experimental

The experimental technique was essentially the same as described previously.<sup>1</sup> The precipitation processes were followed by light scattering measurements with the Pul-

frich photometer combined with the Zeiss tyndallometric attachment.  $% \left[ {{\left[ {{{\rm{T}}_{\rm{T}}} \right]}_{\rm{T}}}} \right]$ 

The activity measurements were performed with the potentiometric arrangement ulready described. A rotating paraffined Ag-AgBr electrode of the electrolytic type was used. The electrodes were prepared as the AgI electrodes. The (unparaffined) AgBr electrode also shows deviations from the theoretical, although smaller than for the Ag-AgI electrode. With paraffined Ag-AgI electrodes practically the same results were obtained (Fig. 2). Therefore in the AgCl systems the Ag-AgI electrode was used. The standard was a saturated calomel electrode.

Ordinary unparaffined AgI and AgBr electrodes do not follow the Nernst formula in the region of pI 5 to pAg 5. Neither by rotation of the electrodes, nor by keeping the rotating electrodes for many hours in a solution of the same pAg, can the theoretically expected potentials be obtained. The paraffined electrodes, which gave a satisfactory indication of the pAg values, were developed by chance.

The precipitating systems for the determination of the negative activity limit were prepared in two different ways: the first method was as follows. To 1000 ml. of the agitated Na halide + NaNO<sub>3</sub> solution a predetermined quantity of 0.01 N AgNO<sub>3</sub> solution was added, producing a sol of the desired concentration of AgBr or AgCl with a pAg > 6.5. Subsequently small amounts of the AgNO<sub>3</sub> solution ware added from a 2-ml. buret at 5-minute intervals. One minute after each addition a 10-ml. sample was taken into a test-tube and the light scatter was followed through longer periods of time up to 7 days. The cell e.m.f. was measured just before a new addition of AgNO<sub>3</sub>.

The second method was analogous to the first except that each system was prepared separately. To 50 ml. of the agitated Na halide + NaNO<sub>3</sub> solution 50 ml. of the AgNO<sub>3</sub> solution was added from a pipet with a constant speed during 3 minutes. The concentration of the solution was prede-

M. Mirnik and B. Težak, Trans. Faraday Soc., 50, 65 (1954).
 M. Mirnik and B. Težak, Arhiv kem., 23, 59 (1951).

termined to give the desired final concentration of AgI,  $NaNO_3$  and the desired pAg.

The coagulation values in the region pI 5 to 10 were determined by preparing 200 ml. of a sol with 0.0002 *M* AgI formed with a desired pAg in the described way. Samples of this sol (5.0 ml.) were mixed with 5.0 ml. of solutions of NaNO<sub>3</sub>, Ba(NO<sub>3</sub>)<sub>2</sub> and La(NO<sub>3</sub>)<sub>3</sub> of various concentrations and the light scatter was measured. The intersections of the tangent on the steepest parts of the 10-minute concentration tyndallograms were taken as the coagulation values.<sup>3,4</sup>

The coagulation values in the region pI 1 to 5 were determined in the same way except that the sols were prepared by mixing equal volumes of sodium halides with AgNO<sub>3</sub> solution plus various concentrations of coagulating electrolyte to produce 0.0005 *M* Ag halide sol.

#### Results

The AgBr System.—For the characterization of the type of precipitation process the plot of the tyndallometric value against the logarithm of time may be used. Figure 1 represents a series of such plots, which differ in the activity of the potential determining ions.



Fig. 1.—The effect of the activity of the potential-determining ions on the plots intensity of scattered light against logarithm of time in the equivalency region of the AgBr system. Concentration of AgBr 0.0001 M; NaNO<sub>3</sub> 0.001 N. Plots of systems with pAg: 7.7, 6.9, 6.6, 6.2, 5.8, 5.0.

A systematic differentiation of the type of process (in the present case the differentiation of the stable process from the isoelectric or equivalency coagulation) can be obtained by plotting the tyndallometric value at a definite time against the pAgvalue. Figure 2 represents an "activity tyndallogram" obtained in this way one minute after addition of each amount of AgNO<sub>3</sub>. The full points were obtained by measurements on systems prepared by the second, and the circles by the first method. The point of intersection of the tangent at the steepest part of these curves with the zero light scattering axis represents the "negative activ-



Fig. 2.—Plots of intensity of scattered light against pAg (activity tyndallograms) representing the isoelectric maximum with the negative activity limit of stability of the AgBr system. Concentration of AgBr 0.0001 M; NaNO<sub>3</sub> 0.001 N; cell, saturated calomel electrode-rotating paraffined Ag-AgBr electrode. Drawn line, first method of preparation of the systems; dashed line, second method (for comparison a paraffined Ag-AgI electrode was used in the later). Time of measurements, 1 minute after each addition of AgNO<sub>3</sub>.

ity limit of stability."<sup>1</sup> The region between the positive<sup>2</sup> and negative activity limits represents the region of isoelectric coagulation (isoelectric maximum).

The values of the negative activity limit of stability obtained with various concentrations of Na- $NO_3$  were used for the construction of the curve in Fig. 4.

The AgCl System.—Two activity tyndallograms obtained in an analogous way for the AgCl system are represented by Fig. 3. The activity limits obtained with various concentrations of NaNO<sub>3</sub> were used for the construction of the composite Fig. 4. Above 0.01 N NaNO<sub>3</sub> it was impossible to measure the negative activity limit. The apparent coagulation values of Na<sup>+</sup> in the AgCl system are too low<sup>3</sup> (ref. 3, II, Fig. 6).

The AgI System.—The negative activity limit and the coagulation values as well as the influence of the concentration of NaNO<sub>3</sub> were determined previously<sup>1</sup> and the results are inserted in Figs. 4 and 5. The coagulation values<sup>3,4</sup> of Na<sup>+</sup>, Ba<sup>2+</sup> and La<sup>3+</sup> were determined by the aid of the 10minute concentration tyndallograms (AgI = 0.0005 M, pI 1–5; AgI = 0.0001 M, pI 5–10) and inserted into Fig. 5.

<sup>(3)</sup> B. Težak, et al., This Journal, 55, 1557, 1567 (1951).

<sup>(4)</sup> B. Težak, et al., ibid., 57, 301 (1953).



Fig. 3.—Plots of the intensity of scattered light against pAg (activity tyndallograms) representing the isoelectric maximum with the negative activity limit of stability of the AgClsystem. Cell, saturated calomel electrode-rotating paraffined Ag-AgI electrode. Concentration of AgCl, first method of preparation, drawn line, 0.001 M; second method, dashed line, 0.0001 M. Concentration of NaNO<sub>3</sub>, 0.001 N. Time of measurements, 1 minute after each addition of AgNO<sub>4</sub>.

#### Discussion

The time tyndallograms as represented in Fig. 1 for the AgBr system and in Figs.<sup>5</sup> 5 and 6 and Fig.<sup>6</sup> 1 for the AgI system, show that the stable processes (*i.e.*, processes with halide activities higher than the activity of the negative limit of stability) have roughly constant critical times, after which the tyndallometric values start to increase. In the AgI system the critical time values lie in the region of a few days (log<sub>10</sub> t-3 to 4); for the AgBr system this time is in the region of a few hours at about log<sub>10</sub> t-2 (Fig. 1). For the AgCl this time is still shorter at log<sub>10</sub> t  $\sim$  1.

The negative activity limits of various halides plotted against the activity of potential determining ions at various concentrations of neutral electrolyte are represented by Fig. 4. The difference between the values of various halides is of the same order of magnitude as the determination errors of the limits of stability and the standardization differences between various electrodes and amounts



Fig. 4.—The influence of the concentration of the NaNO<sub>3</sub> on the negative activity limit of stability of the AgI (circles), AgBr (full points) and AgCl (circles with points) systems. Cell, saturated calomel electrode-rotating paraffined Ag-AgBr or AgI electrode, concentration of Ag halides, 0.0001 M.

in the region of best reproducibility ([NaNO<sub>3</sub>]  $\sim 10^{-2}$  to  $10^{-3}$  N) to about  $\pm 5$  mv. From this it may be concluded that the coagulation induced at the negative limit is caused by the destruction of the double layer causing stability and by the subsequent formation of the layer in which the equilibrium with the Ag activities is established. Thus the layer causing stability should be in all three cases equal.

If the coagulation values of the coagulating ions,  $(e.g., ^{3}$ II, Figs. 4, 5, 6; ref. 7, Fig. 2) are expressed as concentrations of the counterions present (e.g., $Na^+$  from  $NaI + NaNO_3$ ) the plot of coagulation value against pI (Fig. 5) for monovalent ions would be practically constant from pI to pAg 8, for bivalent ions from pI 2.7 to pAg 7.2 and for trivalent from pI 4.1 to pAg 6.3. Experimental evidence for this statement is also provided by Figs.<sup>8</sup> 1 and The values 1, 2.5 and 4.1 are practically equal 2. to the negative logarithms of the coagulation val ues for  $Na^+$ ,  $Ba^{2+}$  and  $La^{3+}$ . They represent the limit of the so-called concentration maximum, i.e., the coagulation induced with the counterions of the potential-determining electrolyte (NaI,  $BaI_2$ ,  $LaI_3$ ).

On the other hand the negative activity limit of stability may be represented as a function of the concentration of neutral electrolyte. The negative limit moves toward higher pAg values when

- (7) B. Težak, Disc. Faraday Soc., 18, 199 (1954).
- (8) K. F. Schulz and B. Težak, Arhiv kem., 26, 187 (1954).

<sup>(5)</sup> M. Mirnik and B. Teżak, Arhiv kem., 21, 109 (1949).



Fig. 5.—The influence of pI upon the coagulation values  $Na^+$ ,  $Ba^{2+}$  and  $La^{3+}$  and upon the negative activity limit of stability in the AgI system. Ordinate: logarithm of the concentration of the neutral coagulating cation. Abscissac: pI or pAg of the cell: "Saturated calomel electrode-Ag-AgI electrode." Concentration of AgI: 0.0005 M, pI 1 to 5; 0.0001 M, pI 5 to 10.

the concentration of the neutral electrolytes approaches their constant coagulation values. The activity limit seems also to be independent of the valency of the counterions as well as their size in low concentrations of the neutral electrolytes. This was checked with  $Cd(NO_3)_2$  and  $Ba(NO_3)_2$  with no other cation present in the concentration 0.0001 N.

Figure 5 shows that no smooth and continuous transition from the function of the activity limit (vertical part) into the function of coagulation val-

ues (horizontal part) occurs and that a very well expressed discontinuity can be observed. This may be considered as a confirmation of the opinion that a sharp distinction between the mechanism of the isoelectric coagulation and the mechanism of coagulation with neutral electrolytes should be made. Previously<sup>1</sup> this was concluded from the difference of the adsorption capacities measured on suspensions which were obtained by both coagulations.

## ON THE EQUATION OF MOTION OF A SPHERICAL PARTICLE IN A CENTRIFUGAL FIELD

#### By G. Narsimhan

Department of Chemical Engineering, Laxminarayan Institute of Technology, Nagpur University, Nagpur, India Received February 14, 1956

The equations of motion of a particle settling in a centrifugal field, under ultimate streamline and eddying conditions have been completely solved. Subsidiary expressions have been derived to compute the optimum feed rate to continuous centrifuges. In deriving the analytical expression for the velocity of a particle settling ultimately under eddying conditions, an appropriate boundary condition has been chosen, recognizing the fact that the particle has successively passed through the streamline and buffer zones involving different force fields before encountering fully developed eddying resistance. This important fact appears to have been overlooked by previous investigators.

The critical mathematical relationship governing the velocity of migration of a particle of a dispersed phase in a continuous medium was first developed

by Stokes, as the law that bears his name.<sup>1</sup> Am-

(1) G. G. Stokes, "Mathematical and Physical Papers," Trans. Cambridge Phil. Soc., Vol. 9, 1901, Part II.

Nov., 1956

bler<sup>2</sup> analyzed the mathematical aspect of continuous centrifuges for predicting the performance of industrial equipment. There have been relatively few fundamental studies on the dynamics of particles in a centrifugal field, when compared with the availability of a large amount of data for performance characteristics of industrial machines. Coulson and Richardson<sup>3</sup> have indicated the general equation of motion of suspended particles in a centrifugal field and given the approximate solution. The present paper will deal with the derivation of a rigorous analytical solution of the general equation of motion with the help of appropriate boundary conditions.

The rate of phase separation in a centrifuge is considerably greater than that obtained with gravitational settling but the particles do not attain a constant terminal velocity because the accelerating force increases as the particles approach the walls of the basket.

Figure 1a represents a section of a tubular centrifuge of radius  $x_w$ . Under the action of centrifugal force developed when the basket is rotated at high speed, the surface of the liquid contained in the basket takes on the shape of a paraboloid. The equation of a section of the surface through the center of rotation is

$$y = \frac{\omega^2 / x^2}{2g} + y_0 \tag{1}$$

At high speeds of rotation, the slope of the liquid surface is very high and therefore the liquid surface is almost vertical. The paraboloid is not complete

	NOMENCLATURE
A	constant
B	constant
d	particle diameter, ft.
g	acceleration due to gravity, $ft./sec.^2$
Ή	height of the centrifuge, ft.
$k_1 k_1$ etc.	constants
p	a function
Q	vol. rate of flow, $ft.^3$ /sec.
t	time, sec.
v	velocity, ft./sec.
x	
y i	Cartesian coördinates
z	

Greek symbols

$\alpha_1, \alpha_2$	roots of the eq. 3
β, λ	constants
ω	angular velocity, sec. $^{-1}$
ρ	density lb./ft. <sup>3</sup>
μ	viscosity lb./ft. sec.
φ	function, defined by eq. 23

and  $y_0$  is negative. This condition is represented in Fig. 1b.

Consider a fluid element at a distance y from the bottom of the basket, rotating with the angular velocity  $\omega$ . Let the radius of the inner surface of the liquid be  $x_i$ . For a spherical particle of diameter d, density  $\rho_s$ , settling under streamline conditions, the equation of motion of the particle in the radial direction is

$$\frac{\pi d^3}{6} (\rho_s - \rho) x \times \omega^2 - 3\pi\mu d \times \frac{\mathrm{d}x}{\mathrm{d}t} - \frac{\pi d^3}{6} (\rho_s - \rho) \frac{\mathrm{d}^2 x}{\mathrm{d}t^2} = 0 \quad (2)$$

(2) C. M. Ambler, Chem. Eng. Prog., 48, 150 (1952).

where the first term of LHS represents the centrifugal force, the second, the drag and the third, the accelerating force.

Dividing throughout by  $\frac{\pi d^3}{6}(\rho_{\rm s}-\rho)$ , equation 2 may be rewritten as

 $\frac{\mathrm{d}^2 x}{\mathrm{d}t^2} + \frac{18\mu}{d^2(\rho_s - \rho)} \times \frac{\mathrm{d}x}{\mathrm{d}t} - \omega^2 x = 0$ 

The primitive of the above equation may be written as

$$x = A \exp(\alpha_1 t) + B \exp(\alpha_2 t)$$
(4)

where  $\alpha_1$  and  $\alpha_2$  are the roots of the equation 3

$$\alpha_{1} = \frac{-9\mu}{d^{2}(\rho_{s} - \rho)} + \left\{ \frac{9\mu}{d^{2}(\rho_{s} - \rho)} \right]^{2} - \omega^{2} \left\{ \frac{1}{2} \right\}^{1/2}$$
(5)  
$$\alpha_{2} = \frac{-9\mu}{d^{2}(\rho_{s} - \rho)} - \left\{ \frac{9\mu}{d^{2}(\rho_{s} - \rho)} \right]^{2} - \omega^{2} \left\{ \frac{1}{2} \right\}^{1/2}$$
(6)

Let the following boundary conditions be imposed on the general solution

When 
$$x = x_i$$
,  $t = 0$ 

In introducing the second boundary condition an assumption has to be made. It is clear from inspection of eq. 2 that the particle does not attain a terminal velocity because the accelerating force increases as the particle travels toward the centrifuge wall. However, if this free term can be neglected, as being small in comparison with the others, then the particle velocity at the centrifuge wall can be calculated as equal to  $\lambda \omega^2 / x_w$ . Equation 4 can be differentiated with reference to t and the differential set equal to the above quantity. This would provide the second boundary condition: when  $t = t_m$ ,  $(dx/dt)_m = \lambda \omega^2 / x_w$  where

$$\lambda = \frac{d^2(\rho_a - \rho)}{18\mu} \tag{6A}$$

and  $t_m$  represents the minimum time the particle stays in the centrifugal field. Introducing the first boundary condition in eq. 4

$$x_1 = A + B \tag{7}$$

Introducing the second boundary condition

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \lambda^2 \omega x_{\mathrm{w}} = A \alpha_1 \exp(\alpha_1 t_{\mathrm{m}}) + B \alpha_2 \exp(\alpha_2 t_{\mathrm{m}}) \quad (8)$$

Solving 7 and 8

$$A = [\lambda \omega^2 x_w \exp(-\alpha_1 t_w) - \alpha_1 \beta x_i] \frac{1}{\alpha_1(1-\beta)}$$
(9)  
$$B = - [\lambda \omega^2 x_w \exp(-\alpha_1 t_w) - \alpha_1 x_i] \frac{1}{\alpha_1(1-\beta)}$$

where

$$\beta = \frac{\alpha_2}{\alpha_1} \exp \left[ (\alpha_2 - \alpha_1) t_{n_1} \right]$$
(10)

The particular solution of 3 is given as

$$x = \frac{1}{\alpha_{1}(1-\bar{\beta})} \left\{ \left[ \lambda \omega^{2} x_{w} \exp[-\alpha_{1} t_{m}) - \alpha_{1} \beta x_{1} \right] \exp(\alpha_{1} t) - \left[ \lambda \omega^{2} x_{w} \exp[-\alpha_{1} t_{m}) - \alpha_{1} x_{1} \right] \exp(\alpha_{2} t) \right\}$$
(11)

An expression relating the velocity of the particle to its radial position can be derived from the above equation on differentiation.

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{1}{1-\beta} \left[ \lambda \omega^2 x_{\mathrm{w}} \left\{ \exp \alpha_{\mathrm{l}} (t - z_{\mathrm{n}}) - \frac{\alpha_{2}}{\alpha_{1}} \exp \left( \alpha_{2} t - \alpha_{1} t_{\mathrm{m}} \right) \right\} + x_{\mathrm{i}} \left( \alpha_{2} \exp \alpha_{2} t - \beta \alpha_{1} \exp \alpha_{1} t \right) \right] \quad (12)$$

(3)

<sup>(3)</sup> J. M. Coulson and J. E. Richardson, "Chemical Engineering," Vol. II, Pergamon Press, Ltd., London, 1955, p. 462.



Fig. 1.—Liquid surface during centrifugal separation: a, low speed,  $y_0 + ve$ ; b, high speed,  $y_0 - ve$ ; c, particle path.

The time a particle takes to reach the wall is  $t_{\rm m}$ . This may be determined from 10 after substituting the terminal conditions. Therefore

$$x_{\mathrm{w}} = \frac{1}{1-\beta} \left[ \lambda \omega^2 x_{\mathrm{w}} \left\{ 1 - \exp\left(\alpha_2 - \alpha_1\right) t_{\mathrm{m}} \right\} - x_{\mathrm{i}} \left\{ \beta \exp\left(\alpha_1 t_{\mathrm{m}}\right) - \exp\left(\alpha_2 t_{\mathrm{m}}\right) \right\} \right]$$
(13)

On the assumption that  $\beta$  can be neglected as small, it can be shown that

$$t_{\rm m} \simeq \frac{1}{\alpha_2} \log_{\rm e} \left[ \frac{x_{\rm w}}{x_{\rm i}} \left( 1 - \frac{\lambda \omega^2}{\alpha_1} \right) \right]$$
 (14)

Equation 14 is helpful in determining the optimum feed rate to the centrifuge to give a clear discharge. One need not assume a constant settling velocity to be operative at all times during the motion of the particle.

If the height of the basket is H, the volume retained in the basket at any time is  $\pi(x_w^2 - x_i^2)H$ .

If the volumetric rate of flow is Q ft.<sup>3</sup>/sec., the residence time

$$t_{\rm R} = \frac{\pi (x_{\rm w}^2 - x_{\rm i}^2)H}{Q}$$
(15)

For clear discharge, it is obvious that  $t_{\rm R} \ge t_{\rm m}$ . The condition  $t_{\rm R} = t_{\rm m}$  for the smallest particle gives the optimum feed rate,  $Q_0$ .

$$Q_0 = \frac{\pi (x_w^2 - x_i^2) H}{t_m}$$
(16)

The equation of motion of the particle under

turbulent conditions is

$$\frac{\pi d^3}{6} (\rho_s - \rho) \omega^2 \times x - 0.22\rho \, \frac{\pi d^2}{4} \left(\frac{\mathrm{d}x}{\mathrm{d}t}\right)^2 - \frac{\pi d^3}{6} (\rho_s - \rho) \frac{\mathrm{d}^2 x}{\mathrm{d}t^2} = 0 \quad (17)$$

where the second term denotes the drag force under eddying conditions. Dividing throughout by  $(\pi d^3/6)(\rho_s - \rho)$  and rewriting

$$\frac{\mathrm{d}^2 x}{\mathrm{d}t^2} + \frac{0.33\rho}{\mathrm{d}(\rho_{\mathrm{s}} - \rho)} \left(\frac{\mathrm{d}x}{\mathrm{d}t}\right)^2 - \omega^2 x = 0 \qquad (18)$$

Substituting

$$\frac{\mathrm{d}x}{\mathrm{d}t} = p; \frac{\mathrm{d}^2x}{\mathrm{d}t^2} = p \cdot \frac{\mathrm{d}p}{\mathrm{d}x}$$

Equation 18 may be transformed as

$$p \frac{\mathrm{d}p}{\mathrm{d}x} + k_1 p^2 - k_2 x = 0 \tag{19}$$

where

$$k_1 = \frac{0.33\rho}{d(\rho_8 - \rho)}; \ k_2 = \omega^2$$

Equation 19 can be rewritten after substituting  $p^2 = \phi$ . Accordingly

$$\frac{\mathrm{d}\phi}{\mathrm{d}x} + 2k_1\phi - 2k_2x = 0 \tag{20}$$

The integrating factor is

$$\exp(\int 2k_1 dx) = \exp(2k_1 x) \tag{21}$$

Therefore

$$\phi \exp(2k_1 x) = \int 2k_2 x \exp(2k_1 x) dx + A_1 \quad (22)$$

$$\phi = p^2 = \left(\frac{\mathrm{d}x}{\mathrm{d}t}\right)^2 = \left(\frac{k_2}{k_1}\right)x - \frac{k_2}{2k_1^2} + A_1 \exp(-2k_1 x)$$
(23)

or

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \left[\frac{k_2}{k_1}x - \frac{k_2}{2k_1^2} + A_1 \exp\left(-2k_1x\right)\right]^{1/2} \quad (24)$$

In applying a suitable boundary condition to evaluate the constant  $A_1$ , in eq. 24, it must be remembered that the general equation of motion that eq. 17 represents is for point condition and only for a particle settling under eddying resistance. In as much as the particle settling from rest passes through the streamline and buffer regions before encountering fully developed eddying resistance, the appropriate velocity term, necessary to evaluate  $A_1$ , should either be the lower or upper critical velocity corresponding to Reynolds numbers 0.1 and 800, respectively. The eddying resistance becomes fully developed for Reynolds number greater than 800. For simplicity, it will be assumed that beyond the lower critical velocity,  $v^*$ , the general equation of motion will be governed by eq. 17. Let the distance traversed by the particle, in the streamline region, to attain this critical velocity be  $x^*$ .

On applying the boundary condition,  $x = x^*$ , when  $dx/dt = v^*$ 

$$A_{1} = \left[ v^{*2} - v_{m}^{2} \frac{x^{*}}{x_{w}} + \frac{\omega^{2} d^{2} (\rho_{\theta} - \rho)^{2}}{0.22 p^{2}} \right] \exp \left[ \frac{0.66 \rho x^{*}}{(\rho_{\mathfrak{s}} - \rho) d} \right]$$
(25)

Equation 24 may be rewritten as

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \left[ v_{\mathrm{m}^2} \frac{x}{x_{\mathrm{w}}} - \frac{k_2}{2k_1^2} + \left( v^{*2} - v_{\mathrm{m}^2} \frac{x^*}{x_{\mathrm{w}}} + \frac{k_2}{2k_1^2} \right) \exp\left( -2k_1(\overline{x-x}^*) \right) \right] \quad (26)$$

Equation 26 defines precisely the magnitude of the particle velocity in the turbulent region as a function of its radial position beyond  $x^*$ . This equation is difficult to solve to provide a relationship between distance traversed and time. However, on the assumption that the magnitude of the term in the exponent is large, eq. 26 may be simplified as

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \left[v^{*2} + \frac{v_{\mathrm{m}}^2}{x_{\mathrm{w}}}(x - x^*)\right]^{1/2} \tag{27}$$

The general solution of the above equation is

$$\frac{2x_{w}}{v_{m}^{2}}\left[v^{*2}+\frac{v_{m}^{2}}{x_{w}}\left(x-x^{*}\right)\right]^{1/2}=t+B_{1} \quad (28)$$

Applying the boundary condition that  $t = t_m$  when  $x = x_w$ , B can be evaluated.

The particular solution of eq. 27 may hence be given as

$$\frac{2x_{\rm w}}{v_{\rm m}^2} \left[ \left\{ v^{*2} + \frac{v_{\rm m}^2}{x_{\rm w}} \left( x_{\rm w} - x^* \right) \right\}^{1/2} - \left\{ v^{*2} + \frac{v_{\rm m}^2}{x_{\rm w}} \left( x - x^* \right) \right\}^{1/2} \right] = (t_{\rm m} - t) \quad (29)$$

The above equation defines the distance traversed by the particle as a function of time under ultimate eddying conditions. The time taken by the particle to reach the centrifuge wall may be evaluated from eq. 29 by specifying any set of values for t and x. The condition that  $t = t^*$  when  $x = x^*$ , gives  $t_m = t^* + \frac{2x_w}{v_m^2} \left[ \left\{ v^{*2} + \frac{v_m^2}{x_w} (x_w - x^*) \right\}^{1/2} - v^* \right]$  (30)

By substituting the value of  $v^*$  in eq. 12 and then inserting the calculated value of  $t^*$  in eq. 11,  $x^*$ may be obtained;  $v^*$  is approximately equal to  $0.1(\mu/d\rho)$ .

Equation 30 is useful in determining the optimum feed rate to the centrifuge. The optimum feed rate is obtained as

$$Q_0 = \frac{\pi [x_w^2 - x_i^2] H}{t_m}$$
(31)

The maximum velocity of the particle can be calculated from eq. 17 as

$$v_{\rm m} = \left[\frac{d(\rho_{\rm s} - \rho)x_{\rm w} \times \omega^2}{0.33\rho}\right]^{1/2} \tag{32}$$

A more rigorous procedure in analyzing the dynamics of a particle in a force field would be to divide the region into streamline, buffer and turbulent zones and then solve the general equation of motion, choosing the appropriate term to define the resisting force. The transition from streamline to buffer zone and from buffer zone to turbulent zone occurs at Reynolds numbers 0.1 and 800, respectively. This would help satisfy the boundary conditions and, depending upon the ultimate settling conditions, the time of migration can be computed by adding the residence periods for the particle in appropriate zones.

The general equation of motion for a particle settling under such conditions that the Reynolds number is between 0.1 and 800 may be written as

$$\frac{rd^3}{6} \left(\rho_{s} - \rho\right) \omega^2 \times x - \left[3\pi\mu d\frac{\mathrm{d}x}{\mathrm{d}t} + C_{\mathrm{D}} \frac{\pi d^2 \rho}{8} \left(\frac{\mathrm{d}x}{\mathrm{d}t}\right)^2\right] - \frac{\pi d^3}{6} \left(\rho_{s} - \rho\right) \frac{\mathrm{d}^2 x}{\mathrm{d}t^2} = 0 \quad (33)$$

A complete solution of the above differential equation has not been attempted here, because eq. 33 is itself rather approximate, due to the doubtful validity of the resisting force made up of the second and third terms.

#### Discussion

The general equation of motion of a particle in a centrifugal field, under streamline conditions, has been solved completely to provide eqs. 11 and 12. On the assumption that, in the case of a particle settling ultimately under eddying conditions, only two zones need be considered, namely, the streamline and turbulent, eqs. 26 and 29 have been derived.

In calculating the optimum feed rate in industrial centrifuges a constant velocity is usually assumed to be operative for all the time the particle takes to reach the centrifuge wall and hence provide a means for comparing centrifuge performance.<sup>2</sup> But it is now possible to calculate with more accuracy the time taken for the smallest particle to reach the wall. Equations 16 and 31 are more reliable to calculate optimum feed rate than existing equations.

Finally, it may be mentioned that in assessing the centrifuge performance, one usually assumes that the angular velocity is constant throughout. But there might be a slight decrease in its magnitude from the centrifuge wall to the inner surface consequent on the shear transferred to the central air space by the rapidly revolving inner liquid angular velocity in the direction perpendicular to the axis of rotation, causing the settling particle to assume a curved path instead of a straight one

surface. In such cases there may be a gradient of (Fig. 1c). The shear transferred may be evaluated if the system is considered as one where the air is blown at equivalent velocity over a plane surface. Investigation into this effect is desirable.

## THE MICROPORE STRUCTURE OF ARTIFICIAL GRAPHITE<sup>1</sup>

#### By C. N. Spalaris<sup>2</sup>

Engineering Department, General Electric Company, Richland, Washington Received February 27, 1956

The surface characteristics of artificial graphite were investigated by means of nitrogen adsorption-desorption isotherms Changes in surface area, pore size distribution and density of graphite were studied as a function of oxidation. It was concluded that the binding materials used in the manufacture of graphite are largely responsible for the majority of the pores The variation in the pore size distribution with increasing oxidation must play an important role in the rate present. and/or mechanism of graphite oxidation.

In the study of heterogenous reactions between artificial graphite and gases it was decided that information concerning the surface characteristics of graphite was necessary. In the past, several attempts have been made to correlate the rates of carbon dioxide-graphite oxidation with its surface characteristics, but the data reported are only fragmentary.<sup>3-5</sup> Moreover, the artificial graphite used in the experiment reported here is of a different type from that used by other investigators.

The surface characteristics of five kinds of artificial graphite were investigated. These studies include the determination of surface area, pore size distribution, density and the changes of these properties taking place upon successively higher oxidation.

#### Methods and Materials

A standard B.E.T. all-glass vacuum apparatus was used to obtain the data for the surface characteristics. Nitrogen gas was used as an adsorbent to obtain the adsorption-desorption isotherms. The surface area was determined desorption isotherms. The surface area was determined from the analysis of the adsorption isotherms using the B.E.T. method.<sup>6</sup> The pore size distribution curves were b.E.1. method.<sup>2</sup> The pole size distribution curves were obtained from the analysis of the nitrogen desorption iso-therms using the B.J.H. method.<sup>7</sup> Some of these isotherms were analyzed by the modified B.J.H. method developed by C. Pierce.<sup>8</sup> Density studies were made at  $25.0 \pm 0.1^{\circ}$ by helium immersion using a container whose volume was determined to the nearest 0.02 cm.<sup>3</sup>. The volume difference before and after the graphite sample was placed in the container was the volume of the solid sample. The density was then calculated using the volume and the weight of the sample.

The CO<sub>2</sub>-graphite oxidation studies were made in a horizontal combustion furnace at a controlled temperature of  $1000 \pm 3^{\circ}$ . The temperature was recorded with a chromelalumel thermocouple, its welded junction being imbedded in the center of the graphite sample.

The Graphite Samples.-All of the graphite samples used in this experiment were artificial, high purity, Acheson

(1) Presented before the Division of Colloid Chemistry, 128th A.C.S. National Meeting, September 11, 1956, Minneapolis, Minnesota.

(2) General Electric Co. APED, San Jose, California

(3) E. A. Gulbransen and K. F. Andrew, Ind. Eng. Chem., 44, 1039 (1952). (4) P. L. Walker, Jr., R. J. Foresti and C. C. Wright, ibid., 45, 1703

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(5) P. L. Walker, Jr., F. Rusinko, Jr., and E. Raats, THIS JOURNAL. 59, 245 (1955).

(6) S. Brunauer, P. H. Emmett and E. Teller, J. Am. Chem. Soc., 60, 309 (1938).

(7) E. P. Barrett, L. G. Joyner and P. P. Halenda, ibid., 73, 363 (1951).

(8) C. Pierce, THIS JOURNAL, 57, 149 (1953).

type. The types of samples used and some of their physical properties are listed in the Table I.

#### TABLE I

SOME PHYSICAL PROPERTIES OF GRAPHITE USED IN THIS EXPERIMENT

	Graphitiza- tion temp.,	X-Ray Co spacing,	Ash content,
Type <sup>a</sup>	°C.	Å.	%
CSF	2800	6.71	0.037 to
TS-GBF	2500	6.74	0.084
CS-GBF	2500	6.72	
$\mathbf{KC}$	2800	6.71	
WSF	2700	6.72	

<sup>a</sup> The abbreviations used in the above table for the graph-ite samples are as follows: CSF, Cleves Coke (Petroleum Coke), standard pitch used for binder, purified by the "F" process; CS-GBF, Cleves Coke, standard pitch, gas baked, purified by the "F" process; TS-GBF, same as CS-GBF except Texas Coke (a petroleum coke) is used instead of Cleves Coke; KC, Kendall coke and Chicago pitch; WSF, Whiting coke, standard pitch, purified by the "F" process.

The purification process "F" is achieved by circulating "Freon-12" around the graphite bars, which are held at a temperature of about 2500°.

Commercially obtained gases (N2 and He) used for the surface characteristics were purified by passing them through a tube filled with copper turnings heated to 450°, then through a bubbler filled with concentrated sulfuric acid and finally through a liquid nitrogen trap. Liquid nitrogen of good purity was obtained commercially.

#### **Results and Discussion**

The surface area of graphite, calculated by using the B.E.T. method, was found to be between  $0.3\bar{0}$ and 1.00  $m.^2/g$ . for formed cylindrical samples of 1 cm. in diameter and 10 cm. long. The surface area values depend greatly upon the temperature of outgassing and the type of graphite sample. The surface area of all graphites used was found to increase with increased outgassing temperature, particularly in the range of 25 to  $500^{\circ}$  (Fig. 4). The increase in surface area is very small beyond the outgassing temperature of 500°. All of the outgassing in this experiment was made between 450 and 550°.

All types of artificial graphite examined possess a structure consisting of pores with radii smaller than 200 Å. termed the micropore structure. These micropores seem to be an intrinsic property of the manufactured graphite. It can be seen in Fig. 1 that artificial graphite has a large number of



Fig. 1.—Pore size distribution curves for CSF graphite sample.

micropores in the 20 to 35 Å. pore radius region. All graphites examined exhibited this property although the relative size of this pore size peak varies with the type of graphite. The hysteresis loops of the nitrogen desorption isotherms on graphite were found to take place at relative saturation pressures of 0.40 to 0.55 (Fig. 5). These hysteresis loops are generally associated with the presence of micropore structure. The shapes of pore size distribution curves do not change appreciably with the size of a given graphite sample. The intensity of the peaks in these curves increased upon subdivision or pulverization of formed graphite due to the fact that more pore volume is available per unit weight after a given sample is pulverized.

Absolute density determinations, using the helium displacement method, indicated that the density values of artificial graphite were about 3 to 9% lower than the density of the crystallites as calculated from X-ray measurements. Density was found to increase with the degree of pulverization.

The density and surface area of all types of graphite studied increased upon oxidation, this effect being most marked during the initial stages of oxidation (Figs. 2,3).

Figures 1 and 6 show the variation of pore size distribution of artificial graphite as a function of stepwise oxidation. The abscissa of the pore size distribution curves represents pore radius expressed in Å. (ångström units). The ordinate, however, is not self-explanatory. The value  $\Delta V/\Delta R$  is obtained from another curve, the so-called "cumulative pore volume curve." For this curve the radius r in ångström units is plotted as an abscissa, and the volume in pores of radius equal to or larger than r is plotted as an ordinate. The quantity  $\Delta V/\Delta R$  is the slope of this cumulative pore volume curve for a given value of r. Thus  $\Delta V/\Delta R$  represents an intensity factor of volume in pores equal to or larger than r, and this value is expressed in (cm.<sup>3</sup>/g.)/Å. For further details the original paper should be consulted.<sup>7</sup>



Fig. 2.—Variation of surface area with increasing oxidation of a typical graphite sample and its corresponding coke flour.



Fig. 3.—Effect of oven oxidation on the density of CSF graphite.



Fig. 4.—Effect of outgassing temperature on the surface area of graphite.

It is evident from Figs 1 and 6 that the pore size distribution changes markedly as the result of oxidation. These variations in the micropore distribution are believed to be caused either by removal of blockages from pore entrances previously unopened or by enlargement of existing pores. Types of graphite other than CSF have also exhibited this behavior when oxidized. Although the 20–35 Å, pore radius peak is present in all types of the artificial graphite examined, it does not vary uniformly in magnitude upon stepwise oxidation,



Fig. 5.—A typical nitrogen gas adsorption-desorption isotherm for artificial graphite. Sample outgassed at  $450^{\circ}$ .





The peak observed at 110 to 170 Å. increased with increasing oxidation up to about 6% and then decreased on further oxidation.

For the majority of the samples, the surface area found by the summation of the area in the pores less than 170 Å. in radius, agreed within 2% with the surface area calculated using the B.E.T. method.<sup>6</sup> A similar agreement has been observed by Barrett, Joyner and Halenda<sup>7</sup> for their various samples.

It was proposed that the rapid initial increase of density and surface area on slight oxidation was due to the removal of blockages from the entrance of previously inaccessible pores. These blockages are probably formed as a result of the mixing process of coke flour with pitch (used as binding material) and the subsequent graphitization.

To test the hypothesis of the role of binding material in the micropore characteristics of graph. ite, 600 Mesh TS-GBF coke flour heated to 2800° was subjected to stepwise greater oxidation and its surface area and pore size distribution were determined for each step. The initial increase of density and surface area of flour with increasing oxidation was found to be very small as compared to that of formed graphite samples made from the same type of flour. Upon further oxidation, the surface area of coke flour remained about constant while the surface area of the formed graphite continued to increase but at a slower rate than recorded initially. These results can be seen in Fig. 2. Experiments with two other types of coke flour and their corresponding graphites yielded similar results. These were CS-GBF and CSF type.

It was found that the majority of micropores are formed by the binding of crystallites with the various binding materials used in the manufacture of graphite. Coke flours (powder) used in the manufacture of graphite, have a relatively small initial surface area despite their small particle size. In contrast, even if graphite is pulverized to lesser degree than these coke flours, its surface area magnitude is found to be at least two times that of coke This difference in surface area magnitude flours. exists because graphite particles possess large numbers of micropores whereas coke flours do not. Nitrogen desorption isotherms on coke flours indicate the presence of only a small number, or none at all, of pores in the range of 20 to 200 Å. radius. This has been proven by the absence of hysteresis loops in the desorption isotherms of coke flours.

An attempt was made to correlate the surface characteristics with  $CO_2$ -graphite oxidation rates. Surface characteristics, in general, do play an important role in the graphite oxidation kinetics. It was found in our experiments that the increase in surface area causes the rate of  $CO_2$ -graphite oxidation to increase. Further correlation of oxidation rates with pore size distributions could not be realized with the data presently available. It is expected that such a correlation is difficult because upon stepwise oxidation the size of pores opened are not consistent from sample to sample for each successive oxidation step. It is illustrated in Figs. 1 and 6 that each successive step of oxidation produces a different type of surface heterogeneity, which is likely to influence considerably the graphite-gas reaction mechanism and/ or rate.

It is suspected that the nature of binding material itself may have an influence on the graphite oxidation reactions. Although experimental evidence is scant, other factors that might be different in any given graphite sample are method of manufacture, temperature of graphitization, particle size before "binding" or the presence of impurities. These factors may account in part for the variation in the values of the surface properties for the various types of graphite studied and thereby influence the oxidation reactions. Acknowledgment.—The author wishes to thank D. H. Curtiss of General Electric Company for his helpful suggestions in preparing this paper.

### THE SOLUBILITY OF HYDROGEN IN DIBORANE

By Jih-Heng Hu and George E. MacWood

Contribution of the McPherson Chemical Laboratory of The Ohio State University, Columbus, Ohio Received March 8, 1953

The solubility of hydrogen in liquid diborane was determined in the temperature range 113-181 °K. and the pressure range 0-40 atm. The solubility is found to increase with temperature. The heat of solution at infinite dilution ranges from 386-601 cal./mole.

#### Introduction

As a part of the program of determining thermodynamic properties of boron hydrides in progress in this Laboratory, the solubility of hydrogen in liquid diborane has been investigated over a range of temperature 113–181°K. and a range of pressure 0– 40 atm.

#### Experimental

Apparatus.—The apparatus for determining the solubility of hydrogen in liquid diborane consisted of two parts: (1) the system for attaining equilibrium and sampling, and (2) one for measuring the amounts of hydrogen and diborane both in the liquid and gas phases. A schematic diagram of the former part is shown in Fig. 1. The pipet (P) which contained the liquid was made of a heavy-walled copper tube capable of withstanding pressures up to 150 atm. It was 9 in. long and its inner diameter was 1 in.

To achieve equilibrium fairly rapidly, a circulating pump was incorporated into the system. It operated electromagnetically and consisted of a coil (D), a bellows (U), and iron rod (W). The upper half of the rod could move into the coil (D); the lower half of the rod passed through a hole at the bottom of the bellows and was attached to a disk (V). An O-ring was placed on the disk. All parts were enclosed in a stainless steel case. One end of the coil (D) was grounded and the other end taken out of the case through an insulated plug with Teflon packing and connected to a 130volt d.c. line. The current was interrupted periodically. When the circuit was closed, the rod was attracted into the coil, and the O-ring sealed off the hole in the bellows. As the rod moved further into the coil, it compressed the bellows and forced gas to flow into an exchange coil immersed in the cryostat liquid. After the gas had been cooled to the temperature of the cryostat, it entered into the bottom of the pipet in fine streams. On open circuit, the rod dropped under its own weight and opened the hole in the bellows, allowing gas to enter. To minimize fluctuations in pressure, a reservoir of 600 cc. volume was used as a buffer.

The pressure of the system was measured with a gage calibrated in this Laboratory against a dead-weight gage. The temperature was obtained with the aid of a standard thermocouple soldered into the thermocouple well just below the liquid level. To obtain the desired temperature, the freezing points of ethyl alcohol and methylcyclohexene were used at temperatures 158.3 and 146.2°K., respectively. The other temperatures were obtained by using dimethyldifluoromethane (Freon 22) as a cryostat liquid. A container approximately 2 in. in diameter and 30 in. in length containing liquid nitrogen was partially immersed in the Freon. By keeping the liquid nitrogen in the container at a certain level, and, at the same time, bubbling air through the cryostat liquid at a suitable rate, the desired temperature could be maintained within a few tenths of a degree. The bubbling of the air served a dual purpose both as a heat compensator and as a stirrer.

The analyzing system consisted of five Pyrex flasks. The volumes of two of the flasks were calibrated with water. All other volumes were calibrated against these two, using hydrogen. The accuracy of calibration is estimated to be



Fig. 1.—System for obtaining equilibrium and sampling.

better than one part in two thousand. All the glass flasks were immersed in a water-bath. The pressure was measured with a mercury manometer using a Gaertner cathetometer.

with a mercury manometer using a Gaertner cathetometer. **Procedure.** (a) Vapor-Liquid Equilibrium.—The cryo-stat was first cooled to near the freezing point of diborane (108°K.), and 1.3 moles of diborane of 99.9% purity were condensed into the pipet (P) through the valves m, f and c. Valves m and c were then closed, and the system was evacuated to high vacuum through valves d and g. At the same time, the cryostat was warmed to the temperature at which the experiment was to be carried out. Electrolytic hydrogen from the storage cylinder was introduced into the system through coil (L<sub>2</sub>), which was immersed in liquid nitrogen to through valves f, a and b, it was bubbled through the liquid diborane in the pipet (P). When the gage ( $G_1$ ) showed the desired pressure, valve f was closed and valve c opened. The entire system was then in communication. The circulating pump was connected to a 130-volt d.c. line. It operated at a speed of two strokes per minute, and each stroke compressed approximately 10 cc. of gas into the liquid phase. In order to avoid excessive heat generated by the magnet, a mixture of ice and water was placed in the outer jacket of the pump. The time required to attain equilibrium in the system was approximately 80 to 90 minutes. The temperature of the pipet (P) was recorded

every five minutes, and the temperature for each experiment was the average of the recorded temperatures of the pipet during the run with a slight emphasis on the last few readings. The deviations of the temperature readings were usually  $0.3^{\circ}$ K. After equilibrium had been achieved, the circulating pump was stopped, valves a, b and c were closed and the system was ready for liquid sampling. The liquid sampling was done by opening the needle valve n and liquid was allowed to flow into the capillary line. After three to five seconds, needle valve n was closed. The liquid sample was collected in the tube S, which had been evacuated and cooled to liquid nitrogen temperature. The cryostat was then heated to approximately 160°K., at which temperature the vapor pressure of diborane became sufficiently large (ca. 1/2 atm.), so that no liquid remained in the capillary line.

(b) Analysis.—The liquid sample was allowed to remain in the tube S for 15 minutes. Valve j was then opened, and the hydrogen was pumped into a calibrated volume in the analyzing system through a liquid nitrogen trap  $L_s$  by means of a Toepler pump. It usually required approximately 20 pumpings to reduce the hydrogen in the liquid sample to a negligible amount. The sample was then allowed to melt so that any hydrogen trapped in the solid diborane would be liberated. During the melting, valve i was closed to prevent diborane from condensing back into the capillary line. The sample was then cooled to liquid nitrogen temperature, and the residual gas was added to the same volume in the analyzing system. The process was repeated until no trace of hydrogen was found by further melting.

The calibrated volume in the analyzing system was immersed in a water-bath, the temperature of which was controlled to within 0.01°. The pressure of the hydrogen was measured by a manometer using the Gaertner cathetometer. All readings were in reference to a standard meter bar. By this means, the pressure was read to within 0.1 mm. From these data, the number of moles of hydrogen could be calculated from its equation of state.

After the amount of hydrogen in the liquid sample was determined, the gas was evacuated from the system. Tube S was then warmed to room temperature and the diborane was pumped into the analyzing system. The number of moles of diborane was determined in the same manner. No decomposition of diborane was detected during this process, which usually required approximately one hour.

The diborane was usually present in the gas phase in small quantities. In order that it could be measured conveniently, the entire gas mixture in the reservoir was analyzed. Since the calibrated volume in the analyzing system was insufficient to accommodate all the hydrogen in the reservoir, it was necessary to measure it in several expansions. A part of the hydrogen was expanded into the entire calibrated volume of the analyzing system (ca. 5 liters). When the pressure reached approximately one atmosphere, the expansion was stopped, the pressure measured, and the gas discarded. A second portion of hydrogen was expanded into the analyzing system. It was necessary to repeat this process three to five times, depending on the pressure of the system. By this procedure, less than 5% of the gas remained in the system. From the measured pressure of this gas, the number of moles of hydrogen remaining in the reservoir could be calculated from a previously determined relation between the number of moles of hydrogen in the reservoir and its pressure. The reservoir was then isolated, and the gas in the remainder of the system was pumped into the analyzing system and its quantity determined.

The system was then evacuated. When high vacuum was obtained, the diborane in the reservoir was condensed into the trap  $L_3$ . Since the volume of this trap was considerably smaller than that of the reservoir, the transfer of the material into the analyzing system was greatly facilitated. Valve k was closed, the trap warmed, and the diborane introduced into the analyzing system with the aid of the Toepler pump. The molar quantity was determined in the same manner as for hydrogen.

When the analyses of both liquid and gas phases were completed, all diborane taken out of the pipet was condensed into the reservoir. By adjusting the cryostat temperature and starting the circulating pump, most of the diborane was condensed back into the pipet. The residue was removed. The next run was always started with no diborane in the reservoir, because more time was required for the system to reach equilibrium when an excessive amount of diborane was present in the reservoir.

#### Results

The experimental results of this investigation are recorded in Table I and are summarized in Fig.

#### TABLE I

#### SOLUBILITY OF HYDROGEN IN LIQUID DIBORANE

$T_{1}$	Total pressure,	f2°',	$N_1'$	f <sub>2,7</sub>	$N_{2d}$	$f_2/N_2''$
° K.	atm.	atm.a	× 104¢	atm.b	$\times 10^{3d}$	$\times 10^{-3}$
115.49	8.77	8.78	6	8.77	<b>2</b> .590	3.385
112.34	10.14	10.15	4	10.15	2.969	3.418
112.43	11.45	11.46	2	11.46	3.365	3.406
113.82	15.14	15.16	2	15.16	4.435	3.418
114.51	21.00	21.11	2	21.11	6.182	3.470
113.46	21.41	21.45	2	21.45	6.285	3.413
112.66	<b>26</b> , $61$	<b>26</b> , $68$	2	26.67	7.501	3.556
112.85	34.13	34.25	2	34.24	8.694	3.939
112.08	41.98	42.16	1	42.16	9.667	4.361
Av. temp.	113.12°	К.				
123.83	6.74	6.76	14	6.74	2.330	2.893
123.95	14 , $42$	14.50	8	14.48	4.842	2.990
123.92	19.98	20.11	6	20.10	6.841	2.938
124.24	25 , $58$	25.78	6	25.77	8.469	3.042
124.46	34.06	34.42	6	34.40	11.180	3.077
124.23	42.12	42.67	6	42.65	13.554	3.147
Av. temp.	124.10°	К.				
134.94	7.03	7.04	<b>24</b>	7.02	2.834	2.477
134.93	13.56	13.64	<b>20</b>	13.62	5.381	<b>2</b> , $530$
135.13	20.59	20.78	15	20.75	8.230	2.521
134.80	27.16	<b>27</b> , $49$	16	27.44	10.757	2.551
134.95	33.74	34.25	13	34.21	13.073	2.617
134.95	42.46	43.26	12	43.21	16.129	2.679
Av. temp.	$134.95^{\circ}$	к.				
145.91	5.48	5.50	166	5.41	${f 2}$ , $458$	2.199
145.66	9.13	9.17	114	9.07	4.152	2.184
146.19	20.66	20.89	52	20.78	9.307	2.233
146.55	25.44	25.78	47	25.66	11.338	2.263
146.75	32.44	33.01	46	32.86	14.406	2.281
146.01	41.91	42.86	40	42.69	18.326	2.329
Av. temp.	$146.21^\circ$	K.				
158.43	4.04	4.05	705	3.77	1.954	1.928
158.32	9.94	10.00	245	9.76	5.106	1.911
158.30	14.95	15.09	177	14.82	7.634	1.941
158.15	21.23	21.50	138	21.21	10.854	1.954
158.33	28.21	28.68	105	28.38	14.541	1.952
158.35	34.13	34.82	100	34.48	17.622	1.957
159.26	41.49	42.52	85	42.16	21.377	1.972
Av. temp.	$158.31^{\circ}$	K.				
169.55	7.79	7.82	721	7.27	4.337	1.676
169.86	14 60	14.74	350	14.23	8.427	1 689
169.88	21.41	21.70	281	21.10	12,433	1 697
169.97	28.74	29.26	220	28 64	17 083	1 676
169.69	35.82	36.63	195	35 94	21 139	1 700
169.71	41.98	43 10	184	43 34	24 527	1 726
Av. temp.	169.78°	K.	101	10.01	21:021	1.120
181.56	8 31	8 36	1473	7 17	4 900	1 463
181.68	14 09	14 21	863	13 03	8 921	1 462
181.42	20.12	20.38	565	19.27	13,143	1 466
181.55	26 88	27 36	460	26.15	17 661	1 481
181.55	35 82	26 66	390	35 30	23 562	1 498
181.73	41 69	42 82	370	41 32	27 194	1 590
Arr. toman	101 500	12	0.0	11.00	-1.101	1.040

Av. temp. 181.58°K.

<sup>a</sup>  $f_2^{\circ}$  is the fugacity of pure hydrogen at a pressure equal to the total pressure. <sup>b</sup>  $f_2$  is the partial fugacity of hydrogen. <sup>c</sup>  $N_1'$  is the mole fraction of diborane in the vapor phase. <sup>d</sup>  $N_2''$  is the mole fraction of hydrogen in the liquid phase.

2, in which the mole fraction of hydrogen in the liquid phase is plotted against the partial fugacity of hydrogen for the temperatures corresponding to the various isotherms measured.

#### Theory

**Partial Fugacity of Hydrogen.**—The partial fugacity of hydrogen in the vapor phase can be calculated from the relation

$$\ln \frac{f_2}{f_2^*} = \frac{1}{RT'} \int_{p^*}^p \bar{V}_2 \, \mathrm{d}p \tag{1}$$

where  $f_2$  and  $f_2^*$  are the partial fugacities of hydrogen in the gaseous mixture at temperature T and at total pressures p and  $p^*$ , respectively, and  $\overline{V}_2$  is its partial molal volume. The integration is carried out at constant composition.

If the second virial coefficient of the mixture is denoted by B and the numbers of moles of diborane and hydrogen by  $n_1$  and  $n_2$ , the total volume of the mixture V is given by

$$V = (n_1 + n_2) \left(\frac{RT}{p} + B\right) \tag{2}$$

The partial molal volume of hydrogen is, therefore

$$\overline{V}_2 = \left(\frac{\partial V}{\partial n_2}\right)_{n_1} = \frac{RT}{p} + B + (n_1 + n_2) \left(\frac{\partial B}{\partial n_2}\right) \quad (3)$$

For a binary mixture

$$B = N_1^2 B_1 + 2N_1 N_2 B_{12} + N_2^2 B_2 \tag{4}$$

where  $B_1$  and  $B_2$  are the second virial coefficients of pure diborane and pure hydrogen and  $B_{12}$  is a similar quantity due to the interaction between diborane and hydrogen molecules.  $N_1$  and  $N_2$  are the mole fractions of the respective components.

Using eq. 4, the partial volume  $V_2$  becomes

$$\overline{V}_2 = \frac{RT}{p} + B_2 - (B_1 - 2B_{12} + B_2)N_1^2$$
 (5)

Inserting eq. 5 into 1 and performing the integration gives

$$\ln \frac{f_2}{f_2^*} = \ln \frac{p}{p^*} + \frac{B_2}{RT} \left( p - p^* \right) + N_1^2 (p - p^*) \gamma \quad (6)$$

where

$$\gamma = -\frac{B_1 - 2B_{12} + B_2}{RT} \tag{7}$$

As  $p^*$  goes to zero, keeping the composition fixed,  $f_2^*$  approaches  $N_2p^*$  and eq. 6 becomes

$$\ln f_2 = \ln N_2 p + \frac{B_2}{RT} p + \gamma N_1^2 p$$
 (8)

Since  $B_2p/RT$  and  $\gamma(N_1{}^2p/RT)$  are small quantities, eq. 8 can be written, neglecting the second and higher powers of these quantities

$$f_{2} = N_{2}p\left(1 + \frac{B_{2}p}{RT}\right)(1 + \gamma N_{1}^{2}p)$$
(9)

or

$$f_2 = N_2 f_2^{\circ} (1 + \gamma N_1^2 p) \tag{9'}$$

where  $f_2^{\circ}$  is the fugacity of pure hydrogen at T and p. If the term containing  $N_1^2$  can be neglected, eq. 9' reduces to that given by Lewis and Randall.<sup>1</sup> The values of the second virial coefficients of hy-



drogen were taken from the literature.<sup>2</sup> The second virial coefficients of diborane have been determined at temperatures above its boiling point in this Laboratory.<sup>3</sup> From these values, assuming the Lennard-Jones 6-12 potential, the depth of the potential,  $\epsilon$ , was found to be  $1.882 \times 10^{-14}$  ergs and the second parameter  $b_0$  (=  $(2\pi/3) Nr_0^3$ ,  $r_0$  being the equilibrium distance) is 394.5 cm.<sup>3</sup>. To determine  $B_{12}$ , the interaction potential was assumed to be determined by the two relations<sup>4</sup>

and

$$b_{12} = \frac{1}{2}(b_1^{1/3} + b_2^{1/3})^3$$

 $\epsilon_{12} = (\epsilon_1 \epsilon_2)^{1/2}$ 

Then using published tables<sup>4</sup> giving the second virial coefficient as a function of the parameters  $\epsilon_{12}$  and  $b_{12}$ ,  $B_{12}$  was obtained. The calculated values of  $B_1$  and  $B_{12}$ , together with those for  $B_2$ , are given in Table II. The values of  $B_1$ , calculated with these constants, are in good agreement with the experimentally determined values between the boiling point of diborane and room temperatures.

The partial fugacities of hydrogen reported in Table I have been calculated with the aid of eq. 9'.

Vapor-Liquid Equilibrium. (a) Isotherms.— Consider the equilibrium between the vapor and liquid phases for the two-component system diborane-hydrogen at constant temperature. Under these conditions, the condition for equilibrium of hydrogen between the two phases is

$$\mu_2' = \mu_2'' \tag{10}$$

<sup>(1)</sup> G. N. Lewis and M. Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, N. Y., 1923, p. 226.

<sup>(2)</sup> H. W. Woolley, R. B. Scott and F. G. Brickwedde, J. Research Natl. Bur. Standards, 41, 379 (1948).

<sup>(3)</sup> Unpublished work, Leo J. Paridon and G. E. MacWood.

<sup>(4)</sup> J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, "Molecular Theory of Gases and Liquids," John Wiley and Sons, Inc., 1954.

	SECOND	VIRIAL	L COEFFICI	ENTS	
°K.	$B_{1,}$ cm. <sup>3</sup>	${}^{B_{2,}}_{{ m cm.}^{3}}$	$B_{12}, cm.^{3}$	$-(B_1 + B_2 - 2B_{12})$	$\gamma$
113.12	-1385.5	1.1	-119.6	1145.2	0.1234
124.10	-1179.5	3.2	-95.9	984.5	. 0966
134.95	-1018.1	5.0	- 76.9	859.3	.0775
146.21	-886.2	6.4	-60.5	758.8	. 0632
158.31	-768.7	7.8	-45.9	669.1	.0516
169.78	-676.5	8.8	-34.3	599.1	. 0430
181.58	-597.1	9.7	-24.0	539.4	.0362

where  $\mu_i$  is the chemical potential of the ith component, the single prime and double prime refer to the vapor and liquid phases, respectively. Hence, for an isothermal change, one obtains

$$RT \operatorname{dln} f_{2}' = \left(\frac{\partial \mu_{2}'}{\partial p}\right)_{N_{2}',T} \operatorname{d} p + \left(\frac{\partial \mu_{2}'}{\partial N_{2}'}\right)_{p,T} \operatorname{d} N_{2}' = \left(\frac{\partial \mu_{2}''}{\partial p}\right)_{N_{2}'',T} \operatorname{d} p + \left(\frac{\partial \mu_{2}''}{\partial N_{2}''}\right)_{p,T} \operatorname{d} N_{2}'' \quad (11)$$

Assuming that hydrogen in the liquid phase obeys a generalized Henry's law, *i.e.* 

$$f_2'' = k N_2'' \tag{12}$$

eq. 11 becomes

$$d\ln f_2' = \frac{\overline{\mathcal{V}}_2}{RT} dp + d\ln N_2'' \tag{13}$$

Integrating, one finds

$$\ln N_{2}'' = \ln \frac{f_{2}'}{k} - \frac{1}{RT} \int_{p_{1}^{\circ}}^{p} \overline{V}_{2} \, \mathrm{d}p \qquad (14)$$

(b) Isobars.—For an isobaric change, one finds



$$\frac{\left(\frac{\partial \mu_2^{0'}}{\partial T}\right)_{N_2',p} \mathrm{d}T + RT \,\mathrm{d}\ln f_2' = \left(\frac{\partial \mu_2''}{\partial T}\right)_{N_2'',p} \mathrm{d}T + \left(\frac{\partial \mu_2''}{\partial N_2''}\right)_{T,p} \mathrm{d}N_3'' \quad (15)$$

Now, under the assumption that eq. 12 is satisfied and that the vapor phase satisfies the solution law eq. 9', eq. 15 becomes

$$d \ln \frac{f_2'}{N_2''} = \frac{(\bar{H}_2^{0'} - \bar{H}_2'')}{RT^2} dT$$
(16)

where the superscript 0 indicates the standard state value. Remembering eq. 12, this becomes

$$\frac{\mathrm{dln}\;k}{\mathrm{d}T} = -\frac{\bar{H}_{2^{0}}{}^{"}-\bar{H}_{2}{}^{"}}{RT^{2}} = -\frac{\Delta\bar{H}_{s}}{RT^{2}} \qquad (17)$$

where  $\Delta H_s$  is the partial molal heat of solution at infinite dilution.

(c) Heats of Solution.—In Fig. 3, the values of  $f''/N_2''$  corresponding to each isotherm have been plotted against  $p - p_0$  where p is the total pressure of the system and  $p_0$  is the vapor pressure of pure diborane at the temperature of the isotherm. By extrapolation of f''/N'' to its value at  $p - p_0$  equal to zero, k, Henry's law constant, is obtained. The values thus obtained are reported in Table III.

Using these values of k, it has been found that, within 1%

$$\log k = 6.704 + 7.618/T - 1.581 \log T \quad (18)$$

Hence

$$\Delta \bar{H}_{*} = 30.68 - 3.141T \tag{19}$$

The values of  $\Delta H_*$  at the various experimental temperatures are also reported in Table III.

#### $T_{ABLE} III$

#### HENRY'S LAW CONSTANTS AND HEATS OF SOLUTION

Temp., °К.	$k_{\mathrm{obsd}}, \\ \mathrm{atm.}^{-1}$	$k_{\text{calcd,}}$ atm. <sup>-1</sup>	$\Delta \vec{H}_{s},$ cal./mole
113.12	3358	3349	386
124.10	2867	2853	420
134.95	2425	2471	455
146.21	2160	2155	490
158.31	1910	1883	528
169.78	1672	1674	564
181.58	1435	1442	601

#### Discussion

One rather striking observation is the increase in the solubility of hydrogen with temperature at constant pressure. This behavior is not as unusual as one might think at first glance. It frequently occurs in systems, such as  $N_2-H_2$ ,<sup>5</sup> CO- $H_2$ ,<sup>5</sup> CH<sub>4</sub>- $H_2$ ,<sup>6</sup>  $N_2$ -He,<sup>7</sup> for which the temperatures involved are above the critical point of the solute.

Another fact of interest with respect to this system is that the partial molal volume of hydrogen is approximately 20 cm.<sup>3</sup>, which is 8 cm.<sup>3</sup> less than that of liquid hydrogen at its boiling point. This is what one might expect for a liquid of such high internal pressure.

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## THE KINETICS OF THE THERMAL DECOMPOSITION OF SODIUM NITRATE<sup>1</sup> AND OF THE REACTION BETWEEN SODIUM NITRITE AND OXYGEN

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The kinetics of the thermal decomposition of sodium nitrate and of the reaction between sodium nitrite and oxygen were investigated in the presence of argon and oxygen, at atmospheric pressure, over the temperature range of 600 to 780°. The rate of reaction was followed by observing changes in the volume of the systems as a function of time at constant pressure. Mass spectrometric analyses revealed that the gases formed during the decomposition of sodium nitrate consisted of nitrogen, oxygen and small quantities of nitrogen dioxide. The nitrogen and some of the oxyger were due to the decomposition of sodium nitrite and sodium superoxide, intermediate products of the decomposition of sodium nitrate. From the investigation of the reaction between sodium nitrite and oxygen it was found that equilibrium was attained between sodium nitrate, sodium nitrite and oxygen below 700°. Above 700° the oxidation reaction was followed by the decomposition of sodium nitrite. Although the reaction velocity increased with temperature, the extent of reaction decreased with increasing tem-In the extent of reaction velocity increased with temperature, the extent of reaction decreased with increasing temperature. From the temperature dependency of the equilibrium constants, the heat of reaction for the formation of one mole of sodium nitrate from sodium nitrite and oxygen was calculated to be -24.5 kcal. per mole. The rate process for the oxidation reaction appears to be surface dependent, as indicated by the effect of varying the area of contact between gaseous oxygen and the sodium nitrite melt. The kinetics involves a first order reversible reaction with respect to sodium nitrate of a strategies of activity more determined for the oxidation and accomparities protection and a more solid protection with respect to solid protection. and sodium nitrite. The energies of activation were determined for the oxidation and decomposition reactions and a reac-tion mechanism is proposed. The entropies and free energies of activation and the nitrogen to oxygen bond energy in sodium nitrate were also determined.

#### Introduction

Previously, investigations of the thermal decomposition of sodium nitrate dealt with the identification of the gaseous and solid products over various temperature ranges.<sup>3-6</sup> Although there is considerable interest in the high temperature reactions of this compound, especially in the field of munitions, there is apparently a lack of fundamental work concerning the kinetics and the mechanism of the decomposition at normal pressures. In this investigation the reactions of sodium  $nitrite^{7-10}$  in argon and oxygen also were studied in order to clarify the origin of the gaseous products as well as the kinetics and the mechanism of the decomposition.

#### Experimental

The sodium nitrate and sodium nitrite were of C.P. grade

The apparatus for this work consisted of a stainless steel thimble (reaction vessel) within a Vycor tube which is connected to a dual system consisting of a gas buret and compensating tube separated by a controlling manometer. The dual system of gas burets makes possible the continual observance of the rate process during the collection of the gaseous decomposition products.

For measuring changes in volume of the system, while automatically maintaining a constant pressure," two plati-num wires were sealed in the intervening manometer and connected to an electronic relay,12 used to operate a sole-

(1) This paper was presented, in part, before the Division of Physical and Inorganic Chemistry at the National Meeting of the American Chemical Society in Cincinnati, Ohio, April 6, 1955.

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noid valve<sup>13</sup> (see Fig. 1). When there is a small increase in pressure, mercury-wire contact is made on the compensating tube side of the manometer, opening the solenoid valve. The mercury level in the gas buret falls until the original pressure of the system is restored, at which point the mercury-wire contact is broken and the solenoid valve closes. The change in the mercury level is a measure of the increase in volume at the initial pressure of the system. For reactions involving decreases in volume, the solenoid valve opens when the mercury-wire contact is broken. The posi-tion of the mercury leveling bulb is adjusted so that when the solenoid valve is open the mercury level in the buret will A layer of mineral oil, one cm. thick, is used to coat the rise. upper surface of the mercury in the gas buret to minimize reaction with  $NO_2$ . It was determined experimentally that losses of NO<sub>2</sub> are almost completely eliminated, in this manner, within the limits of the experimental times used in the decomposition studies. The gases were determined by mass spectrometric analyses and the solid residues by X-ray diffraction and chemical methods.

The mass spectrometer was the G.E. Analytical Model and the instrument was calibrated with  $O_2$ ,  $N_2$ , NO,  $N_2O$  and  $NO_2$ . The results were confirmed by comparisons with synthetic mixtures of the gases in question.

The Vycor vessel, containing a stainless steel reaction tube, is heated in a resistance furnace which is regulated to  $\pm 2^{\circ}$  by means of an indicating pyrometric proportioning controller. The vessel is also provided with an invertible side arm, located out of the heating zone, which contains the sample prior to the reaction. When the furnace has at-tained the desired temperature and the apparatus is filled with the appropriate gas the side arm is inverted, allowing the sodium nitrate or nitrite crystals (approximately 0.5 g.) to drop into the stainless steel tube where the reaction ensues. All the reactions are carried out at approximately one atmosphere of pressure and in a stainless steel reaction vessel having an inside diameter, i.d., of 1.60 cm., unless otherwise stated.

The Chevenard automatic photographic recording thermobalance was used to obtain the thermograms for sodium nitrate and sodium nitrite in air. The sample weight was approximately 0.5 g. and the reaction was carried out in a Coors crucible (glazed) No. 000. The temperature of the furnace was increased at a rate of 15° per minute, and is noted at the timing marks at 2-minute intervals. The bal-ance was calibrated with standard 100 and 200 mg. weights and the furnace cover adjusted so that buoyancy effects were negligible.

#### Results and Discussion

Figure 2 is a graph of the change in weight of so-

(13) Automatic Switch Co., Valve #826212.





Fig. 1.—Apparatus: G, water jacket; H, gas buret, 100 ml.; I, controlling manometer (mercury); J, compensating tube; K, platinum leads; L, solenoid valve (stainless steel); M, controlling relay (thyratron); N, leveling bulb; O, to reaction vessel; P, to gas buret; Q, sample container; R, furnace; S, to vacuum and gases; T, stainless steel reaction vessel; U, Vycor vessel.

dium nitrate heated in air vs. temperature. Decomposition, as indicated by losses in weight of the sample, commenced slowly at 600° and was rapid at temperatures exceeding 756°. At 910° the reaction was complete and the total weight loss, 0.277 mg., corresponds to the formation of sodium oxide. The discrepancy between the observed and theotical values is 2.3%.

Figure 3 is a graph of the increase in volume of the individual gases formed as a function of time, due to the decomposition of sodium nitrate in argon, over the temperature range of 650 to 780°. Mass spectrometric analyses of the decomposition gases, which were collected periodically, showed the presence of oxygen, nitrogen and small quantities of nitrogen dioxide. The analytical data are presented in Table I. Several of the points for oxygen, not given in Table I, were obtained by taking the difference between the total volume and the volume of nitrogen plus nitrogen dioxide. The presence of nitrogen dioxide may result from the reac-



Fig. 2.—Thermogram of sodium nitrate in air; weight loss (mg.) vs. temperature (°C.); timing marks at 2 min. intervals; rate of temperature increase,  $15^{\circ}$  min.<sup>-1</sup>.



Fig. 3.—Rate of decomposition of  $NaNO_3$  in argon at contant pressure (one atm.); volume (ml./g.) S.T.P. vs. time (min.).

	Temp., °C.	Gas	Temp., °C.	Gas
0	650	$O_2$	⊠ 750	N2
$\otimes$	650	$N_2$	Z 750	$NO_2(N_2O_4)$
$\triangle$	700	$O_2$	$\diamond$ 780	$O_2$
$\mathbb{A}$	700	$N_2$	<b>9</b> 780	$N_2$
	750	$O_2$		$NO_2 (N_2O_4)$

tion between oxygen and nitric oxide. During the initial stages of the reaction oxygen is the principal gas formed; as the reaction proceeds the proportion of nitrogen increases. The data indicate that the primary stage of the decomposition of sodium nitrate involves predominantly the formation of sodium nitrite and oxygen. X-Ray analyses of the solid residues corroborate these findings. The use of a reaction vessel having a smaller inside diameter, 1.30 cm., had little effect on the reaction rate.

Since sodium nitrite is a product of the decomposition of sodium nitrate, its thermal decomposition was investigated, in argon, over the temperature range of 650 to 780°. The results are shown in Fig. 4, a graph of the increase in volume of the gaseous products vs. time. The decomposition gases were found to consist of nitrogen and oxygen.<sup>14</sup> During the initial stages of the reaction, nitrogen is the predominant gas formed; however, as the reaction progresses the relative quantities of oxygen increase. Relatively good reproducibility of the data is indicated from duplicate experiments carried out at 700°. These results, in addition to the orangebrown color of the decomposing liquid, indicate that the nitrogen formed during the decomposition of sodium nitrate probably originates from the breakdown of sodium nitrite to an intermediate superoxide and nitrogen. The increased proportion of oxygen, as the decomposition of sodium nitrite proceeds, may be accounted for by the decomposition of the superoxide to sodium oxide and oxygen.

X-Ray analyses revealed the presence of sodium nitrate in the solid decomposition products of sodium nitrite. The intensitities of the reflections for sodium nitrate and nitrite were weak due to extensive decomposition, but a pattern was not observed for the oxides. The oxides, therefore, appear to exist in the amorphous state. The formation of sodium nitrate is not attributed directly to the decomposition of sodium nitrite since sodium nitrate is unstable at the experimental temperatures. A reasonable explanation is, however, that when the mass cools, sodium superoxide oxidizes sodium nitrite to the nitrate and itself is reduced to a peroxide or oxide.

Since nitrogen dioxide was not observed during the decomposition of sodium nitrite, in stainless steel, the formation of nitric oxide and/or nitrogen dioxide resulted principally from the decomposition of sodium nitrate. This reaction takes place to a small extent upon heating sodium nitrate as indicated in Table I and Fig. 3.

A graph of the change in weight of sodium nitrite, heated in air, vs. temperature is shown in Fig. 5. At approximately  $620^{\circ}$  the oxidation of sodium nitrite by oxygen becomes apparent as indicated by increases in sample weight. The maximum weight is attained at 740°. Further increases in temperature resulted in weight losses due to decomposition, which are relatively rapid above 780°. At 920° the decomposition was complete. The total weight loss, 0.327 mg., corresponds to the forma-



Fig. 4.—Rate of decomposition of  $NaNO_2$  in argon at constant pressure (one atra.); volume (ml./g.) S.T.P. vs. time (min.).

	Temp., °C.	Gas	Temp., °C.	Gas
	650	$O_2$	$\triangle$ 750	O2
Ò	650	$N_2$	$\overline{\bigtriangleup}$ 750	$N_2$
×	700	$()_2$	⊗ 780	$O_2$
	700	$N_2$	O 780	$N_2$



Fig. 5.—Thermogram of sodium nitrite in air; weight loss (mg.) vs. temperature (°C.); timing marks at 2 min. intervals; rate of temperature increase,  $15^{\circ}$  min.<sup>-1</sup>.

tion of sodium oxide. The difference between the observed and theoretical values is 2.2%.

The effect of oxygen on the high temperature behavior of sodium nitrite over the temperature range of 600 to 780 ° is shown in Fig. 6. Rather than decomposition, as occurs in argon, a decrease in volume is observed due to the formation of sodium nitrate. At 780 and 750° a secondary reaction involving the decomposition of sodium nitrite is indicated. This is evident from the initial decrease in the volume of the systein, followed by an increase in volume resulting from the evolution of nitrogen and some oxygen. The amount of sodium nitrate present when the rate of change in volume is zero,

<sup>(14)</sup> When the reaction was carried out at  $600^{\circ}$  in a platinum crucible, in nitrogen, traces of NO and/or NO<sub>2</sub> were also observed. This is in qualitative agreement with the results reported by Oza and Walawalker.<sup>10b</sup>



Fig. 6.—Rate of reaction between NaNO<sub>2</sub> and O<sub>2</sub> at constant pressure (one atm.); volume (ml./g.) S.T.P. vs. time (min.); temp., °C.: ⊠, 600; ⊗, 650; ♢, 650; □, 700; △, 750; ⊙, 780.

and the time for the attainment of this condition, both increase as the temperature is decreased. Although the rate of oxidation increases with temperature, the extent of reaction decreases with increasing temperature. At 600, 650 and 700°, after a period of time which increases with decreasing temperature, the volume of the system remained constant, indicating that equilibrium had been attained between sodium nitrate, sodium nitrite and oxygen. This was confirmed by X-ray analyses of the residues which indicated only the presence of sodium nitrate and sodium nitrite. Duplicate experiments, at 650°, showed good reproducibility of the data.

On the basis of the amount of oxygen at equilibrium, as determined from the above experiments, equilibrium constants were calculated. For this purpose the standard states of the salts were taken as pure molten sodium nitrate and sodium nitrite at the same temperature and pressure. The melt is assumed to approach ideality and the activity of each component was taken as equal to its mole fraction. The assumption of ideality is made since the nitrate and nitrite ions are both univa-

TABLE	Ţ
TUDDE	- 4

THERMAL DECOMPOSITION OF NaNO3 IN ARGON (ONE

		ATMOSPHERE;	)	
Temp.,	Time,	Volur	ne (ml./g.) S.T	
°C.	min.	Oxygen	Nitrogen	$NO_2(N_2O_4)$
650	160	10.0	0.8	0.1
700	12	23.5	0.5	0.1
700	102	31.5	4.3	0.1
750	15	50.4	0.1	2.1
750	168	69.0	8.3	2.4
780	13	59.3	5.1	6.1
780	123	98.3	30.5	8.7
780	142	100.1	36.9	8.7

lent, occupying approximately the same space due to rotation at high temperatures and the cation is common to both salts. Furthermore, in general,

#### TABLE II

Thermodynam	IC FUNCTIONS AND R.	ATE CONSTANTS
1. Net reaction	: $NaNO_2(1) + 1/2O$	$_2(g) = NaNO_3(1)$
Temp., °C.	Change in free energy $\Delta F$ , kcal. mole <sup>-1</sup>	Equilibrium constant K., NNaNO3/NNANO2
600	-3.54	5.88
650	-1.77	2.61
700	-0.668	1.41
2. Reaction: N	$\operatorname{SaNO}_2(1) + \operatorname{O}_2(g) \rightarrow 1$	$NaNO_3(1) + O(g)$
	Free energy of activation	Rate constant
Temp., °C.	$\Delta F_1^{\ddagger}$ , kcal. mole <sup>-1</sup>	$k_{1}'$ $ imes$ 104, sec1
600	67.7	2.55
650	70.4	4.52
700	73.0	8.42
3. Reaction	h: $NaNO_{3}(l) \rightarrow NaN$	$O_2(1) + O(g)$
Temp., ° C.	Free energy of activation $\Delta F_2$ ;, kcal. mole <sup>-1</sup>	Rate constant $k_{2}' \times 10^{5}$ , sec. <sup>-1</sup>
600	70.8	4.35
650	72.3	17.3
700	73.8	59.7

systems approach ideal behavior at elevated temperatures.<sup>15</sup> The standard state of oxygen is taken as one atmosphere fugacity since the oxygen pressure was constant, one atmosphere, throughout the reaction. Consequently, the equilibrium constant,  $K_{e}$ , is equal to the ratio of the mole fractions, N, of sodium nitrite and sodium nitrate for the reaction between one mole of sodium nitrite and oxygen to form one mole of sodium nitrate.

$$K_{e} = \frac{N_{NaNO_3}}{N_{NaNO_2}} \tag{1}$$

(15) S. Glasstone, "Textbook of Physical Chemistry," D. Van Nostrand Company, Inc., New York, N. Y., 1946, p. 713. The values of the equilibrium constant vary inversely with temperature and are given in Table II.

From a graph of the logarithm of the equilibrium constants vs. the reciprocal of the absolute temperature, Fig. 7, the heat of reaction for the formation of one mole of sodium nitrate from the reaction between sodium nitrite and oxygen was calculated to be -24.5 kcal. per mole. This is in good agreement with the calculated value, -25.6 kcal. per mole, based upon the heats of formation of sodium nitrate (solid), -111.5 kcal. mole<sup>-1</sup>, and sodium ni-trite (solid), -85.9 kcal. per mole.<sup>16</sup> Other investigators have found that equilibrium exists between lithium nitrate, lithium nitrite and oxygen just above the melting point of lithium nitrate and calculated the heat of reaction for the formation of one mole of lithium nitrate from lithium nitrite and oxygen to be 25.1 kcal. per mole.<sup>17</sup> The change in free energy for the reaction between sodium nitrite and oxygen to form sodium nitrate varies from -3.54 kcal. mole<sup>-1</sup> at 600° to -0.67 kcal. mole<sup>-1</sup> at  $700^{\circ}$  (see Table II).

By carrying out the oxidation in a vessel having a smaller inside diameter (1.30 cm.), the rate of reaction was decreased by 40%, which is approximately proportional to the decrease in the contact area between the melt and the gaseous phase. This indicates that the reaction is heterogeneous occurring, principally, on the surface of the melt between oxygen (gas) and sodium nitrite (liquid).

For the deviation of a rate expression the following relationship is considered.

NaNO<sub>2</sub> + 
$$\frac{1}{2}$$
 O<sub>2</sub>  $\stackrel{k_1}{\underset{k_2}{\longleftarrow}}$  NaNO<sub>3</sub> (2)

 $k_1$  and  $k_2$  = rate constants

The rate of the forward reaction 
$$v_1$$
 is

$$v_1 = k_1 \, \Omega_{O_2}^{1/2} \, \Omega_{NaNO_2} \tag{3}$$

 $Q_{0}$  = fugacity of oxygen

 $\Omega_{NaNO_2}$  = surface activity of sodium nitrite, moles NaNO<sub>2</sub>/

The activity of sodium nitrite is dependent on the amount of sodium nitrite at the surface of the melt and is proportional to its mole fraction. The fugacity of oxygen is independent of the activity of sodium nitrite and remains essentially constant during the reaction. Therefore, the rate equation takes the form

$$v_1 = k'_1 N_{NaNO_2} = k'_1 (1 - x/a)$$
(4)

 $k_1' = a$  new rate constant

- x =moles sodium nitrate in the melt

a = moles sodium nitrate plus moles sodium nitritex/a = mole fraction of sodium nitrate in the melt(1 - x/a) = mole fraction of sodium nitrite in the melt

The rate of decomposition of sodium nitrate is given in equation 5.

$$v_2 = k_2 \Omega_{N_a N O_a} = k'_2 N_{N_a N O_a} = k'_2 x/a$$
(5)

The activity of sodium nitrate is taken as equal to its mole fraction,  $N_{NaNOi}$ , since the melt is assumed



Fig. 7.—Temperature dependency of equilibrium constant; log equilibrium constant  $K_e vs. 1/T \times 10^3$ , °K.<sup>-1</sup>.

to be ideal. The rate of formation of sodium nitrate is

$$d(x/a)/dt = k'_1 (1 - x/a) - k'_2 x/a$$
 (6)

At equilibrium  $v_1 = v_2$ . From these relationships the following rate expression is obtained for the case where initially only sodium nitrite is present (x/a = 0 at t = 0)

$$k'_1 = (x_e/at) \ln x_e/(x_e - x)$$
 (7)

 $x_{\rm e}$  = amount of sodium nitrate at equilibrium. If one starts with pure sodium nitrate, an identical expression for  $k_2'$  is obtained,  $x_e$  and x being replaced by  $y_e$  and y, which refer to moles of sodium nitrite. Figure 8 shows the results of substituting the experimental data in equation 7 and plotting  $(x_e/a) \ln x_e/(x_e - x)$  as a function of time. The points fall along a series of straight lines showing good agreement between the theoretical and observed results.

From a graph of the logarithm of the rate constants,  $k'_1$ , vs.  $T^{-1}$ , Fig. 9, the activation energy was



Fig. 8.-Kinetics of reaction between sodium nitrite and oxygen  $(x_e/a)$  ln  $x_e/(x_e - x) \times 10^1$  vs. time, min.

calculated to be 20.7 kcal. mole<sup>-1</sup>. The rate constants,  $k'_{2}$ , for the decomposition of sodium nitrate to sodium nitrite and oxygen were calculated from the relationship between the equilibrium constant,  $K_{e}$ , and the rate constants (see Table II).

$$K_{\mathbf{e}} = k_1'/k_2' \tag{8}$$

The graph,  $\log k_2 vs. T^{-1}$ , for the decomposition of sodium nitrate is plotted in Fig. 9. The activation

<sup>(16)</sup> National Bureau of Standards: Circular 500, Selected Values of Chemical Thermodynamic Properties, by F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, February, 1952.

<sup>(17)</sup> M. Centnerzwer and M. Blaumenthal, Bull. inter. acad. polon. ci.; sci. math. nat., No. 8-9, 470 (1936).



Fig. 9.—Temperature dependency of the rate constants: O, left coördinate, log  $k_2'$  vs.  $1/T \times 10^3$ , °K.<sup>-1</sup>;  $\triangle$ , right coördinate log  $k_1'$  vs.  $1/T \times 10^3$ , °K.<sup>-1</sup>.

energy was calculated from the slope of the line to be 44.7 kcal. mole<sup>-1</sup>.

The dissociation energy<sup>18</sup> of oxygen, 118.2 kcal. mole<sup>-1</sup>, is considerably greater than the activation energy for the formation of sodium nitrate from sodium nitrite and oxygen, 20.7 kcal. mole<sup>-1</sup>. From this it is clear that a reaction mechanism involving the oxidation of nitrite by atomic oxygen, formed from the dissociation of molecular oxygen, is not probable. Consequently, the energetics and reaction kinetics favor the following mechanism for the oxidation and decomposition reactions.

Oxidation:

$$NaNO_2 + O_2 \xrightarrow{k_1^n} NaNO_3 + O$$
 (9)

$$O + NaNO_2 \xrightarrow{R_1^*} NaNO_3$$
 (10)

Decomposition:

(

$$NaNO_3 \xrightarrow{k_2^{\circ}} NaNO_2 + ()$$
(11)

$$) + \text{NaNO}_3 \xrightarrow{k_2^2} \text{NaNO}_2 + O_2$$
 (12)

 $k_1^*, k_1^b, k_2^*, k_2^*$  = rate constants. The reaction, 20  $\rightarrow O_2$ , is of minor importance due to the negligibly small concentration of atomic oxygen with respect to the concentration of nitrate and nitrite. The above sequence of reactions is in agreement with the observed kinetics in two respects: reactions (9) and (11) should be slow compared to (10) and (12), respectively; and from general kinetic considerations.

$$v_1 = k_1^* \mathfrak{A}_{\mathsf{NaNO}_2} \mathfrak{A}_{\mathsf{O}_2} + k_1^* \mathfrak{A}_{\mathsf{NaNO}_2} \mathfrak{A}_{\mathsf{O}} - k_2^* \mathfrak{A}_{\mathsf{NaNO}_3} \mathfrak{A}_{\mathsf{O}} - k_2^* \mathfrak{A}_{\mathsf{NaNO}_4} (13)$$

 $v_1$  = velocity of over-all oxidation reaction. The concentration of atomic oxygen, an unstable intermediate, is assumed to be essentially constant during most of the reaction (stationary state approximation). On this basis the activity of oxygen is incorporated into the rate constant. The fugacity of molecular oxygen is also constant at one atmos-

(18) L. Pauling, "Nature of the Chemical Bond," Cornell Univerity Press, Ithaca, N. Y., 1948, p. 61. phere of pressure. Therefore, the rate of formation of sodium nitrate is

$$v_{1} = K_{1}^{n} \Omega_{NaNO_{2}} + K_{1}^{h} \Omega_{NaNO_{2}} - K_{2}^{h} \Omega_{NaNO_{3}} - k_{2}^{h} \Omega_{NaNO_{3}} = (K_{1}^{n} + K_{1}^{h}) \Omega_{NaNO_{3}} - (K_{2}^{h} + k_{2}^{h}) \Omega_{NaNO_{2}}$$
(14)

- - - 1

where  $(K_1^{\circ} + K_1^{\circ})$  and  $(K_2^{\circ} + k_2^{\circ})$  correspond to  $k_1^{\prime}$  and  $k_2^{\prime}$  in equation 6.

The entropies and free energies of activation were determined from equations 15 and 16 assuming that  $\Delta H^{\ddagger}$  is approximately equal to the energy of activation  $\Delta E^{\ddagger}$ .

$$k'_{1} \text{ or } k'_{2} - kT/h \ e^{\Delta S^{\dagger}/R} e^{-\Delta H^{\dagger}/RT}$$
(15)  

$$h = \text{Planck's constant}$$
  

$$\Delta H^{\ddagger} = \text{heat of activation}$$
  

$$k = \text{Boltzmann's constant}$$
  

$$R = \text{gas constant}$$
  

$$\Delta S^{\ddagger} = \text{entropy of activation}$$
  

$$\Delta F^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$$
(16)

 $\Delta F^{\ddagger}$  = free energy of activation, kcal. mole<sup>-1</sup>

The entropies of activation at  $650^{\circ}$  were calculated to be -53.8 and -29.8 c.u., for the forward and reverse reactions, respectively. The corresponding values for the free energies of activation vary from 67.7 to 73.0 kcal. mole<sup>-1</sup> and 70.8 to 73.8 kcal. mole<sup>-1</sup>, Table II.

A study of the decomposition of sodium nitrate at 700° in an oxygen atmosphere appears to confirm the above treatment and interpretation. After a period of 40 minutes equilibrium was attained and the equilibrium constant,  $K'_{e}$ ,  $N_{\text{NaNO}_2}/N_{\text{NaNO}_3}$ , was found to equal 0.342. Figure 10 shows the linear relationship obtained by plotting  $(y_e/a) \ln y_e/(y_e - y)$  vs. time. The rate constant for the decomposition was determined from the slope of the line to be 5.60  $\times 10^{-4}$  sec.<sup>-1</sup> and is in good agreement with the value obtained from the study



Fig. 10.—Kinetics of the decomposition of sodium nitrate in oxygen;  $(y_e/a) \ln y_e/(y_e - y) \times 10^4 vs.$  time, min.

of the oxidation of sodium nitrite,  $5.97 \times 10^{-4}$  sec.<sup>-1</sup>. The rate constant for the oxidation reaction is  $1.64 \times 10^{-3}$  sec.<sup>-1</sup>, approximately two times greater than that found by studying the reaction between sodium nitrite and oxygen,  $8.42 \times 10^{-4}$  sec.<sup>-1</sup>. This is attributed to a catalytic effect of traces of nitric oxide which was formed during the early stages of the decomposition. Nitric oxide reacts with oxygen to form nitrogen dioxide which reacts with sodium nitrite to form sodium nitrate and nitric oxide. The reactions may be represented as

$$NaNO_2 + NO_2 = NaNO_3 + NO$$
(17)

Nov., 1956

$$NO + 1/2O_2 = NO_2$$
 (18)

$$NaNO_3 = NaNO_2 + O$$
(19)

$$O + NO = NO_2$$
 (20)

The value for the energy of the nitrogen to oxygen bond in sodium nitrate may be calculated from the dissociation energy of oxygen,<sup>18</sup> 118.2 kcal. mole<sup>-1</sup>, and the energies of activation by the following considerations

$$E_{(N...O..O)} - E_{O_2} = 20.7 \text{ kcal. mole}^{-1}$$
 (21)

$$E_{(N,\ldots,0,\ldots,0)} = 20.7 + 118.2 = 138.9 \text{ kcal. mole}^{-1}$$
 (22)

$$E_{(N \dots O \dots O)} E_{N-O} = 44.7 \text{ kcal, mole}^{-1}$$
 (23)

$$E_{(N-0)} = 138.9 - 44.7 = 94.2 \text{ kcal. mole}^{-1}$$
 (24)

 $(N \dots O) = bonds$  in transition state. The assumption is made that the temperature dependency of the rate constants for reactions (10) and

(12) are small compared to reactions (9) and (11) due to the unstable nature of atomic oxygen. The value for the nitrogen to oxygen bond in sodium nitrate determined from the heat of dissociation of oxygen and heats of formation of sodium nitrate and nitrite (solid)<sup>15</sup> is 84.7 kcal. mole<sup>-1</sup>. This discrepancy can be attributed to the assumptions used in the above calculations.

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## THIOCYANATE COMPLEXES OF LEAD AND THALLIUM IN SOLUTION

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Polarographic studies of the reduction of lead ions in thiocyanate-perchlorate mixtures of constant ionic strength have shown the existence of the species PbSCN<sup>+</sup>, Pb(SCN)<sub>2</sub> and Pb(SCN)<sub>4</sub><sup>-</sup> in these solutions. The over-all formation constants at 25° and an ionic strength of 2.00 M are  $K_1 = 3.5$ ,  $K_2 = 7.5$  and  $K_4 = 7$ . The ion Pb(SCN)<sub>3</sub><sup>-</sup> appears to have a formation constant of the order of 0.1 under the same conditions. Similar studies on thallous ion in nitrate-thiocyanate mixtures show evidence only for un-ionized thallous thiocyanate with a formation constant of about 2.6.

Lead and particularly thallium show relatively little tendency to form complexes with thiocyanate ion in solution, as evidenced by the close correspondence of the half-wave potentials in dilute thiocyanate solutions with those in "non-complexing" electrolytes.<sup>1,2</sup> For this reason, polarographers have in general assumed the non-existence of complex formation between these metals and thiocyanate, even in relatively concentrated solutions. The conductivity data of Böttger,<sup>3</sup> however, suggest the existence of the  $PbSCN^+$  with a stability comparable to that of the PbCl+ ion, and the solubility measurements by Bell and George<sup>4</sup> lead to a formation constant of 6.3 for the species TISCN at 25°. In order to see if the polarographic method could shed further light on this problem, we have studied the dependence of the half-wave potentials of lead and thallium as a function of thiocyanate ion activity in solutions of constant ionic strength.

#### Experimental

Apparatus and Materials.—Measurements were made either with a Sargent Model XII recording polarograph without damping and equipped with a wave spreader<sup>5</sup> to expand the voltage scale, or a manual apparatus similar to that of Lingane and Kolthoff.<sup>6</sup> The dropping electrodes were fabricated of commercial marine barometer tubing and

(5) T. W. Gilbert and D. N. Hume, Anal. Chem., 24, 431 (1952).

(6) J. J. Lingane, J. Am. Chem. Soc., 61, 825 (1939).

**Technique.**—The general method of operation was similar to that described in previous papers.<sup>7-9</sup> The half-wave potentials were estimated from plots of log  $[(i_d - i)/i]$ *versus E*, in which duplicate samples checked to within 1 mv. All values were corrected for *iR* drop in the cell. Good straight lines with slopes in close agreement with the theoretical values were obtained in the above plots, and it was concluded that both systems showed satisfactory reversibility.

#### **Results and Discussion**

Lead Thiocyanate.—The half-wave potential and diffusion current of lead were measured in the cell

		NaClO4	$1.9 \ M$	NaClO <sub>4</sub>	NaClO₄	(2-x) M	
Hg	$Hg_2$	NaCl	0.1 M	2.0 M	NaSCN	x M	d.
	$\overline{\mathrm{Cl}_2}$	HClO₄	0.001	HClO₄	HClO₄	$0.001 \ M$	m
		-	M	0 001 M	Pb(ClO₄)	$5 \times 10^{-4}$	e

for values of x from 0 to 2.00 M in steps of 0.1 M. Gelatin (0.01%) was used as a maximum suppressor. The negative shifts in half-wave potential observed

(7) D. N. Hume, D. D. DeFord and G. C. B. Cave, *ibid.*, **73**, 5323 (1951).

(8) H. M. Hershenson, M. E. Smith and D. N. Hume, *ibid.*, **75**, 507 (1953).

(9) R. E. Frank and D. N. Hume, ibid., 75, 1736 (1953).

<sup>(1)</sup> I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1952.

<sup>(2)</sup> J. O. Hibbets and S. S. Cooper, Anal. Chem., 26, 1119 (1954).

<sup>(3)</sup> W. Böttger, Z. physik. Chem., 46, 521 (1903).

<sup>(4)</sup> R. P. Bell and J. H. B. George, Trans. Faraday Soc., 49, 619 (1953).



Fig. 1.—Analysis of half-wave potential of lead in thiocyanate-perchlorate mixtures in the range of thiocyanate molarity 0.0 to 1.0.



Fig. 2.—Analysis of half-wave potential of lead in thiocyanate-perchlorate mixtures at higher concentrations.

were small (4 mv. in 0.1 M thiocyanate, 35 mv. in 1.0 M thiocyanate and 63 mv. in 2.0 M thiocyanate), but very clear-cut and not explainable merely on the basis of changes in activity coefficient of lead ion in these solutions. The data were subjected to analysis by the method of DeFord and Hume<sup>10</sup> and the results are presented in Table I and graphically in Figs. 1 and 2. Because the complexes involved are very weak and consequently the potential differences small, the effect of experimental error on the interpretation of the results is greater than in previous studies. In order to reveal the contribution due to personal bias in estimating slopes and intercepts, the data were analyzed by two persons working independently of each other, one doing the analysis directly on the two duplicate series of measurements and the other taking points from a smoothed curve of  $F_0(x)$ which incorporated both sets of data. The resulting K values were in remarkable agreement ( $\pm 0.5$ unit) indicating the effect of personal equation to be small, even in the interpretation of difficult cases.

The curves in Fig. 1 show clearly that up to about 0.5 M thiocyanate,  $PbSCN + and Pb(SCN)_2$ are the only important species formed. At higher thiocyanate concentrations, the contribution of  $Pb(SCN)_4$  becomes important. The best estimates of the formation constants were taken as  $K_1 = 3.5$ ,  $K_2 = 7.5$  and  $K_4 = 7$ . The formation constant of the  $Pb(SCN)_3$ -ion is small—too small to be evaluated with any degree of confidence by this method. It may safely be stated to be less than 1.0 and is probably not much greater than 0.1. In its behavior with thiocyanate as a complexing ligand, lead closely resembles cadmium and zinc in this respect. In complexes with chloride, however, lead like cadmium forms a relatively stable MX<sub>3</sub><sup>-</sup> ion but not the  $MX_4^{=.11}$ 

Thallous Thiocyanate.—The half-wave potential of the thallous ion was found to vary only very slightly with sodium nitrate concentration, the shift being -12 mv. going from 0.1 to 1.0 M sodium nitrate supporting electrolyte. This shift is of the order of magnitude which might be expected from junction potential and activity coefficient changes and was interpreted as indicating negligible nitrate complex formation. In sodium thiocyanate solutions, however, the change was three times as great and at high thiocyanate ion concentrations the half-wave potential was observed to be shifting markedly to more negative values. Accordingly measurements were made of the half-wave potential of  $0.001 \ M$  solutions of thallous nitrate in sodium nitrate-sodium thiocyanate mixtures at a constant ionic strength of  $2.00 \ M$ . The changes in halfwave potential were quite small, e.g., 30 mv. due to 1 M thiocyanate ion, indicating the complexformation to be weak. Only a single "complex," TISCN, with formation constant of 2.6 was shown conclusively to be present by the analysis (Table II and Fig. 3). The determination, based on such small potential differences, is necessarily rather uncertain, but the existence of the species TISCN is clearly evident and the agreement with the re-

(10) D. DeFord and D. Hume, J. Am. Chem. Soc., 73, 5321 (1951).
(11) P. Kivalo, Suomen Kemistilehti, B28, 155 (1955).

TABLE I

	Analysis	s of $E_{1/2}$ of	LEAD IN THIOD	YANATE-PERCHI	LORATE MIXT	URES AT $\mu =$	2.00	
SCN(M)	$E_{1/2}(v.)$	Is/Ic	$F_0(X)$	$F_0(X)^a$	$F_1(X)$	$F_2(X)$	$F_{\delta}(X)$	$F_4(X)$
0.00	-0.4611	1.00	(1.00)	(1.00)	$[3, 5]^{b}$	$(7,5)^{b}$	$[\sim 0]^{b}$	[7] <sup>b</sup>
. 10	4650	1.02	1.38	1.38	3.80	3 0		
. 20	4688	1.02	1.41	2.00	5.00	75		
. 30	- 4740	1.03	2.81	<b>2</b> , $70$	5.67	72		
. 40	4760	1.10	3.52	3.60	6.50	7.5		
. 50	4790	1.14	4.60	4.60	7.20	7.4		
. 60	4832	1.25	7.00	6.70	9.50	10.9	5.7	9.5
. 80	4896	1.32	12.2	11.7	13.4	12.4	6.1	7.6
. 90	4922	1.39	15.6	14.9	15.4	12.4	5.4	6.0
1.00	4956	1.29	19.0	18.5	17.5	13.0	6.5	6.5
1.10	4985	1.22	22.6	23.4	20.7	15 6	7.4	6.7
1.30	5064	1.16	36.9	39.0	29.2	19 8	9.5	7.4
1.40	5091	1.18	49.9	49.9	34.9	22.4	10.6	7.6
1.70	5172	1.16	92	92	54	30	13	7.6
1.80	5220	1.15	108	108	59	31	13	7.3
1.90	5227	1.15	141	141	74	37	15	8.0
2.00	5244	1.19	165	165	82	39	16	8.0

<sup>2</sup> Taken from smooth curve drawn through  $F_0(X)$  values in previous column. <sup>b</sup> By extrapolation to (X) = 0.

sults of Bell and George is as good as can be expected under the circumstances.

TABLE II						
Analysis	OF $E_{1/2}$ of	THALLI	um(I) in	THIOCYANATE-		
	NITRATE N	IXTURES	AT $\mu = 2$ .	00		
$\mathrm{SCN}(M)$	$E_{1/2}(v.)$	Is/Ic	$F_0(X)$	$F_1(X)$		
0.00	-0.472	1.00	(1.00)	[2.6](extrap.)		
. 10	473	1.00	1.04			
. 20	483	0.99	1.52	2.6		
. 30	487	1.01	1.81	<b>2</b> .7		
. 60	494	1.06	2.50	2.5		
1.00	504	1.12	3.90	2.9		
1.30	510	1.15	5.06	3.1		
2.00	519	1.18	7.31	3.1		

The above results indicate that the use of thallium as a "pilot ion" in polarography must be made with some caution. The half-wave potential is definitely not independent of supporting electrolyte composition when thiocyanate is present, and one might expect similar behavior to be found in solutions of other complex-forming anions if the half-wave potential measurements were made correspondingly precise.

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Fig. 3.—Analysis of half-wave potential of thallous ion in thiocyanate-nitrate mixtures.

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## DIELECTRIC PROPERTIES OF LOWER-MEMBERED POLYETHYLENE GLYCOLS AT LOW FREQUENCIES

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The dielectric properties of seven polymeric homologs of glycol from ethylene glycol to heptaethylene glycol have been measured at the frequencies of 0.5 to 50 kc./sec. by means of a conductance capacitance bridge. The measurements were made on liquid, supercooled liquid and solid states of these polyethylene glycols over the temperature range from -70 to  $+60^{\circ}$ . In the liquid state the dielectric constant for each polyethylene glycol showed the equilibrium or static value to be dependent on temperature, being smaller, the higher the homolog of polyethylene glycol. It was found empirically that the variation of static dielectric constant for these polyethylene glycols was linear with the reciprocal absolute temperature. In the crystalline solid the dielectric constant showed small values of 3 to 4 almost independent of the type of polyethylene glycol. In the case of tetraethylene glycol the dielectric dispersion and absorption which can be expressed by the "lemniscate" formula was observed in the supercooled liquid state.

#### Introduction

Although some extensive investigations have hitherto been carried out on the dielectric properties of high polymers,<sup>1a-d</sup> dielectric measurements of lower polymeric homologs have not been made. It may be important for studying the dielectric properties of high polymers to obtain some information about the dielectric behavior of lower polymeric homologs.

In this research some dielectric measurements have been attempted on lower polymeric homologs of polyethylene glycol. Polyethylene glycols HO- $[CH_2CH_2O]_{n-1}CH_2CH_2OH$  are characterized by a very hydrophilic or water-soluble nature and have relatively large dielectric constants. This hydrophilic property may arise from the two end hydroxyl groups and the polyoxyethylene group. Some physical properties of polyethylene glycols have been reported by Hibbert and his co-workers, and others.<sup>2</sup> However, there are no available data on dielectric properties of polyethylene glycols.

The present work was undertaken to determine the static dielectric constants of lower homologs of polyethylene glycol and examine the variation of their dielectric properties with the series of homologs.

#### Experimental

Materials.—The seven homologous polychylene glycols from ethylene glycol to heptaethylene glycol were prepared by the fractional distillation of commercial products from Carbide and Carbon Chem. Co. Since possible impurities present in the commercial glycols used are water and homologous glycols, and since the glycols used herein form no azeotropic mixture with water, it is relatively easy to obtain each homologous polyethylene glycol by fractional distillation of commercial products dried over a suitable drying agent.

Commercial ethylene glycol was purified by drying over freshly dehydrated sodium sulfate and three successive fractional distillations at a reduced pressure, retaining only the middle fraction, and finally recrystallized twice; b.p.  $83.0^{\circ}$  (8 mm.); m.p.  $-12^{\circ}$ ; lit. m.p.  $-13^{\circ}$ ,<sup>2</sup>  $-13.2^{\circ}$ ; density  $d^{20}$ , 1.1150; lit.  $d^{20}$ , 1.1136.<sup>2</sup> Commercial diethylene

(3) A. F. Gallaugher and H. Hibbert, J. Am. Chem. Soc., 58, 813 (1936).

glycol and triethylene glycol were purified in the same way as ethylene glycol. Diethylene glycol: b.p.  $117.2-117.5^{\circ}$ ; (7 mm.); m.p.  $-6^{\circ}$ ; lit. m.p.  $-8^{\circ},^2 -10.1^{\circ}.^3$  Triethylene glycol: b.p.  $144 \pm 1^{\circ}$  (6 mm.); m.p.  $-8^{\circ}$ ; lit. m.p.  $-4.3^{\circ},^4 -7.2^{\circ},^2 -9.4^{\circ}3$ ; hydroxyl value 748 (theoretical 747.5).

Tetracthylene glycol and higher homologs were prepared by several successive fractional distillations of "Polyethylene Glycol 300" and "Polyethylene Glycol 400" from Carbide and Carbon Chem. Co. under a reduced pressure of nitrogen, to avoid oxidation by air at high boiling temperature. Finally, each homolog was purified by two or more fractional recrystallizations, retaining only the crystalline portion. Tetraethylene glycol: b.p.  $154 \pm 1^{\circ}$  (2 mm.); m.p.  $-3^{\circ}$ ; lit. m.p.  $-6.2^{\circ}{}_{2}^{2} - 9.4^{\circ}{}_{3}$ ; hydroxyl value 581 (theoretical 578.0). Pentaethylene glycol: b.p.  $184 \pm 1^{\circ}$ (2 mm.); m.p. range -2 to 0°; lit. m.p.  $-8.7^{\circ}{}_{3}$ ; hydroxyl value 472 (theoretical 471.1). Hexaethylene glycol: b.p.  $214 \pm 1^{\circ}$  (2 mm.); m.p. range 5 to 7°; lit. m.p.  $2.1^{\circ}{}_{,2}^{2}$  $1.3^{\circ}{}_{3}^{3}$ ; hydroxyl value 378 (theoretical 397.6). Heptaethylene glycol: b.p.  $237-244^{\circ}$  (2 mm.); m.p. range 10 to  $12^{\circ}{}_{3}$ ; lit. m.p.  $7.7^{\circ}{}_{3}^{3}$ ; hydroxyl value 330 (theoretical 343.9). These glycols are very hygroscopic, so that refined semples

These glycols are very hygroscopic, so that refined samples were always kept in a desiccator just before use to prevent them from absorbing moisture.

Apparatus and Measurements.—Capacitance and conductance measurements were made on the liquid and solid states of glycols at temperatures from -70 to  $+60^{\circ}$  over the frequency range of 0.5-50 kc. with an impedance bridge of the parallel resistance type which has been described elsewhere.<sup>5</sup> The measuring cell used consisted of two concentric platinum cylinders whose empty capacitance was about 30  $\mu\mu f$ ., and was calibrated with several standard liquids.<sup>5</sup> The accuracy of the dielectric constant was within  $\pm 0.5\%$ . The bridge used was rather suitable for measurements of high conductance which ranged from 0.1 to 1000  $\mu$ mhos.

To check the value of equivalent high frequency conductance in measurements of dielectric absorption, the equivalent capacitance  $C_p$  and conductance  $G_p$  for parallel combination were measured on a series combination of resistance  $R_s$  and capacitance  $C_s$  as a function of frequency. It is easily shown that  $C_p$  and  $G_p$  are related to  $C_s$  and  $R_s$ by the equations

$$C_{\rm p} = \frac{C_{\rm s}}{1 + (\omega T_{\rm s})^2}, \frac{G_{\rm p}}{\omega} = \frac{C_{\rm s}\omega T_{\rm s}}{1 + (\omega T_{\rm s})^2} \text{ and } T_{\rm s} = R_{\rm s} C_{\rm s}$$

where  $\omega$  is the angular frequency equal to  $2\pi$  times frequency f and  $T_s$  is the time constant for given  $C_s$  and  $R_s$ .

Therefore, plots of  $G_{\rm p}/\omega$  versus  $C_{\rm p}$  as a function of frequency must fall on a semi-circle for given  $C_{\rm s}$  and  $R_{\rm s}$ , and plots of log  $(G_{\rm p}/\omega C_{\rm p})$  versus log f must give a straight line with a slope of unity, whose intercept with the line for log  $(G_{\rm p}/\omega C_{\rm p}) = 0$  gives the frequency corresponding to the reciprocal of the time constant. The test plots of  $G_{\rm p}/\omega$ 

(5) N. Koizumi and T. Hanai, Bull. Inst. Chem. Research, Kyoto Univ., 33, 14 (1955).

See (a) R. E. Burk and O. Grummitt, "The Chemistry of Large Molecules," Interscience Pub. Inc., New York, N. Y., 1943, Chap. VI;
 F. H. Müller and Chr. Schmelzer, Ergeb. exakt. Natur., 25, 359 (1951); (c) F. Würstlin, Kolloid-Z., 134, 135 (1953); (d) A. R. von Hippel, "Dielectric Materials and Applications," John Wiley and Sons, Inc., New York, N. Y., 1954, Chap. V.

<sup>(2)</sup> Cited in G. O. Curme, Jr., and F. Johnston, "Glycol," Reinhold Publ. Corp., New York, N. Y., 1952, Chap. 1, 3 and 7.

<sup>(4)</sup> Carbide and Carbon Chem. Co., "Physical Properties of Synthetic Org. Chemicals," 1956 ed.

Temp	Dielectric constant $\epsilon$ of glycols								
°C.	Ethylen	e,	Diethylene	Triethylene	Tetraethylene	Pentaethylene	Hexaethylene	Heptaethylene	
			Liquid a	and supercool	$\operatorname{ed} \operatorname{liquids}^a$				
60	31.58 (lit.6)	33.42	24.83	19.18	16.53	14.83	13.28	12.45	
50	33.21 (lit. <sup>6</sup> )	35.28	26.40	20.11	17.26	15.55	13.86	13.01	
35	35.86° (lit.6)	38.41	28.90	21.94	18.84	16.86	14.92	13.96	
<b>20</b>	38.66 (lit. <sup>6</sup> )	41.82	31.69	23.69	20.44	18.16	16.00	14.85	
5		45.70	34.81	25.60	22.24	19.60	17.14	15.83	
- 5		<b>48</b> , $50$	37.12	<b>27</b> , $00$	23.55	20.67	18.00	16.66	
-20		53.01	40.69	29.36	25.51	22.30	19.48	17.90	
				$\operatorname{Solid}^b$					
-10			3.93	4.45	3,80	4.61	3.96	3.96	
-20		3.73	3.47	3.60	3.49	4.21	3.91	3.91	
-30		3.52	3.32	3.43	3.36	3.99	3.87	3.88	
-40		3.43	3.24	3.39	3.34	3.82	3.83	3.85	
-50		3,37	3.21	3.41	3.36	3.66	3.73	3.79	
-60		3.33	3.21	3.37	3.27	3.31	3.39	3.56	
-70		3.31	3.21	3.24	3.14	3.24	3.27	3.41	
~									

<b>m</b>	T
TABLE	
TUDDU	-

Dielectric Constants of Homologous Polyethylene Glycols

<sup>a</sup> Static dielectric constants. <sup>b</sup> Values at 5 kc. <sup>c</sup> Interpolated value.

versus  $C_p$  and log  $(G_p/\omega C_p)$  versus log f obtained for a series combination of a carbon resistor and a mica condenser were consistent precisely with the predicted forms. It was, of course, checked beforehand that the resistor and the capacitor alone had no frequency dependent value.

This procedure will be useful to check whether the measuring set gives systematic errors in measurements of the equivalent high frequency conductance for dielectric absorption or not.

#### **Results and Discussion**

Liquid.—The dielectric constants observed for polyethylene glycols at 5 kc. are listed in Table I.

These glycols showed a sharp change in dielectric constant at the melting point, giving small values in the solid state which were almost independent of kinds of glycol.

In the liquid and supercooled liquid states above temperatures of about  $-30^{\circ}$ , the dielectric constant showed no variation with frequency, within the present frequency range, corresponding to the static dielectric constants, and showed the normal decreasing tendency with increasing temperature which is characteristic of dipolar liquids. The higher the homolog of polyethylene glycol, the smaller was the dielectric constant.

Considering that the main contribution to the dielectric polarization of liquid polyethylene glycol may be due to the orientation polarization of hydroxyl groups, it is a reasonable result that higher polyethylene glycols, having fewer hydroxyl groups per cc., show smaller dielectric constants.

There are no available data on the dielectric constants of polyethylene glycols. Although Åkerlöf's data<sup>6</sup> for ethylene glycol are accepted as the static dielectric constants, the values observed in this work were somewhat larger than those of Åkerlöf, as given in Table I.

For associated liquids such as polyethylene glycols which involve strong intermolecular hydrogen bonding, the relation between the dielectric constant and the dipole moment may be considered quantitatively in terms of the Kirkwood relation- $\rm ship^7$ 

$$\frac{(\epsilon-1)(2\epsilon+1)}{9\epsilon}\frac{M}{d} = \frac{4\pi N}{3}\left(\alpha + \frac{g\mu^2}{3kT}\right)$$

where M is the molecular weight, d the density, NAvogadro's number,  $\alpha$  the optical polarizability,  $\mu$ the dipole moment in liquid state and g the correlation parameter.

The calculated value of the effective dipole moment in liquid  $g^{1/2}\mu$  for each polyethylene glycol increased with the increasing number of the polymeric member, as shown in Table II.

#### TABLE II

LIQUID MOMENTS OF POLYETHYLENE GLYCOLS BY KIRK-WOOD'S RELATIONSHIP

Glycol	Liquid moment $g^{1/2}_{\mu} \times 10^{18}$ e.s.u. at 20°
Ethylene	4.87
Diethylene	5.50
Triethylene	5.58
Tetraethylene	5.84
Pentaethylene	6.05
Hexaethylene	6.14
Heptaethylene	6.35

Uchida, Kurita, Koizumi and Kubo<sup>8</sup> have recently measured the dipole moment of the same specimens used herein in dioxane solution and discussed the relation between the dipole moment and the molecular structure. The results showed the same tendency of the dipole moment to increase.

It was found that the observed dielectric constants for all the polyethylene glycols used were very linear with the reciprocal of absolute temperature T in a temperature range from -30 to  $+60^{\circ}$ . The numerical values of the dielectric constant for the individual polyethylene glycols are given as a function of 1/T by the formulas.

(7) J. G. Kirkwood, J. Chem. Phys., 7, 911 (1939); Trans. Faraday Soc., 42A, 7 (1946).

(8) T. Uchida, Y. Kurita, N. Koizumi and M. Kubo, J. Polymer Sci., in press.

<sup>(6)</sup> G. Åkerlöf, J. Am. Chem. Soc., 54, 4130 (1932).

Ethylene glycol	e	=	20700	$\times$	1/T	_	28.75
Diethylene glycol	e	=	16797	Х	1/T	—	25.59
Triethylene glycol	€	=	10912	Х	1/T	—	13.57
Tetraethylene glycol	€	=	9731	Х	1/T	—	12.75
Pentaethylene glycol	ε	=	8074	Х	1/T	—	9.40
Hexaethylene glycol	e	=	6552	Х	1/T	-	6.38
Heptaethylene glycol	e	=	5700	$\times$	1/T	-	4.62

The maximum difference between the observed values and those calculated by the above formula was within  $\pm 0.5\%$ , being of the order of the experimental error in this work.

The linear relation of dielectric constant to 1/T was presented by Morgan and Lowry,<sup>9</sup> and Cole, et al.<sup>10</sup>; no theoretical basis was given. The present authors have also found that this linear relation holds for many other dipolar liquids. Yasumi and Komooka<sup>11</sup> recently have developed a theory on the dielectric constant of polar liquids which gives the linear relation of dielectric constant to 1/T.

The conductivity for polyethylene glycols measured together with the dielectric constant in the liquid state was also independent of frequency within the present frequency range, corresponding to d.c. conductivity. In many cases it is often difficult to make absolute measurements of the conductivity of a pure organic liquid, since any trace of ionic impurity affects the conductivity considerably. In the present work the numerical value of conductivity was reproducible within 10% irrespective of the purification run.

The conductivity for homologous polyethylene glycols decreased with higher members of the homologous series except in the case of diethylene glycol, as given in Table III.

#### TABLE III

D. C. Conductivities of Homologous Polyethylene  $G_{LYCOLS}$  at  $20^{\circ}$ 

D.c. conductivity $\sigma \times 10^{8}$ , mho cm. <sup>-1</sup>				
This research	Lit.12			
16	$116(25^{\circ})$			
3.1				
8.4				
4.7				
3.0				
1.3				
1.0				
	D.c. conduc mho This research 16 3.1 8.4 4.7 3.0 1.3 1.0			

It appears likely that most of the d.c. conductivity for glycols is attributable to the proton conduction mechanism by the intermolecular hydrogen bonding of the hydroxyl group. Therefore, for higher polyethylene glycols the number of hydroxyl groups per unit volume becomes smaller, resulting in the lower d.c. conduction.

Only diethylene glycol showed relatively small conductivity, being of the order of that for pentaethylene glycol. This small d.c. conductivity might be caused by intramolecular hydrogen bonding between two end hydroxyl groups, which would make the diethylene glycol molecule ring-

(9) S. O. Morgan and H. H. Lowry, THIS JOURNAL, 34, 2385 (1930).
(10) F. X. Hassion and R. H. Cole, J. Chem. Phys., 23, 1756 (1955);

D. J. Denney and R. H. Cole, *ibid.*, 23, 1767 (1955).
 (11) M. Yasumi and H. Komooka, *Bull. Chem. Soc. Japan*, 29, 407

(1956).
 (12) R. M. Müller, V. Raschka and M. Wittmann, Monalsh. Chem.,

(12) R. M. Müller, V. Raschka and M. Wittmann, Monalsh. Chem., 48, 659 (1927). like. Accordingly, in the case of diethylene glycol one of the two end hydroxyl groups would take part in d.c. conduction effectively. The thermal evidence for the intramolecular hydrogen bonding of diethylene glycol already has been reported by Hibbert and his co-workers.<sup>13</sup>

It appears, of course, that intramolecular hydrogen bonding is also possible in the case of higher polyethylene glycols.

As for the temperature dependence of the conductivity for polyethylene glycol, plots of log  $\sigma$  versus 1/T showed some deviation from linearity. Discussion of this point is given in the last section of the paper.

Solid.—On cooling polyethylene glycols through the melting point, the liquid state continued in various temperature ranges, and the dielectric constant rose gradually, but at a temperature of about  $-30^{\circ}$  below the melting point the liquid solidified into a crystalline state, giving a small value of 3 to 4 as shown in Table I.

This indicates that in the crystalline solid of polyethylene glycol most of the molecular dipoles are rotationally frozen or have no freedom of orientation to the electric field.

It was often noted that diethylene, triethylene and tetraethylene glycols supercooled until about  $-50^{\circ}$ , setting to a transparent vitreous state. This vitreous state continued for several hours when no external mechanical shock was given, and thereafter a white portion of spherical form, that is, a nucleus of polycrystal, appeared in the vitreous solid. But the nucleus grew too slowly, and a few days would have been necessary for the whole system to crystallize at about  $-50^{\circ}$ . On warming up to about 20°, however, the nucleus of crystal grew very rapidly. Such behavior of crystallization also has been found for isobutyl chloride<sup>14</sup> and glycerol.<sup>15</sup> It was considered that due to the very high viscosity of the vitreous state the rearrangement of molecules hardly occurred at a low temperature, but at a higher temperature below the melting point the decrease in viscosity made the molecular rearrangement, and thus the crystal growth, relatively easy.

In dielectric measurements of the solid state, it is important to attain thermal equilibrium. For this reason, when the temperature of the surrounding bath around the measuring cell was changed and set to a desired value, the measurements were made at a time interval of ten minutes or more until no variation of dielectric constant was observed with the lapse of time. Particularly at the temperature just below the melting point it was often noted that the temperature equilibrium was attained after ten hours or more. The values as shown in Table I are those obtained in this way.

For the lower glycols such as ethylene, diethylene and triethylene glycols the dielectric constant was about 3.3 in the crystalline solid state, decreasing only slightly with decreasing temperature within a temperature range from the melting point to  $-70^{\circ}$ , and no dielectric loss was observed.

(13) A. F. Gallaugher and H. Hibbert, J. Am. Chem. Soc., 59, 2514, 2521 (1937).

(14) A. Turkevich and C. P. Smyth, *ibid.*, **64**, 737 (1942).

(15) A. K. Schulz, Z. Naturforschg., 9a, 944 (1954),



Fig. 1.—Plots of  $\epsilon''$  versus  $\epsilon'$  for supercooled tetraethylene glycol. Numbers beside plots denote frequency in kc. Solid curve was drawn by eq. 1 for the case:  $\epsilon_0 = 33.7$  (at  $-56^\circ$ ),  $\epsilon_{\infty} = 4.0$  and  $\pi\beta/2 = 35^\circ$ .

On the other hand, in the case of those higher polyethylene glycols such as penta-, hexa- and heptaethylene glycol, the dielectric constant showed a value of about 3.8 near  $-40^{\circ}$ , decreasing at lower temperatures, and becoming about 3.3 at  $-70^{\circ}$ .

It was considered that the drop in the dielectric constant near  $-60^{\circ}$  for higher polyethylene glycols was due to a small dielectric dispersion, because the high frequency conductance increased appreciably, associated with the drop in the dielectric constant. The maximum dielectric loss was estimated to be of the order of 0.1 at 5 kc., too small to be measured with accuracy in the bridge used. Therefore the loss data are not given here.

Although no conclusive interpretations can be made, there are two possible explanations for the small dielectric dispersion observed for the higher polyethylene glycols. First, it can be considered that freedom of orientation of the polarization due to twisting of the molecular chain around the long axis is possible only for higher polyethylene glycols. Another possibility is that a small dielectric dispersion is caused by the dipole groups of amorphous solid present in the crystalline solid. The more gradual change in the dielectric constant at the melting point shows that a distribution of molecular size occurs.

A similar small dispersion of the dielectric constant in the solid state has been reported for some other solids, long chain esters,<sup>16</sup> ether,<sup>17</sup> amorphous polymers<sup>18</sup> and partially crystalline polyesters.<sup>19</sup>

**Dielectric Relaxation.**—As mentioned in the previous subsection, polyethylene glycols supercooled easily in some temperature ranges and showed a very high viscosity with decreasing temperature. In such a viscous or vitreous state dielectric dispersion and absorption would be

(19) F. Würstlin, Kolloid-Z., 110, 71 (1948).

expected for polyethylene glycols at the present experimental frequencies.

In fact, the dielectric dispersion was appreciably noted for these glycols below  $-40^{\circ}$  at frequencies of about 50 kc. However, the supercooled state was not always stable during the dispersion measurements, and crystallization occurred spontaneously.

In some cases with triethylene and tetraethylene glycols a stable supercooled state was realized for a time long enough to measure the complex dielectric constant  $\varepsilon^*$  as a function of frequency. The observed values of the complex dielectric constant for tetraethylene glycol are plotted in a complex plane in Fig. 1.

The loci of  $\epsilon^* (= \epsilon' - j\epsilon'')$  for tetraethylene glycol fitted approximately to the "lemniscate" formula which has been given for supercooled propylene glycol and glycerol by Davidson and Cole.<sup>20,21</sup>

$$\epsilon^* - \epsilon_{\infty} = \frac{\epsilon_0 - \epsilon_{\infty}}{(1 + j\omega\tau)^{\beta'}}, \ 1 \ge \beta > 0 \tag{1}$$

where  $\epsilon_0$  is the static value,  $\epsilon_{\infty}$  the limiting value at the high frequency side,  $\tau$  the most probable relaxation time,  $\beta$  a parameter for the distribution of relaxation times and j and  $\omega$  have the usual significance.

From eq. 1 the real and imaginary parts of the dielectric constant,  $\epsilon'$  and  $\epsilon''$ , are given as

$$\begin{aligned} & \epsilon' - \epsilon_{\infty} = (\epsilon_0 - \epsilon_{\infty})(\cos \phi) \cos \beta \phi \\ & \epsilon'' = (\epsilon_0 - \epsilon_{\infty})(\cos \phi)^{\beta} \sin \beta \phi \end{aligned}$$

where  $\tan \phi = \omega \tau$ .

Then, putting  $\theta = \tan^{-1}[\epsilon''/(\epsilon' - \epsilon_{\infty})]$ , one obtains another expression for the frequency dependence of  $\epsilon^*$  in the dielectric relaxation of "lemniscate" type

$$\omega \tau = \tan \left( \theta / \beta \right) \tag{2}$$

<sup>(16)</sup> R: W. Crowe and C. P. Smyth, J. Am. Chem. Soc., 72, 5281 (1950).

<sup>(17)</sup> A. Schallamach, Nature, 158, 619 (1946).

<sup>(18)</sup> E.g., ref. 1a, p. 450.

<sup>(20)</sup> D. W. Davidson and R. H. Cole, J. Chem. Phys., 19, 1484 (1951).

<sup>(21)</sup> S. Takahashi suggested that eq. 1 for  $\beta = 0.5$  corresponds to Bernoulli's lemiscate: Research Electrotech. Lab. Japan, No. 539, p. 60 (1953).



Fig. 2.—Logarithm of relaxation time  $\tau$  versus 1/T and  $1/(T - T_{\infty})$  ( $T_{\infty} = -108^{\circ}$ ) for supercooled tetraethylene glycol: O, values for supercooled state observed in this work; O, values obtained from microwave data.24

Accordingly, log-log plots of  $\tan(\theta/\beta)$  versus  $\omega$ must give a straight line with a slope of unity.

Although the lemniscate formula fitted to the complex locus of dielectric relaxation for tetraethylenc glycol more precisely than the ordinary circular arc rule,<sup>22</sup> strictly speaking, a slight deviation was noted: The solid curve in Fig. 1 which is calculated for the case that  $\epsilon_0 = 33.7$  at  $-56^{\circ}$ ,  $\epsilon_{\infty} = 4.0$  and  $\pi\beta/2 = 35^{\circ}$ , fitted to the dispersion data for  $-56^{\circ}$ at the low frequency side, but at higher frequencies rather fitted to those for  $-62^{\circ}$ . Checking the frequency dependence of  $\epsilon^*$  by eq. 2, log-log plots of  $\tan(\theta/\beta)$  versus frequency showed slightly smaller slopes than unity.

It seems that the exact expression for dielectric relaxation of supercooled tetraethylene glycol would involve a more complicated distribution function of relaxation times than those derived from lemniscate formula and circular arc rule. The fact that a parameter  $\beta$  for tetraethylene glycol was smaller, about 0.4, than those of 0.66 and 0.6 for propylene glycol and glycerol, respectively,<sup>20</sup> indicates the existence of a more broad distribution of relaxation times for tetraethylene glycol. This feature is likely related to the non-rigid molecular chain of tetraethylene glycol consisting of a fairly flexible polyoxyethylene group  $-[CH_2CH_2O]_n$ -.8

The most probable relaxation time  $\tau$  was obtained from the frequency for log  $\tan(\theta/\beta)$  equal to zero. According to the rate theory of Eyring,<sup>23</sup> logarithm of

 (22) K. S. Cole and R. H. Cole, J. Chem. Phys. 9, 341 (1941).
 (23) S. Glasstone, K. J. Laidler and H. Eyring, "Theory of Rate Processes," McGraw-Hill Book Co., New York, N. Y., 1941, Chap. IX.

 $\tau$  is to be linear with the reciprocal absolute temperature 1/T; however, some systematic deviation was found for the case of tetraethylenergy glycol, as shown in Fig. 2. If  $\log \tau$  was plotted against  $1/(T - T_{\infty})$  where  $T_{\infty}$  is a parameter, it was found that the variation of log  $\tau$  was approximately linear with  $1/(T - \tau)$  $T_{\infty}$ ) (Fig. 2), as is the case for propylene glycol and glycerol.<sup>20</sup>

Therefore, the temperature dependence of  $\tau$ was given by the expression

$$\tau = A \exp[B/(T - T_{\infty})]$$
(3)

where A and B are parameters whose numerical values are given in Table IV. This situation would show literally that  $\tau$  becomes infinitely large at the temperature  $T_{\infty}$  or that  $T_{\infty}$  is a characteristic temperature where the orientation polarization disappears owing to the infinitely slow relaxation process.

It is also a noticeable feature that a similar relation to that in the relaxation process was found for the temperature dependence of conductivity  $\sigma$  of tetraethylene glycol; the plots of log  $\sigma$  versus 1/T for polyethylene glycols were slightly convex upwards, but the plot of log  $\sigma$  versus  $1/(T - T_{\infty})$  for tetraethylene glycol was a straight line, within the experimental error. Hence, the expression of the form of eq. 3 is also valid for the temperature depen-

dence of conductivity.

#### TABLE IV

PARAMETERS OF TEMPERATURE DEPENDENCE OF RELAXA-TION AND CONDUCTION PROCESSES FOR TETRAETHYLENE GLYCOL

Measurement	Temp. range (°C.)	A	(°K.)	${}^{T_{\infty}}_{(^{\circ}K.)}$
Dielectric	$-62 \sim +50$	$1.028 \times 10^{-13}$	994	165
Conductivity	$-20 \sim +60$	$2.96 \times 10^{-5}$	-829	165

Considering that the d.c. conductivity of polyethylene glycol is caused mainly by the proton conduction mechanism which requires the rearrangement of the hydroxyl group, it might be plausible that  $T_{\infty}$  is  $-108^{\circ}$  for both relaxation and conduction processes (Table IV) and both the dipole orientation and the proton conduction hardly occur at the temperature of  $T_{\infty}$ .

It has been reported also by Davidson and Cole<sup>20</sup> and Schulz<sup>11</sup> that eq. 3 is applicable for the viscous flow or the rheological process in supercooled glycerol.

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<sup>(24)</sup> N. Koizumi, to be published.

#### THE EFFECT OF PRETREATMENT ON THE ACTIVITY OF $\gamma$ -ALUMINA. ETHYLENE HYDROGENATION I.

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Dehydrated  $\gamma$ -alumina catalyzes ethylene hydrogenation, its catalytic activity increasing as drying time and temperature are increased. The activation energy for hydrogenation decreases from about 14 kcal./mole after 450° drying, to 6 kcal./ mole, after drying at 650°. The dried catalyst is very sensitive to poisoning by water; the extent of poisoning increases as the temperature at which water is added increases, to about 350°. About 0.15 wt. % water is sufficient for complete poisoning; this corresponds to coverage of about 2% of the total alumina surface.

#### I. Introduction

Of the metal oxides used to catalyze hydrocarbon reactions, alumina plays the most diversified role. Little commercial use is made of alumina alone, however; it is usually used as a support for a second oxide or a metal (chromia-alumina, reforming catalysts), or as the "active" component in ad-mixture with an "inert" oxide (silica-alumina). Though considerable progress has been made in understanding the over-all properties of such mixed systems, few data are available that bear on the catalytic properties of alumina alone.

This paper presents the results of a study of the effect of pretreatment, dehydration and rehydra-tion on the activity of high purity  $\gamma$ -alumina for the hydrogenation of ethylene. Alumina from the same preparation has also been used to study the effect of like pretreatment on its activity for hydrogen-deuterium exchange. These latter data are presented in Part II.

The reaction studied, the hydrogenation of ethylene at subatmospheric pressure, was chosen for the following reasons. a. The reaction was believed to be straightforward hydrogenation and to involve little side reaction. b. The course of reaction may be followed manometrically. c. The reaction products lend themselves to mass spectrometric analysis. d. The reaction involves the use of sufficiently high temperatures that results should be comparable with usual studies of hydrocarbon reactions. e. The equilibrium is sufficiently in the direction of ethane formation that the back reaction does not introduce a complicating factor in the kinetics of the reaction.

The  $\gamma$ -alumina used was a laboratory preparation of very low impurity content: this high purity was necessary in order to ascribe experimental results to the alumina itself, and not to any impurities, such as iron, which are ordinarily present in amounts of the order of a few tenths of a per cent.

#### II. Experimental

A. Preparation of Alumina.-Commercial aluminum isopropoxide was distilled under reduced pressure and a heart-cut hydrolyzed with an isopropyl alcohol-water mixture. The gelatinous aluminum hydroxide was filtered, dried at  $105^{\circ}$ , and then dried for two hours at  $450^{\circ}$  in a current of dried, filtered air.

During all stages of the preparation, drying and storage, precautions were taken to minimize pickup of inorganic impurities. Analysis of the final product indicated that the preparation was of high purity; it contained 0.03 weight % sodium, calculated as Na<sub>2</sub>O, and 0.003 weight % iron, calculated as Fe<sub>2</sub>O<sub>3</sub>.

B. Ethylene-Hydrogen Composition.—The gas charged was a commercial blend, analyzing 43.6% H<sub>2</sub>, 55.2% C<sub>2</sub>H<sub>4</sub>

was a commercial blend, analyzing 43.6% H<sub>2</sub>, 55.2% C<sub>2</sub>H<sub>4</sub> and 1.2% C<sub>2</sub>H<sub>6</sub>. It was charged to a storage bulb in the re-action system through a bed of Drierite held at  $-78^{\circ}$ . C. Experimental Procedure.—The experimental setup is shown schematically in Fig. 1. The reaction tube, A, was fabricated from silica and was connected to the system through a graded seal. About 0.5-g. sample of alumina dispersed over about 1 g. of silica wool was charged to tube A



Fig. 1.-Schematic drawing of experimental system.

The procedurc used was as follows: the catalyst was dried at  $450^{\circ}$  under constant high vacuum ( $<10^{-3}$  mm.) for the desired time and then isolate 1. The furnace was then adjusted to the desired run temperature. The gas blend was taken into the calibrated bulb V, and then expanded into A; volumes were chosen such that the pressure in the reaction volumes were chosen such that the pressure in the reaction system was about 500 mm. at run temperature. Starting with the admission of the blend to A, readings were taken on manometer M at regular time intervals. After reaction, the gas in A was expanded into the Toepler pump P. The volume of P was about ten times that of A, assuring a repre-sentative sample. The sample in P was compressed into semula tuba D for analysis by mass speatrometer. sample tube D for analysis by mass spectrometer.

Treatment of the catalyst after an experiment varied with the purpose of the run. To show the effects of consecutive runs, the sample was evacuated at run temperature for 15 minutes before starting the next experiment. To show the effect of poisoning by added water, the catalyst was evacuated for 15 minutes at run temperature, brought to 350°, water added and the mixture held at 350° for one hour. The gas blend was then added and an experiment carried out in the usual fashion.

After a day's experiments the catalyst was evacuated overnight (16 hours) at the desired temperature. All reactions involving a given drying temperature were carried out before the catalyst was ever subjected to a higher drying temperature.

D. Catalyst Analysis.—Physical measurements carried out on the catalyst included determination of the surface area as a function of time and temperature of evacuation and the X-ray diffraction patterns after drying.<sup>1</sup> The hydrogen content after drying was determined by equilibration with a measured volume of deuterium at  $450-650^\circ$  for two hours.

#### **III.** Experimental Results

A. Effect of Drying on the Physical Properties of Alumina. 1. Water Content.—Individual samples of alumina, approximately 2 g. in weight, were evacuated for varying times at 450, 550 and  $650^{\circ}$ ; the residual water contents were then determined by equilibration with deuterium at the evacuation temperature. Isotopic equilibrium in the gas phase was reached in all cases. The residual water contents, calculated from the exchange data, are shown in Table I, column 3. The loss of "water" from  $\gamma$ -alumina is a slow process; to remove the same absolute increment requires increasingly more drastic conditions as the water content of the catalyst decreases.

2. Surface Area.—The surface areas of samples dried for varying times at 450, 550 and 650° were measured by the BET method and are shown in Table I, column 4. Though there appears to be a trend toward a decrease of area with increase in drying time and temperature, the spread of the data falls within the experimental errors of the measurement.

#### Table I

CATALYST WATER CONTENT AND SURFACE AREA AS A FUNCTION OF DRYING CONDITIONS

Drving co	nditions	Cata	alvst
Temp., °C.	Time, hr.	Wt. % H <sub>2</sub> O remaining	Surface area, m.2/g.
450	16	2.29	304
	64	1.80	<b>2</b> 94
550	16	1.25	305
	64	0.98	290
650	16	0.61	293
	93	0.37	284

3. X-Ray Diffraction Patterns.—The X-ray diffraction pattern of the alumina before use was compared with that of the sample at the end of the experimental work, which had received a total heat treatment of 540 hours at temperatures from 450– 650°. Both materials showed essentially identical patterns of alumina conforming with data reported in the ASTM X-Ray Diffraction Data (1950 edition), indicating no change had occurred in crystallographic structure as a result of the prolonged heating.

B. Effect of Catalyst Pretreatment on its Hydrogenation Activity. 1. Effect of Drying on Activity.—Catalyst activity increases with increase in temperature and time of drying. Typical data showing pressure decrease during hydrogenation are presented in Fig. 2. The initial reaction rates, presented in Table II, were calculated from rectifying plots of the experimental data. These reaction rates include a small amount of cracking which occurs simultaneously with the formation of ethane. The magnitude of this effect decreases

(1) X-Ray diffraction patterns were determined on a NORELCO Unit, operating at 40 kw. and 20 ma. A 114.6 mm. diameter camera was used; exposures were for four-hour periods. with increased drying temperature. After  $450^{\circ}$  drying, as much as 25% of the over-all rate is due to cracking; after  $550^{\circ}$  drying, however, cracking contributes about 5% to the over-all rate; and after  $650^{\circ}$  drying, cracking is less than 2%.

#### TABLE II

INITIAL RATE OF REACTION (MM. PRESSURE DECREASE/ MINUTE) AS A FUNCTION OF CATALYST DRYING TEMPERA-TURE AND REACTION TEMPERATURE

Drying temp., °C	250	Reaction temp., °C.	450
450		$2\pm 1$	$10 \pm 1$
550	$11 \pm 3$	$40 \pm 3$	$120\pm13$
650	$57 \pm 8$	$127 \pm 9$	$278\pm12$

From the data of Table II the activation energy and the pre-exponential term in the Arrhenius expression were calculated as a function of catalyst drying temperature. These values are shown in Table III. The values calculated after 450° drying are only approximate because of insufficient precision in measuring these low rates.

#### TABLE III

Activation Energy and Pre-exponential Factor of the Reaction in the Range 350-450° for Several Drying Temperatures

	Dryin	с.	
	450	550	650
Activation energy, kcal.	$\sim 14$	9.0	5.9
Pre-exponential factor <sup>a</sup>	15.8	6.0	1.7
<sup>a</sup> Arbitrary units.			

The data of Table II were determined using alumina that had been evacuated for sixteen hours at the drying temperature indicated. If consecutive experiments are carried out, with evacuation for 15 minutes between runs, the catalyst activity decreases continuously, as seen in Fig. 3. The fractional decrease of the second experiment, relative to the first run on catalyst evacuated for 16 hours, is approximately constant regardless of drying temperature or reaction temperature. This is seen in Table IV, in which the ratios of initial rates of the second and first runs (for a first run of five minutes) are presented. Within the over-all errors of the measurements, all the data for experiments carried out after 550 and 650° drying show a constant ratio. The low rate of reaction after  $450^{\circ}$ drying and the much larger contribution of cracking are believed to be the cause of the wider spread in these data.

#### TABLE IV

ACTIVITY OF THE SECOND RUN EXPRESSED AS THE FRACTION OF THE ACTIVITY OF THE INITIAL RUN

Drying temp., °C.	Reaction temp., °C. 250 350				
450		0.50	1.0		
550	0.63	0.60	0.73		
650	0.61	0.59	0.74		

The decrease in catalyst activity obtained in consecutive experiments with 15-minutes evacuation between experiments is not found if the alumina is pumped 16 hours between runs. In this case the activity returns to its original level within an experimental spread of about  $\pm 10-15\%$ . Traces of a yellow oil are found on the walls of the reaction vessel just outside the heated zone.

2. Effect of Water Addition on Activity.—Water added back to dried alumina has a marked inhibiting effect on activity. The magnitude of the decrease in activity depends on the amount of water added and the temperature at which it is added.

a. Temperature at Which Water Is Added.-To establish quantitatively the effect of water, experiments were carried out in the following way: the catalyst was dried overnight at 550° with vacuum, the temperature lowered to 250°, and a standard hydrogenation run started. The experiment was terminated after five minutes, the catalyst evacuated at 250° for 15 minutes, and then water added and a run carried out as before. In a parallel experiment, after the five minute hydrogenation run, the catalyst was again evacuated and then the temperature was raised to  $450^{\circ}$  and water added, and, subsequently, a run carried out at 250°. In like manner, experiments at a temperature of 350° were carried out in which water was added at 350 and  $450^{\circ}$  after initial runs at 350° for five minutes.

The reason for this procedure stemmed from the fact that the standard deviation among runs is in the order of  $\pm 10\%$ . However, as shown by the data of Table III, the ratio of any two successive runs is constant within about 5 or 6%. Therefore, from the observed rate for the initial five minute run the theoretical rate for a succeeding run could be calculated, and the rate of the actual second run, which was poisoned by water addition, could be compared with this theoretical second This procedure was used to calculate the run. data for runs after 550 and 650° drying. After  $450^{\circ}$  drying, since the absolute rates were quite low and poorly reproducible, water was added directly after drying without the intervening five minutes run.

Results of these experiments, Table V, show that the temperature at which the alumina is treated is important and that water does not show its maximum effect below about  $350^{\circ}$ . Above  $350^{\circ}$ little further effect is seen.

In view of these data all subsequent water poisoning experiments involved addition of water at run temperature, except for experiments carried out at  $250^{\circ}$ , in which case water was added at  $350^{\circ}$ .

b. Poisoning as a Function of Water Concentration.—Data showing the extent of poisoning (based on the theoretical #2 run) as a function of water concentration are given in Table VI.

Water exerts a profound effect on the ability of alumina to catalyze the hydrogenation of ethylene, as little as 0.03 wt. % water (based on catalyst weight) reducing the rate by about a third. Addition of 0.15 wt. % water is sufficient to almost completely inhibit the reaction.

An interesting point brought out by the data of Table VI is that a given amount of water added to the alumina causes roughly the same fractional decrease in rate of reaction, despite variations in drying temperature or reaction temperature. For



Fig. 2.—Reaction rate as a function of catalyst drying temperature; reaction at 450°, catalyst drying temp.:  $\odot$ , 450°;  $\Box$ , 550°;  $\Delta$ , 650°.





#### TABLE V

POISONING AS A FUNCTION OF THE TEMPERATURE AT WHICH WATER IS ADDED

Wt. % water added	Temp. at which water is added, °C.	% of Theor. ∦2 Run				
Dryir	ng at 550°; reaction at 2	250°				
0.032	250	73				
.032	450	60				
.065	250	<b>62</b>				
.065	450	0				
. 215	250	10				
	450	0				
Dryir	ng at 550°; reaction at 3	350°				
0.03	350	69				
0.03	450	69				

example, in the case of catalyst poisoned with 0.03 wt. % water, after 550° drying the rate had been reduced to 60–69% of the theoretical rate compared to 57–74% when dried at 650°. In like manner, addition of 0.065 wt. % water decreased the rate to 0–36% for 550° dried catalyst and 18–43% for 650° dried material. With 0.15 wt. % water the rate is reduced to 0–3% for 550° dried catalyst.

TABLE VI

Reaction Rates as % of Theoretical #2 Run as a Function of Amount of Water Added to the Dried Catalyst

Drying temp	Wt. % water	Rea	action temp	°C.
°C.	added	250	350	450
450	0		100	100
	.030		0	$(\sim 30)^{a}$
	.069			$(\sim 20)^a$
	.11			0
550		100	100	100
	.015		88	
	.030	60	69	59
	.065	0	36	10
	. 154		0	3
	.25			0
650		100	100	100
	.030	57	74	71
	.069	43	43	18
	.14	0	13	<b>2</b>
	.25		0	<1

<sup>a</sup> For explanation see text.



Fig. 4.—Relative amount of hydrogenation over  $\gamma$ -alumina dried at 450°:  $\nabla$ , reaction at 450°;  $\odot$ , reaction at 350°;  $\triangle$ , reaction at 250°.



Fig. 5.—Relative amount of hydrogenation over  $\gamma$ -alumina dried at 650°:  $\nabla$ , reaction at 450°;  $\odot$ , reaction at 350°;  $\triangle$ , reaction at 250°.

3. Product Distribution after Reaction.-In Figs. 4 and 5 the partial pressure of ethane in the system at the end of an experiment (calculated from the final pressure and the mass spectrometric analysis) is plotted against the actual pressure decrease. For the pure hydrogenation reaction each mm. decrease in pressure means a mm. of ethane has been formed, and the dotted line in each figure corresponds to this ideal case. The points plotted show the observed relationship, and the extent to which the points lie off the dotted line is a measure of the extent of the side reaction in the system. For reactions carried out after 650° drying, there is no effect of either time or extent of reaction on the product distribution, and the reaction is essentially quantitative at all times. Complete reaction corresponds to a pressure decrease of 250 mm. With 450° dried catalyst, the ethane formation is also linearly related to pressure decrease regardless of the amount of reaction, but the occurrence of side reactions is evident.

Runs made consecutively with 15 minute pumping between runs show little difference in product distribution from runs made with 16 hours pumping intervening. With the shorter pumping time, the rates of consecutive runs decrease, but the ethane/methane ratio remains relatively constant. Water-poisoned alumina also gives the same product distribution as does the active catalyst—the only difference lies in the relative rates of reaction.

C. Self-hydrogenation of Ethylene.—A dismutation reaction occurs when ethylene alone is charged to the dried alumina; products both lower and higher in molecular weight are formed. Typical analyses of the gaseous product are given in Table VII. The rate of reaction, measured by pressure decrease, is about one-third that of the ethylene–hydrogen blend for alumina dried at  $450^{\circ}$ and about one-tenth for  $550^{\circ}$  dried alumina. A few experiments were carried out in which the selfhydrogenation was studied on water-poisoned catalyst. Here, too, water is a poison for the reaction; 0.07 wt. % water decreased the reaction rate to one quarter that of non-poisoned catalyst (for reaction at  $450^{\circ}$  after  $550^{\circ}$  drying).

#### IV. Discussion

A. Effect of Drying on the Physical Properties of  $\gamma$ -Alumina.—The physical properties of  $\gamma$ alumina after prolonged heat treatment are noteworthy in three respects: one, even after heating at 650° for several hundred hours, there is no change in the X-ray diffraction pattern; two, there is no change in surface area after heating at 650° for 93 hours; and, three, it is very difficult to completely dehydrate the alumina even at such elevated temperature, and, as the "water" content decreases, it becomes increasingly difficult to reduce the amount by the same absolute increment. For example, after 64 hours drying at 550°, the alumina contains the equivalent of 0.98 wt. %water; 16 hours of drying at  $650^{\circ}$  reduces this by 0.37% to a level of 0.61 wt. % water; a further 77 hours at  $650^{\circ}$  reduces this value by only 0.24 to 0.37 wt. % water.

Taking the diameter of an  $O^{=}$  ion as 2.8 Å., there are about  $44 \times 10^{20}$  oxide ions in the surface

TABLE	VII
TUPTE	

PRODUCT ANALYSES FROM SELF-HYDROGENATION OF ETHYLENE

Cat. drying temp., °C.	Wt. % $H_2O$ added to cat.	Run temp., °C.	Time of run, min.	Final ∆P in system, mm.	H <sub>2</sub>	CH4	C <sub>2</sub> II <sub>6</sub>	C2H4	Ca	C₄
450	0	450	60	81	16.7	4.2	15.5	56.5	3.8	2.7
550	0	450	30	95	4.0	2.3	20.4	68.4	2.7	2.0
550	0.067	450	60	36	3.9	0.4	3.3	89.3	1.0	1.9

of a gram of alumina of  $300 \text{ m.}^2/\text{g}$ , area. Each surface oxygen must be associated with a proton to satisfy the requirements of electrical neutrality. This corresponds to 6.6 wt. % water required for surface saturation. This figure does not include interstitial water of the crystal structure, or physically sorbed water.

This rough calculation stresses the fact that, on high-temperature drying, the catalyst surface must be left in a strained, high-energy condition due to loss of hydroxyl groups as water. However, this surface condition of strain is relatively stable even toward water addition, for there is a definite temperature dependency for poisoning by water (*i.e.*, relief of strain). Very schematically, one might represent the dehydrated surface in the following manner

$$\begin{array}{ccc} OH & OH & O \ominus \\ -O-Al-O-Al-O- \xrightarrow{\Delta} & -O-Al-O- \xrightarrow{\Delta} & -O-Al-O- + If_2O \end{array}$$

or

Mills and Hindin<sup>2</sup> and Weyl<sup>3</sup> have already noted that dehydration of oxide catalysts leaves the surface in a strained condition and that the relief of this strain may be the driving force leading to some catalytic reactions by this surface.

B. Effect of Dehydration on Catalyst Activity. —The increase in activity of  $\gamma$ -alumina on dehydration can come about in one of two ways: either (1) by an increase in the number of active sites of the same strain energy; or (2) by an increase in the number of higher energy sites.

If the number of active sites formed is related to the amount of water lost, the data rule out the possibility that there is an increase only in the number of sites. This is deduced in the following way: between 450 and 550° drying, the water content of the alumina decreases from 1.8 to 0.98%; from 550 to  $650^{\circ}$ , from 0.98 to 0.37% (Table I). At the same time, the activity increases (for  $450^{\circ}$  reaction) from 10 to 120, and 120 to 278 (Table II); that is, there is an absolute increase of 110 "units" for a water loss of 0.8%, and a further increase of 158 "units" for a further loss of 0.6%. In other words, with increase in drying temperature, the reaction rate increases more rapidly than the water content decreases. The increase in activity is due, therefore, to creation of sites of higher strain energy. This accounts for the decrease in the apparent activation energy for reaction (Table III), since the

(2) G. A. Mills and S. G. Hindin, J. Am. Chem. Soc., 72, 5549 (1950).

activation energy is the thermal energy of gas molecules and solid catalyst needed to supply the difference between the total energy required for the rate-determining step and the strain energy of the solid.

Only those sites of greatest energy play an appreciable role in reaction. Once the catalyst has been dried to, say,  $650^{\circ}$  only those sites created at  $650^{\circ}$  are important; those created at, say,  $450^{\circ}$ , play little or no role. This accounts for the decrease in pre-exponential factor upon increased drying (Table III) if one assumes that this factor is proportional to the number of sites active under the test conditions. As the drying temperature increases, fewer new sites are formed, in line with the decrease in dehydration, but these sites are of sufficiently higher energy that for practical purposes, only they take part in reaction.

From the data it is not possible to reach any decision as to whether high-energy sites are created from low-energy sites or whether the low-energy sites remain, and high-energy sites arise from previously inactive sites.

Although the catalytic activity originates from the strained surface remaining after dehydration, the detailed structure of the catalytic sites is not certain. The geometric requirements for twopoint adsorption of ethylene on adjacent aluminum loss are satisfied by the corundum structure, in which the closest aluminum-aluminum distance is  $\sim 2.8$  A. Assuming adsorption of this type, the aluminum-carbon bonds would be 1.8 Å. long, with the usual carbon tetrahedral angle. This is entirely feasible, since in the aluminum alkyls the aluminum-carbon distance varies from 1.85-2.0 Å. A second possibility, which seems intuitively less probable, is two-point adsorption to an aluminum atom and to the "odd" oxygen left after dehydration. Structures can be drawn satisfying the required geometry; there is, however, no evidence for such adsorption.

Two-point adsorption to two bare aluminum sites leads to a picture for water poisoning in qualitative agreement with the experimental data, namely, that addition of a given amount of water to the dried catalyst destroys more sites than were originally generated by removal of the same amount of water. This follows from the fact that *two* moles of water must be removed to give *two* bare aluminum atoms, *i.e.*, *one* active site; addition of *one* mole of water destroys only *one* aluminum site, but this is sufficient to prevent any reaction.

There is a possibility that the activity of  $\gamma$ alumina may be due to formation of an *n*-type semiconductor, through loss of oxygen atoms on drying.<sup>4</sup> If such is the case, oxygen should act as

(4) W. Hartmann, Z. Physik, 102, 709 (1936).

<sup>(3)</sup> W. A. Weyl, Trans. N. Y. Acad. Aci., [II] 12, 245 (1950).

a catalyst poison. Though the effects of oxygen pretreatment were not investigated in this work, study of the hydrogen-deuterium exchange reaction showed no effect of oxygen. Therefore, it appears that an oxygen-deficient structure is not required for this catalytic activity of alumina.

The data show that  $\gamma$ -alumina should not be considered an inert support for any reaction involving either hydrocarbons and/or hydrogen, for, obviously, it possesses the ability to activate both, especially in systems maintained at very dry conditions. Furthermore, this result has an important implication for other systems: since this catalytic behavior of alumina arises out of the strained condition of the dehydrated surface, it may be expected that other "inert" oxides (for instance, silica, magnesia or zirconia) will act in a similar manner under the proper conditions of prior dehydration to set up the required strained surface. Quantitative differences would be expected among the various oxides, due to such factors as strength of binding of metal to oxide ions, energy required to remove hydroxyl groups, etc., but, qualitatively, they should all show the same general type of reaction. Holm and Blue<sup>5</sup> have shown that this similarity of behavior exists among a large number of oxides in the catalysis of hydrogen-deuterium exchange and that alumina is a catalyst for ethylene hydrogenation, though its activity is not comparable to that of chromia-alumina. Simi-larly, Parravano, Hammel and Taylor<sup>6</sup> have shown that a silica-alumina cracking catalyst is

(5) V. C. F. Holm and R. W. Blue, Ind. Eng. Chem., 43, 501 (1951); 44 107 (1952).

(6) G. Parravano, E. F. Hammel and H. S. Taylor, J. Am. Chem. Soc., 70, 2269 (1948).

effective for hydrogenation of the ethylenic double bond at  $345^{\circ}$ .

C. The Effect of Coke on Catalyst Activity.— During an experiment coke is laid down on the catalyst in amounts that vary with catalyst drying temperature; the higher the drying temperature, the less coke is deposited in unit time. This coke is not completely removed by short (15 minutes) periods of evacuation at the reaction temperature, but it can be removed, at least from the catalytically active sites, by overnight evacuation at temperature. After such treatment, the catalyst is still black, though its initial activity has been recovered.

The decrease in activity caused by coke deposit on the catalyst is quite remarkable in one regard. As shown in Table IV, the decrease in activity after an initial run of five minutes is the same fraction of the original activity, regardless of the catalyst drying temperature or the temperature at which the reaction is carried out. Stating this in another fashion, only the same fraction of active sites is coked, though the extents of reaction vary by a factor of ten or more, and the amounts of coke actually deposited on the catalyst vary with the length of run and catalyst pretreatment. This may mean that the slow step in the reactions leading to coke formation is not very temperature-dependent, and is also essentially independent of the state of strain of the alumina surface.

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## THE EFFECT OF PRETREATMENT ON THE ACTIVITY OF γ-ALUMINA. II. HYDROGEN-DEUTERIUM EXCHANGE

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 $\gamma$ -Alumina catalyzes hydrogen-deuterium exchange at temperatures as low as  $-124^{\circ}$ , far below those at which exchange with catalyst hydrogen occurs. The catalytic activity is increased by vigorous drying, and it is poisoned by addition of water back to the dried catalyst. The poisoning effect of water increases with the temperature of addition, up to about  $350^{\circ}$ ; chemisorbed hydrogen poisons the exchange reaction, whereas oxygen shows no effect. These results argue that the activity of  $\gamma$ -alumina does not arise from an oxygen-deficient structure, but instead from the high-energy, strained surface remaining after dehydration. There is a direct parallelism between the effects of pretreatment on exchange activity and on activity for ethylene hydrogenation, despite the several hundred degrees difference in temperatures at which the two reactions are carried out.

#### I. Introduction

Part I of this series discussed the effects of dehydration and rehydration on the catalytic activity of high-purity  $\gamma$ -alumina for ethylene hydrogenation. The present paper presents results of a study of the effects of the same pretreatment for hydrogen-deuterium exchange.

Exchange reactions serve as a sensitive and simple means for investigating activated sorption of reactants by a catalyst surface. Hydrogendeuterium exchange over hydrogenation catalysts has been extensively studied for this reason, since activation of hydrogen for exchange may be expected to parallel activation for hydrogenation.

The available information showing the effects of pretreatment on the activity of  $\gamma$ -alumina for hydrogen exchange is quite limited. Holm and Blue<sup>1</sup> have demonstrated that  $\gamma$ -alumina is active for hydrogen-deuterium exchange, and that this activity is markedly increased when the catalyst dry-

(1) V. C. F. Holm and R. W. Blue, Ind. Eng. Chem., 43, 501 (1951); 44, 107 (1952).
ing temperature is raised from 400 to 800°. A decrease in catalyst activity occurs if the dried alumina is exposed to a humid atmosphere at room temperature; exposure to dried air has no effect on activity. From this, it was concluded that removal of water is responsible for the high activity which is characteristic of alumina after high temperature drying.

In view of the paucity of data, a program was initiated which had as its aim to determine the effect on the rate of hydrogen-deuterium exchange of the following variables: 1, catalyst drying temperature; 2, water addition to the catalyst after drying; 3, pretreatment of the catalyst *in vacuo*, oxygen and hydrogen.

#### II. Experimental

Figure 1 is a schematic drawing of the apparatus used in this research. The alumina was mechanically spread over silica wool, and charged to tube S. So far as possible, the filling was designed to minimize the dead space; the inlet and outlet tubes were made of very small cross-section, relative to S, for the same reason. A number of different portions from one batch of the alumina was used during the course of the work; the weights of the several samples varied from 0.2 to 1.2 grams. The volume of gas charged was 16.3 cc. (STP), yielding a pressure of about 380 mm. in the system when the reaction tube was held at  $-78^{\circ}$ .

The  $\gamma$ -alumina used was described in Part I. It is a very pure  $\gamma$ -alumina of high area (0.03% Na<sub>2</sub>O, 0.003% Fe<sub>2</sub>O<sub>3</sub>, 300 m.<sup>2</sup>/g.), prepared by hydrolysis of aluminum isopropoxide.

The hydrogen-deuterium blend used (approximately 50-50) was purchased from the Stuart Oxygen Co. after allocation from the AEC. It was charged to the storage bulb after passage through dried Houdry catalyst S-45 at  $-123.5^{\circ}$ . This material is a synthetic silica-alumina used in catalytic cracking. The oxygen used was dried in the same manner. Helium was purified by passage through activated charcoal at  $-195^{\circ}$ .

Experiments were carried out generally in the following manner. The  $\gamma$ -alumina was dried overnight (16 hr.) at the desired temperature under constant vacuum (<10<sup>-3</sup> mm.). The catalyst, after some cooling, was immersed in a bath held at -78°, and helium was admitted to about 200 mm. pressure. After 30 minutes cooling (this length of time had been shown to be sufficient to cool the catalyst to the bath temperature), the helium was removed by evacuation for two minutes. The hydrogen-deuterium blend was then added, by expansion from bulb A.

After reaction for the desired time, the gas was expanded into bulb B and then compressed into tube C for mass spectrometric analysis. The design of the equipment was such that reactions could be carried out for very short times, of the order of five seconds, if desired. Further, the volume of bulb B was about one liter, ensuring a representative gas sample for analysis.

After the experiment, tube S was evacuated for two minutes, while still in the  $-78^{\circ}$  bath. A fresh charge of hydrogen-deuterium was added, and the reaction again carried out for some other desired time. After the series of experiments was carried out, the  $-78^{\circ}$  bath was replaced by one at  $-99.6^{\circ}$  (31% chloroform plus 69% trichloroethylene, cooled with liquid nitrogen), helium added to 200 mm. pressure, and the sample cooled to this new run temperature. After the series of experiments was carried out at  $-99.6^{\circ}$ , with a two minute evacuation period between runs, the sample was cooled to  $-123.5^{\circ}$  (*n*-butyl chloride cooled to a slush with liquid nitrogen) and a final series of experiments performed. With both the  $-99.6^{\circ}$  and the  $-123.5^{\circ}$  bath, temperatures throughout the runs were constant to  $\pm 0.1^{\circ}$ , as measured by an ethane vapor pressure thermometer.

#### **III.** Experimental Results

The variables studied were: (1) catalyst drying temperature, (2) water addition to the dried catalyst, and (3) pretreatment of the catalyst *in vacuo*, oxygen and hydrogen. Results of experiments de-



Fig. 1.—Schematic drawing of apparatus.

signed to evaluate the effects of these variables are as follows.

(1) The Effect of Catalyst Drying Temperature on Catalytic Activity. The temperature at which  $\gamma$ -alumina is dried determines its activity for hydrogen-deuterium exchange. Before examining the data, the word "activity" requires definition. In an isotopic exchange reaction, the reaction is always of apparent first order, regardless of the true order.<sup>2,3</sup> Thus, neglecting isotope effects, the rate constant, k, is calculated from the equation

$$k = -\frac{\ln (1 - HD/HD_{\text{equil}})}{2t}$$

If one calculates the rate constant for hydrogendeuterium exchange over  $\gamma$ -alumina in a series of experiments carried out as previously described (consecutive experiments for increasing times, with two minute evacuation between experiments), it is found that k is not constant, but instead decreases rapidly after the first experiment, and then levels off slowly with increasing number of experiments. A typical example of this behavior is seen in Table I.

#### TABLE I

#### RATE CONSTANT DETERMINED IN A SERIES OF CONSECUTIVE EXPERIMENTS

Conditions: catalyst dried at  $650^\circ$ ; reaction temperature  $-123.5^\circ$ ; experiments carried out consecutively for indicated times, with two minute evacuation between experiments.

Experi- ment	Reaction time, sec.	Rate constant, min. <sup>-1</sup> at -123.5°
1	15	0.064
<b>2</b>	30	.028
3	60	.022
4	120	. 023
5	180	. 021

(2) H. A. C. McKay, Nature, 142, 997 (1938).

(3) R. B. Duffield and M. Calvin, J. Am. Chem. Soc., 68, 557 (1946).

In view of these results, the catalyst activity has been arbitrarily defined as follows: the "initial" activity is that which is determined in a reaction carried out for 15 seconds on a freshly dried catalyst; the "steady-state" activity is that which is determined in a reaction carried out over the catalyst after it has been in contact with the reactant gases for two minutes.

Returning to the effect of drying temperature on activity, the data of Table II show that at  $-78^{\circ}$  the "initial" activity increases with increase in drying temperature; however, for the test temperature,  $-99.6^{\circ}$ , the "initial" activity goes through a maximum as the drying temperature is increased. The "steady-state" activity, on the other hand, is greatest when the catalyst is dried at 550°, regardless of the test temperature (Table III).

#### TABLE II

INITIAL RATE AS A FUNCTION OF CATALYST DRYING TEMPERATURE

Drying temp.,	Rate constan	t, min1, at
450	0.22	<0.2
550	<b>2</b> .6	1.2
650	3.6	0.8

#### TABLE III

STEADY-STATE RATE AS A FUNCTION OF CATALYST DRYING TEMPERATURE

Drying temp., °C.	-78°	Rate constant, min -99.6°	<sup>1</sup> , at -123.5°
450	0.18	0.079	0.033
550	1.2	.38	.076
650	0.83	. 21	. 021

Surprisingly long drying times are required to reach a constant level of catalyst activity despite the high temperatures used. For example, about 80 hours evacuation at 450° are needed to reach constant activity; during this period, activity increases with drying time. Similarly, activity increases with drying time at 550°: about 32 hours drying yield maximum activity. At 650°, about 16 hours drying are required.

A question which arises from the exchange data concerns the extent of catalyst hydrogen participation in the reaction at temperatures of -78 to  $-123.5^{\circ}$ . It is possible to set an upper limit on the fraction of catalyst hydrogen which enters the reaction, from hydrogen and deuterium weight balances on the products of the reaction (Table IV). For alumina dried at 450, 550 and 650°, the maximum

#### TABLE IV

WEIGHT BALANCE ON GASEOUS PRODUCTS

Drying temp., °C.	112, vol. %	vol. %
Original H <sub>2</sub> -D <sub>2</sub> blend	$45.7 \pm 0.8$	$54.3 \pm 0.8$
450	$45.0 \pm .5$	$55.0 \pm .5$
450, H₂O poisoned <sup>a</sup>	$45.1\pm.3$	$54.9 \pm .3$
550	$45.4 \pm .4$	$54.6 \pm .4$
550, H₂O poisoned <sup>a</sup>	$45.1 \pm .2$	$54.9 \pm .2$
650	$45.5 \pm .2$	$54.5 \pm .2$
550, H₂O poisoned <sup>a</sup>	$45.5 \pm .1$	$54.5 \pm .1$

<sup>a</sup> The alumina had been poisoned by treatment with water after drying.

amounts of catalyst hydrogen which could have exchanged were 3, 5 and 10% respectively.

These values were calculated as follows: the weight balances of Table IV were determined for a large number of experiments in which about 0.200 g. of alumina was used as the catalyst. It is known that this alumina still contains 1.8 wt. % of water of constitution after 64 hours of evacuation at  $450^{\circ}$ 1.0 wt. % water after 64 hours at 550°, and 0.4 wt. % water after 64 hours at 650°.<sup>4</sup> About 0.6 mg. of hydrogen was added in the gas mixture. Assuming a 1% absolute error in the gas analyses, the figures quoted above were calculated as the maximum that could have taken part in reaction. It should be noted that these data were determined for reactions that were allowed to proceed for varying times (15 seconds to 15 minutes), to varying extents of equilibrium (2-85%) and at temperatures of -78, -99.6 and  $-123.5^{\circ}$ . The samples indicated with an asterisk, Table IV, were ones in which the alumina had been treated with water, after drying (to be discussed below, Section 3). The maximum amount of water added in any experiment was about 0.1 wt. % based on catalyst weight. The amount of hydrogen introduced in this way, therefore, has little effect on the calculation.

(2) The Effect of Pretreatment in Oxygen and Hydrogen on Catalytic Activity.—Since the initial rate of the exchange reaction is greater than the steady-state rate, hydrogen (and deuterium) sorbed at low temperatures acts as a catalyst poison. Experiments were, therefore, carried out to determine the effects of hydrogen treatment and of oxygen treatment on activity for catalyst that had been dried for 16 hours at 650°.

a. After overnight drying at  $650^{\circ}$ , the catalyst was cooled to run temperature  $(-99.6^{\circ})$  in hydrogen, oxygen or helium. After 2 minute pumping at  $-99.6^{\circ}$ , the exchange reaction was carried out.

b. After drying, the catalyst was cooled in hydrogen from 650 to 30°, evacuated at 30°, then again cooled in hydrogen from 30 to  $-99.6^{\circ}$ . After pumping, the exchange was carried out.

The results of this series of experiments, seen in Table V, show the following.

1. Oxygen sorbed at any temperature from 650 to  $-99.6^{\circ}$  is either (a) not a poison or (b) removed by 2 minute evacuation at  $-99.6^{\circ}$ . This may be seen by a comparison of experiments 1 and 3. The initial and equilibrium rates are the same in the two experiments within the experimental error.

2. Hydrogen is a catalyst poison, and the poisoning effect is greater for hydrogen sorbed at high temperature than for hydrogen sorbed at low temperature; compare experiments 2 and 5 with experiment 1. There is no difference in extent of poisoning by hydrogen when sorbed at  $30^{\circ}$  than when sorbed at  $-99.6^{\circ}$ , as shown by comparison of the equilibrium rates of experiments 1 and 5.

3. Hydrogen sorbed at high temperature,  $650^{\circ}$ , can be removed by evacuation at  $30^{\circ}$ , as seen by comparing experiments 4 and 5. Hydrogen sorbed at  $-99.6^{\circ}$  is not removed by evacuation for 2 minutes at this temperature as shown by the constancy

(4) S. G. Hindin and S. W. Weller, THIS JOURNAL, 60, 1501 (1956).

of the steady-state rates in experiments 1 and 3.

Since hydrogen sorbed at low temperature is not removed to any appreciable extent by short periods of pumping at low temperature, experiments were carried out to determine the effect of pumping time on desorption of hydrogen. These experiments were performed in the following manner. A sample of  $\gamma$ -alumina dried at 650° was cooled to  $-99.6^{\circ}$  in helium in the usual way, pumped for two minutes, and then an exchange experiment carried out for 15 seconds. Six consecutive runs were made, with the time of pumping between experiments varied, as shown in Table VI. In each case, the exchange experiments were allowed to proceed for 15 seconds.

#### TABLE V

EFFECT OF PRETREATMENT IN OXYGEN AND HYDROGEN ON CATALYTIC ACTIVITY

		for r	eaction cant, $-99.6$	nin, -, irried ° for
Exp.	Catalyst pretreatment <sup>a</sup>	1 min.	2 min.	10 min.
1	Cooled in He from 650 to $-99.6^{\circ}$	0.61	0.14	0.12
2	Cooled in $H_2$ from 650 to $-99.6^{\circ}$	.04	.04	.04
3	Cooled in $O_2$ from 650 to $-99.6^{\circ}$	. 55	. 12	.11
4	Cooled in $H_2$ from 650 to 30°, pumped at 30°, then cooled in $H_2$ from 30 to $-99.6^{\circ}$	. 12	. 12	.11
5	Cooled <i>in vacuo</i> from 650 to 30°, then cooled in $H_2$ from 30 to $-99$ 6°	. 12	. 11	.12

 $^a$  The catalyst was evacuated at 650° for 16 hours before each experiment.

#### TABLE VI

Effect of Pumping Time in Recovering from Hydrogen Poisoning at  $-99.6^{\circ}$ 

Conditions: catalyst dried at  $650^{\circ}$ ; all reactions carried out for 15 sec. at  $-99.6^{\circ}$ , time of pumping between runs as indicated in table.

Pumping time, min.	Rate constant, min. <sup>-1</sup>
0	0.67
$2^a$	.18
<b>2</b>	.15
15	. 20
30	. 23
2	. 15
2	. 16

<sup>a</sup> Experiments are consecutive.

The results, shown in Table VI, indicate that hydrogen sorbed at  $-99.6^{\circ}$  is only slightly desorbed at this temperature. Thus, the fresh catalyst showed a rate constant of 0.67 min.<sup>-1</sup>; after hydrogen poisoning, the rate was reduced to about 0.16 min.<sup>-1</sup>. The effect of 30 minutes pumping was to increase the rate to only 0.23 min.<sup>-1</sup>. The amount of hydrogen sorbed at  $-99.6^{\circ}$  is quite small; experiments showed that not more than 2-3 µmoles per gram of catalyst is taken up. This is sufficient to cover only a small fraction (less than 1%) of the available alumina surface. 3. The Effect of the Dehydration of the Dried Catalyst on Catalytic Activity.—Water added to dried  $\gamma$ -alumina is a marked poison for the exchange reaction, when added at somewhat elevated temperatures. The magnitude of the poisoning effect depends not only on the amount of water added, but also on the temperature at which rehydration is carried out; as the temperature is raised, a given amount of water shows a larger poisoning effect.

a. Extent of Poisoning as a Function of Temperature of Rehydration.-The effect of temperature of rehydration on inhibition of reaction is shown by the data of Table VII. The experiments were carried out in the following manner: 0.30 wt. % water was added at 30° to a sample of alumina that had previously been dried at 450°. The catalyst was cooled in helium to  $-78^{\circ}$ , and a series of exchange experiments carried out. After evacuation following the last experiment, the system was closed, the temperature raised to 100°, and the catalyst held at this temperature for one hour. The sample was then again cooled to  $-78^{\circ}$ , and a series of exchange experiments performed. In like manner, the temperature was raised to 200 and  $300^{\circ}$  and the exchange studied after each temperature increase.

It is seen in Table VII that water does not show its maximum poisoning effect until a temperature of  $300^{\circ}$  or higher is reached. This effect is not due to poisoning by hydrogen, since hydrogen was not allowed in contact with the catalyst at a temperature above  $-78^{\circ}$ .

#### TABLE VII

Effect of Temperature of Rehydration on Activity

Conditions:  $450^{\circ}$  dried catalyst treated with 0.30 wt. % H<sub>2</sub>O. Mixture held for 1 hour at indicated temperatures before reaction.

Temp. of catalyst		% HD.	at -78°	
+ H <sub>2</sub> O, °C.	0.50 min.	2.0 min.	5.0 min.	30.0 min.
30	35.4	44.6	$46.0^{a}$	
100	11.8	23.2	41.6	
200	<b>2</b> , $0$	4.8	16.2	
300	<b>0</b> . $2$	0.2	0.3	0.5

<sup>a</sup> This value corresponds to equilibrium.

Alumina that has been treated with water at high temperature is stable to further water treatment at lower temperature. As shown in Table VIII, a sample of alumina was treated with 0.1 wt. % water at 30° after initial drying at 450°. As expected, there is a marked decrease in activity when the catalyst temperature is raised to 450°. If a further 0.2 wt. % water is then added at 30°, there is little effect of this later addition.

In the experiments shown in Tables VII and VIII, the catalyst was held at high temperature for periods of 1 to 2 hours. Later work showed this long holding time was not needed, for poisoning takes place very rapidly at high temperature. This was shown by an experiment in which the dried catalyst with 0.1 wt. % water added was held at 450° for 2 minutes, cooled and reaction carried out at  $-78^{\circ}$ . The catalyst temperature was then again raised to 450° and held for 4 hours, then the ex-

#### TABLE VIII

#### EFFECT OF TEMPERATURE OF WATER ADDITION

Conditions: 0.1 wt. % H<sub>2</sub>O added to dried catalyst at 30° and reaction carried out at  $-78^{\circ}$ . Mixture held 1 hour at 450°, then experiment carried out. Then a further 0.2 wt. % H<sub>2</sub>O added.

	% HD, at −78°		
Temp. of catalyst + H <sub>2</sub> O,	0.50	2.0	
°C.	min.	min.	
0.1 wt. % at 30	43.7	45.4	
0.1 wt. % at 450	9.6	25.4	
Further $0.2$ wt. $\%$ at $30$	9.0	<b>23</b> , $9$	

change again studied at  $-78^{\circ}$ . Results of the two runs were identical within the experimental error.

b. Extent of Poisoning as a Function of the Amount of Water Added.—In view of the previous results showing the effect of rehydration temperature on poisoning, all further work was carried out on a system in which water was added to the dried catalyst at  $450^{\circ}$ , the temperature held at  $450^{\circ}$  for one hour, and then exchange experiments performed. At such conditions it is found, Table IX, that water is a very effective poison for the exchange reaction over dried  $\gamma$ -alumina. For example, about 0.1 wt. % water reduces the initial rate to only 10% of the rate on dried catalyst, regardless of catalyst drying temperature; as little as 0.024 wt. % water decreases the activity to about one-half of that of the freshly-dried catalyst.

#### TABLE IX

POISONING AS A FUNCTION OF AMOUNT OF WATER ADDED

	Rate constant, min1						
NT	-	78°	-99.6°	$-123.5^{\circ}$			
Wt. %	Tota	Steady	Steady	Steady			
$\Pi_2 O$	Init.	State	State	State			
	450°	dried catal	yst				
0	0.22	0.18	0.079	0.033			
0.024	.088	.058	.023	.008			
.048	. 026	. 023	.008	.002			
.085	.017	.017	.007	.002			
550° dried catalyst							
0	2.6	1.2	0.38	0.076			
0.024	1.63	1.04	.27	.049			
.048	0.92	0.70	.17	.032			
. 085	<b>0</b> , $22$	0.20	.058	.015			
	650°	dried catal	yst				
0	3.6	0.83	0.21	0.021			
0.024	0.71	. 56	. 10	.012			
. 048	. 68	. 45	. 12	.014			
.085	. 39	.34	. 093	.012			

On the other hand, the poisoning measured by the steady-state rate does show a dependence on drying temperatures; the higher the drying temperature (*i.e.*, the more sites available), the lesser is the percentage reduction in activity for a given weight of water. Even in the case of the 650° dried catalyst, however, addition of 0.1 wt. % water decreases the rate by more than 50%.

It should be remembered that 0.1 wt. % water is sufficient to cover only about 2% of the available alumina surface, indicating that the active surface of  $\gamma$ -alumina is of the order of a few per cent. of the total available surface, provided there is no interaction between sites.

The data of Table IX show that water competes for the active sites with chemisorbed hydrogen; as the amount of water added is increased, the difference between the initial and the equilibrium rates decreases, until at about 0.1 wt. % water, the two become equal. However, water poisons sites that are not poisoned by hydrogen; this is concluded from the fact that the steady-state rate of the freshly-dried catalyst is materially reduced by addition of water.

4. Temperature Dependence of the Reaction Rate.—The activation energy computed from the steady-state rates for both freshly-dried and for water-poisoned  $\gamma$ -alumina varied from 2.5 to 4.5 kcal./mole, and showed no trend with the drying temperature or extent of water poisoning.

#### IV. Discussion

The effects of dehydration on the physical properties of  $\gamma$ -alumina have already been discussed in Part I. It was shown that drying at 650° does not affect either the surface area or the crystallographic structure of  $\gamma$ -alumina. It was further pointed out that after drying at high temperatures, the catalyst surface is left in a strained, high-energy state, due to loss of hydroxyl groups as water. The relief of this strain is the driving force leading to reaction.

It has sometimes been suggested that the catalytic activity of  $\gamma$ -alumina, which is known to be an n-type semi-conductor,<sup>5</sup> derives from the formation of an oxygen-deficient structure on drying. The data of Table V rule out this interpretation of the exchange activity, since treatment of the dried catalyst with oxygen over the temperature range  $650 \text{ to } -100^{\circ} \text{ has no effect on activity. Were oxy-}$ gen deficiencies formed on drying, it is difficult to see why they would not have disappeared on treatment of the catalyst in oxygen. The experiments of Holm and Blue,<sup>1</sup> showing that humid air poisons the dried catalyst whereas dried air has no effect on activity, are consistent with the results of this study. Further indirect evidence that exchange activity is not related to defects formed by loss of oxygen arises from the data of Russell and Stokes,<sup>6</sup> who point out that dried alumina chemisorbs much more hydrogen than it does oxygen.

The maximum found in the steady-state rate after drying at 550° (see Table III) may be explained in the following manner. An efficient catalyst is one that adsorbs the reactant and product molecules sufficiently strongly to activate them, but not so strongly that the product molecules cannot be desorbed. If active sites of increasing energy are formed by drying at increasing temperatures, above some temperature the sites may bind hydrogen too strongly to permit desorption, resulting in the above-described maximum. Holm and Blue<sup>1</sup> show a similar maximum with  $\gamma$ -alumina when the drying temperature is increased from 650 to 800° though their interpretation of the data differs from that presented here. An alternative explanation to theirs for the non-occurrence of a maximum for silica-alumina with increase in drying temperature is that the maximum for silica-alumina would occur at temperatures higher than those studied. Prac-

(5) W. Hartmann, Z. Physik, 102, 709 (1936).

(6) S. A. Russell and J. J. Stokes, Jr., J. Am. Chem. Soc., 69, 1316 (1947).

#### TABLE X

# A Comparison of the Effects of Pretreatment of $\gamma$ -Al<sub>2</sub>O<sub>3</sub> on its Activity to Catalyze Hydrogen Exchange and Ethylene Hydrogenation

I	Pretreatment		Effect Hydrogen exchange	on	Ethylene hydrogenation
1.	Increasing drying temp.	1.	Initial activity in- creases; Steady- state activity goes through a max.	1.	Activity increases
2.	Addn. of water to dried catalyst	2.	Water is a poison; ca. $0.1$ wt. $\%$ water decreases the reaction rate to $10\%$ of its initial value	2.	Water is a poison ca. 0.1 wt. % water almost completely in- hibits reaction
3.	Temp. of water addn.	3.	Water must be added at a temp. of ca. 300° to show its max. poison- ing effect	3.	Same
4.	Poisoning as a func- tion of amount of water added	4.	Active sites are poisoned by addn. back to the catalyst of lesser amounts of water than were originally removed	4.	Same

tically, of course, this maximum might occur at some point beyond the sintering temperature, and so not be accessible to experimental investigation. It must also be remembered that Holm and Blue carried out most of their activity testing at temperatures much higher than those used in this research, and these higher temperatures could appreciably affect the state of adsorption of hydrogen on the alumina surface.

In both the dehydration of alcohols over  $\gamma$ -alumina<sup>7</sup> and the exchange of molecular hydrogen with surface hydroxyl groups,<sup>8</sup> reactivity increases initially with increase in catalyst drying temperature and then goes through a maximum with further increase. Wicke's interpretation of the exchange data<sup>8</sup> parallels that presented in this report.

Russell and Stokes claim<sup>6</sup> that high temperature  $(700-900^{\circ})$  sorption of hydrogen by  $\gamma$ -alumina increases with increasing drying temperature and that there is evidence of an irreversible reaction of hydrogen with alumina at these higher temperatures. The present data (Table V, compare expts. 1, 4 and 5) show no evidence of an irreversible reaction, at least at 650°; if hydrogen is irreversibly sorbed, it is not held on those sites which catalyze the exchange reaction.

The fact that poisoning by water shows a marked temperature dependence (Tables VII and VIII) is presumably due to an initial non-specific adsorption of water on catalytic sites of varying energies. At low temperatures, the water is "stuck" on the sites it first hits; at higher temperatures, however, the adsorbed water has sufficient mobility to distribute itself preferentially on the sites of highest energy (*i.e.*, of highest activity) and thus to cause maximum poisoning. This interpretation is consistent with the result (Table IX) that when the most active sites are poisoned by water, adsorbed hydrogen no longer acts as a poison and the initial and steady-state rates become equal.

The close correspondence of these data with the results of water poisoning in the ethylene hydrogenation reaction (Part I) merits emphasis. In both cases, water shows maximum poisoning effect only when added at temperatures of  $300^{\circ}$  and higher; water added at room temperature is not a poison. Also, in the ethylene hydrogenation reaction, about 0.1 wt. % water is sufficient to completely inhibit reaction; in the hydrogen-deuterium exchange reaction, addition of about 0.1 wt. % water reduces the initial rate to about 10% of the rate on non-poisoned catalyst.

Here, again, the explanation previously given for the poisoning effect of water (active sites formed by loss of water are poisoned by addition back to the catalyst of smaller amounts than were originally removed) is applicable.

Holm and Blue<sup>1</sup> reported values for the activation energy of exchange which were 12 kcal./mole after  $400^{\circ}$  drying and decreased to 3 kcal./mole after  $650^{\circ}$  drying. This result disagrees with the relatively constant activation energy observed in the present work. The origin of the disagreement may reside either in the much higher test temperatures used by Holm and Blue, or in a significant difference in drying procedure. Holm and Blue dried their samples for 16 to 29 hours; in the present work, drying was continued until a condition of constant activity was reached, which required as much as 80 hours at  $450^{\circ}$ .

One feature of the hydrogen exchange reaction is of special interest. Exchange will proceed between molecular hydrogen and deuterium over  $\gamma$ -alumina at temperatures at which deuterium will not exchange with catalyst hydrogen. This phenomenon is found with other catalysts, chromia,<sup>9</sup> barium hy-dride<sup>10</sup> and promoted ircn catalyst,<sup>11</sup> and a like effect has also been found in the  $O_2^{16}-O_2^{18}$  exchange over some oxides. Two possible explanations can be advanced to explain this effect. One is that molecular hydrogen is adsorbed in a different state (perhaps atomically) than catalyst hydrogen and that exchange does not occur between the nonequivalent species. Alternately, the adsorbed hydrogen may be capable of exchange with catalyst hydrogen, but does so only with that catalyst hydrogen which is in its immediate neighborhood. Since the catalyst hydrogen is not mobile at test temperatures, the amount of it which is able to exchange is so small compared with the amount of added hydrogen gas that it is not detected by analysis.

A comparison of the effect of pretreatment of  $\gamma$ -

(9) S. E. Voltz and S. Weller, J. Am. Chem. Soc., 75, 5227 (1953).
(10) L. Wright and S. Weller, *ibid.*, 76, 5305 (1954).

(11) J. T. Kummer and P. H. Emmett, THIS JOURNAL, 56, 258 (1952).

(12) E. R. S. Winter, J. Chem. Scc., 1522 (1954).

<sup>(7)</sup> W. S. Brey and K. A. Krieger, *ibid.*, **71**, 3637 (1949).

<sup>(8)</sup> E. Wicke, Z. Elektrochem., 53, 279 (1949).

alumina on exchange activity with the effects of like pretreatment on activity for ethylene hydrogenation<sup>4</sup> is shown in Table X. The direct parallelism between the activity of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> for those two widely-differing types of reactions is especially striking when one considers that the exchange reaction is carried out in the region of  $-100^{\circ}$  and the hydrogenation reaction at  $+450^{\circ}$ . This

strongly suggests that the same sites on the catalyst surface are involved in both reactions.

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## THE LIGHT SCATTERING BEHAVIOR OF THREE DIMENSIONAL NETWORK GELS<sup>1</sup>

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A sensitive and versatile light scattering photometer was constructed and utilized for studies on the scattering behavior of three-dimensional networks. The polyglyceryl sebacate and polyglyceryl hexahydrophthalate systems were studied in detail throughout the course of the polymerization. Difficulties encountered were: formation of crystallites as a result of unreacted monomer, extraneous inhomogeneities arising from motes, onset of light absorption, and the appearance of a blue excited fluorescence. By eliminating these complications, it was demonstrated that such systems, though as rigid as polymer in bulk, behave in the light scattering sense as simple liquids. Weight average molecular weights of the polyesters measured prior to the gel point were significantly larger than those obtained by cryoscopic means. Limitations of the light scattering method as a means of obtaining information on the molecular composition of solids is discussed.

#### Introduction

If trifunctional molecules such as glycerol are allowed to react with bifunctional molecules, such as dibasic acids, using certain ratios of reacting groups, *e.g.*, two moles of glycerol to three moles of acid, a polymer is formed, and at a certain welldefined stage in the course of the polycondensation, the reaction mixture changes abruptly from a viscous liquid to an elastic gel. In such a reaction, the functionality of the polymer molecule increases with increase in size. Therefore, some of the molecules present can become indefinitely large. These macro structures will extend throughout the volume of the polymerized system and their sizes on the molecular weight scale can be considered to be infinite. Such structures are called infinite networks.<sup>4,5</sup>

The course of the polycondensation can be followed by end-group analytical methods such as titration, and this fact enables one to approach the gelation point carefully and systematically. Further reaction past the gel point increases the amount of the infinite network and reduces the quantity of fluid within the system to the point where the gel becomes very inelastic and begins to resemble a rigid solid. Such systems have been studied intensively from the point of view of their practical applications but very little fundamental work has been reported on them in the literature. This is no doubt due to the extreme difficulty of manipulating such systems. Their insolubility in

(1) Dissertation of Joseph Yudelson submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Illinois Institute of Technology, 1955. Presented before the Division of Polymer Chemistry, 126th meeting of the A.C.S., New York, September, 1954.

(5) P. J. Flory, J. Am. Chem. Soc., 63, 3083 (1941).

all solvent systems prevents the application of most physico-chemical techniques.

It is the purpose of this work to examine the light scattering behavior of these systems from the beginning of the reaction when the mixture consists of small molecules, to the end when the infinite network is formed and the system has changed from one with definite liquid properties to one which has the characteristics of an insoluble elastic solid. In this way, it is hoped that information will be obtained that will aid in the interpretation of scattering results from bulk systems.

#### Choice of Systems

To form a three-dimensional network polymer, a molecule with three or more functional groups must react with one whose functionality is at least two. Because of the ready availability of glycerol and pentaerythritol, an alcohol was used as the branching molecule and allowed to react with dibasic acids and acid anhydrices. A large number of polyester systems were investigated with no success insofar as light scattering was concerned because: (1) they were strongly light absorbing, especially in the 400-550 m $\mu$  region, and/or (2) crystallization of unreacted monomer occurred upon cooling to room temperature. However, if glycerol was used as the branching molecule, the crystallization complication was virtually eliminated except at low extents of reaction. Glycerol in a nitrogen atmosphere reacted with sebacic acid or hexahydrophthalic anhydride, with alkane sulfonic acids as catalyst, and gave polymers whose absorbances in the region of long visible wave lengths were small.

All polyester systems were found to be fluorescent throughout much of the visible spectrum. For those reported here, the fluorescent intensity at 575 m $\mu$  was approximately the same order as the scattering intensity, but at 607 m $\mu$  it was negligibly

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<sup>(4)</sup> W. H. Carothers, Chem. Revs., 8, 402 (1931).

small. Most of the measurements reported in this paper were made at the longer wave length.

#### Experimental

Materials.—Glycerol (Eastman Kodak) was distilled under nitrogen at 13 mm. and the middle fraction boiling at  $171-173^{\circ}$  collected. Sebacic acid (Eastman Kodak, m.p.  $134^{\circ}$ ) was used without further purification. Its neutralization equivalent was 101.1 (theor. 101.12). Redistilled hexahydrophthalic anhydride was kindly provided by the National Aniline Division of the Allied Chemical and Dye Corp. Its neut. equiv. was 77.3 (theor. 77.1) as determined by titrating an acetone solution with aqueous NaOH using thymolphthalein as indicator. A sample of "mixed alkane sulfonic acids" was kindly supplied by the Indoil Chemical Co. Its neut. equiv. was 110, and for reaction purposes it was considered to be a compound having a molecular weight of 110. Matheson prepurified nitrogen was used in the polymerizations and all solvents were doubly distilled. Benzene was crystallized twice by successively freezing out about onehalf the original amount.

Cleaning Materials for Light Scattering Use.—Due to the unusual nature of the substances used (insofar as light scattering is concerned) special cleaning procedures had to be devised. A Servall SS-1 angle centrifuge was used to eliminate dust. The centrifuged liquids or solutions were checked for optical cleanliness by examination at low angles when illuminated by the strong unfiltered beam in the photometer.

Glycerol was heated to  $130^{\circ}$  and centrifuged for four hours at top speed. The catalyst was always dissolved in it before heating so as to avoid a separate cleaning procedure. For each polycondensation the centrifuged solution was weighed directly from the centrifuge into an optically clean cell by means of a clean pipet. Sebacic acid was cleaned by making up an 8% solution in ethanol, filtering through a sintered glass filter of medium porosity to remove fibrils, then centrifuging at top speed for 30 minutes. The optically clean solutions were transferred by pipet to a beaker and placed into a vacuum desiccator. The pipet and beaker had been cleaned previously and all air passed into the desiccator after removal of solvent was filtered through an ultra-fine sintered glass disc. The neutralization equivalent of sebacic acid that had undergone the cleaning procedure was 101.5, indicating negligible reaction with the solvent. Hexahydrophthalic anhydride was heated to 100° and the molten material centrifuged for two hours. It remained fluid (m.p. 35°) through out the centrifugation and was weighed into the cell in the same manner as glycerol.

Light Scattering Photometer and Cell.—The nature of this study required that the photometer be able to work over a wide range of wave lengths, take measurements quickly, and use a scattering cell that was rugged enough to withstand the conditions imposed by a condensation polymerization. A 100 watt concentrated arc lamp (M-100) (Western Union Telegraph Co., Water Mill, N.Y.) was used as a light source. This lamp has essentially a continuous spectral distribution and is especially intense in the red. Transmission interference filters (Baird Associates, Cambridge Mass., Fish-Schurman Corp., Germany) were used to isolate the light scattering wave lengths. The incident beam passed through  $\epsilon$  series of lenses and diaphragms to produce a well collimated circular beam 7 mm. in diameter which was monochromatized and passed into the cell. The scattering volume was defined by two circular diaphragms (4.8 and 13.7 mm. in diam.) which were the limiting apertures for the scattered radiation. They were limiting apertures for the scattered radiation. They were set 81 mm. apart so that the limiting plane angle of ac-ceptance of the receiver system was 6°. The scattered light impinged on a 1P21 photomultiplier tube whose output was read directly on a Rubicon galvanometer #3414 (sens. 0.0018 ua./mm.). An Ayrton shunt extended the range for higher intensity readings. A regulated power supply es-sentially similar to that used by Hadow and co-workers<sup>6</sup> supplied the voltage for the photomultiplier. It utilized a negative feedback circuit in which a small amount of the negative feedback circuit in which a small amount of the incident beam was reflected onto a 1P39 photocell whose photocurrent varied the amplification of the photomultiplier so as to compensate for small changes in lamp intensity.

Cylindrical light scattering cells were constructed as follows: a plane entrance window of 2 mm. optically clear Pyrex was sealed over the end of a 3.5 cm. tube of 16 mm. o.d. which in turn was sealed at right angles to the side of a section of 48 mm. tubing. This was carefully picked from regular stock to be as optically perfect as possible. Previous to this operation, it was sealed at one end which was then heated and drawn in at the center, and the rim ground with carborundum until the cylinder rested perpendicularly on the resulting flat rim. For an exit tube, a modified Raman horn was used: opposite to the entrance tube along its axis, another piece of 16 mm. tubing was sealed to the cylinder, and the end drawn down to a point 3.5 cm. from the juncture to serve as a light trap. The cells were 12 cm. high and had an effective volume of 130 ml. All external parts of the cell not transmitting light were coated with flat black paint. For polymerizations, the cell was covered with a tight fitting Teflon cap which had an opening for an entrance tube. This tube carried nitrogen into the cell, and also served the purpose of removing samples for analysis thus avoiding dust contamination of the system. Measurements of the incident beam intensity were made with the cell removed from the apparatus.

Calibration .- Photometer alignment was checked by observing the fluorescence from a dilute dichlorofluorescein solution which gave galvanometer deflections approximately five times the background intensities. Using the sin  $\theta$ volume correction factor, a symmetrical radiation envelope was obtained with a deviation of less than 1% over the range 25 to 145°. Galvanometer readings were converted into absolute turbidity units by calibration with a 0.25%solution of Ludox (obtained from E. I. du Pont de Nemours and Co.) of unit dissymmetry ratio and negligible depolarization whose transmittance was measured on a Beckman DU spectrophotometer using calibrated 10 cm. cells. The measured turbidity at 365 m $\mu$  was 0.0105 cm.<sup>-1</sup> and its value for longer wave lengths was obtained by the inverse fourth power relationship.<sup>7</sup> The photometer had a sensi-tivity of approximately  $2 \times 10^{-6}$  turbidity unit per galvanometer deflection using incident radiation in the range 443 to 575 m $\mu$ . Sensitivity at 607 m $\mu$  was  $1 \times 10^{-5}$ . The calibration was tested by measuring the scattering from optically clean benzene. Values of the Rayleigh ratio  $(R_{90})$  were 45.0  $\times$  10<sup>-6</sup> and 17.3  $\times$  10<sup>-6</sup> cm.<sup>-1</sup> for 443 and 540  $m\mu$ , respectively, which is in excellent agreement with literature values.<sup>8</sup> The depolarization ratio for benzene using unpolarized incident light was 0.42. A correction factor of 1.05 was used to account for the greater sensitivity of the photomultiplier to horizontally polarized light. A refrac-tive index correction based on the equations of Carr and Zimm<sup>8</sup> and the modifications of Hermans and Levinson<sup>5</sup> was used in all measurements.

Absorption Corrections.—All polyesters were found to be light absorption corrections.—All polyesters were found to be light absorbing, particularly in the region 443 to 540 mµ. Empirical correction factors were obtained by which the observed scattering measurements were corrected to the values that would be obtained if the systems were nonabsorbing. This was done by measuring the scattering intensities from 1% starch solutions before and after the addition of small increments cf concentrated dye (Orange II) solution in the manner of Brice and co-workers.<sup>10</sup> No interaction was observed between the dye and the macromolecules at the non-absorbing wave length (575 mµ). The transmittance of each starch solution to which dye had been added was measured in a Beckman spectrophotometer using 1 cm. calibrated cells. They were measured relative to those of the dye-free starch solution. Glycerol was used as the reference for the polyesters since its refractive index approximated closely that of the polymers. The absorption coefficient measured in this instance was due to both scattering and color absorption. Since the turbidities of the polyesters were relatively small, the absorption coefficient could be considered to be due to color absorption only.

Fluorescence.—Fluorescent radiation was observed in all the systems studied. Its intensity was very large when 443 m $\mu$  excitation was used, and practically zero for 607 m $\mu$ 

75, 824 (1953).

<sup>(6)</sup> H. J. Hadow, H. Sheffer and J. C. Hyde, Can. J. Res., 27B, 791 (1949).

<sup>(7)</sup> G. Oster, J. Polymer Sci., 9, 525 (1952).

<sup>(8)</sup> C. I. Carr and B. H. Zimm, J. Chem. Phys., 18, 1616 (1950).

<sup>(9)</sup> J. J. Hermans and S. Levinson, J. Opt. Soc. Am., 41, 460 (1951).
(10) B. A. Brice, G. C. Nutting and M. Halwer, J. Am. Chem. Soc.,

excitation. It was detected by placing in the scattered beam a filter (test filter) having a sharp cut-off to zero transmittance at a wave length slightly longer than that of the incident beam. These filters had virtually zero transmittance for the scattered light and very high transmittance for the fluorescent radiation. A Kodak Wratten light filter #34A was used for 607 m $\mu$ , a Corning color filter #2408 for 575 m $\mu$ , and a Corning #3480 for 540 m $\mu$ . In order to re-duce the amount of fluorescent radiation falling on the photomultiplier when scattering intensities were measured, a filter arrangement was used which involved a filter (elimination filter) in the incident beam and the interference filter in the scattered beam before the photomultiplier. The elimination filter had a sharp cut-off to zero transmittance at a wave length slightly shorter than that trans-mitted by the monochromatic interference filter, but with relatively high transmittance for light passed by the inter-ference filter. For a non-fluorescent system, the same galvanometer deflection is obtained if the above filter arrange-ment is used or if both elimination and interference filters are placed in the incident beam. This is an extremely sensitive test for the presence of fluorescence in scattered light. Where it is present, the galvanometer reading is larger for the case where both interference and elimination filters are placed in the primary beam. A Corning filter #2412 was used as elimination filter for 607 m $\mu$ , and #3480 for 575 m $\mu$ . This method was ineffectual for lower wave lengths (540 m<sub> $\mu$ </sub>, etc.) because of the magnitude of the fluorescence rela-tive to the scattered light. However, at 575 m<sub> $\mu$ </sub> its use en-abled qualitative measurements to be made. Since the fluorescent radiation excited by 607 m<sub> $\mu$ </sub> was found to be negligible by the samplifue test described above the value negligible by the sensitive test described above, the values reported for this wave length were obtained without the elimination filter.

**Preparation** of **Optically Homogeneous** Gels.—Poly-merizations were conducted in an oven whose tempera-ture was kept constant within 2°. Nitrogen was passed into the oven by means of a glass tube which was connected to the gas inlet tube of the cell by a spherical ground glass joint. Extents of reaction were determined by removing samples with the gas inlet tube, chilling quickly in an erlenmeyer, dissolving in chloroform and titrating with alcoholic NaOH using microburets and phenolphthalein as indicator. The end-points were very sharp. A sample of the fluid polymer was placed in 1 cm. calibrated Beckman cells when scattering measurements were made in order to determine the color correction factors. After the gel point, these factors were obtained by extrapolation and the changes throughout the course of the reaction were small. Dust, gas bubbles and crystallization must be avoided in the preparation of each system. Dust was effectively removed by the cleaning procedures described. The number of transfer operations was kept to an absolute minimum and all equipment was rendered as dust-free as possible. Crystallization was avoided by running the reaction to an advanced extent before beginning scattering measurements. This extent was determined experimentally in each case. Bubbles of nitrogen and water vapor were removed before the gel point by placing the cell into a vacuum desiccator immediately upon removal from the oven. Since it is impossible to remove entrapped bubbles after the infinite network has formed, it was necessary to stop the flow of nitrogen before gelation occurred, remove all bubbles, then continue the reaction with the nitrogen tube removed. At this point, a shorter tube was used which passed a current of nitrogen over the surface of the reaction mixture. This carried off water vapor and effectively excluded oxygen from interfering with the polymerization. If this was not done, the transmittance of the system was greatly decreased and the fluorescent intensity increased. Other details concerning the preparation of the infinite networks are included in the experimental results section.

Molecular Weights.—Light scattering molecular weights were determined for polyester samples obtained immediately before the gelation point. Acetone was used as solvent. The specific refractive increments were obtained by a differential refractometer based on a design by Brice and co-workers.<sup>11</sup> It was calibrated by means of sucrose solutions and by hydrocarbon samples (methylcyclohexane, 2,2,4-trimethylpentane) obtained from the National Bureau of Standards. Concentrations of the polymer solutions were determined by heating 10-ml. samples at  $70\,^\circ$  for 6–12 hours.

#### **Experimental Results**

Color Absorption Correction.—This correction is divided into two parts: (1) the correction factor at a scattering angle of  $90^{\circ}$ , and (2) its angular dependence. For a given absorbance at any angle, it is defined by

$$C = \frac{\text{scattered intensity in absence of dye}}{\text{scattered intensity in presence of dye}}$$
(1)

This was determined for each cell over a wide range of absorbances. Plotting the natural logarithm of eq. 1 as a function of the absorption coefficient  $\alpha$  (where  $\alpha = 1/L \ln 1/T$ , *T* is the transmittance of an absorbing solution in a spectrophotometric cell having an optical path length *L*) of the absorbing macromolecular system gave a straight line for values of  $\alpha$  less than 0.15 cm.<sup>-1</sup>. Therefore the correction factor in this range can be written

$$C = \exp(\alpha k) \tag{2}$$

where k is the slope of the logarithmic plot and equal in this case to 8.65 cm. It is readily seen that k corresponds to the total path length travelled by a light beam of zero width which enters the cell and is scattered from the center of the cylindrical portion to the wall. The path length for this particular cell as measured by ruler and calipers was 8.7 cm. As the absorption coefficient increases beyond 0.15 cm.<sup>-1</sup> the correction factor given by eq. 2 becomes too large. Fortunately the absorbances for the polyesters studied were less than this value for wave lengths of 540 m $\mu$ and greater.

The correction factors were determined for each angle and a small degree of angular dependence was observed. It increased for angles less than 90° and decreased for those greater than 90°. The lower the transmittance of the colored macromolecular solution, the more pronounced was the effect. This increase in the attenuation of light scattered in the forward direction has been discussed by Tonnelat<sup>12</sup> and treated in detail by Frank and Ullman.<sup>13</sup> However, at an absorbance of 0.14 cm.<sup>-1</sup> the change in the correction factor with angle was approximately 5% from its 90° value for the extreme positions of 25 and 145°. For this work, the correction factor was considered to be independent of angle.

**Polyglyceryl Sebacate** (**PGS**).—When sebacic acid and glycerol were allowed to react in a 1:1 mole ratio of hydroxyl to carboxyl groups, the resultant polyester on cooling became opaque due to crystallization and no scattering measurements could be made. It was necessary to use a larger proportion of hydroxyl groups in order to obtain transparent systems. With a hydroxyl:carboxyl ratio of 1.28, it was possible to obtain a noncrystalline system on cooling if the extent of reaction<sup>14</sup> was greater than 0.77. This corresponds to

- (12) J. Tonnelat and H. Batsch, Compt. rend., 231, 960 (1950).
- (13) H. Peter Frank and R. Ullman, J. Opt. Soc. Am., 45, 471 (1955)
   (14) Extent of reaction is defined as
  - tent of reaction is defined as

#### no. of ester groups

(11) B. A. Brice and M. Halwer, J. Opt. Soc. Am., 41, 1033 (1951).

no. ester groups + no. unreacted carboxyl groups

Nov., 1956

the point "A" in Fig. 1. The data for this figure were obtained by measuring the extent of reaction as a function of time for compositions and conditions similar to those used in the preparation of the polyesters for light scattering measurements. No attempt was made in these cases to render the reagents dust-free. The lengths of time necessary to reach the gelation points shown in Fig. 1 are less than those required in the scattering studies, for in the latter case the cell was removed from the oven and cooled so that scattering measurements could be made.

Heating the cell containing the mixture of alcohol and acid described above for 100 minutes at 160° brought the extent of reaction to 0.792. After cooling to room temperature, scattering measurements were made and the horizontal and vertical components of scattered light using unpolarized incident radiation are shown in Figs. 2 and 3. The correction factors described in the Experimental section have been applied to all scattering intensity measurements before plotting. A further 100 min. of heating at 160° raised the reaction extent to 0.852 at which point the system became extremely viscous. The gelation point for this system was p = 0.855 (see Fig. 1). Entrapped bubbles were removed and the reaction was continued (after scattering measurements were taken) for 90 minutes at 180°. After this period, the polyester lost all fluid properties at the elevated temperature indicating that gelation had occurred. The scattering envelopes obtained on cooling are shown in Figs. 2 and 3. The light scattering measurements obtained immediately before the gelation point were only very slightly less than those measured at p =0.88 and were not put in Figs. 2 and 3 for the sake of clarity.

Carrying the reaction further caused considerable contraction of the gel and fractures appeared at the gel-glass interface and scattering measurements could not be made. Cleaning the cell revealed the system to be uniformly gelled with the exception of the upper 2 mm. which was somewhat harder than the contents of the lower region. The PGS gel had the resiliency of soft rubber. Titrating a sample of the insoluble gel gave a reaction extent of 0.88. Samples of PGS gel remained clear for approximately two months after which time a haze developed. This was probably due to crystallization of unreacted and partially reacted sebacic acid residues.

Scattering measurements were also obtained on PGS systems in which the initial hydroxyl to carboxyl ratios were 2:1 and 3:1. In these cases, gelation could not occur because of the excess of hydroxyl groups. The values of the Rayleigh, dissymmetry and depolarization ratios for different extents of reaction are listed in Table 1.

**Polyglyceryl Hexahydrophthalate** (PGP).—In this system it was possible to allow the alcohol and acid to react in a 1:1 ratio of functional groups with no crystallization difficulties. Fifteen minutes of heating at  $160^{\circ}$  was required for homogeneity of the reactants to occur and the first set of scattering measurements were taken at an extent of 0.491 (which corresponds to point "A" of Fig. 1).



Fig. 1.—Kinetics of the polycondensations leading to gelation.



Fig. 2.—Angular variation of horizontal component  $(H_u)$  for polyglyceryl sebacate (PGS);  $\lambda$  607 m $\mu$ .



Fig. 3.—Angular variation of vertical component  $(V_u)$  for polyglyceryl sebacate (PGS);  $\lambda$  607 m $\mu$ .

Light	SCATTER	ING RESUL	TS OF T	HE POLY	LYCERY	l Seba-
		CATE (P	GS) Sy	STEM		
		(i) (OH)/(	COOH	) = 1.28		
				$R_{90} \times$		
λ (m//)	n	(cm, -1)	С	$10^{5a}$ (cm, $-1$ )	i45/1126	Øn
607	0 790	0 0457	1 45	3 70	2 11	0 40
607	0.852	0.0439	1.43	3.90	1.64	0.44
607	0.88	0.0439	1.43	4.06	1.55	0.42
575	0.852	0.0650	1.69	c	1.96	0.35
575	0.88				1.77	0.34
		(ii) (OH)/	(COOH	() = 2.0		
607	0.795	0.0376	1.35	3.33	2.18	0.38
607	0.879	0.0371	1.35	3.42	2.08	0.37
575	0.795	0.0592	1.61	с	2.62	0.32
575	0.879	0.0565	1.58		2.34	0.37
		(iii) (OH)/	(COOE	I) = 3.0		
607	0.772	0.0136	1.12	3.24	2.24	0.38
607	0.946	0.0202	1.18	2.74	1.31	0.47
607	$0.946^{b}$	0.0202	1.18	2.74	1.19	0.47
575	0.946	0.0278	1.25	с	1.72	0.42
575	0.946 <sup>b</sup>	0.0330	1.31		1.39	0.44

TABLE I

<sup>a</sup> Corrections for background scattering were made by subtracting the scattering intensity obtained with clean glycerol. <sup>b</sup> Centrifuged 3 hr. (see Discussion section). <sup>c</sup> Values for 575 m $\mu$  were uncertain due to fluorescence.



Fig. 4.—Angular variation of horizontal component  $(H_u)$  for polyglyceryl hexahydrophthalate (PGP);  $\lambda$  607 m $\mu$ . ( $V_u$  was independent of angle and equal to 23 and 31 units at p = 0.49 and 0.77, respectively).

The initial reaction between the anhydride and glycerol was extremely rapid in the same manner as reactions between phthalic anhydride and primary alcohols.<sup>15</sup> The viscosity of this system was much higher than that of PGS and at room temperature it solidified to a brittle glass-like solid. This caused the necessary manipulations to be

(15) E. F. Siegel and M. K. Moran, J. Am. Chem. Soc., 69, 1457 (1947).

much more difficult as compared with the PGS After the first set of scattering measurecase. ments had been taken, the reaction was continued to p = 0.745, a value very close to the gel point (0.755) which had been observed in test runs (see Fig. 1). The gas bubbles were removed, the homogeneous system was heated at 190° for 60 minutes, and gelation occurred. Upon cooling, the final set of scattering measurements were made. The important ratios are listed in Table II. The horizontal component is shown in Fig. 4 and the vertical component was constant over the entire angular range and equal to 31 galvanometer divisions. Scattering measurements were also obtained on PGP systems in which the initial hydroxyl to carboxyl ratios were 2:1 and 3:1. These are listed in Table II.

#### TABLE II

#### LIGHT SCATTERING RESULTS OF THE POLYGLYCERYL HEXA-HYDROPHTHALATE (PGP) SYSTEM

#### (i) (OH)/(COOH) = 1.0

λ		α		$R_{90} \times 10^{5a}$			
(mµ)	p	(cm1)	C	(cm1)	145/1135	φu	
607	0.491	0.0182	1.17	3.58	1.00	0.53	
607	0.77	0,0212 <sup>b</sup>	1.20	5.06	1.07	0.60	
575	0.491	0.0315	1.31		1.01	0.50	
5 <b>7</b> 5	0.77	$0.0429^{b}$	1.44		0.98	0.57	
		(ii) (OH)	/(COO	H) = 2.0			
607	0.516	0.0151	1.14	4.18	1.01	0.52	
607	0.752	0.0166	1.15	5.28	1.02	0.50	
607	0.922	0.0309	1.30	6.55	1.05	0.53	
		(iii) (OH)	/( <b>C</b> 00	H) = 3.0			
607	0.623	0.0186	1.17	4.45	1.01	0.52	
607	0.808	0.0181	1.17	5.79	1.04	0.52	

 $^{\rm a}$  Same background corrections as in PGS.  $^{\rm b}$  Measured at extent of 0.719.

The scattering intensities were observed to decrease with increase in temperature for all systems studied. When the cell was removed from the oven, scattering measurements were taken at the angles 45, 90 and 135° as the cell cooled. The scattering intensities increased for these three angles with cooling and, when equilibrium was reached, the measurements reported above were taken. The length of time for equilibrium was dependent on the extent of reaction, increasing with larger extents. In the PGP case (OH)/(COOH) = 1.0, 35 min. was required at p = 0.49 and 80 min. at p = 0.77. The scattering intensity increased 63 and 67%, respectively, over the cooling period. The effect was much less pronounced for the PGS system. However, the dissymmetry ratio for the latter case increased as the cell cooled. The negative temperature coefficient was virtually absent in all cases where an excess of hydroxyl groups were used to avoid gelation. The depolarization ratios in all cases re-

mained constant throughout the cooling process. **Molecular Weight Determinations.**—Fluorescence was detected in the acetone solutions of the polymers when an incident beam of 475 m $\mu$  was used, but none was observed at 540 m $\mu$ . This latter wave length was used in all molecular weight determinations. It was not necessary to correct for color absorption. The solutions had a dissymmetry ratio of unity and negligible depolarization Nov., 1956

 $(\varphi_u = 0.03)$ . The Debye equation was used in the following form

$$\frac{Hc}{\tau} = \frac{1}{M} + 2 Bc \tag{3}$$

where:  $H = 32\pi^3 n_0^2 (dn/dc)^2/3 N\lambda^4$ ,  $\tau =$  turbidity (corrected for solvent scattering),  $n_0 =$  index of refraction of solvent (1.359), N = Avogadro's no.,  $\lambda = 5.40 \times 10^{-5}$  cm., (dn/dc) = specific refractive increment, c = concn. in g. solute per ml. soln., M = weight average molecular weight, B = second virial coefficient.

The refractive index correction due to calibration with water solutions was 3%. Equation 3 was extrapolated to infinite dilution without difficulty and the pertinent molecular weight results are listed in Table III.

#### TABLE III

LIGHT SCATTERING RESULTS FOR MOLECULAR WEIGHT DETERMINATIONS

System	p	dn/dc	$\frac{11}{10^{5}}$	$(Hc/\tau)_{c=0}^{(Hc/}\times 10^{4})$	M₩	${}^B imes_{10^4}$
		0 100	1 00	1 00	F700	00

 Polyglyceryl
 sebacate
 0.846
 0.129
 1.99
 1.83
 5700
 29

 (OH)/(COOH)
 =
 1.28

 Polyglyceryl
 hexahy 0.741
 0.127
 1.92
 2.12
 4800
 14

drophthalate (OII)/(COOH) = 1.0Polyglyceryl hexahy- 0.922 0.127 1.92 3.43 2900 11 drophthalate (OII)/(COOH) = 2.0

#### Discussion and Conclusions

Gelation-Points.—The gelation of PGP at p = 0.755 is less than the value obtained by Wekua<sup>16</sup> for polyglyceryl phthalate (0.79 at 180°). Kienle and co-workers<sup>17</sup> using 190° found p = 0.786 at the gel point for the same case. No catalyst was used in either of these cases in contrast to the conditions employed in this work. No cases were found in the literature where hexahydrophthalic anhydride was used as the acid.

For the conditions observed in the PGP preparation, Flory<sup>5</sup> demonstrated that the branching coefficient ( $\alpha_b$ ) becomes equal to the square of the extent of reaction.

$$\alpha_{\rm b} = p^2 \tag{4}$$

Letting  $\alpha_b = 0.50$  which is the condition for formation of infinite networks, the theoretical reaction extent at which gelation should occur is 0.71 and the experimental value found is seen to be higher. For the PGS case, we have

$$\alpha_{\rm b} = p^2 / 1.28$$
 (5)

Letting  $\alpha_b = 0.50$  gives a theoretical gelation point at p = 0.80 and the experimental value was 0.855. The fact that the observed gelation points were

The fact that the observed gelation points were reached at higher than the theoretical extents of reaction can be explained as a failure of the systems to rigorously fulfil certain assumptions made in the Flory treatment, namely, equal reactivity of groups and absence of intramolecular condensation. The secondary hydroxyl group of glycerol is less reactive than the primary groups, and the reactivity of a hydroxyl group is reduced by the condensation of one of its neighbors. Also, a fraction of the total reaction inevitably gives rise to some intramolecular condensation which does not contribute toward the growth of the polymer molecules.

Light Scattering Behavior.—Comparing Figs. 2, 3 with 4 and the data concerning the variation with angle of  $V_{\mu}$  for PGP, it is apparent that the radiation envelope for PGS is asymmetrical about  $90^{\circ}$  and that for PGP is definitely symmetrical. The asymmetry in the sebacate case becomes less pronounced as gelation occurs. The same behavior was noted in the cases where the hydroxylcarboxyl ratio was such that only relatively small molecules could be formed and such systems should possess symmetrical scattering envelopes. Since the centrifugation of the reactant mixture (Table I, part iii) markedly reduced the dissymmetry ratio at both wave lengths, it can be concluded that the asymmetry in this system must be due to the small amount of foreign inhomogeneities that were always present. Examination of these systems at low angles always revealed the presence of a very small quantity of motes. It is likely that these inhomogeneities were due to small amounts of crystallized sebacic acid residues. As the reaction progressed, the concentration of these crystallites decreased and the radiation envelope tended to become less asymmetrical. It must be emphasized that for all experiments, samples of the glycerol and sebacic acid used were examined in the photometer for the presence of motes and were found to be clean. Further proof that these motes were crystallites was the fact that the dissymmetry ratios of these systems were lower than those reported in Table I when measured immediately after removal from the oven.

In the PGP case, no inhomogeneities were observed throughout the course of the light scattering experiments. The dissymmetry ratios can be considered to be constant and equal to unity throughout the course of the polymerization. The deviations from unity listed in Table II appear to be within experimental error. This is further verified because the ratios for the non-gelation experiments fluctuated in the same manner. Rayleigh's ratio increased with the extent of reaction and its magnitude was of the order of that found in liquids such as benzene and carbon disulfide. The depolarization ratios are all greater than 0.50 and appear to increase with increasing extents of reaction. Such large depolarization ratios are characteristic of liquids whose scattering intensities are of the order of  $10^{-4}$  turbidity unit.

**Theoretical.**—Smoluchowski's<sup>18</sup> equation for the scattering of light from liquids can be written as

$$\frac{ir^2}{I_0} = \frac{\pi^2 RT \beta}{2 N \lambda^2} \left( \varphi \frac{\partial \epsilon}{\partial \varphi} \right)_T^2 \left( 1 + \cos \theta \right) F(\varphi_\mu)$$
(6)

The left side of eq. 6 represents the intensity of scattering at a distance r from a unit volume of liquid,  $\epsilon$  is the optical dielectric constant,  $\varphi$  the density,  $\beta$  the isothermal compressibility, and  $F(\varphi_{\mu})$  represents the scattering contribution from the anisotropy of the scattering units. The constant term (with respect to angle) of the right side is identified with the component of scattered light whose electric vector is vertical to the plane of

<sup>(16)</sup> K. Wekua and W. Klausch, Farbe u. Lack, 59, 85, 138 (1953).

<sup>(17)</sup> R. H. Kienle and F. E. Petke, J. Am. Chem. Soc., 62, 1053 (1940).

<sup>(18)</sup> M. Smoluchowski, Ann. Physik, 25, 205 (1908).

observation. The term dependent on the scattering angle refers to the horizontal component of scattered radiation. Now the  $V_u$  data for the PGP system represents the constant term of eq. 6. The angular variation of the horizontal component as described in Fig. 4 is predicted by eq. 6 when the anisotropy of the scattering centers is taken into account. Therefore, it must be concluded that three-dimensional network systems behave as liquids in the light scattering sense if they are free of optical inhomogeneities such as motes, crystallites, and inclusions of air. In a liquid, a fluctuation in density on the positive side is immediately accompanied by a fluctuation on the negative side and the time mean value of these fluctuations is zero for volume elements of arbitrary size. Equation 6 is based on just such a model. In a polyester gel system, the fluctuations must be considered to be quasi-permanent because of the large viscosity value of the medium, but the gels nevertheless behave optically as supercooled liquids. The agreement between eq. 6 and the experimental data for PGP shows that the gels are amorphous. In this respect they compare with amorphous solids such as are discussed by Bhagavantam.<sup>19</sup>

The increases in scattering intensity that were observed as the polyesters cooled to room temperature are contrary to the temperature dependence that would be predicted from eq. 6. Now, on cooling the systems showed a large amount of contraction. Thus the isothermal compressibility should decrease causing the scattering intensity to decrease. Also, the anomalous temperature effect can be attributed to an increase in the dielectricdensity term. The density of the system increases on cooling, and since this variable is present as a squared term, it could well account for the temperature-scattering effect.

The weight average molecular weights described in Table III are much larger than number average values (1000–1500) obtained<sup>20</sup> for similar systems

(19) S. Bhagavantam, "Scattering of Light and the Raman Effect," Chemical Publishing Co., New York, N. Y., 1942, p. 77.

(20) R. H. Kienle, P. A. van der Meulen and F. E. Petke, J. Am. Chem. Soc., 61, 2258 (1939).

prior to their gelation points. This is further evidence of the existence of a small number of very large molecular structures in the reaction mixture immediately before gelation occurs. The depolarization ratios for acetone solutions of the polyesters were very small (0.03) in contrast to the values for the polyesters in bulk. In general, the depolarization for liquids is five or more times greater than that exhibited by the molecules in the gaseous state. Benzene has a depolarization ratio of 0.045 in the gaseous state<sup>19</sup> and a value of 0.42 was obtained in this work for liquid benzene. Hence dissolution of the polyesters is analogous to the evaporation of a liquid. The large depolarization values obtained are therefore due mainly to intermolecular effects and cannot be connected directly with the inherent anisotropy of the scattering molecules.

Light Scattering from Solids.—Debye and Bueche<sup>21</sup> have reported light scattering results from Lucite, polystyrene and glass. They found relatively large dissymmetries and a residual intensity at large scattering angles which was attributed to small inhomogeneities. From our studies it appears that the residual intensity is the scattering of the pure solid and this was measured in the PGP system. The scattering behavior of PGS on the other hand, was very similar to the results of Debye and Bueche.

Because of the overwhelming effect of foreign inhomogeneities on the radiation envelopes from condensed systems, it appears that very little information can be obtained about the molecular properties of solids by light scattering unless these inhomogeneities are removed. We can conclude that the scattering behavior of optically clean amorphous solids is identical with that of liquids.

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(21) P. Debye and A. M. Bueche, J. Chem. Phys., 13, 1423 (1950).

## STABILITY OF FERROUS HYDROXIDE PRECIPITATES

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The stability of ferrous hydroxide precipitates at temperatures up to 316° has been investigated. Pure ferrous hydroxide in contact with solutions of potassium chloride containing either excess ferrous ion or excess hydroxyl ion and with rigorous exclusion of oxygen were found to be completely stable for periods up to six months at temperatures below 100°. When precipitated with nickel hydroxide the spontaneous reaction  $3Fe(OH)_2 \rightleftharpoons Fe_3O_4 + H_2 + 2H_2O$  takes place at ordinary temperatures with an activation energy of  $10.2 \pm 1$  kcal./mole. Excess hydroxyl ion completely inhibits the reaction. At temperatures in the range 150-210° pure ferrous hydroxide decomposes according to the above reaction with a conveniently measurable rate. The activation energy was measured and found to be  $30 \pm 3$  kcal./mole. In this temperature range silica and hydroxyl ion in the supernate inhibit the decomposition. By X-ray structure analysis and microscopic examination  $\alpha$ -iron was identified in the magnetite crystals formed in the thermal decomposition of the ferrous hydroxide at 178°

#### I. Introduction

Many references to the importance of the chemistry of ferrous hydroxide to iron corrosion can be found in the literature.<sup>3</sup> In addition this compound is thought to play a part in the chemistry of the Edison nickel-iron accumulator.<sup>4</sup> While the room temperature stability of precipitates of pure ferrous hydroxide is fairly well established (see below), the literature contains virtually no data as to its stability above 100°.

In 1933 Schikorr<sup>5</sup> studied the decomposition of ferrous hydroxide, which he assumed to take place according to the reaction

$$3 \operatorname{Fe}(\mathrm{OH})_2 \rightleftharpoons \operatorname{Fe}_3 \mathrm{O}_4 + \mathrm{H}_2 + 2 \mathrm{H}_2 \mathrm{O} \tag{1}$$

by measuring the amount of hydrogen evolved from the precipitated solid over long periods of time. In his experiments air was carefully excluded and the precipitate was not separated from the supernatant solution. Schikorr observed a slow evolution of hydrogen when the supernate contained excess ferrous ion, but in the presence of excess base no reaction occurred. Although some of his experiments ran for as long as 75 days, the maximum yield was about 16% of the theoretical amount of hydrogen calculated from reaction (1). As a result of these studies the reaction (1) is referred to in the literature as "Schikorr's reaction."

Fricke and Rihl,<sup>6</sup> in a review of the properties of ferrous hydroxide, reported that the pure white precipitate is oxidized by water at room temperature. Evans and Wanklyn<sup>7</sup> investigated the reaction further in 1948. Using a somewhat more elaborate method of preparing the precipitates of ferrous hydroxide, these investigators found them to be stable at all temperatures up to  $100^{\circ}$ , even in the presence of excess ferrous ion in the supernate. However, a reaction resulting in the evolution of hydrogen and the formation of magnetite was found to take place when certain salts were present.

(1) Now at the Chemistry Research Department, Research Laboratory, General Electric Co., Schenectady, New York.

(2) Operated by the General Electric Company for the U. S. Atomic Energy Commission.

(3) (a) U. R. Evans, "Metallic Corrosion, Passivity and Protection," Edward Arnold and Co., London, 1946, p. 209; (b) U. R. Evans, Engineering, (May 8, 1953).

(4) (a) J. T. Crennell and F. M. Lea, "Alkaline Accumulators," Longmans, Green and Company, London, 1928, p. 83; (b) O. Glesmer and J. Einerhand, Z. Elektrochem.. 54, 302 (1950).

(5) G. Schikorr, Z. anorg. allgem. Chem., 212, 33 (1933).

NiSO<sub>4</sub>, PtCl<sub>2</sub> and Na<sub>2</sub>S "catalyzed" the reaction when present in the solution. The finely divided metals platinum, copper and nickel were also effective "catalysts." Leussing and Kolthoff,<sup>8</sup> in a recent study of the solubility of ferrous hydroxide, report that the precipitate remains pure white at room temperature for periods of time up to several weeks.

The decomposition of the dried precipitate at  $200^{\circ}$  was observed by Goldberg<sup>9</sup> in 1914. Hüttig and Möldner<sup>10</sup> obtained similar results in a more thorough study in 1931.

In the present paper we report the results of a study of the thermal decomposition of slurried ferrous hydroxide at temperatures up to 316°. This covers the temperature range of interest in considerations of the mechanism of corrosion of iron in high-temperature water. In addition, we describe a brief study of the very interesting "catalysis" of this reaction by coprecipitated nickelous hydroxide.

#### II. Experimental

Pure white ferrous hydroxide was precipitated by mixing ferrous chloride and potassium hydroxide solutions in the absence of oxygen. These solutions were prepared by the method of Evans and Wanklyn, <sup>7</sup> *i.e.*, by the electrolysis of a one molar potassium chloride solution using an iron anode (99.99% Fe) and a platinum cathode. The water used to prepare the potassium chloride was purified by passing it through a bed of deoxygenating resin and then a bed of deionizing resin.<sup>11</sup> The oxygen content of the water was <0.1 ppm. The electrolysis cell, shown in Figure 1, consists of two compartments joined by a one molar potassium chloride bridge. The anode compartment is separated from the bridge by a sheet of anion-exchange resin<sup>12</sup> while a cation exchange resin<sup>12</sup> is used at the cathode junction. Potassium chloride solution was admitted to each compartment of the cell in an atmosphere of argon. Electrolysis was carried out at a constant voltage of 10–12 v., adjusted to give a fixed current of 120 ma. At the anode the current density ranged from 20 to 50 ma./cm.<sup>2</sup>, the higher values arising from the smaller area of a partially dissolved anode. On completion of the electrolysis the resulting FeCl<sub>2</sub> and KOH solutions were passed through stopcocks into evacuated Pyrex reaction cells where the precipitation of Fe(OH)<sub>2</sub>

(10) G. F. Hüttig and H. Möldner, Z. anorg. Chem., 196, 177 (1931).

(11) "Duolite S-10" resin, Chemical Process Co., Redwood City, California, and "Amberlite" MB-I resin, Rohm and Haas Co., Philadelphia, Pa., respectively.
(12) "Amberplex" ion-exchange resins, Rohm and Haas Co., Phila-

(12) "Amberplex" ion-excharge resins, Rohm and Haas Co., Philadelphia, Pa.

<sup>(6)</sup> R. Fricke and S. Rihl, ibid., 251, 414 (1943).

<sup>(7)</sup> U. R. Evans and J. N. Wanklyn, Nature, 162, 27 (1948).

<sup>(8)</sup> D. L. Leussing and I. M. Kolthoff, J. Am. Chem. Soc., 75, 2476 (1953).

<sup>(9)</sup> R. Goldberg, Dissertation Dresden, 1914, cited in H. B. Weiser, "Inorganic Colloid Chemistry," Vol. II, John Wiley and Sons, New York, N. Y., 1935, p. 87.



Fig. 1.—Schematic diagram of apparatus used in the preparation of pure ferrous hydroxide precipitates: X, stopcocks; A, cell for making up and degassing KCl solution; B, anode chamber; C, cathode chamber; D, anion-exchange membrane; E, cation-exchange membrane; F, connected to argon supply; G, reaction cell.

took place. The cell volume was ca. 100 cc. Excesses of either FeCl<sub>2</sub> or KOH were produced by discarding the solution in one compartment after a specified time of electrolysis, then refilling and continuing the electrolysis. A total of 0.003 mole of FeCl<sub>2</sub> was produced for all experiments; and for convenience the amounts of FeCl2 or KOH left in solution after precipitation of the  $Fe(O\hat{H})_2$  are expressed as a per cent. of this number, e.g., "per cent. ex-cess KOH." The solution volume varied, but usually amounted to about half the cell volume and was determined exactly at the end of each run. In the ''catalysis'' studies

the Fe(OH)<sub>2</sub> was precipitated in a Pyrex cell to which was affixed a small mercury manometer so that the rate of hydrogen evolution could be observed. Prior to the pre-cipitation of  $Fe(OH)_2$  the catalyst and a Pyrex enclosed magnetized stirring bar were placed in the cell. During precipitation constant magnetic stirring was employed. Samples stirred constantly throughout a run and samples stirred only during mixing of reactants gave identical re-sults. These experiments were run in a constant temperature bath (controlled to  $\pm 0.1^{\circ}$ ) and pressure inpressure increases were followed on a cathetometer.

Preliminary experiments at elevated temperatures in Pyrex cells indicated that the decomposition of  $Fe(OH)_2$  is

inhibited by the presence of silica. Consequently Pyrex cells with platinum or gold cups in them to contain the ferrous hydroxide were used in these experiments. The cell was evacuated before ferrous hydroxide was precipitated in the platinum cup. Immediately after precipitation the constriction in the entry tube was sealed, and the cell was placed in a stainless steel autoclave and the autoclave thrust bolts were tightened with a torque wrench. The autoclaves were equipped with needle valves through which helium was admitted and gas samples taken. After an autoclave con-taining a sample cell had been thoroughly flushed with helium the breakoff tip in the top center of the sample cell was punctured by means of an iron rod pushed through the valve port of the autoclave. The rod was removed, the valve stem inserted and the valve was closed after a measured pressure of helium was introduced. After heating in an oven at the desired temperature (controlled to  $\pm 2^{\circ}$ ) for a specified time the autoclave was quenched in water. The gas was then expanded into a known volume and the pressure recorded before a sample of gas was taken for analysis. The autoclave was then pumped out and refilled with helium for additional hydrogen evolution data. The hydrogen content of the gas samples was determined by analysis on a General Electric analytical mass spectrometer. A more complete discussion of the autoclave design and sampling techniques will be found in another report.<sup>11</sup>

#### III. Results

#### "Catalysis" Experiments.-The stability of fer-

(13) D. L. Douglas and F. C. Zyzes, "Corrosion of Iron in High Temperature Water," presented at the High Purity Water Corrosion Symposium, General Meeting of the National Association of Corrosion Engineers, New York City, March 13, 1956. rous hydroxide at room temperature was affirmed. A ferrous hydroxide precipitate containing a 10%excess of ferrous chloride was left standing for six months with neither a change in the appearance of the precipitate nor the evolution of hydrogen. This is in agreement with Evans and Wanklyn<sup>7</sup> and Leussing and Kolthoff.8 However, when nickel chloride was added to the ferrous chloride before precipitation a very rapid evolution of hydrogen (identified mass spectrometrically) was The hydrogen was observed to come observed. from the precipitate and not the supernatant solution. After an hour or two the reaction ceased entirely. Cupric chloride and cobaltous chloride, when used in the same way, caused very slow evolution of hydrogen for a period of days. No hydrogen was observed with PdCl<sub>2</sub>, ZnCl<sub>2</sub> or MnCl<sub>2</sub>.

A series of rate measurements was carried out using NiCl<sub>2</sub>·6H<sub>2</sub>O as a "catalyst," since a measurable quantity of hydrogen is produced in a few minutes after precipitation. The procedure consisted of adding three millimoles of ferrous chloride to a cell containing a predetermined quantity of NiCl<sub>2</sub>·6H<sub>2</sub>O and adding enough KOH, with constant stirring, to precipitate 90% of the mixture. A deficiency of base was used because the transfer of solutions was not quantitative to better than 1 or 2% and even a slight excess of base completely "killed" the reaction. Immediately after the addition of the base a pure white precipitate was observed which soon turned greenish-black and finally black as the evolution of hydrogen continued. Tested with a magnet the black precipitate proved to be strongly magnetic. Using a standard mixture containing 0.0003 mole of NiCl<sub>2</sub> (designated as 10% excess NiCl<sub>2</sub>) added to the 0.003 mole of FeCl<sub>2</sub> the effect of temperature on the reaction rate was determined. In addition, the effects of varying the amount of NiCl<sub>2</sub> "catalyst" and of varying the order of addition of reactants and "catalyst" were studied. Typical results are presented in graphical form in Fig. 2. The effect of temperature on the rate of hydrogen evolution of the 10% excess NiCl<sub>2</sub> runs is shown in Fig. 3. From the plots rates were determined from slopes of the initial linear portions of the curves. The data are given in Table I. From the rate constants an Arrhenius plot was made (Fig. 4) giving an apparent activation energy of  $10.2 \pm 1$ kcal./mole.

A few comments are in order relative to the results depicted in Fig. 2. The first concern the low yields obtained. In all cases the reaction stopped after a few hours—no more hydrogen being evolved over the course of several days. If the three millimoles of ferrous ion were to react quantitatively according to the reaction

#### $3 \text{Fe}(\text{OH})_2 \rightarrow \text{Fe}_8 \text{O}_4 + \text{H}_2 + 2 \text{H}_2 \text{O}$

then one millimole or 22.4 cc. (STP) of hydrogen would be evolved. The largest yield obtained in any of the experiments amounted to about 20%of this and most were in the region of 10%. This is actually in accord with the original results of Schikorr, his yields being about 16% at the end of 75 days. Separate experiments showed that 0.1% NiCl<sub>2</sub> produced no detectable reaction in two days; while 1.0% NiCl<sub>2</sub> added to the three millimoles of  $FeCl_2$  resulted in the evolution of about 0.25 cc. (STP) of hydrogen in two days. From these and the results shown in Fig. 2 it is seen that there is an approximate direct correlation between the extent of reaction and the amount of NiCl<sub>2</sub>. The results at 50% excess NiCl<sub>2</sub> are an unexplained exception. EVOLVED However, it is significant that the yield of hydrogen was always less than or equal to the amount of ROGEN nickel coprecipitated with the iron. In several cases the extent of ferrous ion oxidation was checked after cessation of the hydrogen evolution by dissolving the precipitate in excess acid, adding a known excess of standard potassium dichromate

solution and back titrating with standardized ferrous sulfate solution. Invariably the calculated unreacted ferrous ion corresponded within experimental error to the dichromate titer. In general increasing the ratio of NiCl<sub>2</sub> to FeCl<sub>2</sub> increased the initial rate of hydrogen evolution. By analysis of the final supernatant solutions it was established that all of the nickel was in the precipitate.

#### TABLE I

Rate Constants for the Evolution of Hydrogen from Ferrous Hydroxide Coprecipitated with 10% Nickel

Temp.,	$\Delta P / \Delta t a$	V cc	$k, cc. H_2$ (STP) $\times 10^2$	logk
0.1	0.16	55 6	1 17	_ 1 022
0.1	0.10	00.0	1.17	-1.902
0.1	0.13	55.3	0.95	-2.024
24.95	1.05	39.3	5.43	-1.265
24.9	1.12	47.0	6.93	-1.159
24.85	0.59	64.5	5.01	-1.300
24.8	0.50	56.0	3.68	-1.434
40.4	1.72	54.8	12.4	-0.906
40.4	2.75	<b>25</b> , $8$	9.34	-1.025
54.7	3.74	44.1	21.7	-0.664
54.7	3.99	52.2	27.4	-0.562

 $^{\rm a}$  Pressures have been corrected to  $273\,^{\circ}{\rm K}.$  and corrected for vapor pressure of water.

The reaction was inhibited, but not completely so, when the catalyst was added after precipitation of the ferrous hydroxide. Addition of NiCl<sub>2</sub> immediately after the ferrous hydroxide had been precipitated yielded 0.5 cc. of hydrogen in one hour (Fig. 2), while a precipitate that had aged for two hours before the addition of NiCl<sub>2</sub> produced only 0.4 cc. of hydrogen in 20 hours. When ferrous chloride was added after nickel hydroxide had been precipitated, the reaction was retarded also as is shown in Fig. 2. The addition of hydrogen to the cell immediately after coprecipitation of nickel and iron hydroxides had no affect on the yield.

An attempt was made to increase the yield of the reaction by homogeneous precipitation<sup>14</sup> of the ferrous hydroxide and nickel hydroxide. In the first experiment the anode compartment solution was added to a cell containing 0.5 g. of urea and the usual 10% (0.0003 mole) of NiCl<sub>2</sub>. After sealing, the cell was heated in a water-bath at 90-100°. Precipitation accompanied by hydrogen evolution began after abcut one hour, the first precipitate being black and magnetic. This behavior continued for approximately an hour after

(14) L. Gordon, Anal. Chem., 24, 459 (1952).



Fig. 2.—Nickel chloride "catalysis" of Schikorr's reaction at 24.9  $\pm$  0.1°: expt. 10, 20% NiCl<sub>2</sub>; expt. 33, 100% NiCl<sub>2</sub>; expt. 36, 10% NiCl<sub>2</sub>; expt. 79, 10% NiCl<sub>2</sub>-Ni(OH)<sub>2</sub> precipitated first; expt. 80, 10% NiCl<sub>2</sub>-Fe(OH)<sub>2</sub> precipitated before addition of NiCl<sub>2</sub>; expt. 89, 50% NiCl<sub>2</sub>.



Fig. 3.—Effect of temperature on the rate of hydrogen evolution from ferrous hydroxide coprecipitated with 10% nickel hydroxide (0.0003 mole NiCl<sub>2</sub> + 0.003 mole FeCl<sub>2</sub> precipitated with 0.006 mole KOH).



Fig. 4.—Arrhenius plot of nickel "catalyzed" decomposition of ferrous hydroxide to magnetite and hydrogen; 0.0003 mole NiCl<sub>2</sub> + 0.003 mole FeCl<sub>2</sub>; coprecipitated with 0.006 mole KOH; units of K are cc. (STP) of H<sub>2</sub> per min.

which the precipitate became greenish to white. Precipitation continued for some hours with no further magnetite or hydrogen being formed. It is estimated that the magnetite yield was about 5% of the total iron. Increasing the proportion of nickel to 50% in a second experiment produced substantially the same result, the final gas being composed of 0.6 cc. of H<sub>2</sub> and 28 cc. of CO<sub>2</sub>. The ferrous hydroxide precipitate was quite dense and settled quickly—suggesting homogeneous precipitation as a good method of preparing this solid.

Thermal Decomposition.—The results obtained in the study of the decomposition of ferrous hydroxide at elevated temperatures are shown in Figs. 5 and 6. Below  $100^{\circ}$  the evolution of



Fig. 5.—Thermal decomposition of ferrous hydroxide at elevated temperatures. The curves show total hydrogen (cc. STP) evolved as a function of time and temperature.



Fig. 6.—Thermal decomposition of ferrous hydroxide at high temperatures; effect of silica, ferrous ion and hydroxyl ion.

hydrogen was undetectable, while at temperatures above about 220° the reaction went to completion too rapidly to be followed conveniently. As can be seen in Fig. 5, the reaction rate at 178 and  $208^{\circ}$ decreased with time. The same may be true at the lower temperatures but no long term experiments were carried out to investigate this point. In this plot the data points represent two or more experiments at each temperature except the lowest, 105° and the highest, 316°. The apparent displacement of the start of the reaction from zero time is due to the time required to heat the autoclave to temperature in the oven. This time amounted to from 1 to 1.5 hours depending on the temperature. It is likely that some of the spread in the data is due to this limitation in the method. The low yield at 316° probably was caused by a loss in preparation of the ferrous hydroxide slurry.

Making use of the data given in Fig. 5 a rough determination of the activation energy of the reaction was made. Rates of hydrogen evolution were estimated graphically. In the case of the two highest temperatures, 178 and 208°, the rate in the initial stage of the reaction was used. An Arrhenius plot made using these slopes and the corresponding temperatures yields an activation energy of 30 kcal./mole. The lack of precision in the results makes the uncertainty in this energy equal to about 3 kcal./mole.

Figure 6 summarizes some experiments carried out to study the possible effect of incomplete precipitation on the rate of decomposition of ferrous hydroxide slurries. In addition, results showing the marked inhibiting effect of silica are given. At the lower temperatures an excess of either hydroxyl ion or ferrous ion remaining in solution inhibits the decomposition markedly. Very likely this accounts for some of the spread in the results of the thermal decomposition experiments, since loss of a few per cent. of either the FeCl<sub>2</sub> or KOH solutions was possible by holdup in the glass system. At the higher temperature,  $316^{\circ}$ , excess ferrous ion does not appreciably affect the decomposition. In another experiment the presence of an atmosphere of hydrogen rather than helium in the autoclave did not inhibit the reaction.

Solid reaction product from the high temperature experiments was collected by filtering and washing and an X-ray powder diagram (Debye–Scherrer) made. A full interpretation of the patterns could be given in terms of magnetite alone for runs at temperatures of 168° and below and in terms of magnetite plus small amounts of  $\alpha$ -iron for reactions carried out at 178° and above. In order to confirm the presence of iron, photomicrographs were made of polished sections of the well formed magnetite crystals mounted in Lucite. A few ferrite grains were found among the magnetite crystals. In all cases the ferrite was in contact with magnetite. This interesting phenomenon will be discussed in the next section.

The thermal decomposition of dried  $Fe(OH)_2$ was studied briefly. A ferrous hydroxide precipitate was collected on a glass frit in an evacuated cell, washed with water and vacuum dried. The precipitate did not decompose at a measurable rate below 100°, but at temperatures of 150–200° hydrogen and water were readily produced. The solid reaction product was magnetite. X-Ray analysis failed to show the presence of iron in the magnetite.

#### IV. Discussion

From the results obtained in this study as well as those of previous investigators it is clear that the decomposition of ferrous hydroxide results in the formation of magnetite and hydrogen. This is to be expected from the thermodynamics of the system. Standard free energy changes corresponding to various possible decomposition reactions of ferrous hydroxide are given in Table II. These were calculated from available standard free energies of formation of the compounds.<sup>15,16</sup> Lack of reliable heat capacity data prevented calculation of the free energy changes at higher temperatures, although rough estimates indicated that at 500°K. they are still negative by a few kilocalories.

It appears certain that ferrous hydroxide precipitates can be kept indefinitely at temperatures

(15) K. H. Kelley, "Selected Values of Chemical Thermodynamic Properties," U. S. Bureau of Standards Circular No. 500 (1949).

Properties," U. S. Bureau of Standards Circular No. 500 (1949).
(16) C. J. Smithells, "Metals Reference Book," Interscience Publishers Inc., London, 1955, p. 575.

#### TABLE II

STANDARD FREE ENERGY CHANGES OF REACTIONS OF FERROUS HYDROXIDE

 $\Delta G^{\circ}, \text{ keal.}$ 

	Reaction	$298^{\circ}$ K. (25
(1)	$3 Fe(OH)_2(c) \rightleftharpoons Fe_3O_4(c) + H_2(g) +$	
	$2H_2O(1)$	-9.9
(2)	$2 Fe(OH)_2(c) \rightleftharpoons Fe_2O_3(c) + H_2(g) +$	
	$H_2O(1)$	-3.0
(3)	$Fe(OH)_2(c) + Fe_2O_3(c) \rightleftharpoons Fe_3O_4(c) +$	
	$H_2O(1)$	-6.9
(4)	$4 Fe(OH)_2(c) \rightleftharpoons Fe_3O_4(c) + Fe(c) +$	

 $\frac{11}{4H_2O(1)} = 103O(10) + 10(0) +$ 

below  $100^{\circ}$  if oxygen is rigorously excluded, and if the iron is sufficiently pure. One is inclined to ascribe Schikorr's original results, in which ferrous hydroxide very slowly decomposed partially to magnetite and hydrogen, to an impure iron. At this time it is possible to say very little about the actual mechanism of the reaction which takes place in the presence of nickel (copper and cobalt). In view of the results of the homogeneous precipitation experiments, in which the formation of magnetite ceases even though ferrous hydroxide is continuously precipitated in the presence of nickel ion, it seems unlikely that the effect of nickel is one of a catalyst in the usual sense of the word. For this reason quotation marks have been used in this paper.

A possible explanation of the peculiar low yields in this reaction is that it is very sensitive to pH. The marked effect of excess base in completely inhibiting the reaction supports this hypothesis. This would require that the reaction be heterogeneous, *i.e.*, the reaction take place on the surface of the precipitate with some constituent of the solution participating. The evidence suggests that coprecipitation of the iron and nickel as hydroxides is necessary for the reaction. Adding the nickel chloride after precipitation of the ferrous hydroxide results in some reaction as nickel ion is adsorbed on the surface yielding a coprecipitated iron-nickel hydroxide.

It is possible that the peculiar aging effects noted in other reactions of ferrous hydroxide<sup>17</sup> may be involved in the low yields of the "catalyzed" reaction. The results of the homogeneous precipitation experiments seem to contradict this but may prove not to do so when more is known about the exact changes taking place in the solution during precipitation.

The thermal decomposition of the pure ferrous hydroxide slurries at high temperatures shows some of the same features as the room temperature—nickel "catalyzed" reaction, *e.g.*, excess hydroxyl

(17) O. Bauditsch and L. A. Welo, Naturwissenschaften, 21, 659 (1933).

ion inhibits both. The inhibiting effect of silica may be due to a formation of ferrous silicate on the surface of the hydroxide or to an increase in pHresulting from the dissolution of the glass. In any event the thermal reaction appears to be heterogeneous also.

It is instructive to consider these results in the light of previous studies of the corrosion of pure iron in high temperature water.<sup>13</sup> In these it was found that at  $240^{\circ}$  the corrosion of iron is described by a linear law, indicating that an interface reaction is rate controlling. This reaction may well be the decomposition of ferrous hydroxide to magnetite and hydrogen. One method of establishing whether this is the case would be to measure the activation energy of the corrosion reaction and compare it with that of the thermal decomposition of ferrous hydroxide. This would not prove that Schikorr's reaction is involved in iron corrosion, but would make it very likely.

The iron found in the magnetite produced by the thermal decomposition of ferrous hydroxide indicates that the reaction

$$4 Fe(OH)_3 \rightleftharpoons Fe + Fe_3O_4 + 4H_2O$$

is proceeding simultanecusly. That this reaction may take place at appropriate temperatures was suggested by Pourbaix,<sup>18</sup> his speculation being based on work by Thiesse.<sup>19</sup> The decomposition of ferrous oxide to magnetite and iron, *viz*.

$$FeO \rightleftharpoons Fe_3O_4 + Fe$$

has been studied by Chaudron and co-workers.<sup>20</sup> They report the transformation to take place in the temperature range 250–400°. In the course of a study of the chemistry of ferrous hydroxide at Battelle Memorial Institute the formation of ferrite in the course of the thermal decomposition has been observed also.<sup>21</sup> This reaction merits further study to elucidate the effects of temperature, time of exposure, method of preparation and purity of the ferrous hydroxide and of dissolved salts.

The assistance of the KAPL Metallurgical and Chemical Analysis Activity in performing various analyses is gratefully acknowledged, and particularly the assistance of C. F. Pachucki and L. R. Yetter for mass spectrometer analyses. We are also indebted to Mr. L. M. Osika of Physical Metallurgy, Technical Department, for the X-ray structure analyses.

(18) M. J. N. Pourbaix, "Thermodynamics of Dilute Aqueous Solutions," Trans. J. N. Agar, Edward Arnold and Co., London, 1949, p. 89.
(19) Thiesse, Thesis, Nancy, 1937.

(20) R. Collongues and G. Chaudron, Compt. rend., 234, 728 (1952);
 R. Collongues, R. Sifferlen and G. Chaudron, Rev. Met., 50, 727 (1953).

(21) Private communication from Dr. P. D. Miller, Physical Chemistry and Corrosion Technology Division, Battelle Memorial Institute, Columbus, Ohio.

### SEPARATION OF ORGANIC SOLUTIONS BY THERMAL DIFFUSION

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Thermal diffusion measurements have been made on solutions of aromatic compounds in benzene. In many cases essentially pure benzene was obtained as one product. The interpretation of the results involves the size and configuration of the molecule.

#### Introduction

The use of thermal diffusion to separate liquid mixtures followed shortly after its application to the separation of gaseous isotopes and mixtures by Clusius and Dickel<sup>1</sup> in 1938. Briefly, the process involves subjecting the gaseous or liquid mixture contained between two vertical, closely-spaced plates, or in a narrow annulus, to a horizontal temperature gradient. One component will be slightly enriched at the hot wall and the other component at the cold wall. The temperature gradient causes a horizontal density gradient and thereby a convective flow of material upward along the hot wall and downward along the cold wall. Consequently, the component which was enriched at the hot wall will be concentrated at the top of the apparatus and the component which was enriched at the cold wall will be concentrated at the bottom of the apparatus.

Only a few extensive investigations of the use of the thermogravitational method for separating organic mixtures have been reported. Prigogine and co-workers<sup>2-4</sup> have used the separation process to obtain information about molecular interactions in solutions. Jones and co-workers<sup>5,6</sup> have reported separations of a number of solutions, with emphasis on industrial applications.

Drickamer and co-workers<sup>7,8</sup> have published a number of papers of which only the most recent are given as references.

This investigation was concerned with solutions of several aryl substituted benzenes in benzene. The compounds used—biphenyl, mercury diphenyl, *o*-terphenyl, *p*-terphenyl, bibenzyl, and *trans*-stilbene—are structurally similar to benzene and would not be expected to exhibit much deviation from ideal behavior when dissolved in benzene. The compounds differ from one another mainly in the molecular weight and geometrical arrangement of the groups. They were chosen in the hope that these differences would be reflected in the character of the separations.

#### Experimental

Construction and Operation of the Cell.<sup>9</sup>—The cell con-

K. Clusius and G. Dickel, Naturwissenschaften, 26, 546 (1938).
 I. Prigogine, L. Brouckere and R. Amand, Physica, 16, 577

(1950).

(3) I. Prigogine, L. Brouckere and R. Amand, ibid., 16, 851 (1950).

(4) I. Prigogine, L. Brouckere and R. Buess, ibid., 18, 915 (1952).

(5) A. L. Jones, Petroleum Processing, 6, 132 (1951).

(6) A. L. Jones and E. Milberger, *Ind. Eng. Chem.*, **45**, 2689 (1953).
(7) E. L. Dougherty, Jr., and H. G. Drickamer, THIS JOURNAL, **59**, 443 (1955).

(8) E. L. Dougherty, Jr., and H. G. Drickamer, *ibid.*, 23, 295 (1955).

(9) For a detailed description of the cell and operation see H. F. John, "Separation of Binary Organic Solutions by Thermal Diffusion," Ph.D. Thesis, University of Missouri, 1953. Available from University Microfilms, Ann Arbor, Mich.

sisted of two silver plated copper plates each 1.3 cm. thick with a trifluorochloroethylene polymer gasket (Kel-F). The plate separation was 0.020 cm. The working area of the cell was 6.4 cm. wide and 9.4 cm. high. One plate was heated by radiation, the other cooled by running water.

The variation in temperature of the working surfaces was always less than 0.5°. Two reservoirs were recessed into the cold plate at top and bottom, each with a volume of 5.45 cm.<sup>3</sup>. Samples were removed for analysis by means of a hypodermic syringe.

hypodermic syringe. Analytical Techniques and Materials.—A Bausch and Lomb Abbe Precision Refractometer was used for analyzing the cyclohexane-ethyl alcohol solutions and some of the benzene-bibenzyl solutions.

Analysis by weight was used for the other solutions. Analysis by weight was used for the other solutions. The samples (40–100 mg.) were transferred by means of a hypodermic syringe from the cell to a small weighing bottle and immediately weighed. The benzene was then evaporated and the weight of solid determined. Preliminary investigation on each of the solutions was necessary to determine the conditions which would ensure complete evaporation of the benzene. The benzene-bibenzyl solutions were not particularly amenable to this type of analysis because of tenacious retention of benzene by the bibenzyl. The weighing technique has the advantage of being relatively insensitive to separation of small amounts of impurities into one of the reservoirs which could cause spurious results if such impurities happened to have a refractive index much different from that of benzene.

The ethyl alcohol, cyclohexane and benzene were redistilled from good starting material. The solid compounds —biphenyl, mercury diphenyl, o-terphenyl, p-terphenyl, bibenzyl and *trans*-stilbene—were Eastman Kodak Co. "white label" products. They were used without further purification.

#### Results

Although this investigation was principally concerned with the separation of several solutions of aryl substituted benzenes, some data were taken on the ethyl alcohol-cyclohexane system for purposes of comparison with the results obtained by Prigogine, Brouckere and Amand<sup>3</sup> on the same system using a similar cell. Figure 1 shows the separation as a function of time for three values of temperature difference between the plates.

Concentrations are plotted as the ratio of the weight fraction W of the ethyl alcohol to its initial weight fraction  $W_0$ , which for these experiments was 0.52. Weight fraction was used rather than mole fraction in order to permit direct substitution in the equation for the Soret coefficient. The order of the curves in Fig. 2 is unchanged by conversion to mole fraction.

Time was measured from the instant the heating unit was turned on. It required about five minutes for the cell to reach thermal equilibrium. Curve A is a single run, curves B and C contain the results of several runs.

Only a limited number of samples could be removed without significant depletion of material. In view of this limitation and the convenience of removing samples from the top, the change in concen-



Fig. 2.— $\Delta T = 27.0^{\circ}$ ,  $W_0 = 0.10$ : A, bibenzyl; B, biphenyl; C, trans-stilbene; D, o-terphenyl; E, diphenylmercury. All in benzene.

tration was for the most part followed in the top reservoir, although for all of the separations at least one sample was taken from the bottom reservoir. More complete data were taken, as shown in Fig. 1, for a few separations. For almost all points ( $W_{\text{bottom}}$ +  $W_{\text{top}}$ )/2 =  $W_0$  to within 2%. The separations of the solutions of the aryl benzenes in benzene are reported, as in the case of ethyl alcohol-cyclohexane, as the ratio of the weight fraction of the solid compound in the top reservoir to its initial weight fraction. Figure 2 shows the separation as a function of time for 10 weight %



Fig. 3.—o-Terphenyl-benzene,  $\Delta T = 27^{\circ}$ : A,  $W_0 = 0.01$ ; B,  $W_0 = 0.10$ ; C,  $W_0 = 0.2209$ ; D,  $W_0 = 0.5184$ .



Fig. 4.—o-Terphenyl-benzene,  $\Delta T = 27.0^{\circ}$ ,  $W_0 = 0.7988$ .

solutions of bibenzyl, biphenyl, trans-stilbene, mercury diphenyl and o-terphenyl in benzene. Separations of 1, 10, 22 and 52% solutions of o-terphenyl are shown in Fig. 3. Figure 4 shows the separation of 88% o-terphenyl solution, which is unique among the separations presented here, since the heavier component initially concentrates in the top reservoir. Separations were also performed on 1% solutions of p-terphenyl and trans-stilbene. The separation of p-terphenyl was very similar to that of o-terphenyl, but slightly slower. The value of  $W/W_0$  for p-terphenyl at 25.5 hours was 0.32, as compared to 0.24 for o-terphenyl. The value of  $W/W_0$  for the 1% trans-stilbene after the same time was 0.48.

An inflection in the  $W/W_0$  vs. time curves occurs after about two hours which gives the separations the appearance of having two distinct regions. In order to show the magnitude of this effect more readily, data for the first six hours of some of the separations have been plotted on an expanded scale in Fig. 5. In addition to curves A, C and D, which were shown in Fig. 3, curve E shows the early hours of the separation of a 0.096% o-terphenyl solution with  $T = 38.2^{\circ}$ . Curve B shows the separation of an o-terphenyl solution after the cell was held in a horizontal position for 2.5 hours before being placed in the usual vertical position. The significance of the latter curve will be discussed later. The inflection in the separation curves is more pronounced for 10% solutions of biphenyl, bibenzyl and *trans*-stilbene than for the 10% o-terphenyl solutions, but is much less pronounced in the case of mercury diphenyl.

#### **Discussion of Results**

Current theories of thermal diffusion emphasize the role of energy. In reaction rate theory energy comes in as activation energy.<sup>10,11</sup> In the thermodynamic approach the "net heat of transport" is the important quality as emphasized by Denbigh.

Attention has been given to the size and shape of molecules by Dougherty and Drickamer, but only as these factors are associated with a net heat of transport or introduce a non-randomness in the distribution of molecules in the solution.

Our data show that separation may be large even in solutions which approach Raoult's law in their behavior. Furthermore, the larger and heavier molecules concentrate at the cold wall. This suggests that the controlling process is one of diffusion

(10) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., New York, N. Y., 1911, chapter IX.

(11) K. G. Denbigh, Trans. Faraday Soc., 48, 1 (1952),



Time in hours.

Fig. 5.—o-Terphenyl-benzene: A,  $\Delta T = 27.0^{\circ}$ ,  $W_0 = 0.5184$ ; B,  $\Delta T = 27.0^{\circ}$ ,  $W_0 = 0.1072$ ; C,  $\Delta T = 27.0^{\circ}$ ,  $W_0 = 0.2209$ ; D,  $\Delta T = 27.0^{\circ}$ ,  $W_0 = 0.09646$ ; E,  $\Delta T = 38.2^{\circ}$ ,  $W_0 = 0.09648$ .

toward the hot wall, perhaps due to the fact that the concentration of holes increases in this direction.

In Fig. 2 we find that the heaviest molecule, mercury diphenyl, concentrates to the greatest extent at the cold plate. This we attribute to its large molecular weight causing a slow rate of diffusion.

Next we note that *o*-terphenyl shows marked concentration at the cold plate. This we attribute to the fact that its shape, roughly spherical, results in a high activation energy for diffusion.<sup>7,8,12</sup>

The next three compounds are composed of molecules which can be characterized as linear, in at least one possible configuration. We attribute their more rapid diffusion cut of the cold region as due to the fact that activation energy will be less than for *o*-terphenyl since the elementary process may be one in which the molecule moves only a fraction of its length.

A molecular model of bibenzyl shows that it can assume a configuration approaching that of a cylinder. Persistence of velocity in the diffusion process may then account for its position in the figure.<sup>12</sup>

Figure 3 shows the results for *o*-terphenyl, the only compound which we studied through nearly

(12) R. R. Ewell and Henry Eyring, J. Chem. Phys., 5, 729 (1937).

the entire range of concentration. The curve for the highest concentration of *o*-terphenyl is shown in Fig. 4 with an expanded scale for the ordinate. These two figures indicate that as the concentration of *o*-terphenyl increases it concentrates less and less at the cold plate until finally at the highest concentration the sign of the Soret coefficient is reversed and it is concentrating at the hot plate. This conclusion is based upon the fact that the curve at the highest concentration exhibits the phenomenon called "Forgotten Effect."<sup>13</sup>

During the first part of the separation the *o*-terphenyl goes to the top reservoir as a result of the difference in density produced by the temperature gradient. Later the *o*-terphenyl goes to the bottom reservoir due to the difference in density produced by the concentration gradient. During the entire process, however, the *o*-terphenyl is concentrating at the hot plate.

The explanation for this reversal in sign for the Soret coefficient with concentration may be that as a solution becomes more concentrated in *o*-terphenyl the holes in the solution becomes larger, being determined by that component present in the

(13) S. R. de Groot, Physica, 9, 699, 601 (1942).

L.	EXPERIMENTAL DAT	A AND CALCULA	TED VALU	ES OF BORET CO	DEFFICIENT	rs -	
	<i>a</i> =	0.020  cm., b =	6.4 cm., v	$= 5.45 \text{ cm.}^3$			
System	Slope, sec1	$\eta$ , poises $\times 10^3$	W	$\Delta ho/\Delta T~ imes~10^3$	T	$\Delta T$	$S \times 10$
$C_2H_5OH-C_6H_{12}$	$1.5 imes10^{-6}$	7.36	0.5221	1.08	30.2	14.0	8.5
$C_2H_6OH-C_6H_{12}$	$3.4 imes10^{-6}$	6.56	. 5223	1.08	32.0	21.8	7.1
$C_2H_6OH-C_6H_{12}$	$11 \times 10^{-6}$	6.03	.5147	1.08	32.5	28.4	12
o-Terphenyl-C <sub>6</sub> H <sub>6</sub>	$3.3 \times 10^{-5}$	5.55	.0965	0.978	31.6	27	-22
o-Terphenyl-C <sub>6</sub> H <sub>6</sub>	$3.4 imes10^{-5}$	5.01	.0965	.978	33.0	38.2	-10
o-Terphenyl-C <sub>6</sub> H <sub>6</sub>	$2.8 imes10^{-5}$	7.10	.2209	. 963	31.6	27	-28
o-Terphenyl-C <sub>6</sub> H <sub>6</sub>	$0.38 imes10^{-5}$	15.8	.5184	.738	31.6	27	-18
Hg diphenyl C <sub>6</sub> H <sub>6</sub>	$1.9 imes10^{-5}$	5.26	.0955	1.08	31.6	27	-11
trans-Stilbene C <sub>6</sub> H <sub>6</sub>	$0.61 imes10^{-5}$	5.45	.0996	0.974	31.6	27	- 4.1
Bibenzyl C <sub>6</sub> H₃	$1.2 imes10^{-5}$	5.35	.0938	0.944	31.6	27	- 8.0
Biphenyl C <sub>6</sub> H <sub>6</sub>	$1.5 imes10^{-6}$	5.29	.0965	1.00	31.6	27	- 9.4

TABLE I

EXPERIMENTAL DATA AND CALCULATED VALUES OF SORET COEFFICIENTS

larger concentration. This reduces the activation energy for the process of diffusion of *o*-terphenyl. If the holes in the liquid become larger than molecules of benzene this could increase the activation energy for diffusion of benzene. This last statement follows from the fact that the activation energy is determined in part by the energy liberated as a molecule slips into a hole.

Figure 5 shows a phenomenon which we are not able to explain. Nearly all curves show a break after two or three hours, after which the rate of separation increases. Curve B was obtained by holding the cell with the layer of liquid horizontal for a time long enough to establish temperature and concentration gradients. On turning the cell to the customary vertical position the data still gave a curve showing a break.

De Groot<sup>13</sup> has developed the phenomenological theory of the separation process in such a manner that the Soret coefficient can be obtained from the limiting slope of the separation curve at zero time. The relation, as modified by Prigogine, is

$$S = \frac{D'}{D} = - (\text{slope})720 \ V_{\eta}/(1 - W_0)\beta g_{\rho}(\Delta T)^2 b a^3$$

where a is the plate separation, b is the width of the plates, V is the volume of the top reservoir,  $\Delta T$  is the temperature difference between the two plates,  $\eta$  is the viscosity of the solution,  $\rho$  is the density of the solution,  $\beta = -[(1/\rho)(\partial \rho/\partial T)], g$  is the acceleration of gravity, S is the Soret coefficient, D and D' are the coefficients of ordinary and thermal diffusion, (slope) is the slope of the curve of  $W/W_0$ plotted against time and taken at the extrapolation to zero time,  $W_0$  is the weight fraction at zero time.

Experimental verification of the above relation is generally lacking. Values of Soret coefficients obtained by Prigogine<sup>2,3</sup> using organic solutions are high compared to values determined for similar solutions by methods not involving thermogravitational separations. The data for some of the separations, however, show such scatter that the limits of error may be great enough to allow for the difference. Discrepancies more difficult to reconcile were later found by Prigogine, Brouckere and Buess<sup>4</sup> when Soret coefficients and diffusion constants of heavy water in water were determined by this method. It is of some interest to calculate Soret coefficients using our data, which show less scatter and are more reproducible than other data which we have found in literature. Using limiting slopes taken from curves A, B and C in Fig. 1, along with a value for viscosity at the average temperature of the plates, values of D'/D of  $8-10 \pm 1 \times 10^{-3}$ deg.<sup>-1</sup> are obtained for ethyl alcohol in cyclohexane. These values are very close to the value of  $8 \pm 3 \times 10^{-3}$  deg.<sup>-1</sup> reported by Prigogine using similar experimental conditions.

Values of D'/D similarly calculated for the benzene solutions are given in Table I, using the slope obtained from the very early part of the separation curve. *trans*-Stilbene is an exception since the data taken during the early part of the separation curve were not sufficiently reproducible to enable us to assign a slope to this part of the curve. The sign of the Soret coefficients is negative, since the conventional choice of signs is such that the Soret coefficient is negative when the component for which the coefficient is calculated concentrates at the cold wall.

Our results confirm in two ways the doubt which has been cast upon the De Groot-Prigogine equation for determining Soret coefficients. First, the value for the cyclohexane-ethyl alcohol system agrees closely with Prigogine's value. Doubt has been cast upon this value and those obtained on several similar solutions by the work of Thomaes,14 who determined Soret coefficients by a method not involving thermogravitational separation. His values were in all cases lower than those determined by Prigogine. Second, the values obtained for the benzene solutions are higher than for any known organic or inorganic systems. Unfortunately experimental measurements on these benzene systems by other methods are not available. It appears that more accurate data would not alter these conclusions.

If these high values for Soret coefficient are confirmed they will support the explanation which we have given for our data, since a small difference in probability produced by a difference in concentration over a length comparable to the size of a molecule corresponds to a large concentration gradient.

(14) G. Thomaes, Physica, 17, 885 (1951).

## ENERGETICS OF THE BORANES. III. THE ENTHALPY AND HEAT CAPACITY OF TRIMETHYLAMINE-TRIFLUOROBORANE AS DETERMINED BY THE DROP METHOD

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Enthalpy increments relative to  $0^{\circ}$  were measured for trimethylamine-trifluoroborane by the drop method, using an ice calorimeter. These values were reduced relative to  $0^{\circ}$ K. by comparison with published data for hexamethylethane and hexafluoroethane. Reduced heat capacities for the solid over the range  $80-290^{\circ}$ K. are tabulated. The entropy increment for the formation of the solid salt from the gaseous Lewis acid and base has thereby been evaluated. Enthalpy and entropy increments for reaction of the sequence methylamines with boron trifluoride are tabulated and compared. Estimates were made and justified for those cases where data are lacking.

Due to the current interest in the thermochemical constants of Lewis salts, and particularly in those wherein the acid center is a boron atom, we wish to report some rough data obtained several years ago by means of ar ice calorimeter on trimethylamine-trifluoroborane. Although these data are crude in comparison with values for other compounds obtained by the same method as reported by workers at the National Bureau of Standards, they provide the basis for making reasonable estimates, and help establish a previously suspected trend for the sequence of methyl substituted amine bases.

The Equipment.—The apparatus consists essentially of a precision isothermal calorimeter, heating and cooling units for sample preparation, and associated vacuum lines, the system being set up so that samples could be completely handled *in vacuo*. The calorimeter has a relatively large volume (approximately 150 ml.) and can be used for measuring heat increments of less than 100 cal. with fair precision. It has been employed for the determination of heats of reactions between gases involving quantities of the order 0.002 mole.<sup>1</sup> The calorimeter proper was patterned after the improved model used by the National Bureau of Standards and described by Ginnings and coworkers.<sup>2-5</sup> The gas drying line and the vacuum apparatus used with the calorimeter are of an orthodox design.

Probably the greatest cause of difficulty and the largest source of error in the measurement of relative enthalpies of samples with this equipment is the operation of the lowering device. The sample is supported by a thread or wire wound around a wheel at the top of the cooling unit; this wheel is turned through a vacuum gland and gearing arrangement by operation of an external crank wheel; thus the sample is raised or lowered. But the time required for lowering is much longer and less uniform than had been hoped, and occasionally even more serious failures in operation were experienced. The incorporation of any lowering device into a vacuum system involves complications, but vacuum operation of the calorimeter is essential only for measuring heats of reaction. For relative enthalpies the method employed by Ginnings and co-workers for handling sodium is quite satisfactory.<sup>5</sup>

During the time the sample is being lowered from the cooling unit to the calorimeter it takes up heat from the surroundings. It is possible to correct for most of this heat by making measurements first on the empty container and then on the container with sample. The difference is taken as the enthalpy change of the sample. There remains some error, since the heat capacity of the sample keeps the temperature difference between the container plus sample and its surroundings greater for the same lowering time; hence the enthalpy difference measurements will be somewhat low in magnitude. With a lowering time of 1/4 second Ginnings and co-workers<sup>2</sup> found the error to be slightly greater than 0.02% at 900°, for a sodium sample. Assuming the time of fall in this apparatus, after leaving the cooling well and before entering the calorimeter, to be 6 to 7 seconds, we obtained a rough estimate of 0.6% for the error from this source at liquid nitrogen temperature, using a copper sample. With a sample of lower heat conductivity the error will be less. If a series of relative enthalpies over a range of temperatures are determined in this manner and plotted, the heat capacities derived from the slope of this curve will be in error to a somewhat greater extent than the error in enthalpy.<sup>2</sup>

Relative Enthalpy of Copper at Liquid Nitrogen Temperature.—With a lowering time of 20 seconds for both an empty container and the container filled with copper, the mercury expelled by the copper sample at  $-193.7^{\circ}$  was 6.81 g. With ten second lowering times the weights obtained were 6.85 g. at  $-193.8^{\circ}$  and  $6.83_{5}$  g. at  $-193.4^{\circ}$ . The heat capacity data of Keesom and Onnes from 14.51 to  $89.38^{\circ}$ K.,<sup>6</sup> and of Griffiths and Griffiths from 90 to  $290^{\circ}$ K.,<sup>7</sup> as well as the few values given by Nernst and Lindemann,<sup>8</sup> were plotted against temperature. The  $C_{\rm p}$  curve was drawn and the enthalpy increment from T to  $0^{\circ}$  was determined by graphical integration. At  $-193.4^{\circ}$  the relative enthalpy is -974.9 c.l. per gram atom; for a 29.000-g. sample the expected weight of mercury is

(6) W. H. Keesom and H. E. Onnes, Leiden Communications, 14, No. 147a (1915).

(7) E. H. Griffiths and E. Griffiths, Proc. Roy. Soc. (London), 90A, 557 (1914).

(8) W. Nernst and F. A. Lindemann, Z. Elektrochem., 17, 817 (1911).

<sup>(1)</sup> R. E. McCoy and S. H. Bauer, J. Am. Chem. Soc., 78, 2061 (1956).

<sup>(2)</sup> D. C. Ginnings, T. B. Douglas and A. F. Ball, J. Research Natl. Bur. Standards, 45, 23 (1950).

<sup>(3)</sup> D. C. Ginnings and R. J. Corruccini, ibid., 38, 583 (1947).

<sup>(4)</sup> T. B. Douglas and A. W. Harman, NBS Report No. 4333, Sept., 1955.

<sup>(5)</sup> D. C. Ginnings and R. J. Corruccini, J. Research Natl. Bur. Standards 38, 593 (1947).

therefore 6.88 g. Similarly for  $-193.7^{\circ}$  the expected weight of mercury is about 6.89 g. The individual heat capacity values from the literature may easily be in error by as much as 0.2%, and it is probable that no better accuracy should be claimed for the graphical value of the relative enthalpy. The precision of enthalpy measurements for an approximately constant lowering time has been found to be of the same order, and errors from sources other than the lowering time are probably at least as small.

Relative Enthalpies and Approximate Entropy at 0° of Trimethylamine-Trifluoroborane.—Trimethylamine-trifluoroborane was prepared by mixing commercial trimethylamine and boron trifluoride in a three-necked flask according to the procedure of Nichols.<sup>9</sup> The crude product was purified by recrystallization from benzene solution followed by sublimation *in vacuo* at about 150°, the more volatile materials being discarded. This procedure, developed and tested by Laubengayer and Heiderick<sup>10</sup> yields a compound of high purity. The sample used was a middle cut from the second sublimation; it was sealed in the Pyrex container under vacuum.

Measurements were made with the empty container, and the container with sample, at the temperature obtained with liquid nitrogen and solid carbon dioxide, and at room temperature (about 19°). The net values for the sample are listed in Table I, determined by difference between full and empty container. In plotting the data the individual points were coded as to lowering time, and insofar as possible the curves were drawn for a ten second lowering time. All values in Table I are for equal lowering times of both empty and filled containers.

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INTEGRAL ENT	HALPY INCREMENTS
Initial sample temp., °K.	Int. enthalpy increments cal./mole
79.4	-5610
195.0	-2850
292.2	+ 754

Except for the error due to the finite lowering time, the errors in this experiment should be the same as in the work with copper. Those errors which are independent of temperature become more important as the quantity of heat measured decreases in magnitude. Nevertheless the precision at the  $CO_2$  temperature for a given lowering time appears to be close to 0.1% of the net quantity of heat; thus even at this temperature random errors apparently are small. It is expected that the systematic error due to lowering time is less for trimethylamine-trifluoroborane than for copper, because the ratio of heat conductivity to heat capacity is much lower for the compound.

Interpretation of Enthalpy Data.—While the amount of data obtained is too limited to permit a complete analysis of the thermal properties of trimethylamine-trifluoroborane, or to yield highly

(9) G. M. Nichols, Ph.D. dissertation presented to the Graduate School of Cornell University, Dept. Chem. (1947).

(10) A. W. Laubengayer and E. W. Heiderick, private communication. precise values of the entropy of this compound, several semi-quantitative conclusions can be reached.

Thermally Me<sub>3</sub>N:BF<sub>3</sub> should be similar to Me<sub>3</sub>- $C-CF_3$ , with which it is almost identical sterically; regrettably, no heat capacity data are available for the latter compound. Trimethylamine-trifluoroborane should be intermediate between hexamethylethane and hexafluoroethane in some respects, though differing from this interpolation because of its polar character, and very likely because of details of packing of the less symmetric molecules in the crystals. The molar heat capacities of hexafluoroethane from 11.51 to  $170^{\circ}$ K.<sup>11</sup> and hexameth-ylethane from 12.12 to  $301.6^{\circ}$ K.<sup>12</sup> were plotted against temperature, and the curves were extrapolated to  $0^{\circ}$ K. Hexafluoroethane has a simple transition at 103.98°K.; the heat of transition is 893 cal. per mole. Hexamethylethane has a transition at  $152.5^{\circ}$ K.; the data in this vicinity appear to be somewhat affected by the presence of an impurity.<sup>12</sup> The heat of transition is given as 478 cal. per mole. A series of enthalpy values referred to absolute zero, were determined by graphical integration and plotted against temperature (Fig. 1).

As an aid to graphical comparison it was assumed that the  $C_{\rm p}$  and H curves (meaning,  $H_{\rm T}^{\circ}$  –  $U^{\circ}$ )  $H_0^{\circ}$ ) of trimethylamine-trifluoroborane are intermediate between those of hexafluoroethanc and hexamethylethane from  $0^{\circ}$ K. to the nitrogen temperature. Using this assumption, the experimental enthalpy values relative to  $0^{\circ}$  were converted to enthalpy relative to 0°K. and also plotted in Fig. 1. From the graphical comparison it appears likely that trimethylamine-trifluoroborane has no transition in the temperature range in which data were obtained. The gaps in the data are so large, however, that this conclusion is not wholly certain. This compound has a higher melting point than either reference compound; the same forces which raise the melting point probably raise the temperature at which rotations occur in the crystal. Thus it is plausible that there are no transitions below 19°. Slopes of the enthalpy curve  $(C_p)$  were determined graphically at intervals of about 20°. These values were plotted on a graph along with values for the reference compounds and a smooth curve was drawn. The smoothed values may be in error by about 1 cal. per degree at most points (provided there are no transitions below 19°, as assumed).

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#### $C_{\rm p}$ (Cal. Mole<sup>-1</sup> Degree<sup>-1</sup>)

	С	'p (cal. mole	e -1 degree	-1)	
°K.	Smoothed curve	$C_{\rm p}/T^a$	°K.	Smoothed curve	$C_{ m p}/T^a$
80	16.6	0.208	220	35.4	0.161
100	19.3	. 193	260	38.8	. 149
140	24.2	. 173	290	40.8	. 141
180	29.9	. 166			

 $^{\rm o}$  For values of T up to 80°K.,  $C_{\rm p}{\rm 's}$  were assumed to be the mean of those for hexafluoroethane and hexamethyl-ethane.

<sup>(11)</sup> E. L. Pace and J. G. Aston, J. Am. Chem. Soc., 70, 556 (1948).
(12) D. W. Scott, D. R. Douslin, M. E. Gross, G. D. Oliver and H. M. Huffman, *ibid.*, 74, 883 (1952); cf. G. S. Parks, H. M. Huffman and S. B. Thomas, *ibid.*, 52, 1032 (1930).

Values taken from the  $C_p$  curves were used to compute  $C_p/T$ , and the latter was plotted against the temperature. The entropy of the solid compound at 0°, as obtained by graphical integration, is 49.6 entropy units.

The entropy was also computed by an alternate method. If  $C_p$  and H are continuous functions, as assumed

$$S_{\rm T} = \frac{1}{T} \int_0^T C_{\rm p} dT + \int_0^T \left[ \frac{1}{T^2} \int_0^T C_{\rm p} dT \right] dT$$
$$= \frac{(H_{\rm T}^\circ - H_0^\circ)}{T} + \int_0^T \frac{(H_{\rm T}^\circ - H_0^\circ)}{T^2} dT$$

 $(H_{273.16}^{\circ} - H_{0}^{\circ}) = 6340$ , and (6340/273.16) = 23.2e.u. Values of  $(H_{\Gamma}^{\circ} - H_{0}^{\circ})/T^{2}$  were plotted and the integral was evaluated graphically as 26.4 e.u. Thus  $S_{(\text{at } 0\circ)} = 49.6$  e.u., in agreement with the value obtained by the conventional method. The second procedure has the advantage that only values from the enthalpy curve need be used, rather than its slopes. The agreement between the two methods suggests that the slopes were obtained with a fair degree of accuracy.

Because of the long extrapolation and interpolations necessary in drawing the enthalpy curve, the error in the entropy may be of the order of 3 units. (The low temperature extrapolation contributes heavily to the uncertainty in the entropy, since  $C_p/T$  and  $H/T^2$  are greatest for values of T below the nitrogen point.) From the published data, the entropy of boron trifluoride at 0° was calculated to be 60.6 e.u.<sup>13</sup> Similarly for trimethylamine the ideal gas entropy at 0° is 67.1 e.u.<sup>14</sup> Thus for the reaction

$$Me_3N(g) + BF_3(g) \longrightarrow Me_3N: BF_3(s), \Delta S_{273}^\circ = -78.1 \text{ e.u.}$$

Reduction to the Gas Phase Reaction.-It was desired to calculate the entropy change for this reaction with the product at one atmosphere in the ideal gas state at  $0^{\circ}$ . The entropy of sublimation and the entropy change from the vapor pressure to one atmosphere must be added to that calculated above. The only available data from which the heat of sublimation and the vapor pressure at  $0^{\circ}$ may be estimated are the vapor pressures in the range 100 to 140° measured by Burg and Green.<sup>15</sup> (Unfortunately this range is short and far from  $0^{\circ}$ requiring a long extrapolation to obtain the desired vapor pressure. Furthermore, Burg later found that another portion of their work on trimethylamine-trifluoroborane could not be reproduced 16 so that some doubt is cast upon the validity of their vapor pressure data on this compound.) From the vapor pressure equation given by Burg and Green,  $\Delta H_{\rm vap} = 16.47$  kcal., and log  $p_{\rm mm} = -2.950$  at  $0^{\circ}$ ; whence  $\Delta S_{273}^{\circ} = -44.5 \pm 3$  e.u. for the gas phase reaction. Another estimate (which leads to the same value) for the heat of sublimation may be obtained by comparison with trimethylamine-borane, which appears to be isomorphous with trimethyl-

(14) J. G. Aston, M. Sagenkahn, G. J. Szasz, G. W. Moessen and H. F. Zuhr, J. Am. Chem. Soc., 66, 1171 (1944).

(16) A. B. Burg and co-workers, ONR Technical Report, Project NR 052-050, Univ. of Southern Cal.fornia (1949).



Fig. 1.—Relative enthalpies  $(H_{\rm T}^0 - H_{\rm O}^0)$  versus temperature.

amine-trifluoroborane,<sup>17</sup> and whose heat of sublimation is 13.99 kcal.<sup>18</sup>

On the other hand, when log  $p_{mm}$  is plotted against 1/T, it is found that the data points of Burg and Green do not lie on a straight line. Moreover their equation does not appear to fit the data very well. If the 134 and 140° points, which deviate increasingly from this line, are ignored,  $\Delta H_{vap}$  is found to be 15.0 kcal. and log  $p_{mm} = -2.585$  at 0°. These values give 54.9 e.u. for sublimation, -25.0e.u. for compression, and  $-48.2 \pm 3$  e.u. for  $\Delta S_{273}^{\circ}$  of the gas phase reaction. A computation of the ideal gas entropy of  $Me_3N:BF_3$  in which judicious guesses were made for the internal rotational and vibrational contributions, led to an estimated entropy increment, for the gas phase reaction,  $\Delta S_{300}^{\circ} =$ -46.1 e.u.,<sup>19</sup> which is midway between the above two estimates. In estimating  $\Delta S_{273}^{\circ}$  and  $\Delta H_{273}^{\circ}$  for the gas phase reaction, the heat of sublimation was assumed to be independent of temperature, so that  $\Delta H^0$  and  $\Delta S^0$  of the charge in standard state do not vary with temperature. This error is relatively small for the range over which the heat of sublimation was evaluated.

The Sequence of Enthalpy Increments for Amines.—The available thermodynamic data for the gas-phase reactions of the compounds  $BMe_{3-n}F_n$  with trimethylamine are compared in Table III.

	TABLE II	I	
	$-\Delta H^{\circ}$ , kcal.	− ΔS° (e.u.)	T, °C.
BMe <sub>3</sub> <sup>20</sup>	$17.6 \pm 0.2$	$45.7 \pm 0.5$	100
BMe₂F	$(18.3^{16})$ $(20.5^{16})$	47.2	85
BMeF <sub>1</sub> <sup>15</sup>	$23.1 \pm 2.3$	$47.2 \pm 4.7$	150
BF:	$\{26, 6 \pm 2\}^2$	$48.2 \pm 3$	0
• Our estim	ate based on $\Delta H_{\rm aub}$	= 15.0 kcal. for	the salt.

Our estimate is in accord with the expectation that BF<sub>3</sub> is a stronger acid than its alkyl substituted analogs, and is consistent with the observation that trimethylamine-trifluoroborane is not appreciably dissociated<sup>16</sup> in the temperature range in which the dissociation of trimethylamine-difluoromethylborane is readily measured.<sup>15</sup>

(17) S. Geller, R. E. Hughes and J. L. Hoard, Acta Cryst., 4, 380 (1951).

(18) A. B. Burg and H. I. Schlesinger, J. Am. Chem. Soc., 59, 780 (1937).

(19) A. Shepp and S. H. Bauer, ibid., 76, 265 (1954).

(20) H. C. Brown, H. Bartholomay and M. D. Taylor, *ibid.*, 66, 435 (1944).

<sup>(13)</sup> H. M. Spencer, J. Chem. Phys., 14, 729 (1946).

<sup>(15)</sup> A. B. Burg and A. A. Green, ibid., 65, 1838 (1943).

The available values of the heats of reactions of boron trifluoride with di- and trimethylamines are cited in Table IV.

	TABLE IV	
	$\Delta H^{\circ}_{278}$ to solid, kcal.	Est. $\Delta H^{\circ}_{273}$ to gas, kcal.
$NH_3(g)$	-41.321	-22
MeNH <sub>2</sub> (g)	-42.79	-26
Me <sub>2</sub> NH(g)	$\{-44 \pm 2\}^{\circ}$	-28.2
Me <sub>3</sub> N(g)	$\{-42 \pm 2\}^a$	-26.6
<sup>a</sup> Our estimate.		

The base strength of ammonia in the gas phase would be expected to be appreciably less than that of monomethylamine, as it is with boron trimethyl as the reference acid.<sup>20</sup> When the solid products are compared, hydrogen bonding and high symmetry in the crystal of the ammonia compound might offset this difference in basicity. The experimental measurements and calculations in these two cases were straightforward.<sup>9,21</sup> Since severe steric strain is not expected in the reaction of boron trifluoride with the methylamines, trimethylamine should be about as strong as monomethylamine in the gas phase, and dimethylamine should be stronger, as with boron trimethyl<sup>20</sup> or borane as the reference acid.

For dimethylamine-trifluoroborane, if  $K_p$  for the gas phase reaction is assumed to be 450 at 230°, and  $\Delta S_{273}^{\circ}$  is assumed to be about -45 e.u.,  $\Delta H_{273}^{\circ}$  for the gas phase reaction is approximately -28.2 kcal. If the heat of sublimation is assumed to be 15 or 16 kcal., the heat of reaction to the solid compound at 0° becomes about 43 or 44 kcal. Such a value is in excellent accord with those obtained for the reactions with ammonia and monomethylamine. An uncertainty of the order of 2 kcal. must be assigned, mainly because of the difficulty in estimating the effect of non-ideal gas behavior on the dissociation data. An error of 2 e.u. in the assumed entropy would lead to an error of only 1 kcal. in  $\Delta H_{0}$ .

A check on the above calculation of  $\Delta H^{\circ}_{273}$  for the dimethylamine has been obtained from Nichols' vapor density at 253°.<sup>9</sup> At this temperature and 66.2 mm. total pressure the apparent degree of dissociation was 0.140. Assuming that  $\Delta S^{\circ}_{273} = -45$  e.u.,  $\Delta H^{\circ}_{273}$  is found to be -30.8 kcal. Only a small allowance for non-ideal behavior of the vapor at 253° is required to bring this value into agree-

(21) A. W. Laubengayer and G. F. Condike, J. Am. Chem. Soc., 76, 2274 (1948).

ment with -28.2 within the assigned uncertainty of 2 kcal.

The heat of reaction of dimethylamine and boron trifluoride may also be estimated in another manner. The gas phase heats of reaction of dimethylamine<sup>20</sup> and piperidine<sup>22</sup> with boron trimethyl are very nearly identical, indicating that these bases are almost equally strong. The heat of reaction of piperidine gas with boron trifluoride gas to form the addition compound in piperidine solution has been given as 51 kcal.<sup>23</sup> If the heat of solution is estimated as 5 to 7 kcal., a value of 44 to 46 kcal. is obtained for the heat of reaction of the gases to give the solid product. The value for piperidine may be slightly higher than for dimethylamine because the greater molecular weight of the addition compound may result in a somewhat higher heat of sublimation. We thus reach an estimate which is in good agreement with the above.

With boron trimethyl as reference acid, trimethylamine is weaker than dimethylamine by about 1.6 kcal. If the relative base strengths with regard to boron trifluoride are assumed to be the same,  $\Delta H_{273}^{\circ}$  is approximately -26.6 kcal. for the gas phase reaction and roughly -42 kcal. for the reaction to the solid product. These values fit well in the two series quoted above. On the basis of this estimate of the heat of reaction,  $K_{\rm P}$  should fall to 450 in the neighborhood of 175°. Dissociation should be readily observed below 200°, but difficult to detect below 175° in view of the imperfect behavior of the vapor. Burg's failure to observe dissociation<sup>16</sup> is in accord with this value.

A summary of the crystal structure data for the addition compounds of boron trifluoride with ammonia, monomethylamine and trimethylamine has been presented.<sup>24</sup> The B–N distances quoted (1.60  $\pm$  0.015 Å., 1.57  $\pm$  0.015 Å., and 1.585  $\pm$  0.03 Å., respectively) are consistent with the estimate of relative base strengths of the amines indicated in Table IV. Relative to these amines, boron trifluoride appears to be a stronger acid than boron trimethyl by 8–10 kcal.

Acknowledgments.—This work was supported, in part, by the Office of Naval Research. One of the authors (R. E. McCoy) is also indebted to the NRC for a fellowship.

(22) H. C. Brown and M. Gerstein, ibid., 72, 2926 (1950).

(23) G. R. Finlay, Ph.D. dissertation presented to the Graduate School of Cornell Universty, Dept. of Chem., 1942.

(24) J. L. Hoard, S. Geller and T. B. Owen, Acta Cryst., 4, 405 (1951).

#### 1533

## EFFECTS OF THE SPREADING SOLVENT ON MONOLAYERS AS DETERMINED BY PRESSURE-AREA AND RADIOACTIVITY-AREA ISOTHERMS

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Effects of spreading solvents on pressure-area isotherms for monomolecular films are not completely understood. Experiments with stearic acid show that benzene, *n*-hexane and chloroform cause no significant differences in the intermediate and high-pressure portions of the isotherm. At low pressures, observed differences in isotherm shape could not be directly related to volatility, solubility or polarity of the solvent. At very low pressures, radioactivity-area isotherms for radiostearic acid spread from the three solvents show a non-homogeneous distribution of the monolayer. The uncompressed monolayers seem to consist of large clusters of extremely small islands. During compression, clusters may coalesce and islands may deform to a continuous solid film of low compressibility. The structure, packing and deformation of islands under compression may give rise to the various shapes of the isotherms in the low-pressure region. The solvent could thus alter the shape of the isotherm by affecting the size, shape and distribution of island structures, rather than by being retained in the monolayer.

#### Introduction

In film-balance studies of two-dimensional packing and phase transformation of monolayers, the position and shape of the pressure-area isotherms are fundamental.<sup>1-3</sup> Position determines the apparent area per molecule in the plane of the substrate surface at different stages of compression. Shape reveals the packing characteristics of the film-forming molecules and thus reflects inter- and intramolecular structure. Both position and shape may be altered by retention of spreading solvent.

An ideal spreading solvent would be totally insoluble in water, would be free of film-forming contaminants, would homogeneously disperse the material to be spread, would not be retained in the monolayer, and would not be so volatile as to cause significant errors in measuring the concentration of the solution or the quantity spread. Benzene is widely used because it dissolves many polar compounds only slightly soluble in *n*-hexane. Although chloroform dissolves most polar materials readily, its high volatility and solubility in water make it less suitable.

Most investigators have assumed that the solvents commonly used to spread the film-forming material evaporate almost completely within a few minutes and exert a negligible effect on the isotherm at all pressures. Jaffe<sup>4</sup> placed a number of highly purified solvents on a water surface and measured the pressure of each as a function of time. Benzene exerted less than 0.001 dyne per cm. after four minutes. Archer and LaMer<sup>5</sup> have suggested that solvent molecules may remain in the monolayer, even under pressure. They interpret variations in water-evaporation rate through a film with changing film pressure to be a solvent effect. Solvent molecules are thought to be occluded in the monolayer when the film is spread. They attribute the decrease in the rate of water evaporation with increasing pressure to the expulsion of these occlusions on compression of the film.

Radiation intensity measurements of radiostearic acid monolayers on the water surface were obtained to study monolayer homogeneity at low pressures and large areas per molecule. Beischer<sup>6</sup> has reported the use of monolayers of radiostearic acid as  $\beta$ -particle standard sources. His investigations, however, were made on mono- and multilayers that had been transferred to solid plates at high surface pressures.

To investigate film homogeneity and solvent effects at all pressures, radiostearic acid was spread from three solvents that differ in volatility, solubility and polarity. Both pressure-area and radioactivity-area isotherms were obtained.

#### Experimental

Pressure-area isotherms for radiostearic acid were obtained with benzene, *n*-hexane and chloroform as spreading solvents. A Geiger tube was suspended over the monolayer to obtain radiation intensity at various stages of compression. Modifications in the basic apparatus included a motor-driven compression barrier and a Teflon coating on the trough.

Materials.—C.P. benzene, C.P. chloroform, and Phillips Pure Grade *n*-hexane were distilled twice to separate nonvolatile impurities. Film experiments with each of the three solvents alone showed that remaining impurities were negligible; literature values of solubility, volatility and dipole moment are assembled in Table I.

The radiostearic acid (m.p. 69.6°), from Nuclear Instrument and Chemical Corporation and of the highest purity available, was carboxyl labeled with C-14 and had a specific activity of 0.972 millicurie per millimole. The ion-exchange water used in the trough was in equilibrium with atmospheric CO<sub>2</sub>; it had a pH of 5.8 and a specific conductivity of less than 1 micromho.

Apparatus.—A Cenco Hycrophil Balance of the Langmuir-Adam-Harkins type<sup>1,2</sup> was used. All areas normally waxed before each experiment<sup>7</sup> were permanently coated with Teflon<sup>8,9</sup> except for the mica float and platinum foils; the advantages gained are discussed by Fox and Zisman.<sup>8</sup>

A TGC-1 Geiger tube, supplied by Tracerlab, Inc., was suspended over the trough so that the mica window (5.73 square cm. in area and 2.3 mg. per square cm.) was parallel to the water surface and 2 mm. above it. The tube was placed about 1 cm. from the float and midway between the

<sup>(1)</sup> N. K. Adam, "The Physics and Chemistry of Surfaces," Third Edition, Oxford University Press, Oxford, 1941.

<sup>(2)</sup> W. D. Harkins, "The Physical Chemistry of Surface Films," Reinhold Publ. Corp., New York, N. Y., 1952.

<sup>(3)</sup> S. J. Gregg, "The Surface Chemistry of Solids," Reinhold Publ. Corp., New York, N. Y., 1951.

<sup>(4)</sup> J. Jaffe, J. chim. phys., 51, 243 (1954).

<sup>(5)</sup> R. J. Archer and V. K. LaMer, THIS JOURNAL, 59, 200 (1955).

<sup>(6)</sup> D. E. Beischer, "Beta Particle Standards for Carbon-14 and Other Elements in the Form of Radioactive Monolayers," U. S. Naval School of Aviation Medicine, Naval Air Station, Pensacola, Fla. Project No. NM001 059.16.03 (1950); THIS JOURNAL, **67**, 134 (1953).

<sup>(7)</sup> H. E. Ries, Jr., and H. D. Cook, J. Colloid Sci., 9, 535 (1954).

<sup>(8)</sup> H. W. Fox and W. A. Zisman, Rev. Sci. Instruments, 19, 274 (1948).

<sup>(9)</sup> A Teflon emulsion was baked on the metal surfaces in a process similar to that described by R. B. Dean and K. E. Hayes, J. Am. Chem. Soc., **73**, 5583 (1951).

45

40

35

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20

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10

5

0 15

20

Film pressure, dynes/cm. 25

center of the trough and the rear edge. A conventional scaler and register were used to obtain counts per minute. The reported counting rates do not include background count.

The entire assembly was housed in a double-walled cabi-net.<sup>7</sup> Water temperatures ranged from 21 to 23° but rarely varied more than 0.1° during a single experiment. A 1 r.p.m. electric motor mounted outside the cabinet moved the compression barrier one millimeter in 2.1 minutes.

Procedure.-The Teflon-coated trough, sweeping barriers and compressing barrier were cleaned before each experiment in a vapor degreaser specially constructed for this purpose. The parts were immersed in tetrachloroethylene vapors (121°) until condensation ceased. This treatment was repeated three times with a cooling period after each immersion. The parts were free of cleaning solvent and ready for use as soon as they had cooled to room tempera-The float and foils were cleaned and lightly waxed, ture. the trough was filled with water, and the water surface was swept. The Geiger tube was lowered into place, and the film was spread from a weight pipet.<sup>7</sup>

The compressing barrier was moved toward the float by hand, with 10-minute pauses at selected distances to measure the radiation intensity of the uncompressed film. After pressure first developed, the motor drive was used to give slow, continuous compression for the remainder of the experiment. Film pressure was recorded at convenient intervals that depended on the rate of pressure increase. Above 15 dynes per cm., pressure increased rapidly and 1-mm. in-tervals were selected. The counts during the minute following each pressure reading were recorded. The experiment was terminated when the film pressure dropped.

Inspections for leakage or contamination were made at the end of each experiment. To determine, for each solvent, the small vapor loss from the weight pipet during spreading, the pipet was weighed before and after opening it for as long as ordinarily required for spreading. The proper correction was applied to each experiment.

BENZENE



Area, square ångströms/molecule. Fig. 1.—Pressure-area isotherms for radiostearic acid spread from three solvents. Duplicate experiments for each solvent.

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#### Pressure-Area Measurements

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Figure 1 shows pressure-area isotherms for radiostearic acid spread from benzene, *n*-hexane and chloroform. Each data point represents a pressure and an area calculated directly from measurements on the film. For comparison, the isotherms may be

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TABLE I

Solubility, Volatility	and Dipole	MOMENT (	OF SOLVENTS
	Benzene	n-Hexane	Chloroform
Solvency, g. stearic acid	soluble in		
100 g. solvent, $20^{\circ}$	$2.46^{a}$	$0.5^{b}$	6.0°
Solubility in water, %	$0.085^{d}$	$0.05^{e}$	0.771'
	(20°)	$(25^{\circ})$	(30°)
Vapor pressure at 20°,			
mm.	$75^{o}$	$120^{g}$	$155^h$
Dipole moment, Debye			
units	$0^i$	$0^{j}$	$1.05^{k}$

<sup>a</sup> C. W. Hoerr and A. W. Ralston, J. Org. Chem., 7, 546 (1942). <sup>b</sup> C. W. Hoerr and H. J. Harwood, *ibid.*, 16, 779 (1951). <sup>c</sup> C. W. Hoerr and A. W. Ralston, *ibid.*, 9, 329 (1944). <sup>d</sup> A. Niini, Suomen Kemistilehti, 11A, 19 (1938). <sup>e</sup> H. S. Booth and H. E. Everson, Ind. Eng. Chem., 41, 2627 (1949). <sup>f</sup> P. M. Gross and J. H. Saylor, J. Am. Chem. Soc., 53, 1744 (1931). <sup>e</sup> Interpolated from data contained in American Petroleum Institute Research Project 44, "Sclected Values of Physical and Thermodynamic Properties of Hydrocarbors and Related Compounds," Carnegie Press, Pittsburgh, 1953. <sup>h</sup> E. Beckman and O. Liesche, Z. physik. Chem., 88, 23 (1914). <sup>i</sup> A. Parts, *ibid.*, B4, 227 (1929). <sup>i</sup> L. M. Heil, Phys. Rev., 39, 666 (1932). <sup>k</sup> C. P. Smyth and S. O. Morgan, J. Am. Chem. Soc., 50, 1547 (1928).

divided arbitrarily into three pressure regions; low (zero to 13 dynes per cm.), intermediate (13 to 24 dynes per cm.), and high (above 24 dynes per cm.). The low-pressure region shows two distinct iso-therm shapes; only the benzene isotherm exhibits significant pressure where the area per molecule lies between 26 and 36 Å.<sup>2</sup> At intermediate and high pressures, the isotherms for all three solvents agree in position and shape, within experimental error.

Calculated data from these isotherms are given in Table II. In the low-pressure region, differences in isotherm shape are described by the "convergence pressure," the pressure at which the curved low portion of each isotherm meets the linear intermediate portion or its extrapolated line. This line, when extrapolated to zero pressure, gives areas per molecule and compressibilities that agree well for all solvents. A similar extrapolation of the high-pressure region gives the conventional molecular cross-section area These values, as well as collapse pressures, agree within experimental error for all solvents.

#### TABLE II

MONOLAYER PROPERTIES OF RADIOSTEARIC ACID SPREAD FROM THREE SOLVENTS

	Benzene	n-Hexane	form
Low-pressure region, convergen	nce		
pressure, dynes/cm.	13	1	11
Intermediate-pressure region, e	extrapd.		
area, Å.²/molecule	<b>25</b> . 5	25.0	24.0
$Compressibility^a$	0.0088	0.0089	0.0079
High-pressure region, extrapd.			
area, Å.²/molecule	20.6	20.5	20.2
Compressibility	0.0010	0.0017	0.0016
Film collapse			
Pressure, dynes/cm	42	41	41
Area, Å.²/molecule	19.8	18.8	19.0
		بمبد المغالم	

 $a(a_0 - a_1)/a_0f_1$ , where  $a_0 = \text{extrapolated area at zero}$  pressure and  $a_1 = \text{smaller area at a pressure } f_1$ .



Fig. 2.—Radioactivity-area isotherms for radiostearic acid.

Although the three isotherm types of Fig. 1 show definite and reproducible differences in the lowpressure region, comparison of the convergence pressures of forty-six stearic acid isotherms obtained with all three solvents did not reveal such distinct differences. Isotherms obtained with benzene showed high convergence pressures most of the time, but a few took the shape characteristic of *n*-hexane. Similarly, some of the *n*-hexane isotherms approached those obtained with benzene. All the chloroform isotherms were like those obtained with chloroform in Fig. 1. Thus, the solvent does not wholly determine shape in the lowpressure region, but it evidently influences molecular packing in the monolayer.

#### Radioactivity-Area Measurements

Figure 2 is a plot of the radiation intensity of the monolayer as a function of the apparent area per molecule. Each point is an average area and count over at least a ten-minute period. Ten or more one-minute measurements were averaged when necessary. The dashed curve was calculated by using the representative value of 1000 counts per minute, when the area per molecule is 20 Å.<sup>2</sup>; the product of the ordinate and abscissa value of every point on the curve is 20,000.

At high pressures, again no significant differences in solvent effects are found. At areas above  $35 \text{ Å}^2$  per molecule, however, some of the experimental points fall far below the calculated curve; gross non-homogeneity of the monolayer at low pressures is indicated. Probably the counting rates were low because the film was spread at the end of the trough opposite the Geiger tube. The counting rate could be increased with no increase in pressure by directing a gentle stream of air against

Vol. 60

the water surface and toward the tube. Surfacepotential measurements<sup>10</sup> and electron micrographs<sup>11</sup> of fatty-acid films show the presence of island structures. Ryan and Shepard<sup>12</sup> obtained autoradiographs of radioactive calcium stearate monolayers transferred at low pressures by the Blodgett technique<sup>13</sup>; large islands of liquid expanded phase surrounded by areas of gaseous phase were postulated.

#### Conclusion

The volatility, solubility and polarity of the spreading solvent cannot be directly related to the shape or position of the stearic acid isotherms. At intermediate and high pressures, no effects of solvent are observed; at low pressures, effects which may be influenced by the spreading solvent appear.

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(11) H. E. Ries, Jr., and W. A. Kimball, This Journal, 59, 94 (1955).

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(13) K. B. Blodgett, J. Am. Chem. Soc., 57, 1007 (1935).

The evidence of the pressure-area and radioactivity-area investigations, combined with related studies, suggests that the uncompressed monolayers exist in large clusters of extremely small islands. During compression, the clusters may coalesce and the islands may deform to yield a continuous solid film of low compressibility just before col-The structure, packing and deformation of lapse. islands during compression may give rise to the various shapes of the pressure-area isotherms in the low-pressure region. The spreading solvent used could affect the shape of the isotherm through its effect on the size, shape and distribution of island structures formed during the spreading process, rather than through solvent retention in the monolayer.

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## NON-NEWTONIAN FLOW IN CONCENTRATED SOLUTIONS OF SODIUM DESOXYRIBONUCLEATE<sup>1</sup>

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Non-Newtonian viscosities of salt-free aqueous sodium desoxyribonucleate solutions have been measured by capillary and falling ball methods over the concentration range from 0.19 to  $18.3 \times 10^{-3}$  g./ml. The polymer molecular weight and radius of gyration were 5.8 × 10<sup>6</sup> and 2170 Å., respectively. The viscosities extrapolated to zero shear rate ( $\eta$ ) ranged from 0.195 to 40,000 poises at 25°. The apparent activation energy for flow, calculated from measurements at 5 and 25°, increased approximately linearly with concentration, up to 8.6 kcal. at  $18.3 \times 10^{-3}$  g./ml. From the capillary measurements, taking into account the inhomogeneous shear rate, the dependence of apparent viscosity ( $\eta_a$ ) on shear rate ( $\dot{\gamma}$ ) was calculated. In form, this function agreed with direct measurements by Markovitz and Zapas at one concentration using a cone-and-plate viscosimeter which provides homogeneous shear. At concentrations from 0.75 to 3.06 × 10<sup>-3</sup> g./ml.,  $\eta_a/\eta$  was a function only of  $\dot{\eta}\eta/c$ , similar to that predicted by the theory of Bueche for free-draining flexible coils. At concentrations of 0.19 and 0.38 × 10<sup>-3</sup> g./ml.,  $\eta_a/\eta$  was a function of  $\dot{\gamma}\eta$ , similar in shape to that predicted by the theory of Saito for rigid elongated ellipsoids; and the corresponding rotary diffusion coefficient reduced to water at  $25^{\circ}$  was  $20 \sec ^{-1}$ , in agreement with flow birefringence measurements by Doty and collaborators in very dilute solution. At  $1.5 \times 10^{-3}$ g./ml., 0.2 M sodium chloride diminished the relative viscosity by a factor of 10 without changing  $\eta_a/\eta$  as a function of  $\dot{\gamma}\eta/c$ . At 0.19 and 0.38 × 10<sup>-3</sup> g./ml., the presence of 50.4% glycerol diminished the relative viscosity by a factor of seven and changed the character of the non-Newtonian flow to resemble that predicted by Bueche for shielded flexible coils.

#### Introduction

Most investigations of the viscosity of sodium desoxyribonucleate solutions have been concerned with extremely low concentrations, seeking information about molecular shape or the effects of electrical charges.<sup>3-5</sup> More concentrated solutions, in the range from  $10^{-4}$  to  $10^{-2}$  g./ml., where the molecular domains overlap but there is no ordering with liquid crystal formation, have received little attention except for an earlier paper from this Laboratory.<sup>6</sup> In this range, the dependence of apparent viscosity on shear rate is very

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marked. The interpretation of such non-Newtonian behavior is of interest in connection with current concepts of flow in polymeric systems,<sup>7</sup> especially for concentrated systems where flexible molecules behave more nearly as free draining rather than as shielded coils.

Earlier measurements in this moderately concentrated range<sup>6</sup> were made in 0.2 M aqueous sodium chloride as solvent. The present paper reports data for salt-free aqueous solutions over a wide range of concentrations, as well as some measurements with salt and in a glycerol-water solvent, using a new preparation of sodium desoxyribonucleate. The results are compared with theoretical calculations of non-Newtonian flow of solutions of flexible coiled molecules<sup>7</sup> and rigid rods.<sup>8,9</sup>

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<sup>(1)</sup> Presented in part at the 128th Meeting of the American Chemica<sup>1</sup> Society, Minneapolis, Minn.

<sup>(7)</sup> F. Bueche, J. Chem. Phys., 22, 1570 (1954).

Nov., 1956

#### Materials and Methods

The sodium desoxyribonucleate (SDNA, sample II) was prepared in collaboration with Dr. Sidney Katz, following the method used by Signer and Schwander<sup>10</sup> for their preparation VIII. (Dr. Katz's earlier preparation<sup>11</sup> by the same method is designated sample I.) Sample II, like sample I, was protein-free as tested by the Weber modification of the Sakaguchi reaction. Because of the emphasis on saltfree solutions in this work, a Van Slyke determination<sup>12</sup> for chloride was made to ensure that the sodium chloride used in the course of preparation had been fully removed; this test indicated a sodium chloride content of less than 0.02%. The molecular weight of sample II, determined from light scattering measurements by Dr. Katz together with the value of refractive index increment used by Doty and collaborators,  $^4$  0.188 (g./ml.)<sup>-1</sup>, was 5.8 × 10<sup>6</sup>. The radius of gyration, calculated from the angular dependence of scattering, was 2170 Å. Its relative viscosity at a concenstration of 0.0149% in 10% sodium chloride at  $pH 6.0, 20^{\circ}$ , and an average shear rate of 910 sec.<sup>-1</sup>, was 1.40. The corresponding values for sample I were 5.9 × 10<sup>6</sup> (corrected with the above refractive index increment), 2120 Å., and 1.254. The molecular dimensions of both samples compare well with those of the best preparations studied by Doty and collaborators'; the lower viscosity of sample I suggests that it may have undergone some delayed degradation due to slight enzymatic attack during preparation. This difference between the two samples is also reflected in the zeroshear viscosity in 0.2 M sodium chloride, as will be seen below

The SDNA was stored at 0° with about 6% water content. After 3 years, at the close of the measurements reported here, its relative viscosity in 10% sodium chloride was unchanged. Stock solutions were made up by weight in conductivity water, and their exact concentrations were usually determined by dry weight at 105° in vacuo. Solutions for measurements were prepared by appropriate dilutions, introducing salt or glycerol when required. Mixing was usually accomplished by a very slow magnetic stirrer, the solutions being kept at 0° with a trace of toluene until homogeneous. The pH, measured in every case with a Beckman Model G pH Meter, was  $6.75 \pm 0.1$  for the salt-free solutions with two exceptions (7.1 and 6.45) and  $6.3 \pm 0.3$  for those in 0.2 M sodium chloride. The dependence of viscosity on pH should be slight in this range.<sup>13</sup>

Very dilute salt-free solutions of SDNA have been found by Litt, Simmons and Doty to be susceptible to a denaturation at room temperature similar to that which occurs in the presence of salt at elevated temperatures.<sup>14</sup> However, sufficient ionic strength to protect against this process is supplied by the sodium ions if the SDNA concentration exceeds about  $10^{-4}$  g./ml., which was the lower limit of our concentration range. The solutions for which data are reported here were stable with respect to viscosity for several days at least; in a few cases, dilute solutions displayed decreasing viscosity with elapsed time, and these were discarded.

At SDNA concentrations of  $5.9 \times 10^{-3}$  g./ml. and above, falling ball viscosity measurements were made with small glass spheres, <sup>6,15</sup> of diameter from 0.1 to 1 mm., obtained through the generosity of the Minnesota Mining and Manufacturing Co., and also with stainless steel bearing balls of diameter from 0.038 in. to <sup>1</sup>/<sub>16</sub> in., thus providing a considerable range of shear rates. The diameters of the glass spheres were measured with a microscope, and their density was obtained by weighing on a microbalance; it appeared to be uniformly 3.0 for those free of air bubbles. Nominal viscosities were calculated by the usual Faxén equation.

At concentrations of  $3.0 \times 10^{-3}$  g./ml. and below, viscosity measurements were made with horizontal capillaries

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bent in zigzag shape for compactness and provided with small bulbs at each end.<sup>16</sup> The capillary length was about 150 cm.; the radius, 0.5 or 1.0 mm.; and the bulb volume, about 1 ml. Flow in either direction could be achieved by applying air pressure with reversing stopcocks. This pressure, regulated by a water column manostat, was varied from 6 to 45 cm. of water. An additional effective pressure due to the average liquid head in the viscometer during discharge of a bulb was determined by calibration with a liquid of known viscosity. The calibration, which also furnished the instrument constant embodying the capillary dimensions and bulb volumes, was performed as follows. Flow of a given volume of the standard liquid (a National Bureau of Standards calibrated oil, or olive oil previously studied in an Ostwald viscosimeter) was timed in both directions at various air pressures. A plot of reciprocal time (1/t) against pressure in cm. of water (h) gave for each direction a straight line whose intercept was the average head pressure hy. In subsequent experiments with SDNA solutions, the

In subsequent experiments with SDNA solutions, the viscometer was filled (by a hypodermic syringe) with an identical volume, as indicated by suitable marks on the capillary. Nominal viscosities  $\eta_m$  for the SDNA solutions were calculated from the formula

$$\eta_{\rm m} = K!(h + h_{\rm v}\rho/\rho_{\rm s}) \tag{1}$$

where  $\rho$  and  $\rho_{\rm s}$  are the densities of solution and calibrating oil, respectively. In practice the density ratio was usually unnecessary since the  $h_{\nu}$  term was relatively small.

In addition to the falling ball and capillary measurements in this Laboratory, measurements on two solutions were generously made by Drs. Hershel Markovitz and L. J. Zapas of the Mellon Institute of Industrial Research with their cone-and-plate viscos.meter<sup>17</sup> which provided a homogeneous rate of shear.



Fig. 1.—Nominal viscosity at 25° plotted against maximum shear stress: 1, capillary measurements, concentration  $3.06 \times 10^{-3}$  g./ml.; 2, falling ball measurements,  $11.8 \times 10^{-3}$  g./ml.; 3, falling ball,  $18.3 \times 10^{-3}$  g./ml.

#### **Results and Discussion**

Extrapolation of Viscosity to Zero Shear Rate.— The maximum shear stress  $(\mathfrak{T}_R)$  at the surface of a falling ball was calculated by the formula  $\mathfrak{T}_R =$  $gd(\rho_B - \rho)/6$ , where g is the acceleration of gravity, d the ball diameter, and  $\rho_B$  and  $\rho$  the densities of ball and solution. That at the surface wall of a capillary was calculated as  $\mathfrak{T}_R = rP/2l$ , where P is the driving pressure,  $(k + h_v) \rho g$ ,  $\rho$  being the density of water, r the capillary radius, and l its length. It was found that plots of nominal vis-

(16) We are much indebted to Mr. Robert Zand for making one of these viscosimeters.

(17) H. Markovitz, L. J. Flyash, F. J. Padden, Jr., and T. W. DeWitt, J. Colloid Sci., 10, 135 (1955).



Fig. 2.—Logarithm of relative zero-shear viscosity at  $25^{\circ}$  and apparent activation energy for viscous flow plotted against concentration of SDNA: O, in water;  $\bullet$ , in 0.2 *M* NaCl; tag up, data of Markovitz and Zapas; tags down, data of Katz and Ferry<sup>6</sup> on Sample I.



Fig. 3.—Logarithm of relative zero-shear viscosity at  $25^{\circ}$  plotted against concentration (dilute range): O, in water;  $\oplus$ , in 50.4% glycerol; tagged circles, data of Butler, Conway and James.

cosity  $\eta_m$ , from eq. 1 or from the Faxén equation, against  $\mathfrak{T}_R$  were usually linear, as in Fig. 1; such plots were used for extrapolation to the zero-shear viscosity. In the most dilute solutions, there was some upward curvature. The extrapolated value is of course not affected by the fact that  $\eta_m$  is different from the apparent viscosity which would be measured under homogeneous shear stress (see below).

Dependence of Zero-Shear Viscosity on Concentration and Temperature.—The extrapolated viscosities are given in Table I, and the relative viscosities  $(\eta_r)$  at 25° are plotted logarithmically against concentration in Fig. 2. The increase with concentration is enormous,  $\eta_r$  attaining a value of  $4.5 \times 10^{6}$  at  $18.3 \times 10^{-3}$  g./ml. Presence of 0.2 M sodium chloride does not affect the viscosity at an SDNA concentration of  $10 \times 10^{-3}$  g./ml., but diminishes it markedly at  $1.5 \times 10^{-3}$  g./ml. Such a decrease is certainly to be expected in view of the work of Butler<sup>5</sup> and others; its absence at high concentration probably means that here the counter (sodium) ions contribute enough ionic strength even in the absence of salt so that the lowered viscosity has attained the plateau which is usually seen in plots against salt concentration. Thus the over-all concentration dependence shown in Fig. 2 combines the effects of changing polymer concentration and ionic strength. The data for the earlier sample I in salt lie far below the new data, supporting the conclusion that sample I was somewhat degraded.

In Fig. 3, relative viscosities at lower concentrations at 25° are plotted with an enlarged scale. The data in water fit in rather well with measurements by Butler, Conway and James<sup>5</sup> in a still more dilute range, although information to characterize the sample used by those investigators is not available. The relative viscosities in 50.4%glycerol are much lower than those in water, indicating some denaturative effect of the former solvent; the expectation that the only effect of glycerol would be to increase the solvent viscosity was not fulfilled.

TABLE I

		Zef	RO-SHEAD	r Visc	OSITIES		
-		log10 viscosity, poises					
$\begin{array}{c} \text{Concn.,} \\ \text{g./ml.} \\ \times 10^3 \end{array}$		5°	Salt-free	25°	0.2 <i>M</i> Na 25°	Cl	50.4% Glycerol <sup>a</sup> 25°
0.095							-1.14
0.19			-	0.71			-0.78
0.38			-	0.05			-0.20
				0.16			
0.75				0.51			
1.50	1.61			1.00	0.08		
3.00				1.66 <sup>b</sup>			
3.06				1.58			
5.90		2.75	i	2.45			
10.0					3.50		
11.8		3.92	2	3.51			
12.0				$3.91^{b}$			
18.3		5.03	;	4.60			

 $^a$  Logarithm of solvent viscosity  $-1.29.~^b$  Measurement by Markovitz and Zapas.

From the measurements at two temperatures at the higher concentrations given in Table I, the apparent activation energy for viscous flow  $(Q\eta)$  was calculated, and is plotted in Fig. 2. Here the values for sample II in water and sample I in 0.2 M salt agree rather well, and are notable in that the activation energy in these extremely viscous solutions is not much higher than that of the pure solvent; the maximum value observed, at a concentration of  $18.3 \times 10^{-3}$  g./ml., is 8.6 kcal. The activation energy is an approximately linear function of concentration, as observed for a number of polymers in non-aqueous solvents<sup>18,19</sup>; moreover,

(18) J. D. Ferry, L. D. Grandine, Jr., and D. C. Udy, J. Colloid Sci. 8, 529 (1953).

(19) D. J. Plazek and J. D. Ferry, This JOURNAL, 60, 289 (1956).



Fig. 4.—Reduced nominal viscosity plotted logarithmically against nominal rate of shear reduced to  $25^{\circ}$  for concentrations (g./ml.  $\times$  10<sup>4</sup>) as indicated. Left of dashed line, falling ball measurements; right, capillary measurements; open circles, measurements at 25°; solid circles, at 5°.

this function extrapolates into the value for the pure solvent, as observed for vinyl polymers,<sup>18</sup> rather than a considerably higher value as in cellulose derivatives.<sup>19</sup>

Dependence of Viscosity on Rate of Shear.-While a plot of nominal viscosity against maximum shear stress as in Fig. 1 is convenient for extrapolation, a different representation is preferable to show the shear dependence over wide ranges. We choose a double logarithmic plot of the ratio of nominal to extrapolated viscosity,  $\eta_m/\eta$ , against the nominal rate of shear,  $D = \mathfrak{T}_R/\eta_m$ , as shown in Fig. 4 for several SDNA concentrations in water. This plot also provides a test for a simple interpretation of the temperature dependence of the non-Newtonian flow. If all the rotary diffusion coefficients (or relaxation times) associated with the different molecular mechanisms characteristic of the flow have the same temperature dependence, 20, 21 it should be possible to combine the data at 5° (T)with those at 25° ( $T_0$ ) by plotting  $\eta_m/\eta$  against the reduced nominal rate of shear,  $D_p = D\eta T_0/\eta_0 T$ . Here  $\eta_0$  is the extrapolated viscosity at 25°. The coincidence of the reduced data at the concentrations where  $5^{\circ}$  values are available indicates that the temperature dependence is indeed the same for all the mechanisms.

The shapes of all the curves in Fig. 4 are rather similar. Unfortunately, no quantitative conclusions can be drawn from them, since the nominal viscosity is measured under experimental conditions of inhomogeneous shear rate. For the falling ball measurements, there appears to be no treatment available for deriving the apparent viscosity which would be observed under a homogeneous rate of shear. For the capillary measurements, however, the latter can be calculated from a wellknown equation<sup>22</sup>

(20) J. D. Ferry, J. Am. Chem. Soc., 72, 3746 (1950).

(21) F. J. Padden and T. W. DeWitt, J. Appl. Phys., 25, 1086 (1954).

$$\frac{1}{\eta_{\rm a}} = \frac{1}{\eta_{\rm m}} \left( 1 - \frac{1}{4(1 + d \ln D/d \ln \eta_{\rm m})} \right)$$
(2)

where  $\eta_a$  is the non-Newtonian viscosity  $(\mathfrak{T}/\dot{\gamma})$ corresponding to a homogeneous shear rate  $\dot{\gamma}$  given by  $\dot{\gamma} = D\eta_m/\eta_a$ . By measuring the slopes graphically on Fig. 4,  $\eta_a/\eta$  was calculated and is plotted logarithmically against  $\dot{\gamma}$  in Fig. 5. This figure also shows the non-Newtonian viscosity measured by Markovitz and Zapas at one concentration in an apparatus which provides an experimentally homogeneous shear rate and thus involves no recalculation.

The extreme dependence of apparent viscosity on shear rate is shown not only by the fact that it drops by a factor of 100 but also by the slope on the logarithmic plot, which attains a value of -0.9. A slope of -1, indicated by a dashed line, would represent hydrodynamic instability, the rate of shear becoming independent of shear stress. The similarity in shape of the curves for capillary and cone-and-plate results lends confidence to the derived calculations on the former using eq. 2, even though the two curves at  $3.0 \times 10^{-3}$  g./ml. do not quite coincide.

The shear dependence of apparent viscosity in 0.2 M salt and in 50.4% glycerol was calculated in the same manner, and will be shown in reduced form below.

**Concentration Dependence of Non-Newtonian Behavior: Reduced Variables.**—If the rotary diffusion processes governing the non-Newtonian behavior all have the same dependence on *concentration* as well as temperature, as implied for example in the theory of Bueche,<sup>7</sup> reduced variables analogous to those used for dynamic viscosity<sup>20</sup> should afford superposition of data at different concentrations on a single composite curve. An analogous conclusion was reached by Peterlin<sup>23</sup> in correlating viscosity with flow birefringence in moderately concentrated solutions. The appro-

<sup>(22)</sup> W. Philippoff, "Viskosität der Kolloide," Steinkopff, Dresden, 1942, p. 42.

<sup>(23)</sup> A. Peterlin, J. Polymer Sci., 12, 45 (1954).



Fig. 5.—Reduced apparent viscosity at 25° plotted logarithmically against rate of shear for concentrations (g./ml.  $\times$  10<sup>3</sup>) as indicated: O, capillary measurements;  $\bullet$ , data of Markovitz and Zapas with cone-plate viscosimeter; dashed line, slope of -1.



Fig. 6.—Reduced apparent viscosity at 25° plotted logarithmically against reduced rate of shear. Open circles, in water: pip up, 0.19  $\times$  10<sup>-3</sup> g./ml. (curve 1); successive rotations 90° clockwise, 0.38 (curve 2), 0.75, 1.50, and 3.06  $\times$  10<sup>-3</sup> g./ml. (curve 3). Black circles, in 0.2 *M* NaCl at 1.50  $\times$  10<sup>-3</sup> g./ml. Slotted circles, data of Markovitz and Zapas (curve 4): vertical, 3.00  $\times$  10<sup>-3</sup>; horizontal, 12  $\times$  10<sup>-3</sup> g./ml. Dashed curve, theory of Bueche for flexible coils,  $M = 5.8 \times 10^6$ .

priate logarithmic plot of  $\eta_{a}/\eta$  against  $\dot{\gamma}\eta/c$  is shown in Fig. 6.

The capillary data fall together over the concentration range from 0.75 to  $3.1 \times 10^{-3}$  g./ml., and the composite curve is very similar in shape, though slightly displaced, to that for the cone-and-

plate data at 3.0 and  $12 \times 10^{-3}$  g./m<sup>1</sup>. The data in 0.2 *M* sodium chloride at  $1.5 \times 10^{-3}$  g./m<sup>1</sup>. also fall on the composite curve. It may be concluded that the concentration dependence is the same for all rotary diffusion processes down to a concentration of  $0.75 \times 10^{-3}$ . At lower concentrations, however, there is an increasing change in shape, and the shear dependence becomes less marked.

According to the theory of Bueche, in which non-Newtonian flow is associated with elastic energy storage in a flexible randomly coiled macromolecule, the flow in a concentrated solution being of a "free-draining" character as it is in an undiluted soft polymer, the function plotted in Fig. 6 is given by a series expression with a variable  $\dot{\gamma}\tau_1$  which in our notation is  $(12M/\pi^2 RT)(\dot{\gamma}\eta/c)$ . Here M is the polymer molecular weight and c the concentration in g./ml. The theoretical curve is shown in the figure by a dashed line, which lies fairly close to the observed data although not exactly coincident in either shape or position.

Non-Newtonian Behavior at Low Concentration. —At 0.19 and 0.38  $\times 10^{-3}$  g./ml., where the reduced data of Fig. 6 deviate from the composite curve, the molecules are evidently not sufficiently overlapping in space for the free draining treatment to apply, and the character of the flow is different. In this case there are two possible approaches. One is to consider the molecules as shielded random coils, for which Bueche has developed a series expansion predicting the non-Newtonian viscosity at relatively small shear rates. The other is to consider rigid elongated ellipsoids of revolution, for which the Saito theory<sup>8</sup> of non-Newtonian flow has been evaluated numerically by Scheraga.<sup>9</sup>

The theory for rigid ellipsoids is strictly applicable only to extremely dilute solutions where there is no intermolecular interference and the viscosity differs only slightly from that of the solvent. In the present concentration range, where the relative viscosity is of the order of 10 to 100, the effect of interference might be expected to be accounted for roughly by assuming the rotary diffusion constant to be inversely proportional to the macroscopic viscosity.<sup>24</sup> In this case,  $\eta_a/\eta$  should be, at different concentrations, the same function of  $\dot{\gamma}\eta$ rather than of  $\dot{\gamma}\eta/c$ . In Fig. 7, this expectation is shown to be approximately fulfilled for dilute solutions.

For comparison with the functional form predicted by theory, a double logarithmic plot of the theoretical  $\eta_a/\eta$  against  $\dot{\gamma}/\theta$  (where  $\theta$  is the rotary diffusion coefficient) has been drawn for a very high axial ratio (300) and an arbitrarily chosen value of  $\theta$ . The fit is fairly good and the magnitude of  $\theta$  thus determined, when reduced to water at 25°, is 20.4 sec.<sup>-1</sup>. While any deductions of molecular dimensions from this value could not be taken too seriously,<sup>4</sup> it agrees with the rotary diffusion constants determined by Doty and collaborators<sup>4,25</sup> from flow birefringence, using the same model, for their best DNA samples.

For dilute solutions in 50.4% glycerol, however, the above treatment is not satisfactory. In this case, the shielded coil treatment of Bueche appears to be more applicable. According to the latter theory,  $(\eta_{\rm a} - \eta_{\rm s})/(\eta - \eta_{\rm s}) = 1 - \sqrt{\tau_{0}\gamma}$ , where  $\eta_{\rm s}$ is the solvent viscosity and  $\tau_0$  a relaxation time de-



Fig. 7.—Reduced apparent viscosity for dilute solutions in water plotted logarithmically against product of rate of shear and zero-shear viscosity. Pip up,  $0.19 \times 10^{-3}$ ; pip right,  $0.38 \times 10^{-3}$  g./ml. Dashed curve, Saito theory, axial ratio 300,  $\theta_w = 20.4$  sec.<sup>-1</sup>.

fined below. Plots of  $(\eta_a - \eta_s)/(\eta - \eta_s)$  against  $\sqrt{\dot{\gamma}}$  were in fact roughly linear for two dilute solutions in glycerol, the ordinates extending down to 0.75 and 0.40 at concentrations of 0.19 and 0.38 imes 10<sup>-3</sup> g./ml., respectively. The values of  $au_0$ calculated from their respective slopes are 0.0025 and 0.029 sec. According to theory,  $\tau_0$  is given by  $1.98(r/b)(\eta - \eta_s) \sqrt{MM_0/cRT}$ , where  $M_0$  is the molecular weight of a chain unit and r/b is a measure of the sideways extension of a unit, believed to be about 2 for vinyl polymers. Taking the latter value, and choosing  $M_0 = 400/5$  as the average molecular weight per nucleotide divided by 5 chain linkages, the corresponding calculated values of  $\tau_0$  are 0.003 and 0.005, respectively. These are similar in order of magnitude to the values obtained from the experimental measurements, though no serious comparison can be made in view of the complicated chain geometry.

#### Conclusions

These results may be reasonably interpreted in terms of the current view of the SDNA molecule as a highly extended, rather stiff coil.<sup>4,25</sup>

The low apparent activation energies (Fig. 2) associated with enormous relative viscosities at moderate concentrations reinforce the earlier conclusion<sup>6</sup> that the high viscosity is due primarily to steric interferences of neighboring molecules, and not to strong attractive forces or to a cross-linked structure. Comparison of sample I and sample II shows that a marked viscosity difference, attributed to degradation of sample I, is not accompanied by any difference in flow activation energy.

The success of reduced variables in correlating the dependence of non-Newtonian flow on temperature (Fig. 4) and concentration (Fig. 6), together with the order-of-magnitude agreement with the Bueche theory (Fig. 6), indicates that in the more concentrated solutions flow is accompanied by intramolecular changes of configuration.

<sup>(24)</sup> Cf. M. A. Lauffer, J. Am. Chem. Soc., 66, 1195 (1944).

<sup>(25)</sup> M. Goldstein and M. E. Reichmann, ibid., 76, 3337 (1954).

Thus the coils must have some degree of flexibility; indeed, flow would otherwise scarcely be conceivable with such an overlapping of molecular domains as exists at a concentration of even  $5 \times 10^{-3}$ g./ml. Evidently in the more concentrated solutions the motion of a coil segment is determined largely by the resistance of its surroundings, the difficulty of bending of its own structure being small by comparison. A similar conclusion is reached from analysis of dynamic mechanical properties of these solutions at low frequencies.<sup>26</sup> Whether the flexibility is achieved by occasional hinges in the helix structure<sup>27</sup> is not clear.

In more dilute solutions, however, the inherent stiffness of the coil evidently becomes more important, and the character of the non-Newtonian flow is more consistent with that predicted for a very long rigid ellipsoid (or rod). The rotary diffusion coefficient estimated for this rigid structure is larger than that measured by flow birefringence in extremely dilute solution by a factor which is simply the relative viscosity. The concept of molecular rigidity agrees with conclusions from other measurements in extremely dilute solution, such as the lack of influence of salt on the intrinsic viscosity<sup>5</sup> and the effect of solvent viscosity on flow birefringence.<sup>28</sup>

Effect of Salt.—The coincidence of data with and without salt in the reduced-variable plot of Fig. 6 indicates that, at a concentration of  $1.5 \times 10^{-3}$  g./ml., salt affects the rates of all rotary diffusion processes to the same extent. Thus, the 8-fold drop in macroscopic viscosity occasioned by 0.2 M sodium chloride is accompanied by a similar drop in the resistance to motion of any coil segment through its surroundings. This is consistent with the view that the intramolecular resistance of

(26) F. E. Helders, J. D. Ferry, H. Markovitz and L. J. Zapas, This JOURNAL, 60, 1575 (1956).

(27) J. D. Watson and F. H. Crick, Nature, 171, 737 (1953).

(28) H. Schwander and R. Cerf, Helv. Chim. Acta, 34, 436 (1951).

bending the coil itself is small by comparison at this SDNA concentration, and with the conclusion of Butler, Conway and James<sup>5</sup> that the viscosity drop caused by electrolyte is related to long-range interionic attractions.

Effect of Glycerol.—That glycerol at a concentration of 50.4% causes an intramolecular change is indicated not only by the smaller relative viscosity (Fig. 3) but also by the different character of the non-Newtonian flow in dilute solution, which now resembles that of a shielded coil rather than that of a stiff ellipsoid or rod. This recalls the picture of denaturation of the SDNA molecule<sup>29</sup> as a partial unravelling of the stiff helix and approach toward a random coil configuration. It is also consistent with the observations of Schwander and Cerf,<sup>28</sup> who found that the rotary diffusion constant from flow birefringence was inversely proportional to solvent viscosity for moderate glycerol concentrations but abnormally large for glycerol concentrations over 40%. Evidence of a similar configurational change in concentrated ethanol solutions has recently been reported by Geiduschek and Gray.<sup>30</sup>

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(29) P. Doty, Proc. 3rd Intern. Congress Biocher., Brussels, 1955, p. 135.

(30) E. P. Geiduschek and I. Gray, J. Am. Chem. Soc., 78, 879 (1956).

## THE REACTIONS OF ETHYLENIMINE AND N-METHYLETHYLENIMINE WITH ATOMIC HYDROGEN AND THEIR RELATION TO COMPLEXES IN ACTIVE NITROGEN REACTIONS<sup>1</sup>

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The reactions of hydrogen atoms with ethylenimine and N-methylethylenimine produce mainly hydrogen cyanide and methane in the temperature range 55 to 300°. Some C<sub>2</sub> hydrocarbons are also formed. The hydrogen atom attack probably gives rise to cyclic radicals which subsequently decompose to hydrogen cyanide. This would seem to give credence to the assumption that the attack of active nitrogen on an olefin may form a cyclic complex of structure similar to that of the cyclic ethylenimino radical, prior to the formation of HCN as the main product.

Of the many reactions of active nitrogen with organic compounds that have been studied in this Laboratory, most appear to involve the formation of a relatively long-lived complex between a nitrogen

(1) With financial assistance from the Consolidated Mining and Smelting Company of Canada Limited, Trail, B. C., and the National Research Council, Ottawa.

(2) Holder of a Cominco Fellowship.

atom and the organic molecule. Such a complex was regarded as an essential part of the mechanism even in the first quantitative investigation of the reaction of active nitrogen with ethylene,<sup>3</sup> and forms the basis of a unified mechanism, outlined in a

(3) J. H. Greenblatt and C. A. Winkler, Can. J. Res., B27, 721 (1949).
recent review,<sup>4</sup> for many analogous reactions.

Although the complex probably would have different structures in different types of reactions, an early suggestion<sup>5</sup> was that it might be cyclic in the reactions of active nitrogen with unsaturated hydrocarbons, *e.g.*, for ethylene, the structure

seemed probable. After an investigation of the active nitrogen reactions with the butenes,<sup>6</sup> and during a study of the mercury photosensitized decomposition of ethylenimine at the Illinois Institute of Technology, Dr. C. Luner proposed that the reaction of hydrogen atoms with ethylenimine be investigated, since it might produce a radical similar to the conjectural cyclic complex of ethylene with atomic nitrogen, and that if this occurred, hydrogen cyanide might be expected as a main product of the hydrogen atom-ethylenimine reaction. This possibility initiated the present investigation.

#### Experimental

Ethylenimine and N-methylethylenimine of research grade were supplied by Brickman and Co., Montreal, and were used after single bulb-to-bulb distillations.

The apparatus was a conventional fast flow system similar to that used in the studies with active nitrogen,<sup>3,7</sup> except that the discharge was continuous rather than condensed. The discharge tube and reaction vessel were "poisoned" with 4% phosphoric acid from which excess water was subsequently removed by evacuation. Experimental procedures, including analysis for hydrogen cyanide, were essentially similar to those described previously. Unreacted imine was determined by titration with standard sulfuric acid solution to the methyl red end-point. Samples of the non-condensable products were removed from the gas stream with a Töpler pump.

stream with a Töpler pump. In all experiments, the flow rate of molecular hydrogen was 7.6  $\times$  10<sup>-6</sup> mole/sec., corresponding to a pressure of 0.73 mm. in the reaction vessel, while hydrogen atom concentrations of about 6.5% at 60° and 5% at 250° have been estimated.

### **Results and Discussion**

Hydrogen cyanide was indeed recovered as a main product from the reactions of hydrogen atoms with ethylenimine and N-methylethylenimine. The results are summarized in Figs. 1 and 2. Comparison of the graphs shows that very nearly one mole of HCN was formed for each mole of either imine destroyed.

At low flow rates of ethylenimine, the rates of imine consumption and HCN production were linear with flow rate and independent of temperature, while at high flow rates, the amounts of ethylenimine reacted or HCN formed remained constant at each temperature. Such behavior is typical of a fast reaction in which either reactant is completely consumed in an excess of the other so that the hydrogen atom concentrations are probably given approximately by the plateau values for ethylenimine destruction. Concordant estimates of the atom concentrations were made on the basis of the amounts of HCl produced in the reaction of atomic

(4) H. G. V. Evans, G. R. Freeman and C. A. Winkler, Can. J. Chem., 34, 1271 (1956).

- (5) G. S. Trick and C. A. Winkler, ibid., 30, 915 (1952).
- (6) H. Gesser, C. Luner and C. A. Winkler, ibid., 31, 346 (1953).
- (7) H. Blades and C. A. Winkler, ibid., 29, 1022 (1951).



Fig. 1.—Hydrogen cyanide produced and ethylenimine consumed in the reaction of hydrogen atoms with ethylenimine.

hydrogen with ethyl chloride at 60, 120 and 275°. Thus, to a first approximation, it may be assumed that at high flow rates each H-atom reacted with a molecule of ethylenimine to give one HCN.

Formation of hydrogen cyanide as the main product can be explained by the reaction

$$H + \frac{H_2C - CH_2}{N} \longrightarrow H_2 + HCN + CH_3$$
$$\Delta H = -15 \text{ kcal.}^{\$} \quad (1)$$

in which the primary step is probably abstraction of the imine hydrogen

$$H + \underbrace{\begin{array}{c}H_2C - CH_2\\N\\H\end{array}}_{H} \longrightarrow H_2 + \underbrace{\begin{array}{c}H_2C - CH_2\\N\\N\end{array}}_{H}$$

 $\Delta H = -6 \text{ kcal.} (2)$ 

followed by decomposition of the ethylenimino radical.

$$\frac{H_2C--CH_2}{N} \longrightarrow HCN + CH_3 \cdot \Delta H = -9 \text{ kcal.} (3)$$

Additional reactions of the type

$$H + \frac{H_2C - CH_2}{N} \rightarrow H_2 + \frac{HC - CH_2}{N}$$

might be expected to occur at low flow rates, although at high flow rates, mechanisms involving

(8) Heats of reaction were calculated using the following values: accepted heats of formation of gaseous substances<sup>6</sup> at 25°; heat of formation of ethylenimine = 25 kcal.<sup>10</sup> Heats of formation have been estimated for N-methylethylenimine and the ethylenimino radical by assuming that  $D_{C_2H_4N-H} \approx 97$  kcal. and  $D_{C_2H_4N-CH_1} \approx 73$  kcal. It has also been assumed that the dissociation energy of the N-N bond in the dimer of the ethylenimino radical is roughly equivalent to D-(N-N) in hydrazine.<sup>11</sup>

(9) U. S. Natl. Bur. Standards, Circular 500, "Selected Values of Chemical Thermodynamic Properties," Washington, 1952.

(10) R. A. Nelson and R. S. Jessup, J. Research Natl. Bur. Standards, 48, 206 (1952).

(11) M. Szwarc, Chem. Revs. 47, 75 (1950).



Fig. 2.—Hydrogen cyanide produced and N-methylethylenimine consumed in the reaction of hydrogen atoms with N-methylethylenimine.

successive H-atom reactions would seem to be of relatively little importance since only one hydrogen atom is consumed in forming each molecule of HCN.

Mass spectrometric analyses<sup>12</sup> of the non-condensable products of the ethylenimine reaction showed methane to be present in appreciable quantities, as given in the table.

Temp., °C.	Imine flow, mole/sec. × 10 <sup>6</sup>	Methane flow, mole/sec. $\times$ 10 <sup>a</sup>
55	5.7	1.8
	9.6	2.4
118	2.9	1.7
	5.3	3.1
271	2.9	1.5
	7.5	2.5

Methane could be formed by reaction of methyl radicals, produced in reaction 3, with any excess hydrogen atoms. The amounts of methane found at very low ethylenimine flow rates, where only a fraction of the available H-atoms were required to react with the imine, were in close agreement with the differences between the estimated atom concentrations and the amounts of imine destroyed. But for this concordance it might appear that the methane results at high flow rates imply true atom concentrations considerably higher than those estimated.

If there were an appreciable steady state concentration of ethylenimino radicals, the thermodynamically favorable reaction

$$CH_{3} + \bigvee_{N}^{H_{2}C \longrightarrow CH_{2}} \longrightarrow CH_{4} + HCN + CH_{2}$$
$$\Delta H = -25 \text{ kcal.} \quad (4)$$

might take place. This reaction has the advantage that migration of a hydrogen atom within the ethylenimino radical is unnecessary. It might be favored at high imine flow rates if ethylenimino radicals were concentrated near the jet through which ethylenimine entered the reaction vessel. However, this reaction would hardly compete successfully with the combination of hydrogen atoms and methyl radicals, especially in the presence of excess H-atoms at low imine flow rates, and it seems unlikely that a large proportion of the HCN could be formed in this way. Some of the methane formation might be attributed to reaction 4, followed by subsequent hydrogenation of methylene radicals.

Since production of methane at lower flow rates of imine  $(2.9 \times 10^{-6} \text{ mole/sec.})$  was found to be essentially the same at 118 and 271°, and the values for higher flow rates (>5.3  $\times 10^{-6}$  mole/sec.) showed no consistent trend with temperature, it would appear that there was no significant temperature coefficient for methane production. This indicates that the reaction

$$CH_{3} + \underbrace{\begin{array}{c}H_{2}C - CH_{2}\\N\\H\end{array}}_{H} \longrightarrow CH_{4} + \underbrace{\begin{array}{c}H_{2}C - CH_{2}\\N\\\Delta H = -4 \text{ kcal. (5)}\end{array}$$

which has an activation energy of 4.8 kcal./mole,<sup>13</sup> did not occur appreciably. Furthermore, if reaction 5 occurred extensively, followed by reaction 3, ethylenimine consumption and HCN production would no longer be equivalent to the hydrogen atom concentration, as required by the experimental stoichiometry expressed by reaction 1. The required stoichiometry could be maintained if ethylenimino radicals formed a dimer or reacted with methyl radicals to form N-methylethylenimine to an extent equivalent to the ethylenimine destroyed by reaction 5. However, neither N-methylethylenimine nor dimer was detected by mass spectrometric analyses of a single sample which showed that, apart from HCN and unreacted ethylenimine, the condensable products contained only small amounts of C<sub>2</sub> hydrocarbons (probably ethane and ethylene).

The difference between the amounts of imine destroyed and HCN produced may be due to the reactions

$$2 \xrightarrow{H_2C} CH_2 \longrightarrow H_2C \\ H_2C \longrightarrow N \longrightarrow N_2 + 2CH_2 \longrightarrow N \longrightarrow N_2 + 2CH_2 \longrightarrow \Delta H = -113 \text{ kcal.} (6)$$

which have been suggested by Brinton and Volman,<sup>13</sup> although the dimer of the ethylenimino radical was not detected in the present study. Increase of temperature would favor reaction 3 and the corresponding decrease in ethylenimino radical concentration would be prejudicial to the second order reactions 6 and 7. This would explain the observation that, with increasing temperature, the amount of HCN produced accounted for a slightly larger fraction of the ethylenimine decomposed.

(13) R. K. Brinton and D. H. Volman, J. Chem. Phys., 20, 25 (1952).

<sup>(12)</sup> We are grateful to Dr. H. I. Schiff, of this department, for permission to use the mass spectrometer, and to Mr. G. J. O. Verbeke for the analyses.

The results of the present investigation are in contrast to those obtained in earlier studies with ethylenimine. Brinton and Volman<sup>13</sup> found that the products of the reaction of methyl radicals with ethylenimine were methane, nitrogen, ethylene and the dimer of the ethylenimino radical, while Luner<sup>14</sup> found similar products, as well as hydrogen and small amounts of hydrogen cyanide, from the mercury photosensitized decomposition of ethylenimine. More detailed study of the various systems would seem to be necessary to explain the different types of behavior observed.

Hydrogen atoms attacked N-methylethylenimine much more slowly than ethylenimine. The rates of methylethylenimine destruction and hydrogen cyanide production increased with temperature throughout the range of flow rates used.

Samples of the non-condensable products of the methylethylenimine reaction were analysed with the mass spectrometer to obtain the results

Temp., °C.	Imine flow, mole/sec. $\times$ 106	Methane flow, mole/sec. $\times$ 10 <sup>6</sup>
67	4.3	<b>2</b> , $5$
	11.6	3.0
300	2.7	1.7
	2.7	1.4
	7.2	1.1
	11.6	0.7

Very small amounts of nitrogen were found in all samples.

The amounts of methane produced at about  $300^{\circ}$  preclude the possibility that all the HCN is formed in the reaction

$$H + \underbrace{\begin{array}{c}H_{2}C \longrightarrow CH_{2}\\N\\ H_{2}C \longrightarrow CH_{4}\\H_{2}C \longrightarrow CH_{4}\\N\end{array}}_{N} \longrightarrow CH_{4} + HCN + CH_{3} \quad (8)$$
$$\Delta H = -38 \text{ kcal.}$$

since this would give at least one mole of methane for each mole of HCN. Thus, the occurrence of the reaction

$$H + C_{3}H_{7}N \longrightarrow H_{2} + C_{3}H_{6}N \longrightarrow$$
$$H_{2} + HCN + C_{2}H_{\delta} \quad (9)$$
$$\Delta H = -27 \text{ kcal.}$$

is indicated. It is considered likely that a hydrogen atom is abstracted from the methyl group rather than from one of the carbons in the ring, since subsequent rearrangement would necessitate the migration of a hydrogen atom only, instead of a methyl group.

Ethyl radicals, formed in reaction 9, could then undergo "atomic cracking"

(14) C. Luner, private communication.

$$H + C_2 H_5 \longrightarrow 2CH_3$$
 (10)

with formation of some methane by the reactions

$$\begin{array}{c} H + CH_3 \longrightarrow CH_4 \quad (11) \\ CH_2 + C_2H_4 \longrightarrow C_2H_4 + CH_4 \quad (12) \end{array}$$

The amounts of methane obtained, particularly at high temperature, were larger than could be reasonably accounted for solely on the basis of reactions 9 to 12 although these reactions would explain the observed trend toward lower methane production at high imine flow rates, where fewer H-atoms would be available for secondary reactions. The formation of small amounts of nitrogen suggests, however, that reaction 8 does take place to some extent and that some of the ethylenimino radicals thus formed undergo reactions 6 and 7. Hence, it is apparent that both reactions 8 and 9 occur, although there is little doubt that the latter is predominant.

Mass spectrometric analysis of the condensables showed that very small amounts of  $C_2$  hydrocarbons were produced at 53°, although considerable quantities were formed at 303°, presumably at the expense of methane production.

Small amounts of various higher hydrocarbon products were detected with the mass spectrometer. Their occurrence is probably due to combination of the alkyl radicals

$$CH_{3} + C_{2}H_{5} \longrightarrow C_{3}H_{8}$$
(13)  
$$2C_{2}H_{5} \longrightarrow C_{4}H_{10}$$
(14)

and to the disproportionation reactions 12 and

$$2C_2H_5 \longrightarrow C_2H_4 + C_2H_6 \tag{15}$$

Second-order rate constants were calculated for the methylethylenimine reaction in terms of both the consumption of the imine and the production of hydrogen cyanide, for streamline and turbulent flow. Mean values of the frequency factor and activation energy, cbtained from the Arrhenius plots, were found to be

$$A = 3 \times 10^{12} \text{ cm.}^3 \text{ mole}^{-1} \text{ sec.}^{-1}$$
  
 $E = 4.8 \pm 0.5 \text{ kcal./mole}$ 

These refer to the over-all production of hydrogen cyanide and destruction of methylethylenimine.

Formation of hydrogen cyanide as a main product in the ethylenimine reaction suggests that the transition state in the reaction of active nitrogen with ethylene may be simulated by the ethylenimino radical. This gives considerable credence to the view that analogous cyclic collision complexes are formed in the other active nitrogen reactions with unsaturated hydrocarbons. The ethylenimino radical apparently also occurred in the reaction of hydrogen atoms with N-methylethylenimine although HCN was produced mainly by the decomposition of another cyclic radical. This suggests that other radicals containing nitrogen may tend to decompose to hydrogen cyanide at low pressures,

# ACID DISSOCIATION CONSTANTS OF SUBSTITUTED 1,10-PHENANTHROLINES<sup>1</sup>

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# Contribution from the Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois

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The acid dissociation constants of forty substitution derivatives of 1,10-phenanthroline were determined potentiometrically at 25°. A linear relationship which permits extrapolation of data to find  $pK_a$  values in water for derivatives insoluble in water was shown to be obtained between per cent. dioxane and relative  $pK_a$  values in water-dioxane solutions. The Hammett substituent constants for methyl groups were shown to be additive for multiple methyl substituents.

#### Introduction

The important applications of 1,10-phenanthroline and its numerous substitution derivatives in the field of analytical chemistry have created considerable interest in their physical properties and those of their chelate complexes with various metal ions. Aside from its utilitarian value to the analytical chemist, this information should afford some insight into the related factors of structure and reactivity. At the present time relatively few physical constants of the 1,10-phenanthrolines and of their complexes have been determined. The acid dissociation constant of 1,10-phenanthroline as well as the instability constants of its Fe(II) and Fe-(III) complexes have been determined by Lee, Kolthoff and Leussing.<sup>2</sup> Determinations of these same constants have also been carried out by Brandt and Gullstrom<sup>3</sup> on some 5-substituted 1,10phenanthrolines and on the unsubstituted compound.

The basic strength of a chelate ligand, among other factors of its structure, determines to a large extent the stability of its metal complexes. Some exceptions have been noted to this general rule, but it should remain valid, excluding steric effects, when applied to a given metal ion and a series of closely related chelate molecules. In the case of the metal complexes with various substituted 1,10phenanthrolines it is to be expected that the relative order of stabilities of a given metal complex should be the same as that of the basic strengths of the ligands. This follows from the similarity of the 1,10-phenanthroline derivatives. Any exceptions would most probably result from steric effects introduced by substitution on the phenanthroline ring.

It is proposed that the empirical relationship, log  $k - \log k^0 = \rho \sigma$ , given by Hammett<sup>4</sup> may find application in predicting approximate values of stability constants of the substituted 1,10-phenanthroline metal complexes. Employing the acid dissociation constants of the substituted derivatives of 1,10-phenanthroline to calculate  $\sigma$ -values and the experimental results of Brandt and Gullstrom on stability constants of Fe(II) complexes of 5-substituted 1,10-phenanthrolines to obtain  $\rho$ , it is believed that satisfactory values for the sta-

Soc., 70, 2348 (1948); (b) 70, 3596 (1948).

Book Co., Inc., New York, N. Y., 1940, pp. 184–207.

bility constants of iron(II) complexes of other substituted ligands may be obtained.

A straight-line relationship has been demonstrated between the  $pK_a$  of substituted 1,10-phenanthrolines and the oxidation-reduction potentials of the ferrous-phenanthroline complexes with nitro, methyl, bromo, chloro or phenyl substituents in the 5-position.<sup>3,5</sup> The ruthenium complexes appear to give similar correlation.<sup>6</sup> In general such a relationship is to be expected in the event that the stability constants of both the oxidized and the reduced forms of a complex are linearly dependent on the basicity of the chelate ligand. The acid dissociation constants of the substituted 1,10-phenanthrolines may, therefore, provide for the prediction of approximate oxidation-reduction potentials as well as of stability constants. Such an approach appears attractive in light of the experimental difficulties involved when the water insoluble phenanthroline complexes are to be evaluated.

## **Experimental Methods and Results**

Materials.—The various substituted 1,10-phenanthrolines were prepared either in the laboratories of Temple University<sup>7</sup> or by the G. Frederick Smith Chemical Company following these directions. They had previously yielded correct analyses for carbon and hydrogen, and were considered to be as pure as crystallization procedures afford.

The best available commercial grade of 1,4-dioxane was purified by refluxing over a mixture of sodium hydroxide and silver oxide for 48 hours. The distillate obtained after this treatment was stored over sodium metal; prior to immediate use it was refluxed for at least 24 hours before distilling requisite amounts. The deionized water used was carbon dioxide-free as indicated by pH measurement. Measurement of Acid Dissociation Constants.—A semi-

Measurement of Acid Dissociation Constarts.—A semimicro balance was used to weigh out samples of the 1,10phenanthroline derivatives in exactly 0.125 milliequivalent amounts which were then transferred into 25-ml. volumetric glass stoppered flasks. Using a weight buret samples of standardized hydrochloric acid (equivalent to 0.5-0.6 of the free base added) were weighed into the contents of the flasks. Various amounts of the 1,4-dioxane (at 25°) were delivered by calibrated pipets into the flasks, the contents of the flasks were diluted to the mark with carbon dioxidefree water and the flasks were then stoppered and placed in a thermostat to equilibrate to 25°. All of these operations were performed without appreciable delay in order to minimize the slight tendency for the pH to decrease as CO<sub>2</sub> is picked up by the relatively weakly buffered solutions. The solutions were measured at 25° using a Beckman model G pH meter equipped with a glass-saturated calomel electrode pair. The meter was calibrated immediately before use with Leeds and Northrup Standard Buffer of

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1547

pH 4.01 at 25°. The performance of the instrument was checked periodically using a standard buffer solution of pH 6.86 at 25°. After completion of a series of measurements on any one compound, the calibration was checked using the pH 4.01 buffer once more. It was observed that continued use of the dioxane-water solutions caused the attainment of constant readings to be sluggish. This behavior occurred twice during the entire investigation and was eliminated both times by flushing out the saturated potassium chloride salt bridges with fresh solution. Other than this, no difficulty was experienced in obtaining rapid and reproducible measurements.

Relative acid dissociation constants in the dioxanewater solutions of the conjugate acids of the substituted 1,10-phenanthrolines were calculated from the pH meter readings and the known concentrations of conjugate acid and free base (1,10-phenanthrolines are monobasic). Because the pH meter was calibrated for aqueous solutions, rather than for each particular dioxane solution, the measurements provide only relative pH values for the dioxane solutions. To obtain the acid dissociation constants in water the relative  $pK_a$  values were plotted versus weight per cent. dioxane and the curve extrapolated to zero dioxane. Since activity coefficients were not employed and because of unknown liquid junction potentials the dissociation constants are not thermodynamic values. The ionic strengths

#### TABLE I

#### ACID DISSOCIATION CONSTANTS AT 25°

1,10-Phenanthroline derivative	Concn. limits of dioxane used (% by wt.)	Extrapo- lated pKa	-m
Unsubstituted	0-40	4.86	1.53
4-Bromo-	12 - 40	4.03	1.30
3-Chloro-	12 - 40	3.99	1.50
3-Ethyl-	12 - 40	4.98	1.40
4-Ethyl-	12 - 40	5.44	1.55
3-Methyl-	12 - 40	5.00	1.43
2-Phenyl-	20 - 40	4.90	1.23
3-Phenyl-	20 - 40	4.82	1.67
4-Phenyl-	20 - 40	4.90	1.80
5-Phenyl-	20 - 40	4.72	1.70
4-n-Propyl-	12 - 40	5.45	1.58
3,8-Dibromo-	52 - 68	3.90	1.85
4,7-Dichloro-	40 - 56	3.03	0.56
5,6-Dichloro-	28 - 40	3.47	1.25
4,7-Diethyl-	12 - 40	5.60	1.18
4,7-Dimethoxy-	40-60	6.45	1.60
5,6-Dimethoxy-	0-40	4.42	1.23
2,4-Dimethyl-	12 - 40	5.96	1.55
2,9-Dimethyl-	12 - 40	6.17	1.50
3,4-Dimethyl-	12 - 40	5.62	1.28
3,7-Dimethyl-	12 - 40	5.57	1.33
3,8-Dimethyl-	20-40	5.23	1.68
4,6-Dimethyl-	12 - 40	5.71	1.28
4,7-Diphenoxy-	38-60	5.34	1.98
4,6-Diphenyl-	40-72	4.69	1.90
4,7-Diphenyl-	10-60	4.84	<b>2</b> , $02$
3,4,6-Trimethyl-	12 - 40	5.93	1.55
3,4,7-Trimethyl-	12 - 40	5.99	1.09
3,5,6-Trimethyl-	12 - 40	5.34	0.98
3,5,7-Trimethyl-	12 - 40	5.90	1.18
3,5,8-Trimethyl-	12 - 40	5.27	1.08
2,4,7,9-Tetramethyl-	20 - 40	6.50	1.10
3,4,6,7-Tetramethyl-	12 - 40	6.45	1.25
3,4,6,8-Tetramethyl-	12 - 40	6.07	1.35
3,4,7,8-Tetramethyl-	12 - 40	6.31	1.55
3,5,6,8-Tetramethyl-	12 - 40	5.54	0.65
3,4-Cyclohexeno-	12-40	5.66	1.55
5,6-Cyclohexeno-	12-40	5.30	1.33
3,4-Cyclopenteno-	12-40	5.78	1.58
(3,4),(7,8)-Dicyclohexeno-	40 - 52	6.23	1.73

at which the measurements were made varied from 0.0025 to 0.0030. Judging from a comparison of the attendant error of the experimental procedure and the small error from neglecting activity coefficients at these low and relatively constant ionic strengths, it may be concluded that these values might well be considered thermodynamic constants.

The results are presented in Table I. The lower limits of concentration of dioxane used depended upon solubility requirements; this information is included together with the maximum concentration of dioxane employed in the measurements as an indication of the reliability of the extrapolations. Negative values of the slopes of the linear curves obtained by plotting the experimental data are given in the table also. The slope, m, is here defined as the rate of change of the relative  $pK_a$  values with change in weight fraction of dioxane. Use of extrapolated  $pK_a$  values and the slopes permits comparison to be made of the relative basicities of the 1,10-phenanthrolines as a function of dioxane

# Discussion

To obtain acid dissociation constants referred to water, the data were extrapolated to zero dioxane content. This was necessitated by the insolubility of most of the substituted 1,10-phenanthroline derivatives in water. It was shown experimentally that this technique, although theoretically unjustified as yet, would yield reliable results. Two of the more water-soluble compounds (1,10-phenanthroline and 5,6-dimethoxy-1,10-phenanthroline) permitted study in aqueous solutions and were found to give a linear relationship, at least within experimental error, between relative  $pK_a$  values and per cent. dioxane in the range from 0 to 40% dioxane. The observed linearity is fortuitous and may possibly result from the use of relative instead of absolute acid dissociation constants. The acid dissociation constants of some anilinium salts as determined by Marshall and Grunwald<sup>8</sup> in concentrations of dioxane in water of 0-20% do not vary linearly with respect to per cent. dioxane by weight. Similar non-linearity is given by data of Gutbezahl and Grunwald<sup>9</sup> for anilinium salts in dilute ethanol solutions in water. The dissociation constants of some  $\beta$ -diketones in the system dioxane-water were found to deviate from linearity at lower dioxane concentrations by Van Uitert, et al.<sup>10</sup> In this case non-linearity was suggested to result from a shift to the enol form as the mixed solvent became more Some of the aliphatic carconcentrated in water boxylic acids have been found to give essentially linear dependence of  $pK_a$  with respect to dioxane content in the dilute dioxane solutions.<sup>11</sup>

The order of relative basic strengths of the derivatives of 1,10-phenanthroline is as one would predict. The various substituents produce different effects in electron density on the nitrogen atoms depending on both their nature and position, in keeping with their known effects on other ring systems. In the 2- and 4-positions a phenyl substituent increases the electron density on the ring nitrogens slightly by its tautomeric effect, whereas in the 3and 5-positions its electrophilic effect predominates. The effects of methoxyl groups are similar

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(11) H. S. Harned and R. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1943, p. 581. to those of the phenyl but more pronounced. Halogen substituents exhibit slight tautomeric and pronounced inductive effects. The inductive effects of methyl substituents, which do not give the tautomeric effect, are in accord with previous predictions based on  $\pi$  electron density calculations for 1,10phenanthroline by Longuet-Higgins and Coulson.<sup>12</sup>

Multiple substitutions of methyl groups on 1,10phenanthroline are found to increase its basicity in an additive fashion. To illustrate this, use is made of the substituent constant,  $\sigma$ , which is defined by the expression  $\sigma \equiv pK_a^\circ - pK_a$ , where  $pK_a^\circ$  is the negative log of the acid dissociation constant in water of 1,10-phenanthroline and  $pK_{\rm B}$  is that of the substituted derivative. The additivity of the four individual methyl substituent constants when multiple substitutions are considered is shown in Table II. The calculated values of these four constants were obtained by averaging their individual contributions in all of the methyl derivatives studied. The good agreement, for the most part, of the calculated and experimental values indicates that reasonably accurate values for the acid dissociation constants of the methyl derivatives of 1,10-phenanthroline may be calculated in this way.

Acknowledgment.—The authors wish to express their gratitude to Professor Francis H. Case of

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TABLE II

Additivity	OF	METHYL	SUBSTITUENT	CONSTANTS
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Methyl substituents on		- σ	
1,10-phenanthroline	Calcd.	Obsd.	Difference
<b>2</b>	0.60		
3	. 17	0.14	+0.03
4	. 56		
5	.25		
2,4	1.16	1.10	+0.06
2,9	1.20	1.31	11
3,4	0.73	0.76	03
3,7	.73	. 71	+ .02
3,8	.34	.37	03
4,6	.81	.85	04
3,4,6	.98	1.07	09
3,4,7	1.29	1.13	+ .16
3,5,7	0.98	1.04	06
3,5,6	.67	0.48	+ .19
3,5,8	. 59	.41	+ .18
3,5,6,8	.84	.68	+ .16
3,4,7,8	1.46	1.45	+ .01
3,4,6,7	1.54	1.59	05
3,4,6,8	1.15	1.21	— .06
2,4,7,9	2.32	1.64	+ .68

Temple University for supplying the comp unds reported herein either directly or indirectly through his many outstanding contributions in the synthesis of substituted 1,10-phenanthrolines.

# SORPTION STUDIES ON AMERICAN COALS

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The interpretation of sorption studies on coals has not led to a clear picture of their physical structure. The sorption of inert molecules such as nitrogen and argon at liquid nitrogen temperatures is low, corresponding to surface areas of 0.5 to 15 m.<sup>2</sup>/g. The sorption of polar molecules such as water, alcohols and amines at about room temperature is high, corresponding to surface areas of 50 to 400 m.<sup>2</sup>/g. The present data, obtained from sorption of normal and isobutane at 0°, and nitrogen isotherms at temperatures of -195 to 0°, indicate that the surface areas of coals have some intermediate value. Density measurements show that coals have a sizable pore volume. Sorption of normal butane was considerably greater than that for isobutane on most coals, indicating that at 0° a large fraction of the pores have openings of about 5 Å. Adsorption of nitrogen at -195° was low, indicating that at this temperature the pore openings are smaller, the order of 4 Å. or less. The sorption of polar molecules is apparently complicated by swelling and imbibition, involving weak chemical bonds between the sorbate and polar groups in the coal.

Coal is an amazingly complex substance, and physical and chemical studies have not led to any simple, useful structure of coal. The interpretation of sorption studies is equally difficult. Work of the British Coal Utilisation Research Association<sup>1-5</sup> beginning about 1940 has produced a large amount of pertinent data for sorption on coal; however, the interpretation of these data has led to polemics

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(4) M. Griffith and W. Hirst, Proceedings of a Conference on the Ultrafine Structure of Coals and Cokes, The British Coal Utilisation Association, London, 1944, pp. 80-94.

(5) F. A. P. Maggs, rel. 4, 1944, pp. 95-109.

that have not yet been settled. In addition to the British group, researchers in South Africa<sup>6,7</sup> and the Netherlands<sup>8,9</sup> have contributed valuable experimental data and interpretation. The controversy resulted from the interpretation of the observations that (a) the sorption of inert molecules such as argon and nitrogen at liquid nitrogen temperatures is relatively low corresponding to surface areas of 0.5 to 15 m.<sup>2</sup>/g., and (b) the sorption of polar molecules such as alcohols and amines at about room temperature is high, corresponding to surface areas of 50 to 400 m.<sup>2</sup>/g. The British group

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(7) P. Le R. Malherbe and P. C. Carman, ibid., 31, 210 (1952).

(8) P. Zwietering, A. P. Oele, and D. W. van Krevelen, *ibid.*, 30, 203 (1951).

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believed that the areas from sorption of polar molecules,<sup>10</sup> especially methanol, were correct and that the sorption of inert, non-polar molecules was prevented by the presence of methane in pores<sup>4</sup> or by the slow rate of diffusional processes.<sup>11,12,9</sup> The opposition<sup>13,6,7</sup> suggested that the sorption of inert molecules yielded the correct areas and that the larger sorption of polar molecules results from a weak chemical bonding with the coal. More recent data<sup>11,9</sup> have shown that both of these interpretations are at least partly incorrect. Since the original manuscript was submitted three important papers have appeared. The first<sup>14</sup> clearly demonstrates that activated diffusion is important in the sorption of methane, the second<sup>15</sup> and third<sup>16</sup> papers indicate that carbon dioxide is adsorbed in large amounts at -78 and  $0^{\circ}$  and that normal butane is adsorbed in greater amounts than isobutane.

The present paper gives the results of adsorption studies on a few typical American coals. Pertinent information regarding the pore structure of coal is provided by density measurements and sorption isotherms of normal and isobutane at  $0^{\circ}$  and nitrogen isotherms at -195, -78 and  $0^{\circ}$ .

#### Experimental

The following coals were used: anthracite from Lower Baltimore bed, Luzerne County, Penna.; low-volatile bituminous from Pocahontas No. 3, bed, Wyoming County, W. Va.; Bruceton high-volatile bituminous from Pittsburgh bed, Allegheny County, Penna.; Rock Springs sub-bituminous from D. O. Clark Mine, Sweetwater County, Wyoming; sub-bituminous from Roland and Smith beds, Campbell County, Wyoming; lignite from Upper bed, Harrison County, Texas; Cannel from Elkhorn No. 1, Floyd County, Kentucky.

Included in the study were hand-picked, banded constituents of Bruceton high-volatile bituminous coal and a fraction of Bruceton coal prepared by dissolving coal in boiling phenanthrene, filtering the solution through glass woo, and precipitating with benzene.<sup>17</sup> This fraction comprised 76% of the coal. Analyses of the coal samples are given in Table I.

To prepare coals for sorption studies, it was necessary to remove, as far as possible, water and other sorbed material present in the coal. Degassing *in vacuo* at high temperatures would have led to decomposition of the coal. The standard methods for determining water in coal were not suitable, since water would not have been removed completely, or the coal would have been oxidized or otherwise altered.

Preliminary experiments indicated that evacuation of the coal at 100° circumvents most of these difficulties as oxidation is avoided and the temperature, although adequate to remove sorbed water and gases, is not high enough to cause appreciable decomposition of the coal. Most of the loss in weight occurred in the first hour, after which the weight decreased very slowly. The following procedure was therefore adopted for the pretreatment: For sorption studies the coals were ground to 80 to 100 mesh (U. S. Standard Sieve) and for density measurements to 6 to 8 mesh. The samples were stored in a desiccator until ready for use. The coal was then placed in the sorption or density tubes, evacuated

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Lahiri, Fuel, **35**, 71 (1956). (16) K. A. Kini, "Reports of the 27th International Congress of

Industrial Chemistry," Brussels, 1954, Vol. II, p. 110. (17) C. Golumbic, J. B. Anderson, M. Orchin and H. H. Storch,

(17) C. Golumbic, J. B. Anderson, M. Orchin and H. H. Storch, Bureau of Mines Report of Investigation 4662 (1950). at room temperature for 1 hour, and finally heated *in vacuo* at 100° for 2 hours. The evacuation was performed very cautiously to avoid loss of coal. The weight of the coal after this treatment was used to compute the amount adsorbed per gram, or the densities.

Density measurements were made on the larger particles so that there would be no uncertainty of mercury not penetrating the spaces between particles in the mercury density measurements. On each sample the helium density was determined at 30° by the method of Smith and Rossman.<sup>18</sup> Then the mercury density was determined by admitting mercury at an absolute pressure of 1,140 mm. to the sample after evacuation following the helium density measurement. At this pressure mercury should not penetrate pores of radius smaller than 5  $\mu$ ,<sup>9</sup> and examination of coal particles showed that little if any mercury had penetrated the pores of the coal.

Water sorption measurements at 30 and 35° were made by two methods. In the first method, a standard glass vacuum system was used. The dried sample was contained in a thermostated glass bulb provided with a stopcock and a ground glass joint to permit removal of the bulb for weighing. The water vapor was admitted from a bulb containing distilled water that had been redistilled in the vacuum system and repeatedly frozen, pumped and melted to remove dissolved gases. The pressure of water vapor was measured by an oil manometer. At each sorption point, all coals appeared to reach equilibrium with the vapor in less than 12 hours; however, the samples were equilibrated 18 to 24 hours before weighing. In the second method,<sup>19</sup> the dried samples were exposed in a vacuum desiccator to water vapor from a series of saturated salt solutions with relative vapor pressures ranging from less than 0.1 to 0.98. The desiccator was kept in an air thermostat maintained at  $35 \pm 0.5^{\circ}$ . It was evaluated to a pressure of less than 5 mm. and then closed for equilibration. The time required to attain equilib-rium was considerably longer than for the first method, presumably due to the presence of air. Preliminary experiments indicated that apparent equilibrium was attained at all relative pressures within 2 or 3 days; but to assure attainment of equilibrium, 7 days were allowed for each sorption point. The two methods gave essentially identical results as shown in Fig. 1.

The methanol sorption studies were made at 30° in the glass vacuum system described for the water measurements,



Fig. 1.—Sorption isotherms on coal, where O and  $\Box$  represent water and methanol, respectively. Sorption points are open and desorption points solid. For anthracite, water isotherms from the desiccator, O and vacuum system  $\otimes$ , methods are compared.

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			Composition on moisture-free basis, wt. %					
	Moisture, % (air dry)	Volatile matter	$\mathbf{Ash}$	Hydrogen	Oxygen	Carbon	Nitrogen	Sulfur
Anthracite	2.3	6.0	5.9	<b>2</b> .5	2.0	88.1	0.9	0.6
Low-volatile bituminous	0.7	17.3	7.6	4.2	2.6	83.8	1.2	.6
Bruceton high-volatile bituminous								
Whole coal	1.7	37.1	7.2	5.2	7.3	77.5	1.5	1.3
Anthraxylon	1.5	38.6	1.6	5.4	7.2	83.1	1.6	1.1
Bright attritus	1.1		4.5	5.4	7.2	80.4	1.5	1.0
Dull attritus	1.3	41.0	2.9	5.6	6.2	82.6	1.7	1.0
Fusain	0.6	13.9	8.4	2.6	3.3	84.8	0.4	0.5
Dissolved precipitated			1.0	5.0	6.0	85.5	1.9	0.6
Rock Springs sub-bituminous	3.2	42.3	4.2	5.1	13.3	74.7	1.6	1.1
Sub-bituminous B49480	16.1	43.3	8.6	4.8	17.0	68.0	0.9	0.7
Lignite	18.3	43.5	11.8	4.4	15.3	66.4	1.3	. 9
Cannel	1.3	48.3	5.1	6.1	<b>6</b> . $2$	80.6	1.4	.6

 Table I

 Chemical Analyses of Coals Used for Sorption Studies

with the following modifications: The pressures were determined by a mercury manometer that was read with a cathetometer. Shorter periods, usually 6 hours, were necessary to reach equilibrium. In all cases sorption was continued to constant weight. C.P. grade methanol was used after it had been distilled over ignited calcium oxide and redistilled, frozen and evacuated in the same manner as the water.

The presence of methane or other gases displaced from the coal would have caused errors in the manometer readings. To minimize this effect, the vapor in the system was freed of these gases several times in the course of equilibration. Between the sorption tube and the manometer was a bulb of about ten times the volume of the sorption tube, which was connected to the manometer by a stopcock. To flush inert gases from the sorption tube, the stopcock on the sample tube was closed and the remainder of the system was evacuated. The stopcock on the bulb was then opened and the gas mixture in the sorption tube was expanded into the bulb. Finally, the stopcock on the sorption tube was closed and the bulb evacuated. This procedure was repeated three times, after which the pressure in the manometer was set at its previous value and the sorption was resumed. This method flushed inert gas from the system without desorbing an appreciable amount of water or methanol from the sample; the volume of displaced gas was, however, negligible in all cases.

Nitrogen, normal and isobutane isotherms were determined by the conventional volumetric method,<sup>20</sup> nitrogen isotherms at  $-195^{\circ}$  and in special experiments at -195, -78 and 0°, and butane isotherms at 0°. For surface area determination, the volume of the monolayer,  $V_{\rm m}$ , was obtained by use of the simple B.E.T. equation,<sup>21</sup> where applicable, and by use of a modified B.E.T. equation<sup>22</sup> for isotherms that deviate widely from the simple equation. For isotherms of butanes, the  $V_{\rm m}$  values were taken as the largest amount sorbed at a relative pressure of 0.1.

#### **Experimental Results**

Helium and Mercury Densities.—Helium and mercury densities (Table II) were determined on four representative coals to illustrate the magnitude of the pore volume and porosity. These fragmentary values demonstrate that the pore volume passes through a minimum in the high volatile bituminous range, as has been shown by several previous workers.<sup>3,23</sup>

Sorption Isotherms and Surface Areas.—Methanol and water isotherms of coals are presented in Figs. 1 to 3. Water isotherms of the banded constituents and of dissolved and precipitated

# TABLE II

# POROSITY OF AMERICAN COALS

	Densit	ies dete	ermined	at 30°		
	Moistu basis Oxy- gen	re-free s, % Car- bon	Densi g./ He- lium	ities,ª cc. Mer- cury	Pore vol., cc./g.	Poro- sity,b cc./ cc.
Anthracite Bruceton HVB	2.0 7.3	88.1 77.5	1.538 1.296	1,384 1,263 1,160	C.073 .020	0.100 .0255
Rock Springs SB Lignite	13.3 15.3	74.7 66.4	1.338 1.457	$1.160 \\ 1.192$	.115	.182

<sup>a</sup> Densities are reported for the whole ccal after the drying procedure used for sorption studies. <sup>b</sup> Porosity based on volume of mercury displaced.

Bruceton coal are shown in Fig. 4. Figure 5 presents the sorption of nitrogen on Rock Springs coal at  $-195^{\circ}$ . Figures 6 to 11 present nitrogen isotherms on 6 different coals determined at 3 different temperatures in the following order: -195, -78, 0, -78,  $-195^{\circ}$  without evacuation in the sequence of experiments. In this series the volume absorbed was determined after 1 to 24 hours.

Isotherms of normal and isobutane at  $0^{\circ}$  are given in Figs. 12 to 17. The approach to equilibrium was slow. Each sorption point was taken after 8 to 24 hours. At a given relative pressure, the amount sorbed increased with each sorption-desorption cycle and finally approached relatively constant values after several such cycles.

The water and methanol isotherms (Figs. 1 to 4) were sigmoid-shaped, except for the Langmuir-type isotherm of methanol on anthracite. With this exception, the isotherms exhibited hysteresis. The hysteresis loops did not close at relative pressures of 0.3-0.4, as is usual for porous inorganic materials, but closed at zero relative pressure in several experiments in which the hysteresis was studied in detail.

The sorption of water vapor on hand-picked samples of banded constituents of Bruceton coal (Fig. 4) resulted in isotherms, all of which have the same general shape as the isotherm for whole Bruceton coal, except that the fusain curve increased relatively more in the region of higher pressure. The anthraxylon isotherm most nearly resembles that of whole Bruceton coal, whereas the sorption of water on other constituents was appreciably less. Figure 4 also includes a water isotherm on the extract of Bruceton coal. Although the shape of this

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<sup>(21)</sup> S. Brunauer, P. H. Emmett and E. Teller, J. Am. Chem. Soc., 60, 309 (1938).

<sup>(22)</sup> R. B. Anderson and W. K. Hall, *ibid.*, 70, 1727 (1948).

<sup>(23)</sup> D. H. Moffat and K. E. Weale, Fuel, 34, 449 (1955).



Fig. 2.—Isotherms of water O and methanol  $\square$  on Rock Springs sub-bituminous coal. Desorption points are solid.



Fig. 3.—Isotherms of water O and methanol  $\Box$  on lignite. Desorption points are solid.

isotherm is considerably different from the others in Fig. 4, the amount sorbed was of the same magnitude as that sorbed on whole Bruceton coal or its banded constituents.

With the exception of anthracite, the rate of adsorption of nitrogen at  $-195^{\circ}$  was similar to that observed for argon at  $-183^{\circ}$  by Malherbe,<sup>6</sup> rapid initially and very slow after about 10 minutes. For example, Fig. 5 shows the adsorption of nitrogen on Rock Springs coal. The open circles represent adsorption points taken at approximately 30-minute intervals on the first and second days, and the solid circles represent desorption points taken during the second and third days of the continuous experiment. On the third day the pressure was increased, resulting in the adsorption points marked  $\diamond$  and (on the third and fourth days) the desorption points marked  $\bullet$ . The system was then allowed to equilibrate on an adsorption point at a relative pressure of 0.2 for 9 days. In the first 4 days the



Fig. 4.—Isotherms of water on banded constituents of Bruceton coal and a dissolved and precipitated fraction. Desorption points are solid.



Fig. 5.—Nitrogen adsorption at  $-195^{\circ}$  on Rock Springs coal.

volume adsorbed increased from 0.91 to 1.08 cc.-(S.T.P.)/g. and then remained constant. The desorption curve decreases abruptly in the relative pressure range 0.50–0.55. At the lower relative pressures, the desorption curve has the same shape as the adsorption curve but lies about 0.2 cc. higher. The difference may be due to a slow adsorption during the interval between the determination of first adsorption and desorption points. The adsorption of nitrogen on other coals was studied in less detail, and the surface areas are based on adsorption points taken after 30 minutes. With anthra-



Fig. 6.—Nitrogen sorption on anthracite. Desorption points are solid.



Fig. 7.—Nitrogen sorption on low volatile bituminous coal. Desorption points are solid.

cite, the pressure of helium decreased slowly for more than a week, during the calibration of the dead space of the adsorption tube at  $-195^{\circ}$ . This behavior was not found on other coals. Similarly, the adsorption of nitrogen was very slow and equilibrium was not established in more than one week. The nitrogen area for anthracite was estimated from the amount adsorbed at 0.1 relative pressure after 7 days; it therefore represents a lower limit of the surface area.

Griffith and Hirst<sup>4</sup> suggested that the low sorption of many molecules resulted from the presence of methane in coal which prevented these molecules from penetrating the pores. Water and especially methanol were postulated to have the ability of displacing this methane. If the displacement of methane by methanol is important, the adsorption of nitrogen by coal should be greater after saturation of the coal with methanol and subsequent evacuation; this was not found (Table III). Two



Fig. 8.—Nitrogen sorption on Bruceton coal. Desorption points are solid.



Fig. 9.—Nitrogen sorption on Rock Springs coal. Desorption points are solid.

portions of sub-bituminous coal were dried and evacuated at 100° in the usual way, and a nitrogen isotherm was determined on one portion. Methanol was sorbed on the second portion at 25°, and the pressure was increased during the experiment until liquid methanol was observed in the sorption tube. The sample was in contact with liquid methanol for several days. Then the methanol was removed by evacuation at 100° and a nitrogen isotherm was determined. The two nitrogen isotherms were identical, corresponding to an area of 1.6 m.<sup>2</sup>/g. contrasted with 404 m.<sup>2</sup>/g. from methanol sorption.

Nitrogen isotherms determined without intermediate evacuation at three different temperatures in the order -195, -78, 0, -78 and  $-195^{\circ}$ 

				50	RPTION 1	JATA ON	COAL	s					
		Surface ar	ea, m.	<sup>2</sup> /g.		Vm, cc.(S	.T.P.)/	g.	Liqui	d vol. at s	aturatio	n, cc./g.	Pore
Coal	N2	CH₃OH	H₂O	$n-C_4H_{10}$ (iso- $C_4H_{10}$ )	$N_2$	CH:OH	H₂O	n-C4II10 (iso- C4H10)	N <sub>2</sub>	CH₃OH	H₂O	n-C4H10 (iso- C4H10)	vol., cc./ g.
Anthracite	$ \begin{array}{c} 7 \cdot 4 \\ \cdot 4 \end{array} $ 59.2	239	a	182 (1.7)	1.7 .08 $b$ 13.5	55.2	a	21.0 (.2)	0.001\ <sup>₺</sup> .030∫	0.0840	0.064	0.095° (.001)	0.073
Low-volatile bitumi- nous	$\begin{array}{c} .4 \\ 1.0 \\ 8.8 \end{array}$	110	33.6	5.8 (1.0)	$\begin{array}{c} .09 \\ .22 \\ 2.0 \end{array}$	25.5	11.5	.7 (.1)	.001) <sup>b</sup> .006)	.069	.028	.003 (.001)	ſ
Bruceton, high-vola- tile bituminous	1.5 .7) <sup>b</sup> 5.8)	113	60.8	35 (4.8)	$.34^{\circ}$ $.15^{b}$ $1.32^{\circ}$	26.0	20.8	4.0 (.55)	.001 $.001)^{b}$ .003)	.074 <sup>g</sup>	.0339	.021° (.003)	.020
Rock Springs sub- bituminous	3.0 <sup>e</sup> 29.4∖ <sup>b•d</sup> 39.6∫	192°	115 <sup>e</sup> 136 <sup>d</sup>	139 113	.7 <sup>c</sup> 6.7) <sup>b·d</sup> 9.1	44.4	39.4	16.0 13.0	.021 <sup>ć</sup> .036\ <sup>b</sup> .036\	. 193 <sup>9</sup>	. 105	.129° (.125)°	. 115
Sub-bituminous	1.6 1.6 <sup>e</sup>	404	292	ſ	.36	93.4	100	1	1	.309	. 185	ſ	ſ
Lignite	3.5 3.2 24.6	299	276	80 (15)	.80 .72) <sup>b</sup> 5.6	69.0	94.4	9.3 (1.7)	.007 \b .021∫	.360″	. 190%	.062 (.013)	.153
Cannel	6.5] <sup>b</sup> 8.6∫	ſ	44	84.0 (31)	1.5 1.9	f	15.1	9.7 (3.6)	.004) <sup>b</sup> .004∫	ſ	.002	.065 (.019)	ſ

	TABLE III
	SORPTION DATA ON COALS
g.	$V_{m}, cc.(S.T.P.)/g$

<sup>a</sup> Simple and modified B.E.T. equations do not fit this isotherm. <sup>b</sup> Lowest value for short period of equilibration at  $-195^{\circ}$ . Highest value obtained at  $-195^{\circ}$  after exposure to N<sub>2</sub> at -78, 0 and  $-78^{\circ}$ . <sup>c</sup> Obtained on sample A. <sup>d</sup> Obtained on sample B. <sup>e</sup> Determined at  $-195^{\circ}$  after saturation with methanol at room temperature and subsequent evacuation. <sup>f</sup> Not determined. <sup>e</sup> Liquid volume at saturation exceeds pore volume.



Fig. 10.—Nitrogen sorption on lignite. Desorption points are solid.

(Figs. 6 to 11) give the unusual result previously reported by Maggs<sup>12</sup> and Kini<sup>16</sup> that sorption at a given pressure at -78 and 0° often exceeds that observed for the initial sorption at  $-195^{\circ}$ . Usually periods of equilibration of 1 to 4 hours were used at -195 and 0°, and 8 to 24 hours at  $-78^{\circ}$ . Portions of the same coal samples as used in previous studies were employed, except for Rock Springs coal for which the original sample was lost. The new sample of Rock Springs coal adsorbed considerably more nitrogen at  $-195^{\circ}$  than the original material; however, the sorption of water was about the same (Table III).

The sequence of the sorption experiments is illustrated by Fig. 6. After the dead space determi-



Fig. 11.—Nitrogen sorption on cannel coal. Desorption points are solid.

nations at each temperature, the sample was cooled to  $-195^{\circ}$  and evacuated. Nitrogen was admitted and sorption and desorption points were determined, ending with point A. Then the temperature was increased to  $-78^{\circ}$  and adsorption point B was determined. Sorption and desorption points at this temperature ended at point C, and then the temperature was increased to  $0^{\circ}$  to give point D. Subsequently, the sorption was determined at -78and then  $-195^{\circ}$ . The final sorption measurements at -78 and  $-195^{\circ}$  in Figs. 6 to 11 are represented by dashed curves.

For anthracite (Fig. 6), low-volatile bituminous (Fig. 7), and Bruceton bituminous (Fig. 8) coal the amount of vitrogen adsorbed at 0 and  $-78^{\circ}$  exceeded the sorption in the initial isotherm at  $-195^{\circ}$ , whereas for Rock Springs sub-bituminous and cannel coals the sorption data fell in the usual order, decreasing from -195 to  $0^{\circ}$ . For lignite, the



Fig. 12.—Butane sorption on anthracite 0°. Desorption points are solid.

sorption at  $-78^{\circ}$  exceeded the initial isotherm at  $-195^{\circ}$ , but the sorption at  $0^{\circ}$  was lower.

Sorptions that increase with temperature must be related to rate processes involving activation energies of sufficient magnitude to make the rate very slow at the lower temperatures. In many cases activated adsorptions involve chemical reactions with high activation energies, but for nitrogen on coal activated diffusion (for methane on coal an activation energy of 3.9 kcal./mole was observed<sup>14</sup>) is probably the step responsible for the activated physical sorption. Activated diffusion may be expected for systems containing very small pores, especially those approaching molecular dimensions, such as chabazite.<sup>24-27</sup> On this basis anthracite, low-volatile bituminous, Bruceton bituminous and lignite may be inferred to have pore diameters approaching molecular sizes, whereas Rock Springs sub-bituminous and cannel coals have larger pores.

Comparison of the relative sorption of normal and isobutane is a delicate method for determining magnitude of pores of molecular dimensions; however, the possibility of solution of butanes in waxy constituents of some coals must not be overlooked. The rates of sorption of butanes at  $0^{\circ}$  were slow, and the isotherms approach equilibrium only after several cycles of sorption and desorption, if at all. For cannel, anthracite, low-volatile bituminous, Bruceton bituminous and lignite the sorption of normal butane was considerably greater than that of isobutane. For Rock Springs coal the sorption of the butane isomers was about the same. According to Barrer<sup>25</sup> the effective diameters of normal and

(24) P. H. Emmett and T. W. DeWitt, J. Am. Chem. Soc., 65, 1253 (1943).

(25) R. M. Barrer, Brennstoff-Chem., 35, 325 (1954).

(26) R. M. Barrer and D. A. Ibbitson, Trans. Faraday Soc., 40, 206 (1944).

(27) R. M. Barrer, J. Soc. Chem. Ind. (London), 64, 130, 131, 133 (1945).



Fig. 13.—Butane sorption on low volatile bituminous coal 0°. Desorption points are solid.



Fig. 14.—Butane sorption on Bruceton coal 0°. Desorption points are solid.

isobutanes in penetrating pores are 4.9 and 5.6 Å. On this basis at 0° the first group of coals must have a major fraction of pores with openings between 4.9 and 5.6 Å. in diameter and Rock Springs coal has a pore diameter greater than 5.6 Å.

Studies on dehydrated chabasite<sup>24,27</sup> and Linde molecular sieves 4A and 5A in our laboratory indicate that adsorbents that will adsorb normal butane but not isobutane at 0°, will adsorb nitrogen rapidly at  $-195^{\circ}$ , and the adsorption of nitrogen will have the ordinary dependence on temperature. Low adsorption of nitrogen at  $-195^{\circ}$  and anomalous variation of amount adsorbed with temperature are found only on sorbents that will adsorb neither normal nor isobutane. These pores are assumed to be smaller than 4.9 Å., apparently the order of 4.0 Å., the diameter of the nitrogen molecule. The sorption data on coal do not follow this pattern with the exception of cannel coal. A simple explanation of these phenomena is that pores of most coals de-



Fig. 15.—Butane sorption at 0° on Rock Springs coal. Desorption points are solid.

crease in diameter from about 5 to 4 Å. as the temperature is decreased from 0 to  $-195^{\circ}$ . According to this postulate at  $-78^{\circ}$  the pores should have some intermediate diameter and adsorption of large amounts of carbon dioxide is possible.<sup>16</sup>

Finally, some of the quantitative data in Table III will be compared. The surface areas estimated from nitrogen isotherms at  $-195^{\circ}$  vary from 0.4 to 59.2 m. $^2$ /g., higher areas being obtained after the nitrogen had been exposed to the sample at -78 or  $0^{\circ}.^{28}$  Areas from normal butane at  $0^{\circ}$  were greater than those from nitrogen, and with the exception of Rock Springs coal areas from isobutane at  $0^{\circ}$  were considerably lower than values from the normal isomer. Areas from water isotherms usually were greater than butane isotherms, with the exceptions of equal values for Rock Springs coal and smaller areas from water than from normal butane sorption on cannel coal. Areas from methanol isotherms were the largest in every case.  $V_{\rm m}$  values for different sorbates on the same coal show a similar variability, with the exception of the isotherms for methanol and water for which  $V_{\rm m}$  values are usually more nearly equal than the surface areas. This relationship suggests that the sorption of water and methanol may occur on a fixed number of sites.

The volume sorbed at saturation pressure (actually at a relative pressure of 0.98) computed as normal liquid at that temperature is also presented in Table III. For a given coal, nitrogen volumes where available are lower than values for other adsorbates. Liquid volumes for methanol, water and *n*-butane frequently exceed the pore volume as measured by helium-mercury density method, in one instance by a factor of more than three.

Liquid volumes at saturation that exceed the pore volume may result from one or all of the following factors: expansion of the system of pores



Fig. 16.—Butane sorption on lignite 0°. Desorption points are solid.



Fig. 17.—Butane sorption cannel coal 0°. Desorption points are solid.

due to sorption; imbibition, a mild chemical interaction of sorbate and coal involving a decrease in volume; or contraction of adsorbate. For porous inorganic materials, the liquid volumes at saturation are usually approximately equal for several adsorbates on the same solid. This generalization does not hold for the coal samples studied.

# Discussion

Sorption studies of coal have led to contradictory interpretations regarding the surface area and pore structure of coal. Pertinent experimental evidence in the present paper and in the literature will be examined starting with the least contradictory data. As shown in Table III and by other published data, all coals have an appreciable pore volume as measured by the helium-mercury density method and similar techniques. Zwietering and van Krevelen<sup>9</sup> studied a hituminous coal with a pore

<sup>(28)</sup> The higher areas involving principally gas trapped in the solid at -78 and 0° represent minimum values of the area of the solid, but not the areas accessible to nitrogen at  $-195^{\circ}$ .

volume 0.134 cc./g. (by He-Hg method) in a mercury porosimeter. At a pressure of 1,000 atmospheres, 0.088 cc./g. of mercury entered the coal. With the angle of contact of mercury on coal taken as 140°, pores with openings (diameters) larger than 200 Å. should fill with mercury at 1,000 atmospheres. The distribution curve of pore volume against pore radius showed a maximum at a diameter of 1,000 Å. From the pore distribution curve, a surface area of  $1.1 \text{ m}.^2/\text{g}$ . was calculated compared with an area by nitrogen adsorption at  $-195^{\circ}$  of  $1.8 \text{ m}.^2/\text{g}$ . In view of the assumptions involved in the calculation, the agreement can be considered sufficiently close to support the postulate that most of the surface of the coal sample measured by nitrogen lies in pores with diameters larger than 200 Α.

Nitrogen (Fig. 5) and argon<sup>6</sup> isotherms at about the boiling point of the sorbate have hysteresis loops that close or very nearly close at relative pressures of about 0.4. For these isotherms, average pore diameters may be estimated by the Kelvin equation,<sup>24</sup> using the relative pressure of the steepest portion of the desorption curve. The average pore diameter computed from Fig. 5, 28.3 Å., agrees with values of about 32 Å. from argon isotherms.<sup>6</sup> However, the volume of pores of this average diameter is very small (about 0.001 cc./g. of coal) compared with the total pore volume obtained from density data (Table III and reference 3).

Other measures of average pore diameters indicate that a major portion of the pores have openings in the range of molecular dimensions. The relative sorptions of normal and isobutane in the present paper suggest that pore openings at 0° may vary between 4.9 and 5.6 Å. The activated physical sorption of nitrogen at  $-195^{\circ}$  reported by Maggs,<sup>12</sup> Zwietering and van Krevelen,<sup>9</sup> Kini,<sup>16</sup> and the present paper should not be expected for pores of this size, but for smaller pores the order of 4 Å.

Zwietering and van Krevelen<sup>9</sup> determined the adsorption of nitrogen and methane on the coal described above at 0 to 50° and from the temperature dependence and appropriate assumptions estimated a surface area of 90 m.<sup>2</sup>/g. This calculation in effect assumes that the adsorption at  $-195^{\circ}$ at a given pressure is about 200 times the sorption at 0° which agrees with factors of 50–100 for charcoals. However, our work with nitrogen on Linde molecular sieve 5A indicates a factor of only 13. Thus, the uncertainties of the area of 90 m.<sup>2</sup>/g. may be regarded as relatively large.

Maggs<sup>11,12</sup> postulated that the small adsorption at liquid nitrogen temperatures might result from either activated diffusion of sorbate molecules or closing of pores at the lower temperature. Bangham and Franklin<sup>29</sup> and Maggs<sup>30</sup> determined the coefficient of linear expansion of coal in the vicinity of room temperature to be 3.3 to  $4.2 \times 10^{-5}$  degrees<sup>-1</sup>, and we have determined the linear changes by direct optical measurement of a polished sur-

(29) D. H. Bangham and R. E. Franklin, Trans. Faraday Soc., 42B, 289 (1946).

(30) R. L. Bond, M. Griffith and F. A. P. Maggs, Disc. Faraday Soc., 3, 29 (1948).

face of coal at room and liquid nitrogen temperatures. Although our method was not highly precise, the maximum linear expansion coefficient found for Bruceton coal was  $4.8 \times 10^{-5}$ . Schuyer and van Krevelen<sup>31</sup> measured the linear coefficients of thermal expansion of a series of vitrinites from 20 to  $45^{\circ}$  and observed values decreasing from  $4 \times 10^{-5}$  to  $1 \times 10^{-5}$  for coals increasing in carbon content from 85 to 96%. Thus, in cooling from 0 to  $-195^{\circ}$  the volume of coal decreases by 3% or less.

The present experimental data suggest that pores of coal are about 5 Å. at  $0^{\circ}$  and 4 Å. at  $-195^{\circ}$ . A simple calculation assuming parallel platelets and no change in volume of the coal substance can account for a change of the separation between platelets from 5 to 4 Å. with only a 3% change in volume. The thickness of the platelet was taken as 36 Å. and the separation as 5 Å., corresponding to a surface area of 200 m. $^2$ /g. (actually only half the area of the platelets due to the inability of introducing more than one layer of molecules in a pore of 5 Å.), and pore volume = 0.099 cc./g. The change in volume is then (36 + 5)/(36 + 4) = 1.025 or 2.5%. This simple picture, however, must be regarded as unrealistic, in view of experiments of Zwietering and van Krevelen,<sup>9</sup> who determined specific volumes of a coal by displacement of helium at temperatures from -195 to  $+100^{\circ}$ . The volume increased linearly with temperature yielding a linear coefficient of  $4.2 \times 10^{-5}$ . With this coal, apparently pores were not blocked at the lower temperature nor was there adsorption or slow diffusion of helium as observed by Dryden and in the present paper for anthracite. For this coal the coal substance itself as measured by helium had about the same expansion coefficient as the coal substance plus pores.

Thus, it may be concluded that areas from nitrogen and argon sorption at low temperatures are usually low due to the inability of these molecules to diffuse into the pores at a reasonable rate. Larger areas, but still smaller than might be expected if activated diffusion were not involved, should be obtained from isotherms in which the temperature has been increased to -78 to  $0^{\circ}$  and then decreased again to  $-195^{\circ}$ .

Polar molecules capable of hydrogen-bonding such as water, methanol, ammonia and methylamine are sorbed on coal in larger amounts. Before considering isotherms of this type, we will digress briefly to consider certain characteristics of physical adsorption of non-polar molecules in porous solids that are generally accepted by adherents of the B.E.T. method:

1. On a given adsorbent, isotherms of different adsorbates give essentially the same surface area.

2. For the same adsorbent, the volumes at saturation computed as normal liquid for different adsorbates are essentially equal.

3. The five types of isotherms of Brunauer's classification<sup>32</sup> may be used to characterize, in at least a rough way, the pore structure of the solid.

(31) J. Schuyer and D. W. van Krevelen, Fuel, 34, 345 (1955).

(32) S. Brunauer, "Physical Adsorption," Vol. I, Princeton University Press, Princeton, N. J., 1945.

The shape of the isotherms of water and methanol (in the present paper, for example) and methylamine<sup>7</sup> are not at all characteristic of a system of pores of molecular dimensions. Most of these isotherms are of Type III characteristic of pores of appreciable dimensions. Hysteresis loops on most inorganic solids close at relative pressures of about 0.4, but for polar sorbates on coal the loops usually do not close until the relative pressure is decreased to zero. Surface areas computed from water, methanol and methylamine isotherms on the same coal usually deviate widely. Similarly, the liquid volumes at saturation for a given coal are not equal and often exceed the pore volume by the heliummercury density method appreciably, as shown in Table III. On a South African coal<sup>7</sup> with a pore volume of 0.042 cc./g., the liquid volumes at saturation were 0.142 and 0.396 fcr methanol and methylamine, respectively.

Another disquieting feature of the interpretation of sorption phenomena on coal is the anomalous densities obtained by displacement of liquids, especially water and methanol. Franklin<sup>3</sup> observed that the densities of coals in methanol always exceed the corresponding helium density and that densities in water frequently did. Either the coal or the methanol must decrease in volume and, since coal is known to swell on immersion in methanol, it was assumed that methanol contracts. This contraction was surprisingly large; Franklin calculated that methanol occupies only 40% of its normal liquid volume if the contraction is limited to only the first "adsorbed" layer. For a series of coals the contraction of the methanol was proportional to the heat of wetting of the coal; it corresponded to about 60% of the liquid volume of methanol required to form a monolayer as computed from heat of wetting data. Thus, for methanol there is an intimate relationship between heat of wetting, "surface area" and contraction. Apparently there are no examples of inorganic sorbents in which densities in liquids exceed corresponding helium densities; however, this phenomenon has been observed for water on cellulose and wood and methanol on partly activated wood charcoal.

A simpler explanation than contraction of the immersion liquid is that the liquid penetrates the "solid" structure of coal,<sup>6</sup> either by entering inaccessible pores or by forming a combination with coal in which the volume of the methanol-coal complex is less than the sum of the separate solid and liquid volumes. The latter process may be similar to the interaction of the large ethylenediamine molecule, with coal, which Bangham and Dryden<sup>33</sup> considered to be chemisorption. Similar phenomena appear to occur with water on coal, but the effect may be largely obscured by the inability of water to wet carbonaceous materials. For low rank coal K, n-hexane and benzene appear to penetrate both the accessible pores and the "solid" structure in the same manner as methanol, and for this coal the isotherms of methanol and *n*-hexane yield essentially the same surface areas.<sup>34</sup>

Bond, Griffith and Maggs<sup>30</sup> measured the swelling of coal at saturation pressure, and, for example, coal K expanded 16, 9 and 2% by volume when saturated with methanol, benzene and water. The swelling of this coal in benzene is exceptionally large, apparently reflecting the same anomaly as observed in the density studies. Maggs and coworkers<sup>30,35</sup> gave the following quantitative relationship, said to hold for all coals, for the sorption of water and methanol at saturation pressure

$$V - P = S + C$$

where V is the volume of water or methanol as normal liquid per gram of coal, P is the pore volume (from particle and helium densities) per gram, S is the increase in bulk volume by swelling per gram and C is the contraction per gram as determined by density studies. This equation states that the difference of the liquid volume at saturation minus the pore volume equals the swelling plus volume contraction of the coal-sorbate system.

The fact that coal swells appreciably may explain some of the anomalous features of sorption isotherms, such as the lack of constancy of liquid volumes at saturation for water, methanol and methylamine, and the failure of hysteresis loops to close at relative pressures of 0.3 to 0.4. The lack of agreement between surface areas cannot be explained as easily, since expansion of the pore system<sup>36</sup> should not increase the area appreciably unless this process enlarges void spaces accessible only to helium so that larger molecules can enter. Furthermore, expansion does not provide an explanation for "contraction" of the coal-sorbate system.

As a final topic, evidence is presented that the sorption of polar molecules on carbonaceous solids often gives unusual results that are not typical of physical adsorption. For untreated carbon blacks, surface areas from isotherms of non-polar molecules agree well with areas computed from electron micrographs, assuming the particles to be smooth, solid spheres.<sup>37</sup> The sorption of polar molecules, such as water, methanol, ammonia and methylamine, was strongly a function of the oxygen content. For blacks containing very small amounts of oxygen, the sorption of polar molecules was considerably less than that of non-polar molecules of the same molecular volume, and isotherms of some polar molecules were not S-shaped. The sorption of polar molecules relative to non-polar molecules of the same size increased with the oxygen content of the carbon black. A sample of lampblack contained sufficient oxygen to form about three chemisorbed layers on the surface, and the sorption of water and ammonia was more than four times that of nitrogen. The sorption of methylamine also exceeded that of nitrogen by a significant amount, indicating that the large sorption of polar molecules was not a function of molecular size. On removal of the oxygen complex of lampblack by evacuation at high temperatures, the nitrogen isotherm remained essentially unchanged, whereas the

<sup>(33)</sup> D. H. Bangham and I. G. C. Dryden, Fuel, 29, 291 (1950).

<sup>(34)</sup> S. J. Gregg, Proceedings of a Conference on the Ultrafine Structure of Coals and Cokes, The British Coal Utilisation Association, London 1944, pp. 100-117.

 <sup>(35)</sup> F. A. P. Maggs, *Trans. Faraday Soc.*, 42, 284 (1946).
 (36) W. K. Hall, W. H. Tarn and R. B. Anderson, THIS JOURNAL, 56, 688 (1952).

<sup>(37)</sup> R. B. Anderson and P. H. Emmett, J. Appl. Phys., 19, 367 (1948).

sorption of water and ammonia was greatly decreased. From this information we may conclude that sorption experiments with water, ammonia, methanol and methylamine on carbon black may be useful for studying the oxygen complex,<sup>38</sup> but not for determining surface area. The sorption of water appears to be the most sensitive to changes in oxygen content.

Unusual sorption phenomena have been observed for polar sorbates, such as water, on polymeric carbonaceous materials containing oxygen and/or nitrogen.<sup>39–48</sup> These substances include many natural products, some of which are similar to or may be regarded as possible precursors of coal, and a variety of synthetic polymers. Pertinent results may be summarized as follows.

1. Water sorption usually greatly exceeds nitrogen sorption. Areas of starches from nitrogen isotherms agree with those estimated from micrographs but were less than 1/100 as large as areas from water isotherms.<sup>49</sup> Sorption of water has been used to estimate the number of polar groups in polymeric materials.

2. Water isotherms on these materials and on many coals have similar shapes, including hysteresis loops that do not close until the pressure is decreased to zero.

3. On cellulose surface areas from sorption of water, sulfur dioxide, ammonia and hydrogen chloride are about 200 times the area from nitrogen isotherms.<sup>50</sup>

4. Densities of wood,<sup>51</sup> cotton fibers and viscose rayon<sup>52</sup> determined by displacement of water exceeded helium densities. Early workers<sup>52-54</sup> explained the anomalous water densities by contraction (compression) of the displacing medium. Recent workers,<sup>55,56</sup> however, have regarded the compression hypothesis as unrealistic and have suggested that the contraction arises from interactions

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(47) E. F. Mellon, A. H. Korn and S. K. Hoover, *ibid.*, 70, 3040 (1948).
 (48) I. Pauling *ibid*. 67, 555 (1045).

(48) L. Pauling, *ibid.*. **67**, 555 (1945).

(49) N. N. Hellman and E. H. Melvin, J. Am. Chem. Soc., 72, 5186 (1950).

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Fibers," Elsevier Press New York, N. Y., 1946, pp. 73-86. (56) J. A. Howsman, "High Polymers," Vol. V, Part I, Interscience Publishers, 1954, pp. 393-441. between water and the polymeric material similar to the decrease in volume observed in mixing liquids such as alcohol and water.

Sorption phenomena on natural and synthetic polymers are similar to those on coal with respect to the magnitude of sorption of polar molecules and nitrogen, shape of isotherms, and the type of the hysteresis. The observation that  $V_{\rm m}$  values for water and methanol on a given coal are more nearly equal than surface areas (Table III) may indicate sorption on polar sites rather than coverage of a given area. The sorption of water on dissolved-precipitated Bruceton coal was of the same magnitude as sorption on the raw coal, but the shapes of the isotherms were different. Unless this "solution" process involves only dispersion into relatively large aggregates, the similarities of the isotherms of raw and dissolved-precipitated coal would not be expected. An explanation on the basis of polar sites seems simpler. Another type of imbibition involving hydrocarbons may occur on coals containing large quantities of waxy materials, such as cannel coal and British coal K.

This discussion surely indicates that sorption data on coal are difficult to interpret. The following conclusions are offered, some of which are definite and others tentative:

1. Coals have a sizable pore volume, the porosities varying from 2.5 to 18% on the coals measured.

2. For most coals, an appreciable fraction of the pores have openings (diameters) of 4.9 to 5.6 Å. at 0° and about 4 Å. at  $-195^{\circ}$ .

3. Low-temperature nitrogen isotherms give the area of pores with larger diameters (>4 to 5 Å).

4. The sorption of polar molecules is apparently complicated by swelling and inhibition, and even if these factors are unimportant we may question the physical meaning of surface areas determined by sorption methods in systems of pores of molecular dimensions. Isotherms of water, methanol and methylamine may give a measure of the number of polar groups in coal.

5. Sorption studies have provided useful information regarding the physical and chemical nature of coal. The sorption of either polar or nonpolar molecules may be useful in explaining and controlling physical and chemical processing of coal; however, valid, meaningful relationships will require a keen insight into both the process involved and the nature of sorption on coal.

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# HYDROTHERMAL REACTIONS BETWEEN CALCIUM HYDROXIDE AND AMORPHOUS SILICA IN ATMOSPHERES OF UNSATURATED STEAM

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The study of the hydrothermal reaction between calcium hydroxide and amorphous silica was extended by investigations of the hydrothermal reactions under lowered vapor pressure, *i.e.*, from saturation down to  $\bot$  atmosphere within the temperature range 160-200° for periods of time up to 48 hr., in order to determine the conditions for a possible transformation boundary of the low temperature phase. It was established that there must be a transformation pressure boundary at about 60% of the vapor saturation; at a pressure higher than the boundary pressure a transformation of the low temperature phases into high temperature phases takes place, at lower pressure the low temperature phase remains unchanged even in the presence of an excess of uncombined calcium hydroxide. The high temperature phases are those shown in the earlier investigation. The pressure boundary is independent of the temperature within the range studied. The lowered pressure causes a decrease of the hydrate water of the low temperature compound. The X-ray photographs of the new-formed dehydrated compounds show only those diffraction lines which are characteristic for the low temperature phase indicating that the new, very minute elements are retained in their earlier arrangement, or/and that the repeating patterns of the low temperature phase.

In an earlier paper the present author and collaborators have given their results of the investigations on the hydrothermal reaction between calcium hydroxide and amorphous silica, in an atmosphere of saturated steam and within the temperature range  $120-220^{\circ}$ .<sup>1</sup> The investigation has now been extended to include an examination of the influence on the reaction of varying pressures. On introducing this new factor into the experiments the possibility of varying the conditions increases considerably. The experiments conducted in the present investigation have therefore been restricted to the temperature range of the greatest importance and interest and to a reasonable period of time. The experimental conditions involved are such that estimation of the formation of some minerals and elucidation of the properties of silica may be possible.

#### Experimental

The material and the autoclave earlier described were used.<sup>1</sup> In the experiments mentioned below the autoclave was equipped with two valves connected in series so that the pressure in the autoclave could be lowered to the required value without difficulty. The adiabatic consumption of heat on diminution of the pressure and the heat of vaporization of the excess water were balanced without any lowering of the temperature. This procedure required a rather short period of time (20 min.).

As the lowering of the pressure involves many possibilities for variation of the experimental conditions, the experiments must be limited to the range at the boundary where the low temperature phase B is transformed into high temperature phases within a period of about 48 hr. The experiments were performed at the temperatures 160, 180 and 200°. The experiments were therefore of two kinds. The preliminary experiments showed that the low temperature phase was formed to a considerable extent during the heating-up period (20 min.) leaving only a part of the calcium hydroxide unreacted. The shortest period of time which could be used for the autoclave synthesis was therefore this heating-up period. In this type of experiment the pressure in the autoclave was lowered immediately after the required temperature was attained. These experiments were intended to show whether calcium hydroxide, silica and the low temperature phase could react in an atmosphere of partial vapor pressure.

As the formation of the low temperature phase was complete after 2-3 hr. at  $160-200^{\circ}$  in saturated steam, the other type of experiment was aimed at elucidating the possible formation of new phases originating from the low temperature phase in connection with the lowered pressure. The lowering of the autoclave pressure was therefore performed after a reaction period of 2–3 hr. in saturated steam. The formation of the phases under these conditions was studied for periods of 2 to about 45 hr. Because of the character of the experiments the only reaction mixtures of interest were those containing the molar proportions  $CaO:SiO_2 = 0.67:1, 1:1$  and 1.5:1. The pressure was lowered to about 60 and 30% of that of saturated steam and also down to atmospheric pressure.

### **Results and Discussion**

In the autoclave mixtures of lime and silica several compounds are always formed and, as has been shown earlier, a real equilibrium cannot therefore have been reached within the rather short periods of time employed. The mixtures, however, must indicate a certain succession of formation of the compounds, which is of importance for the estimation of the general reaction calcium hydroxide-silica-water. It can be anticipated that the lowering of the vapor pressure in the autoclave will alter the conditions for the formation of the compounds and there are three essential points which will be discussed here below concerning the compounds formed under a reduced pressure, namely: the consumption of calcium hydroxide available at the actual moment of the reactions, the hydrate water content of the products, and the establishment of the solids formed.

The Combination of Calcium Hydroxide.—In the first type of experiments the autoclave was cooled down immediately when the maximum temperature was attained after the period required for heating up (20 min.). The composition of the reaction mixture after this period may therefore represent the starting point of the reaction at the given temperature. In all experiments at  $160-200^\circ$ with the mixtures of lime-silica 0.67:1 and 1:1 almost all the lime was combined during this short heating-up period (Tables I, II). On the other hand, the mixture of lime-silica ratio 1.5:1 formed immediately after the heating-up period, a silicate which had a molar proportion lime:silica 1.2:1 (Table III). The combination of lime with silica is obviously dependent to a certain degree on the lime available. The active surface of the silica where the ratio is 1.5:1 must be saturated immediately on mixing, and the reaction proceeds during the heating-up period, as indicated by the large excess of uncombined lime compared with that

<sup>(1)</sup> G. O. Assarsson and E. Rydberg, This JOURNAL, 60, 397 (1956).

found in the products from the mixtures poor in lime (0.67:1 and 1:1). The low temperature phase could therefore reach as high a lime saturation as 1.2:1. When the excess of water in the autoclave was removed immediately after the heatingup period, so that the vapor pressure was lowered to about 60% or less, the lime still uncombined was only slowly consumed on continued heating at the lowered pressure. After this treatment (24 hr.) the molar mixtures 0.67:1 and 1:1 contained little or no free calcium hydroxide, while the mixture 1.5:1 gave a silicate somewhat richer in lime (1.3:1) than the phase first formed. The X-ray photographs of all of these silicate phases showed only the pattern of the low temperature phase B.

Saturation of the silica up to a monosilicate composition could be attained by autoclaving the mixtures 0.67:1 and 1:1 at  $160-200^{\circ}$  for about 2-3 hr. On the other hand, the mixtures 1.5:1contained a substantial amount of uncombined lime after such a treatment. In all cases only the reflection lines of the low temperature phase B were found in the X-ray photographs of the silicate formed. The study of the stability of the phase B in an atmosphere of unsaturated vapor was therefore performed with preparations autoclaved for 2 hr. (mixture 0.67:1) or 3 hr. (mixture 1:1 and 1.5:1) in saturated steam at the chosen temperature, whereupon the pressure was lowered to the desired partial pressure.

#### TABLE I

The mixture CaO:SiO<sub>2</sub> = 0.67:1, autoclaved at lowered pressure. Phases: B (low temperature phase) = 1.5-1.0 CaO·SiO<sub>2</sub>·nH<sub>2</sub>O; T, G, X and H, synthetic phases resembling the minerals tobermorite (CaO·SiO<sub>2</sub>·H<sub>2</sub>O) (T); gyrolite (2CaO·3SiO<sub>2</sub>·2H<sub>2</sub>O) (G); xonotlite (3CaO·3SiO<sub>2</sub>·H<sub>2</sub>O) (X), hillebrandite (2CaO·SiO<sub>2</sub>·H<sub>2</sub>O) (H).

SUITE	Pressure

sa	turated	lowered		Free	Ca-silicate			
Time, hr.	Kg./ cm. <sup>2</sup>	Time. hr.	Kg./ cm. <sup>2</sup>	lime % CaO per ign.	molar ratio CaO:SiO H2Oª	) 2: Phase		
			Temp	<b>.,</b> 160°				
0	6.3	0		3.5	0.58:1:1.15	В		
0	6.3	24	4	0	0.67:1:1.00	в		
2	6.3	0		0	0.66:1:1.50	В		
2	6.3	2	4	0	0.66:1:1.40	в		
2	6.3	4	4	0	0.66:1:1.20	В		
2	6.3	46	4	0	0.66:1:0.90	в		
2	6.3	22	2	0	0.66:1:1.00	В		
2	6.3	22	1	0	0.66:1:0.85	в		
Temp., 180°								
0	10.2	0		2.4	0.60:1.0.95	в		
0	10.2	24	6	0	0.66:1:1.05	В		
2	10.2	0		0	0.67:1:1.20	В		
2	10.2	4	6	0	0.67:1:1,20	В		
2	10.2	46	6	0	0.67:1:0.95	B(T, G?)		
2	10.2	22	3	0	0.67:1:0.90	В		
2	10.2	22	1	0	0.67:1:0.85	в		
<b>T</b> emp., 200°								
0	15.8	0		1.2	0.60:1:1.05	в		
0	15.8	8	9	0	0.67:1:1.05	в		
0	15.8	24	9	0	0.67:1:0.75	в		
2	15.8	0		0	0.67:1:1.10	в		
2	15.8	22	12	0	0.67:1:1.20	B (T, G)		
2	15.8	4	9	0	0.67:1:1.15	В		
3	15.8	21	9	0	0.67:1:0.90	B (T, G)		
2	15.8	22	4	0	0.67:1:0.85	в		
2	15.8	22	1	0	0.67:1:0.80	в		

<sup>a</sup> Deviation of the molar ratio from the correct value is caused by small amounts of carbonate.

TABLE	Π
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The n	nixture	CaO:Si(	$)_2 = 1$	1:1, aut	oclaved at low	vered pres
	sure.	Symbo	ls for	the pha	ses see Table I	I
Pre	ssure	Press	ure	Free	Ca-Silicate	
satu	rated	lowe	red	lime	molar ratio	
hr.	cm. <sup>2</sup>	hr.	cm. <sup>2</sup>	per ign.	H <sub>2</sub> O	Phase
	01111		Tem	p. 160°		
0	63	0		4 5	0 90.1.1 50	в
Ň	6.3	4	4	5.6	0.85.1.1.50	B
Ô	6.3	24	4	0.0	1 00:1:1 50	B
3	6.3	0		0	1 00 1 1 50	B
3	63	4	4	0	1 00:1:1 50	B
3	6.3	21	4	Õ	1 00:1:1 25	B
3	6.3	21	2	Ő	1 00 1 1.05	B
3	6.3	21	1	Ő	1.00:1:1.05	В
•	0.0		Ten		0	
0	10.2	٥		55	0 85.1.1 50	в
0	10.2	4	6	4.0	0.88.1.1.05	B
0	10.2		0	0.5	0.03.1.1.05	B
3	10.2	24	0	0.0	0.00.1.1.20	B
3	10.2	4	6	0	0.99.1.1.20	B
3	10.2	21	6	0	1 00 1 1 00	B
3	10.2	45	6	0	1 00.1.0 90	хтв
3	10.2	21	3	0	0 99.1.1 05	R
3	10.2	21	1	0	0.99.1.1.05	B
U	10,2	21	Ten	on. 200	0	2
0	15 0	0		E 0	0 95.1.1 10	D
0	15.0	0		0.3	0.06:1:1.10	в
0	10.0	4	8 0	0.7	0.96.1.0.95	D D
2	15.8	24	9	0.0	0.90.1.0.85	в
2	10.0	21	10	0	0.99.1.1.13	ы утр
2	10.0	21	12	0	0.99.1.0.70	л, 1, D В
2	15.8	4 01	9	0	0.00.1.0.75	ы утв
3	10.0	21	9	0	0.99.1.0.75	R
2	15.0	21	4	0	0.33.1.0.93	B
	O	41		<b>N</b>	0	1.1

The silicates formed from the mixtures 0.67:1 and 1:1 did not show a changed molar ratio lime:silica in any experiments (Table I and II). In most cases the only silicate established in the products was the low temperature phase B. Some exceptions, however, could be shown. The mix-ture 0.67:1 treated at  $180^{\circ}$  for 2 hr. in saturated vapor (10.2 kg.) and after that for 46 hr. in an atmosphere of 60% saturation (6 kg.) recrystallized very slightly. Two other preparations, the mixture 1:1 autoclaved at 180°, first for 3 hr. in saturated vapor (10.2 kg.) and afterwards for 45 hr. at 60% saturation (6 kg.), and also the 1:1 mixture autoclaved at 200°, first for 3 hr. in saturated vapor (15.8 kg.) and afterwards for 21 hr. at 60% saturation (9 kg.), showed rather a substantial recrystallization; the new-formed phases will be discussed more thoroughly below. Thus the experiments show that the low temperature phase B does not undergo a transformation within 45 hr. at  $180^{\circ}$  or 21 hr. at 200° when the vapor pressure is lowered to below 60% of the saturation value. At saturated vapor pressure the trans-formation discernible by X-rays begins within shorter periods of time; for the mixture 0.67:1 and 1:1 within about 30 hr. at 180° and about 10 hr. at 200°. A lowering of the pressure in the autoclave to 60% or less of the saturation value seems to be sufficiently substantial to preclude a recrystallization of the phase B at the temperatures examined. It can therefore be regarded as established that the pressure boundary of the transformation range of the phase B must be close to 6 kg. vapor pressure on autoclaving at 180° for 48 hr. and to 9 kg. pressure on autoclaving at 200° for 24 hr.

The combination of lime in the mixture 1.5:1 has its special interest (Table III). In this case

TABLE III	
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The mixture  $CaO:SiO_2 = 1.5:1$ , autoclaved at lowered pressure. Symbols for the phases see Table I.

Pre	ssure,	Press	ure,	lime	Ca-silicate	
Fime	Kg /	Time	Ka/	70 C3U	Can Sine	
hr.	Cn1.2	hr.	cm. <sup>2</sup>	subst.	H <sub>2</sub> O	Phase
		,	Te	mp., 160	)°	
0	6.3	0		10.0	1.20:1:1.60	В
0	6.3	4	4	8.0	1.30:1:1.70	В
0	6.3	24	4	7.5	1.30:1:1.60	В
3	6.3	0	2.2	7.5	1.30:1:1.90	В
3	6.3	4	4	7.0	1.25:1.1.65	В
3	6.3	21	4	7.0	1.30:1:1.35	В
3	6.3	21	2	4.5	1.35:1:1.25	В
3	6.3	21	1	6.0	1.30:1:1.25	В
			Te	mp., 180	)°	
0	10.2	0		11.0	1.15:1:1.80	В
0	10.2	4	6	7.0	1.20:1:1.40	В
0	10.2	24	6	5.5	1.30:1:1.35	В
3	10.2	0		6.0	1.30:1:1.85	В
3	10.2	4	6	5.0	1.35:1:1.80	в
3	10.2	21	6	5.0	1.30:1:1.30	В
3	10.2	45	6	4.5	1.40:1:1.25	$B(\mathbf{H}, \mathbf{X})$
3	10.2	21	3	5 0	1.35:1:1.20	В
3	10.2	21	1	4.5	1.35:1:1.20	В
			Te	mp., 200	)°	
0	15.8	0		8.5	1,20:1:1,65	В
0	15.8	4	9	7.5	1.25:1:1.50	В
0	15.8	24	9	8.0	1.25:1:1.10	В
3	15.8	0		6.0	1.25:1:1.40	В
3	15.8	21	12	3.5	1.40:1:1.10	H, X, $B(T)$
3	15.8	4	9	5.0	1.30:1:1.45	В
3	15.8	21	9	3.5	1.40:1:1.05	H, X, T,
3	15.8	21	4	4.5	1.35:1:1,10	В
3	15.8	21	1	5.C	1.35:1:1.05	В

there is always an excess of lime. Heating of the samples in saturated vaper at 160-200° for 3 hr. leads to the formation of a silicate having a lime: silica ratio of 1.3:1. Continuation of heating for a further 21 hr. does not generally change this proportion, in spite of the excess of lime. One experiment, however, 200°, 3 hr. saturated vapor (10.2 kg.) followed by 21 hr. 60% saturation (9 kg.), gave a silicate richer in lime (1.4:1). The silicate phases were all shown to be phase B, except the substance just mentioned prepared at  $200^{\circ}$ . The preparation at 180°, 3 hr. saturated vapor and 45 hr. 60% saturation showed a weak indication of beginning recrystallization. Thus, the excess of lime in the reaction mixture is not generally consumed for formation of silicates more rich in lime than the compound formed after 3 hr. autoclaving in the saturated steam. If a recrystallization of the phase B occurs it is connected with a consumption of the uncombined lime. The boundary of the recrystallization of the phase B even in the presence of free lime is at the same pressure and temperature as mentioned above concerning the lime: silica proportion 0.67:1 and 1:1.

The Hydrate Water Content of the Silicates.— At present it seems to be impossible to determine directly or to make a rather accurate calculation of the hydrate water content of the silicates, particularly of those formed in the hydrothermal reaction at lower temperature and during short periods of time, the compounds which here are assigned as the low temperature phase B. The reasons for this are the almost always occurring mixture of several phases in the hydrothermal products and a particle size which can often be sub-microscopical and also difficult to define with the aid of X-rays. The phase B which is the product formed in most of the experiments in the present investigation, has been estimated by Taylor<sup>2</sup> to correspond to the formula  $CaO:SiO_2$ :  $H_2O = 1.0-1.5:1:2.0-2.5$ . The water content depends to a certain degree on the treatment of the substance after the autoclaving. In the present and the earlier investigations the substances were prepared in accordance with the treatment earlier described and the final removal of the last traces of adhering water and acetone or ethyl ether was performed by drying the substance over anhydrous calcium chloride and sedium hydroxide for 24 hr. at a pressure of about 20 mm.<sup>1</sup> Repeated experiments of this kind gave substances with water contents of good agreement.

In the present experiments the phase B prepared in saturated vapor corresponds to a compound containing 1.5 moles of water. The lowered pressure may influence the water content of this phase B. In some experiments, chiefly in those with the reaction mixture 0.67:1, there occurs a certain amount of unreacted amorphous silica, which could also affect the calculation or determination of the water content of the autoclaved products. In the earlier investigation the water content of the amorphous silica, treated in the same way as the reaction mixtures was found to be 6-8%.<sup>1</sup> If it is assumed that the calcium silicate formed on autoclaving this reaction mixture 0.67:1 is a monosilicate hydrate, the amorphous silica remaining, having a water content of 8%, would influence the water content calculated for the silicate only slightly (<0.1 mole H<sub>2</sub>O). The decrease of the water caused by a lowering of the pressure must therefore be due essentially to a dehydration of the silicate hydrates. A comparison of the relation in the three types of mixtures between the temperature, the vapor pressure used for the syntheses and the water content of the silicates formed leads to the following conclusions. The change in water content of the silicates with varying vapor pressure and different periods of reaction time is similar in its general character, when products prepared at the same temperatures are compared. Thus this change is not dependent on the molar ratio of the reaction mixtures which is in agreement with the statement made above that the phase B is the principal component of all the low temperature products. When the pressure is lowered and the reaction period is extended, there is a difference between the water content of the mixtures. The mixtures poor in lime (0.67:1 and 1:1) yield compounds the composition of which approaches to  $CaO:SiO_2:H_2O = 1:1:1$  on the assumption that a monocalcium silicate is formed. The mixture 1.5:1, on the other hand, gives under the same experimental conditions at 160 and 180° a composition corresponding to about  $CaO:SiO_2:H_2O =$ 1.3:1:1.3. When this compound is autoclaved at 200° and at a pressure lower than 60% of vapor

(2) H. F. W. Taylor, J. Cham. Soc., 163 (1953).

saturation the molar proportion of the silicate becomes about 1.3:1:1. Thus in all autoclave experiments with a pressure reduced to 60% or less of the saturation value there is a substantial decrease of the hydrate water of the silicates which have been synthesized earlier in an atmosphere of saturated steam.

Those samples which have undergone a more or less thorough recrystallization during the autoclaving naturally diverge and show a lower water content, substantially due to a formation of silicates with low hydrate water content (those compounds resembling xonotlite or gyrolite, CaO:  $SiO_2:H_2O = 3:3:1$ , respectively, 2:3:2).

The Calcium Silicate Hydrate Formed.-It is expedient to discuss in rather more detail the identification of the phases formed which have to be compared with those of the earlier experiments and with those of the investigations of other authors. The low temperature phase B was regarded, in the earlier paper, as a mixture of two poorly crystallized compounds with somewhat similar patterns, a monocalcium silicate and another silicate more rich in lime, *e.g.*, of the molar ratio 3:2. It has also been questioned whether the phase B could not be a solid solution of two structurally similar phases, but according to Taylor<sup>3</sup> this could not agree with the varying intensities of some of the reflection lines; a more suitable theory according to which the lime exceeding that required for a monosilicate would be adsorbed on the surface of a monosilicate should therefore be accepted (cf. the discussion of Taylor<sup>3</sup> p. 3686). Kalousek<sup>4</sup> has quite recently published an investigation on which he based the opinion that in the low temperature product several phases might occur, having the composition  $CaO:SiO_2:H_2O = 4:5:n, 4:5:5,$ 1:1:n and 5:4:n; the second of these compounds corresponding to the mineral tobermorite. A gellike compound, having the composition 7:4:n, was supposed to occur in some kinds of preparations. Tobermorite was investigated by Claringbull and Hey,<sup>5</sup> who reached the conclusion that the mineral was to be considered as a monosilicate with one mole hydrate water, and after a comparison of X-ray powder spacings of the mineral with those of the "calcium silicate hydrate (I)" the two compounds ought to be considered identical. This conclusion was also drawn by McConnell.<sup>6</sup> Quite recently Megaw<sup>7</sup> published investigations on the crystal structure of tobermorite; the atoms of the mineral are arranged in the form of grooves and ridges, which explains a non-Berzelian formula. the identity of the mineral with the "calcium monosilicate hydrate (I)" was established and the formula of the mineral and of the synthetic compound may accordingly be written CaO:SiO<sub>2</sub>:  $H_2O = 5:6:5$ , or the mineral might be almost identical with the synthetic compound mentioned by Kalousek. There seem, however, to be some objections from a chemical point of view to such a composition for a synthetic compound, but until

all the properties of importance for the estimation of the compound have been established it may be most suitable to here use a more undefined designation: *i.e.*, monosilicate mixed with 3:2 silicate or, shortly, low temperature phase B.

Another synthetic compound, identified as the mineral gyrolite, will be discussed briefly. According to Mackay and Taylor<sup>8</sup> the composition of the mineral is  $CaO:SiO_2:H_2O = 2:3:2$ . The mineral contains, according to the analysis given by these authors, small amounts of impurities chiefly of alumina, as the mineral tobermorite also does. The list of X-ray powder reflection data shows bands of moderate or weak intensities. When the reflections of the synthetic compounds formed during the autoclaving are compared with those of Mackay and Taylor's list some distinct reflections of medium or weak intensities are seen to coincide with those of the bands of the mineral. The identification of any of the synthetic compounds could therefore be expected to involve certain difficulties. The identification of the compound resembling gyrolite would seem to be most easily effected with the aid of the strong reflection lines 22 and 3.65 Å, which do not occur among the lines of the other calcium silicate formed during the syntheses of the present investigation.

Among the high temperature phases of the mixture  $\text{CaO}:\text{SiO}_2 = 0.67:1$  there also occurs an unstable phase with a characteristic X-ray diffraction line at 15.3 Å. It seems to be a transition phase from which the gyrolite-like compound originates. Some more study is necessary, however, before the existance range of this compound is elucidated sufficiently.

The X-ray powder data of the synthetic compounds are given in the diagrams Fig. 1–3. The reflections of the low temperature phase B are those earlier described, showing for example the decreasing intensity of the reflection 5.5 Å. with increasing lime content of the mixture, this also having reference to those photographs which represent the substances prepared at a pressure lowered below 60% of that of the saturated vapor. According to these observations the lowered content of hydrate water does not influence the position or the intensities of the reflection lines measurable in the photographs, nor could any new reflexes be discerned. It is clear from the analyses of Table I-III that the lowering of the pressure obviously lowers the water content of the compounds to a distinct molar ratio. The low temperature phase formed during the first part of the reaction is poorly crystallized, as proved by the X-ray photographs. The water adsorption on the surface of the minute crystals and on the amorphous silica should decrease continuously in accordance with an absorption isotherm. The tables show that a certain equilibrium seems to be approached, obviously depending on the formation of hydrates of lower water content; these new-formed phases, however, cannot be discerned in the photographs and the recrystallization has only led to disintegration of some of the earlier crystals without new formation of complexes with sufficiently repeated

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<sup>(4)</sup> G. L. Kalousek, J. Am. Concrete Inst., 26, 989 (1956).

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<sup>(7)</sup> H. Megaw, Nature, 77, 390 (1956).



Fig. 1.—The mixture  $CaO:SiO_2 = 0.67:1$ , the X-ray reflection lines measured for the preparations. Concerning the phases see Table I.



Fig. 2.—The mixture  $CaO: SiO_2 = 1:1$ , the X-ray reflection lines measured for the preparations. Concerning the phases see Table II.

arrangements of the patterns. A positive estimation of the change of phases is therefore not possible



Fig. 3.—The mixture  $CaO:SiO_2 = 1.5:1$ , the X-ray reflection lines measured for the preparations. Concerning the phases see Table III.

in this case; this is independent of the molar ratio of the calcium silicate hydrates formed, CaO:  $SiO_2$ :  $H_2O = 1:1:1$  as well as 1.3:1:1.

The photograph of the mixture 0.67:1 autoclaved at 200°, 3 hr., 15.8 kg., and afterwards 21 hr., 9 kg. shows a very slight recrystallization of the low temperature phase (Table I, Fig. 1). On the other hand, the compounds formed at the same temperature 200°, 24 hr., 15.8 kg. (saturated vapor) are well crystallized (Fig. 1). The compounds formed are those resembling gyrolite and possibly also tobermorite. After 24 hr. autoclaving some of the low temperature phase must also remain. Some lines would indicate the presence of the xonotlitelike compound but, as other characteristic lines of this compound are missing, it seems to be most probable that it does not occur in this autoclave product. Thus, the X-ray photographs show that this mixture 2:3 autoclaved at 200°, 2 hr. 15.8 kg. and 22 hr. 9 kg., has recrystallized insignificantly, due to the lowering of the pressure.

The mixture 1:1 yielded on autoclaving at 200°, 3 hr. 15.8 kg., 21 hr. 9 kg. a rather well crystallized preparation (Table II, Fig. 2), the X-ray reflections of which are identical in almost all details with those of the preparations autoclaved at 200°, 24 hr., 15.8 kg. (saturated steam). The compounds formed are identified as the compounds resembling tobermorite and xonotlite; gyrolite does not occur as the line 22 Å. is missing.

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The mixture 1.5:1 autoclaved at  $200^{\circ}$ , 3 hr. 15.8 kg., 21 hr. 9 kg., showed substantially the same X-ray reflections as the sample autoclaved at  $200^{\circ}$ , 24 hr., 15.8 kg. (saturated steam, Table III, Fig. 3). The X-ray photographs are very rich in lines; the compounds formed are those resembling hillebrandite, xonotlite and tobermorite; but probably not gyrolite; the two compounds last mentioned

are probably transformed during the autoclaving at 24 hr. in saturated vapor.

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# REDUCTION OF HEXAVALENT CHROMIUM AT THE ROTATED PLATINUM ELECTRODE. PERMEABILITY OF THE FILM FORMED

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The reduction of hexavalent chromium from 0.001 to 0.01 N mineral acid solutions at a rotated platinum electrode gives rise to the formation of a film at the surface of the electrode. The quantity of electricity consumed in its formation indicates the film to be a unimolecular layer of chromic hydroxide. The film prevents further reduction of chromium(VI). In stronger acid solution, well-defined reduction waves are found, the diffusion current being proportional to concentration and corresponding to reduction to trivalent state. The film cannot be removed by simple washing. Its effect on the reduction waves of ferric iron, cupric and cuprous copper, ceric cerium, permanganate, iodine, thallium and oxygen, and on the oxidation waves of iodide, ferrous iron and thallous ions has been studied. The film was found to be practically impermeable to aquo ferric and ferrous iron and cuprous copper species. The difference in permeability allows at a given potential the selective reduction or oxidation of one electroactive species in the presence of another, if the film is permeable to one of the species and impermeable to the other species. Zero current potentials at the filmed electrode may be different from the true oxidation potentials in systems in which the permeabilities of the oxidized and reduced forms are markedly different.

In the voluminous literature on electroplating of chromium from chromium(VI) baths, frequent reference is made to the formation of a resistant film on the surface of the electrode resulting in a low plating efficiency.<sup>1-5</sup> Upon the authority of Müller,<sup>3</sup> Liebreich,<sup>2</sup> and Kasper,<sup>4</sup> the film quite generally has been considered to be composed of basic chromic chromate. From spectrographic and microchemical studies and X-ray diffraction patterns, Cohen<sup>6</sup> concluded that the film was composed of chromic hydroxide or oxide.

Most of the work reported was carried out at a high chromium concentration and at such negative potentials that hydrogen evolved simultaneously.

In the present paper, the reduction of chromium from the hexavalent to the trivalent state was studied at the rotated platinum wire electrode at various acidities and at potentials where no hydrogen evolution occurs. At very low acidity, a film was formed on the electrode which prevented further reduction of chromium(VI). The effect of the film on electroreduction and electroöxidation of various substances was investigated.

#### Experimental

Materials Used.—All chemicals were C.p. A stock solution of potassium dichromate was prepared from a Merck sample. Conductivity water was used in preparing the solutions. Apparatus and Procedure.—A Leeds and Northrup Electrochemograph type E with a chart speed of 5.1 cm./ min. and a polarization rate  $\Delta E/\Delta t$  of 3.33 n.v./sec., was used in obtaining c-v curves. The platinum indicator electrode was a wire 0.014 cm. in diameter and 0.9 cm. long. It gave a diffusion current constant for the reaction  $I^- = \frac{1}{2}I_2 + e^-$  in 0.1 N perchloric acid<sup>7</sup> of 412.5 µa./mmole/l. The electrode was rotated at a speed of 600 r.p.m. by means of a synchronous motor. A saturated calomel electrode (S.C.E.) of large surface area was used as the non-polarizable anode. Measurements were carried out at 25°. All solutions were deaerated with Linde nitrogen without further purification.

Cleaning the Electrode.—A film formed during the electroreduction of chromium(VI) was found to be insoluble in nitric acid in concentrations up to 5 N, or in 1 N hydrochloric acid, and it did not yield a reduction or dissolution pattern on reversing the polarization. The film was removed by anodic treatment for five minutes in about 4 N sodium hydroxide solution using a current of 100 ma. The electrode was washed with conductivity water and oxygen or the oxide film on the surface of the platinum<sup>8</sup> removed by shortcircuiting vs. the S.C.E. in 1 N sulfuric acid until the current dropped to almost zero. After washing with conductivity water such an electrode gave reproducible current-voltage curve.

#### Results and Discussion

Reduction of Chromium(VI). Current-Voltage Curves in Dilute Acid Solutions.—Typical c-vcurves in 0.001 N hydrochloric acid as a supporting electrolyte are shown in Fig. 1. All solutions were free of oxygen. Curve 2 was obtained at a filmfree electrode and polarization was directed from positive to negative potentials. After passing through a maximum the current decreased before hydrogen evolution occurred. A repetition of the experiment without cleaning the electrode yielded curve 3. Apparently the film formed in the first experiment prevented any reduction of chromium-

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(VI). The shape of the c-v curve in solutions of chromium(VI) in 0.001 N hydrochloric acid served as an indicator of the presence of a film. In 0.01 N acid, similar curves were observed as in 0.001 N acid.

Current-Voltage Curves in More Concentrated Acid Solutions.—In solutions 0.1 N in hydrochloric or sulfuric acid well-reproducible reduction waves of normal appearance were observed with well-defined diffusion currents. As an example, some c-v curves in 0.1 N hydrochloric acid are presented in Fig. 2.

The diffusion currents corresponding to the reduction of chromium(VI) to chromium(III), after correction for the residual current, were found proportional to the dichromate concentration (see Fig. 2), the diffusion current constant being 120  $\mu a./meq.$  Cr(VI)/l. Tests for the presence of a film were negative. If the electrode was first covered with a film by electrolysis in 0.001 N acid, a c-v curve of normal appearance was observed (curve 5, Fig. 2). The c-v curve was displaced to more negative values, although the height of the wave remained practically the same. In 1 and 5 N hydrochloric acid, 0.1 and 5 N sulfuric acid, c-vcurves were found similar in appearance to those in Fig. 2. Although well-defined and reproducible diffusion currents were obtained, the shape of the c-v curves indicates that the reaction

 $HCrO_{4}^{-} + 7H^{+} + 3e^{-} = Cr^{+++} + 4H_{2}O$ 

is quite irreversible. The oxidation potential of Cr(VI) in acid medium has been found by Luther<sup>9</sup> and Kolthoff<sup>10</sup> and in the present study to change closely to the theoretical value of 0.140 v. with one unit change in pH. However, this potential has no exact thermodynamic significance and does not agree with the theoretical value calculated from the free energy of the dichromate ion.<sup>11</sup> The c-vcurves at acidities greater than 0.1 N were found to be unaffected by the presence of chromic chromium; no anodic oxidation of chromic chromium occurred up to the oxygen evolution potential. The slope of the c-v curves near the zero-current potential is extremely small (Figs. 1 and 2) and is not changed in the presence of chromium(III). Thus the oxidation potential of chromium(VI) in acid medium is poorly reproducible and greatly dependent upon the pretreatment of the electrode.

Current-Time Curves.—When the current was measured as a function of time at a potential where the diffusion current was observed, the current remained practically constant when there was no interfering film on the surface of the electrode. Upon longer electrolysis a slight decrease in current was observed due to the exhaustion of the electroactive species. However, in 0.001 N acid the current rapidly decreased to zero because the film formed prevents further electrolysis. Apparently the film is impermeable to chromium(VI) in 0.001 N acid but is permeable at higher acidity.

Thickness of the Film.—From several i-t curves in 0.001 N acid under identical conditions, an aver-



Fig. 1.—Current-voltage curves in 0.001 N hydrochloric acid (oxygen-free): (1) residual current; (2)  $2 \times 10^{-6} M$  $K_2Cr_2O_7$  with a clean electrode; (3)  $2 \times 10^{-5} M$   $K_2Cr_2O_7$  with a filmed electrode; (4)  $2 \times 10^{-5} M$   $K_2Cr_2O_7$ , clean electrode, after rotation in a suspension of Cr(OH)<sub>2</sub> (see text).



Fig. 2.—Current-voltage curves in 0.1 N hydrochloric acid (oxygen-free): (1) residual current; (2)  $8 \times 10^{-6} M$  $K_2Cr_2O_7$ ; (3)  $2 \times 10^{-6} M$   $K_2Cr_2O_7$ ; (4)  $4 \times 10^{-6} M$   $K_2Cr_2O_7$ ; (5)  $4 \times 10^{-6} M$   $K_2Cr_2O_7$ , filmed electrode. Insert:  $i_d$  vs. concentration of  $K_2Cr_2O_7$ , with a clean electrode.

age value of 539  $\mu$ coulombs was calculated to be required for the complete formation of the film. This quantity of electricity corresponds to the reduction of

 $\frac{5.39 \times 6.03 \times 10^{19}}{3 \times 96.5 \times 10^3} = 1.12 \times 10^{15} \text{ ions}$ 

of chromium(VI) to the trivalent state. The apparent surface area of the electrode was estimated to be 0.38 cm.<sup>2</sup>. The ratio of the real to the geometric area of a smooth platinum surface has been estimated by different observers to be between 1.5 and 3,<sup>12,13</sup> and a value of 2 is usually taken as an average. Thus the true surface of the electrode will be approximately 0.76 cm.<sup>2</sup>. From X-ray data

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<sup>(11)</sup> W. M. Latimer, "Oxidation Potentials," Prentice-Hall, New York, N. Y., 1952, p. 245.

the number of atoms of platinum per sq.cm. at a platinum surface is calculated to be about  $0.8 \times 10^{15}$  corresponding to  $1.2 \times 10^{15}$  atoms of platinum on the surface of our electrode. Our results indicate that the quantity of electricity necessary for the formation of the film corresponds to the formation of a unimolecular film of chromium(III) on the electrode.

Since the acidity of the solution determines whether or not a film is formed, it is plausible to suggest that deficiency in hydrogen ions is a favorable condition for film formation. Apparently a platinum electrodc has a strong tendency to deposit a film of chromic hydroxide on its surface. The strongly adherent film is formed even at acidities where the hydrolysis of the chromium(III) is incomplete. It is known that several substances deposit from a suspension as a firmly adhering film on a platinum surface. For example, a firmly adherent film of silver halide is deposited on a platinum electrode when it is placed in a colloidal or flocculated (stirred) suspension of silver chloride, bromide or iodide.<sup>14</sup> We have rotated our platinum wire electrode for a few minutes in a suspension of hydrous chromic hydroxide which was prepared by adding 5 ml. of 1 N sodium hydroxide to 20 ml. of 0.5 M chromic chloride solution. The electrode was washed thoroughly with conductivity water. It was then tested for the presence of a film by determining the c-v curve of  $2 \times 10^{-5} M$  dichromate in 0.001 N hydrochloric acid. From curve 4, Fig. 1, it is evident that a film was present on the electrode which interfered with the electroreduction.

The Effect of the Chromic Hydroxide Film on Other Electrode Reactions.—Müller<sup>3</sup> and Kasper<sup>4</sup> claimed that the film prevents the reduction of every species except hydrogen ions, to which it is permeable. From the following experiments it is concluded that the film is more or less permeable to many electro-oxidizable or electro-reducible species.



Fig. 3.—Reduction of potassium permanganate and silver nitrate from 0.1 N sulfuric acid: (1)  $1 \times 10^{-5} M \text{ KMnO}_4$ , clean electrode; (2)  $1 \times 10^{-5} M \text{ KMnO}_4$ , filmed electrode; (3)  $1 \times 10^{-6} M \text{ KMnO}_4 + 2.5 \times 10^{-5} M \text{ AgNO}_3$ , clean clectrode; (4)  $1 \times 10^{-5} M \text{ KMnO}_4 + 2.5 \times 10^{-6} M \text{ AgNO}_3$ , filmed electrode. Insert:  $i_4$  vs. concentration of KMnO}4, with a filmed electrode.

(14) I. M. Kelthoff and J. T. Stock, Analyst, 80, 860 (1955).

The electrode was covered with a film by electrolysis in a  $2 \times 10^{-5} M$  dichromate solution in 0.001 N hydrochloric acid for a few minutes at +0.1 v. vs. S.C.E. until the current had decayed to practically zero. The "filmed" electrode was then washed with conductivity water and dried with a piece of filter paper. Electrodes filmed in this way gave reproducible current values of better than  $\pm 3\%$ .

The effect of the film on the limiting (diffusion) current of various electro-active species is summarized in Table I.

Dependent on the electro-active species, the decrease of the limiting current varies from almost 100% (aquo ferric, ferrous and cuprous) to zero per cent. (silver and thallium).

The limiting current of permanganate for example was found 60% smaller at the filmed electrode than at the clean electrode. If the film represented an ohmic resistance, it would flatten out the shape of the c-v curves but the limiting current should remain unaffected. As an illustration, the c-v curves of permanganate from 0.1 N sulfuric acid as a supporting electrolyte are shown in curves 1 and 2, Fig. 3, at the clean and the filmed elec-trodes. The insert in Fig. 3 illustrates the proportionality between limiting current and concentration at the filmed electrode. The constancy of the limiting current over a potential range of about 0.8 volt illustrates clearly that the decrease in the limiting current cannot be attributed to an ohmic resistance. If this were the case, the limiting current of all electro-active species should be decreased to the same extent. Hence we attribute the film effect to the difference in permeability of the film for the electro-active species. The reduction of aquo ferric and the oxidation of aquo ferrous ions is practically completely suppressed at the filmed electrode at concentrations below  $10^{-4} M$ ; while the limiting currents of silver,  $Tl(I) \rightarrow$  metallic thallive,  $Tl(I) \rightarrow Tl(III)$  ( $Tl_2O_3$ ), are not suppressed. This does not mean that the film is 100% permeable to silver or to thallium ions. After the electrolysis it was observed that the filmed electrode was covered with a layer of silver, thallium or thallic oxide. Since the original film does not represent an ohmic resistance, the electrode reaction can take place without interference once a layer of a metal or a metallic oxide conductor is formed on the electrode. Thus the presence of a layer of a metal (silver) on the filmed electrode, should make possible the reduction of an ion which does not yield a reduction current at the uncovered filmed electrode. This was found to be the case in the electrolysis of a mixture of 5  $\times$  10<sup>-5</sup> M silver nitrate and 2  $\times$  10<sup>-5</sup> M ferric nitrate, in 0.1 N nitric acid as a supporting electrolyte.

At the filmed electrode no reduction wave of ferric iron was observed in the absence of silver. At the clean electrode the iron wave was drawn out and reached a limiting value at the potential where the silver ions yielded a steep wave. In a mixture of ferric and silver nitrate the total diffusion current was found equal to the sum of the two separate waves. At the filmed electrode no reduction wave of ferric nitrate was observed in the mixture, but the

EFFECT OF FILM ON LIMITING CURRENTS OF VARIOUS SPECIES					
System	Supporting electrolyte	Decrease limiting current in %	Electrode reaction		
$10^{-5} M$ iron(III) chloride	0.2 N HCl	Close to 100	$Fe(III) \rightarrow Fe(II)$		
$10^{-5}$ - $10^{-4}$ M iron(III) nitrate	.1 N HNO3	Close to 100	$Fe(III) \rightarrow Fe(II)$		
$10^{-5}$ - $10^{-4} M$ iron(II) sulfate	$.1 N H_2 SO_4$	Close to 100	$Fe(II) \rightarrow Fe(III)$		
$10^{-5} M \operatorname{copper}(\mathrm{II})^{a}$	$.05 \ M \ \mathrm{KCl}$	ca. 80	$Cu(II) \rightarrow Cu(I)$		
		14	$Cu(I) \rightarrow Cu(\circ)$		
$10^{-5} M \text{ copper}(II)$	(Pyridine + KCl)	ca. 80	$Cu(II) \rightarrow Cu(I)$		
		40	$Cu(I) \rightarrow Cu(^{\circ})$		
$10^{-5} M \text{ copper(II)}$	$NH_4Cl + NH_4OH$	28	$Cu(II) \rightarrow Cu(I)$		
		35	$Cu(I) \rightarrow Cu(\circ)$		
$10^{-6}-10^{-5} M$ permanganate	$0.001 N H_2 SO_4$	62	$Mn(VII) \rightarrow Mn(II)$		
$10^{-5} M$ permanganate	$1 N H_2 SO_4$	59	$Mn(VII) \rightarrow Mn(II)$		
$10^{-5} M$ silver	$0.1 M \text{ NaNO}_3$	0	$\Lambda g(I) \rightarrow \Lambda g(\circ)$		
$10^{-5} M$ silver	$0.1 N H_2 SO_4$	0	$\Lambda \mathbf{g}(\mathbf{I}) \rightarrow \Lambda \mathbf{g}(\mathbf{o})$		
$10^{-5} M \operatorname{cerium}(\mathrm{IV})$	$1 N H_2 SO_4$	21	$Ce(IV) \rightarrow Ce(III)$		
$10^{-5} M$ thallium <sup>15</sup>	0.1 N NaOH	0	$Tl(I) \rightarrow Tl(III)$		
	.1 N NaOH	0	$Tl(I) \rightarrow Tl(\circ)$		
Oxygen <sup>16<sup>6</sup></sup>	.1 M KCl	35	$O_2 \rightarrow H_2O_2$		
$10^{-5} M  ext{ iodine}^7$	$.1 N H_2 SO_4$	27	$I_2 \rightarrow 2I^-$		
$10^{-5} M \text{ iodine}^7$	$.1 M \mathrm{KI}$	44	$I_3 \rightarrow I^-$		
$10^{-5} M \text{ iodide}^7$	.1 $N$ HClO <sub>4</sub>	50	$2\mathrm{I}^-  ightarrow \mathrm{I}_2$		

# TABLE I

<sup>a</sup> Same results obtained in 0.01 and 0.001 M KCl as a supporting electrolyte. <sup>b</sup> Result obtained with an electrode  $\sim 1/15$  as sensitive.

total limiting current at potentials where the silver ions are completely reduced was only 10 to 15% less than that observed at the clean electrode. This supports the conclusion that at the silver plated filmed electrode the reduction of iron occurs simultaneously with that of silver ions.

Experiments were also run in appropriate mixtures of permanganate and silver nitrate in 0.1 N sulfuric acid. As illustrated in Fig. 3 the limiting current of permanganate at the filmed electrode was 60% less than that at the clean electrode. In the presence of silver ions the same suppression of the permanganate current was found, but the height of the apparent silver wave became much greater than at the clean electrode (curve 4, Fig. 3). The reason is that further reduction of permanganate can take place once a coat of silver is formed. The total current found in mixtures of permanganate and silver at potentials where silver yields its diffusion current was only slightly less—about 10% at the filmed than at the clean electrode.

When a constituent is present in the solution whose reduction (oxidation) is practically com-pletely suppressed by the film, it will not be co-reduced (or co-oxidized) when another constituent is in the solution whose reduction (or oxidation) can occur at the filmed electrode, unless the latter constituent deposits a conducting layer (metal or, e.g., thallic oxide) on the cathode. Current-voltage curves have been run in mixtures of permanganate and ferric nitrate in a medium of 0.1 N nitric acid. At a clean electrode both permanganate and ferric iron yield a well-defined diffusion current; in a mixture the diffusion current of permanganate is just attained before the drawn-out reduction wave of iron starts (see curve 2, Fig. 4). At the filmed electrode the limiting current of permanganate again was 60% less than at the "clean" electrode, but no reduction of ferric iron was observed at potentials where it yields a diffusion current at the clean electrode. In mixtures of iodine and ferric iron similar results are found, the iodine yielding its reduction wave and diffusion current, while the ferric iron is not reduced at the filmed electrode.

The behavior of copper(II) in media where the reduction of the metal occurs in two steps is quite interesting. The shape of the curve depends on the supporting electrolyte used. As an example the current-voltage curve of cupric copper in a supporting electrolyte of 0.1 N potassium chloride + 0.1 M pyridine is shown in Fig. 5.

The reduction of Cu(II) to Cu(I) was almost completely suppressed by the film. Apparently the Cu(I) formed at the electrode in the first reduction step permeates the film very slowly. In agreement herewith it was found that at a potential of -0.45 v. vs. S.C.E. the current rapidly dropped to the residual current. The sum of the two waves was markedly less at the filmed than at the clean electrode (curves 2 and 3, Fig. 5). The reason is that the diffusion current plateau corresponding to reduction to metallic copper had not been reached at the filmed electrode when hydrogen evolution started. It is of interest to note that this hydrogen evolution under the experimental conditions started at a considerably less negative potential than at the clean electrode. The dissolution pattern (see Fig. 5), curve 4 leaves no doubt that metallic copper is formed on the filmed electrode at a potential of about -0.6 volt. Both the oxidation and reduction waves of copper(I) in acetonitrile<sup>17</sup> from solutions 0.1 M in pyridine and 0.1 M in potassium chloride were almost completely suppressed.

Oxidation Potential at a Filmed Electrode.— At the zero-current potential, the cathodic current is equal to the anodic current. In a thermo-

 <sup>(15)</sup> I. M. Kolthoff and J. Jordan, J. Am. Chem. Soc., 74, 382 (1952).
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<sup>(47)</sup> J. F. Coetzee, Ph.D. Thesis, University of Minnesota, 1955.



Fig. 4.—C-v curves of potassium permanganate and ferric nitrate in a mixture: (1)  $4 \times 10^{-6} M$  potassium permanganate, clean electrode; (2)  $4 \times 10^{-6} M$  permanganate +  $3 \times 10^{-5} M$  ferric nitrate, clean electrode; (3)  $4 \times 10^{-6} M$ permanganate +  $3 \times 10^{-5} M$  ferric nitrate, filmed electrode; supporting electrolyte 0.1 N nitric acid.



Fig. 5.—*C-v* curves of copper(II) in 0.1 *M* pyridine + 0.1 *M* potassium chloride: (1) residual current; (2) 2  $\times$  10<sup>-5</sup> *M* copper, clean electrode; (3) 2  $\times$  10<sup>-5</sup> *M* copper, filmed electrode; (4) dissolution pattern of copper on reversing the polarization, filmed electrode.

dynamically reversible system, this potential corresponds to the oxidation potential of the system. At the rotated platinum electrode the iodideiodine system has been found reversible.<sup>7</sup> Since the permeability of the film to the iodine, iodide and the triiodide was found to be of the same order of magnitude, it would be expected that the oxidation potential of the system would not be affected by the presence of the film. This was confirmed by measuring the potential of a solution 0.01 M in iodide and 0.001 M in iodine in 0.1 M perchloric acid and 0.4 M sodium perchlorate as a supporting electrolyte, which were 10 and 100 times diluted in iodide and iodine.



Fig. 6.—C-v curves of: (1)  $1 \times 10^{-2} M$  Fe<sup>++</sup> +  $1 \times 10^{-2} M$  Fe<sup>+++</sup>, at a clean electrode; (2)  $1 \times 10^{-3} M$  Fe<sup>+++</sup> +  $1 \times 10^{-3} M$  Fe<sup>+++</sup>, at a clean electrode; (3)  $1 \times 10^{-4} M$  Fe<sup>+++</sup> +  $1 \times 10^{-4} M$  Fe<sup>+++</sup>, at a clean electrode (1'), (2'), (3') same at a filmed electrode. Supporting electrolyte 1 N sulfuric acid.

In a system like that composed of ferrous and ferric iron, in which the oxidation and reduction currents of the species are greatly suppressed by the film, the zero current potential at a filmed electrode would be expected to be different from that at a clean electrode, if the rates of oxidation and reduction of ferrous and ferric iron, respectively, are affected in a different manner by the film. If the ratio of the rates of reduction of ferric iron and oxidation of ferrous iron at the filmed electrode were greater than at a clean electrode, the zero current potentials should shift to more positive potentials, the effect increasing with a decrease in the total concentration of the electro-active species. Current-voltage curves of equimolecular solutions of ferrous and ferric iron in 1 N sulfuric acid at the clean and filmed electrode are recorded in Fig. 6. In solutions 0.01, 0.001 and 0.0001 M in each ferrous and ferric iron the zero current potentials at the clean electrode were found to be 0.44, 0.44 and 0.47 volt (vs. S.C.E.), respectively; and 0.45, 0.49 and 0.55 volt at the filmed electrode. As was anticipated the "oxidation potentials" at the filmed electrode were more positive than at the clean electrode, the difference increasing with decreasing iron concentration. It is interesting to note that the oxidation potential of the solution 0.0001 M in ferrous and ferric iron at the clean electrode was found to be 0.03 volt more positive than that of equimolar solutions more concentrated in iron. This difference must be attributed to the irreversible character of the electrooxidation of ferrous and electroreduction of ferric iron. This deviation from the Nernst equation may occur quite generally in incompletely reversible studies and is being studied further.

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# THE SOLUBILITY OF FERROUS HYDROXIDE AND FERRIC HYDROXIDE IN ACIDIC AND BASIC MEDIA AT 25°1

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Contribution from the Department of Chemistry, Wayne State University, Detroit, Michigan

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A method was developed for the preparation in basic solution of pure ferrous hydroxide. Solubility studies on this material showed ferrous hydroxide to possess weak acidic properties. The principal reactions and their related thermodynamic constants have been determined for ferrous hydroxide. The solubility studies of ferric hydroxide indicate it to be indifferent as to either an acid or a base in that the pH of the water solutions of ferric hydroxide were not significantly different than that of pure water. This observation was further supported qualitatively by the identification of the principal species in basic solution as an undissociated molecule. Quantitative support is also indicated by the low value of the primary basic dissociation constant.

The purpose of this investigation was to obtain data on the equilibria of ferrous hydroxide and ferric hydroxide in dilute perchloric acid and sodium hydroxide solutions. Previous work is incomplete and lacking in agreement as evidenced by the following

Ref.	Solubility Fc(OH) <sub>2</sub> product
Whitman, Russell and Davies <sup>2</sup>	$6.7 \times 10^{-5} \ 3 \times 10^{-14}$
Murata <sup>3</sup>	$8.14 imes 10^{-6}$ 2 $ imes 10^{-15}$
Lamb <sup>4</sup>	$1.35 \times 10^{-5}$ 1 $\times 10^{-14}$
Shipley and McHaffie <sup>5</sup>	$3.9 \times 10^{-15}$
Britton <sup>6</sup>	$4.5 \times 10^{-21}$
Elder <sup>7</sup>	$48 \times 10^{-16}$
Krassa <sup>3</sup>	$8.7  imes 10^{-14}$
Arden <sup>9</sup>	$2.4 \times 10^{-11}$
Schrager <sup>10</sup>	$7.0 \times 10^{-13}$
	Solubility product of ferric hydroxide
Britton <sup>6</sup>	$2 \times 10^{-38}$
Elder <sup>7</sup>	$3 imes 10^{-38}$ to $4 imes 10^{-36}$
Kruikov and Awsejewitsch <sup>11</sup>	$7 \times 10^{-37}$
Bezier <sup>12</sup>	$1 \times 10^{-37}$
Evans and Pryor <sup>13</sup>	$3 imes 10^{-36}$

#### Procedure

Preparation of Reagents. Water, Sodium Hydroxide Solutions, Perchloric Acid Solutions.—The preparations of these substances were similar to those described by Gayer and Leider.<sup>14</sup>

Ferrous Chloride Solution.—J. T. Baker 99.90% iron wire, standardizing grade, was introduced into the reaction flask and dissolved in a volume of normal hydrochloric acid insufficient to react completely with the metal. The resultant solution was boiled free of dissolved gases and cooled under pure nitrogen. A small amount of sodium hydroxide was introduced to increase the pH to some value which would result in the complete precipitation of any ferric ion as well as a partial precipitation of ferrous hydroxide. The supernatant iron II chloride solution was filtered into the reaction flask through a fine glass frit.

- (3) K. Murata, J. Soc. Chem. Ind. Japan, 35, 523 (1932).
- (4) A. B. Lamb, J. Am. Chem. Soc., 32, 1214 (1910).

(5) J. W. Shipley and I. R. McHaffie, Can. Chem. Met., 8, 5, 121 (1924).

- (6) H. T. S. Britton, J. Chem. Soc., 127, 2148 (1925).
- (7) L. W. Elder, Trans. Electrochem. Soc., 57, 383 (1930).
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- (11) P. A. Kruikov and G. P. Awsejewitsch Z. Elektrochem., **39**, 884 (1933).
  - (12) D. Bezier, Ann. Chim., 20, 161 (1945).
  - (13) U. R. Evans and M. J. Pryor, J. Chem. Soc., S157 (1949).
  - (14) K. H. Gayer and II. Leider, THIS JOURNAL 77, 1448 (1955).

Ferrous Hydroxide.—The hydroxide was precipitated from strongly basic solution by the addition of dilute ferrous chloride to a saturated solution of sodium hydroxide in an air-free system with vigorous stirring. The precipitate was washed repeatedly with normal sodium hydroxide (oxygen and carbonate-free) until a test for chloride ion with silver nitrate could no longer be obtained. Five additional one-liter washings with normal base completed the preparation of the ferrous hydroxide used for the solubility studies. This technique led to the formation of a coarse-grained precipitate, white by reflection and slightly greenish tinged by transmitted light. Dilutions of the material were made to one-tenth molar base without evidence of darkening when maintained under an oxygen-free atmosphere. The oxide gave a negative test for residual chloride.

Ferric Hydroxide.—Ferric hydroxide was prepared in a microcrystalline form which could be washed extensively without undergoing peptization. The material was deposited from a dilute solution of Baker and Adamson reagent nitrate nonahydrate by a process of hydrolysis. The solution was maintained at the boiling point for a period of several weeks, the volatile components being replaced by conductivity water. This procedure serves to drive the reaction

# $Fe(NO_3)_3 + 2H_2O \longrightarrow FeOOH + 3HNO_3$

toward completion. The precipitated oxide was washed by repeated decantations and introduced into the system together with a few drops of carbonate-free sodium hydroxide. Washing was continued with degassed conductivity water to the absence of the sodium flame test before samples were prepared. The oxide was found to be free of residual nitrate.

residual mirate. Miscellaneous Analytical Reagents.—A standard iron solution was prepared from Baker A.C.S. ferrous ammonium sulfate. A 0.001 molar solution of G. F. Smith reagent 4,7diphenyl-1,10-phenanthroline was prepared according to Smith, McCurdy and Diehl<sup>16</sup> for use in the analysis of solutions containing less than  $10^{-6}$  mole of iron. Other reagents used in the colorimetric procedure, hydroxylamine hydrochloride, sodium acetate and chloroform, were prepared and/or purified as specified by the above authors. A 10% solution of G. F. Smith reagent 1,10-phenanthroline was used as described by Fortune and Mellon<sup>16</sup> for the analysis of solutions containing larger amounts of iron.

Preparation of Samples, Equilibration of Samples, Acid and Base Analysis.—The procedures were similar to those of Gayer and Leider.<sup>14</sup>

Iron Analyses (Colorimetric).—A model B Beckman spectrophotometer was used for the analysis of the equilibrated solutions. Two methods were used to determine the concentration of dissolved iron. The colored complex formed with ferrous iron by 1,10-phenanthroline served for solutions which contained iron at concentrations greater than  $10^{-6}$  molar. The analytical procedure is described by Fortune and Mellon.<sup>16</sup>

Solutions of ferric hydroxide obtained at equilibrium pH values greater than 4 were too dilute to be analyzed with the foregoing reagent. A substituted compound, 4,7-diphenyl-1,10-phenattoroline, develops a similar colored

(15) F. Smith, W. H. McCurdy, Jr., and H. Diehl, Analyst, 77, 418 (1952).

(16) W. B. Fortune and M. G. Mellon, Ind. Eng. Chem., Anal. Ed., 10, 60 (1938).

<sup>(1)</sup> From a dissertation submitted by Mr. Leo Woontner in partial fulfillment of the requirements for the Doctor's degree at Wayne State University.

<sup>(2)</sup> W. G. Whitman R. P. Russell and G. H. B. Davies, J. Am. Chem. Soc., 47, 70 (1925).

complex with divalent iron and the resulting complex can be extracted into organic solvents. A modification of the procedure described by Smith, McCurdy and Diehl<sup>15</sup> was used to obtain analyses of solutions of low iron concentration.

Volumetric Analysis.- The more concentrated iron solutions were checked by titration with standard dichromate solution using sodium diphenylamine sulfonate as internal indicator as described in Willard and Furman.<sup>17</sup>

The evaluation of the activity equilibrium constants in-

volves the following assumptions. (a) The activity of hydronium and hydroxyl ions is accurately reflected in the pH measurements.

(b) Since specific activity coefficients are not available for dissolved species of less than  $10^{-3}$  molal, the activity coefficients of the metal-bearing ion are taken to be unity.

(c) As a first approximation, the activity coefficient of the iron bearing ion is expressed in terms of the coefficients for NaOH and  $HClO_4$ . The activity coefficient of a 1-2 electrolyte by the square of that of a 1-1 electrolyte.

(d) In considering a particular reaction, it is assumed that no other reactions are occurring which involve the metal ion. This assumption must be made since it is impossible to separate concentration of the metal into various ion concentrations. Further it is assumed that only those reactions occur for which it is impossible to calculate equilibrium constants which do not drift.

General Equilibria for Ferrous Hydroxide.--The dissolution of ferrous hydroxide in basic solutions can be attributed to one or more of the following reactions represented by the equations and formulas

$$Fe(OH)_{2(6)} \longrightarrow Fe^{++} + 2OH^{--} K_1 = a_{Fe}^{++}/a_{OH}^{2--} (1)$$

 $\operatorname{Fe(OH)}_{2(s)} \xrightarrow{\leftarrow} \operatorname{FeOH}^+ + \operatorname{OH}^- K_2 = a_{\operatorname{FeOH}}^+ / a_{\operatorname{OH}}^- (2)$ 

 $\operatorname{Fe(OH)}_{2(\mathfrak{d})} \xrightarrow{\longleftarrow} \operatorname{Fe(OH)}_2 \operatorname{aq} \quad K_3 = a_{\operatorname{Fe(OH)}_2} \operatorname{aq}$ (3) $Fe(OH)_{2(s)} + OH^{-}$   $\longrightarrow$   $HFeO_{2}^{-} + H_{2}O K_{4} =$ 

 $a_{\rm HFeO_2}/a_{\rm OH}$  - (4)  $\operatorname{Fe}(OH)_{2(8)} + 2OH^{-} \underbrace{\longrightarrow}_{Fe_{2}O^{-}} + H_{2}O \quad K_{5} = a_{Fe_{2}O^{-}}$  $/a^{2}_{\rm OH}$  (5)

$$\operatorname{Fe}(\operatorname{OH})_{2(\mathfrak{g})} \stackrel{\checkmark}{\longrightarrow} \operatorname{HFe}(\mathcal{O}_2^- + \operatorname{H}^+ K_5 = K_4/K_w$$
(6)

Solubility measurements cannot be used to distinguish between mononuclear and polynuclear species, hence no attempt was made to write equations involving the latter.

# The Data and Calculated Results

The experimental data and the calculated equilibrium constants for ferrous hydroxide are presented in Table I.

#### TABLE I

SOLUBILITY OF FERROUS HYDROXIDE IN SODIUM HYDROXIDE Molar concn. Activity

of sodium Initial	hydroxide Equil.	Molar conen. of iron $\times$ 10 <sup>6</sup>	coefficients for NaOH	$\overset{K_4}{\times 10^6}$	$\stackrel{K_{b}}{\times} 10^{6}$
0.108	0.131	0.108	0.755	8.3	36
. 323	. 316	.275	. 703	8.7	13.6
. 52	. 445	. 356	. 699	8.0	8.8
. 64	.645	. 550	. 683	8.5	6.1
	.774	. 630	.678	8.2	4.8
2.31	2.30	3.17	. 706	13.7	3.0
3.27	3.09	3.92	.782	12.7	2.5
3.37	3.50	4.26	. 825	12.1	2.4
3.37	3.52	4.71	. 831	13.4	2.6
6.76	5.57	9.60	1.08	17.2	3.6
6.76	5.75	10.5	1.10	18.2	3.8

(17) H. H. Willard and N. H. Furman, "Elementary Quantitative Analysis," 3rd ed., D. Van Nostrand Co., Inc., New York, N. Y., 1940, p. 246.

The numerical values calculated for the constants representing reactions 1, 2 and 3 exhibit decided trends and the magnitude of their variation precludes any significant contribution of these reactions to the dissolution of ferrous hydroxide in basic media. The relatively constant value of  $K_4$ up to about one molar sodium hydroxide indicates that the principal reaction in dilute base is

$$\operatorname{Ce}(\mathrm{OH})_{2(\mathfrak{s})} + \mathrm{OH}^{-}$$
  $\operatorname{HFeO}_2^{-} + \mathrm{H}_2\mathrm{O}$  (4)

The average value of  $K_4$  is  $8.3 \times 10^{-6}$  with a corresponding  $\Delta F_{298}^{0} = 6900$  cal. per mole.

For concentrations of sodium hydroxide greater than one-molar, the calculated values for  $K_4$  begin to increase, indicating the inability of this reaction alone to account for the solubility of ferrous hydroxide in higher concentrations of base. Values of  $K_5$ , however, attain constancy at this point and it is evident that the equation

$$\operatorname{Fe(OH)}_{2(s)} + 2OH^{-} \operatorname{sc} \operatorname{FeO}_{2} + 2H_{2}O$$
 (5)

accounts satisfactorily for the reaction in the range 1 to 6 molar base, the highest concentration investigated. The increasing dependence of the reaction on hydroxyl ion as basicity increases is certainly a reasonable one and it might be expected that such a stepwise formation of negatively charged species should take place in the dissolution by base of the dibasic conjugate of an amphoteric substance. The average value of  $K_5$  is  $2.9 \times 10^{-6}$  and  $\Delta F_{298}^0 =$ 7600 cal./mole.

General Equilibria for Ferric Hydroxide.— The dissolution of ferric hydroxide in neutral, acidic or basic solution can be attributed to one or more of the reactions represented by the equations

$$\operatorname{FeOOH}_{(\mathrm{s})} + \operatorname{H}_{2} O \xrightarrow{\hspace{1cm}} \operatorname{Fe}(OH)_{2}^{+} + OH^{-}$$
$$K_{1} = a_{\operatorname{Fe}(OH)_{2}}^{+} a_{OH}^{-} \quad (1)$$

$$FeOOH_{(s)} + 2H_2O \longrightarrow FeOH^{++} + 2OH^{-}$$

$$FeOOH_{(s)} + 3H_2O \longrightarrow Fe^{+++} + 3OH^-$$

$$K_3 = a_{\rm Fe}^{+++} a_{\rm OH}^{3}$$
 (3)

 $FeOOH_{(s)} + OH^{-} \longrightarrow FeO_2^{-} + H_2O$ 

$$\mathbf{K}_{4} = d_{\mathrm{FeO}_{2}} / d_{\mathrm{OH}} \quad (\texttt{4})$$
  
FeOOH<sub>(s)</sub> + 2OH<sup>-</sup>  $\iff$  HFeO<sub>3</sub><sup>-</sup> + H<sub>2</sub>O

$$K_5 = a_{\rm HFcO_3} = /a^2_{\rm OH} - (5)$$
  
FeOOH<sub>(a)</sub> + 30H<sup>-</sup>  $\leftarrow$  FeO<sub>3</sub><sup>-</sup> + 2H O

$$K_6 = a_{\text{FeO}_3} = /a_{\text{OH}}^3 - (6)$$

$$FcOOH_{(s)} + H_2O \iff Fe(OH)_3$$
 aq

$$K_7 = a_{\text{Fe}(0H)_{3a_1}} \quad (7)$$
  
FeOOH<sub>(a)</sub> + II<sup>+</sup>  $\stackrel{\checkmark}{\longrightarrow}$  FeO<sup>+</sup> + H<sub>2</sub>O

$$K_8 = a_{\text{FeO}} + /a_{\text{H}} + (8)$$
  
FeOOH<sub>(8)</sub> + 2H<sup>+</sup>  $\leq$  FeOH<sup>++</sup> + H<sub>2</sub>O

$$K_9 = a_{FeOH} + A^2_{H} + (9)$$
  
FcOOH<sub>(8)</sub> + 3H<sup>+</sup>  $\leq$  Fc<sup>+++</sup> + 2H<sub>2</sub>()

$$K_{10} = a_{\rm Fc}^{+++}/a_{\rm H}^{3}^{+} \quad (10)$$

Evidence for designating ferric hydroxide by the formula FeOOH comes from Wells.<sup>18</sup> Furthermore, the authors felt that little would be lost by neglecting hydration or complex formation. No evidence for polynuclear species was obtained.

(18) A. F. Wells, "Structural Inorganic Chemistry," First Edition, Oxford Press, New York, N. Y., 1947, pp. 62, 350 and 365.

The Equilibria in Neutral and Acid Solution.— The experimental data with the calculated equilibrium constants are presented in Tables II and III.

TABLE II

Гне	Solubility	OF FERRIC	HYDROXIDE I	N PERCHLORIC
		Ac	ID	
Mo perch	lar concn. of loric acid $\times$ 10	Molar concr s of iron $\times$ 1	$1.05 K_7 \times 10^7$	$K_8  imes 10^3$
	0.00046	0.036	3.6	790
	.0066	. 052	5.2	93
	.25	.072	7.2	2.9
	.89	. 12	12	1.4
	3.8	.36	36	0.95
	16	1.8	180	1.00
	45	6.0	600	1.3
4	406	15	1530	0.37
7	714	32	3170	0.45
10	)44	37	3650	0.35

TABLE III

The Solubility of Ferric Hydroxide in Sodium Hydroxide

Molar concn. of sodium hydroxide × 10 <sup>6</sup>	Molar concn. of iron $\times$ 10 <sup>7</sup>	$K_7 \times 10^8$
0.0022	3.6	36
0.016	3.1	31
1.2	2.5	25
4.9	2.9	29
130	2.6	<b>26</b>

An examination of the calculated constants indicates that in the region of neutrality a transition takes place between two concurrent reactions. A plot of the data shows that the values for  $K_7$  become divergent at about  $10^{-5}$  molar hydronium ion while the constant for reaction 8

$$FeOOH_{(s)} + H^+$$
 FeO<sup>+</sup> + H<sub>2</sub>O or  $Fe(OH)_2$ 

tends toward a constant value in this same region. The constancy of  $K_8$  over the perchloric acid range of  $10^{-3}$  to  $10^{-1}$  molar indicates that reaction 8 is the principal reaction in this concentration range. The average value of  $K_8$  over the range  $9 \times 10^{-4}$  to  $5 \times 10^{-2}$  molar acid is  $1.2 \times 10^{-3}$  with a corresponding value of  $\Delta F_{288}^0 = 4000$  cal./mole. Be-

yond one-tenth molar acid, reactions 8, 9 and 10 all seem to contribute to the solubility of the ferric hydroxide. Further the magnitude of the respective constants indicates a roughly equivalent contribution of each species. The solubility measurements alone, however, are incapable of disentangling such simultaneous, competing reactions.

The solubility of ferric hydroxide in basic and neutral solution demonstrates a marked independence of the hydroxyl ion concentration. There is no evidence, in the calculated constants, for amphoteric behavior over the range of basicity studied. The concentration of dissolved iron, to the contrary, decreased 10-fold for a corresponding 200,000-fold increase in basicity. This remarkable constancy is reflected in the value of  $K_7$  representing the solubility-governing reaction

$$FeOOH_{(s)} + H_2O \iff Fe(OH)_3 aq$$
 (7)

The average value of  $K_7$  calculated over the range  $2 \times 10^{-8}$  to  $1 \times 10^{-3}$  molar sodium hydroxide is

 $K_7 = 2.9 \times 10^{-7}$ 

for which

 $\Delta F^{\circ}_{298} = 3900 \text{ cal./mole}$ 

This value is several orders of magnitude greater than those calculated from electrometric titration data. One explanation lies in the fact that the oxide can exist in fairly acid solution. The point at which turbidity appears in such a determination lies between pH 2 and pH 3. Using the respective hydroxyl and iron-bearing ion concentrations at this point results in solubility product values as low as  $10^{-40}$ . An additional reason for the low literature value for the solubility of iron hydroxide lies in the nature of the iron-bearing species in neutral and basic solution. The results of the present investigation demonstrate that the principal substance in solution is an undissociated molecular species. Such a species would not be detected as iron at an indicator electrode which is used to analyze for ferric ion by measurement of cell potentials.

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# THE PASSIVATION OF IRON BY OSMIUM(VIII) OXIDE AND THE ORIGIN OF THE FLADE POTENTIAL

# By G. H. CARTLEDGE

Contribution from the Chemistry Division of the Oak Ridge National Laboratory. Oak Ridge, Tennessee

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Osmium(VIII) oxide in dilute aqueous solution was found to raise electrolytic iron to a passive potential. The potential equaled the thermodynamic value for the Os(IV)-Os(VIII) couple under favorable circumstances, but was sensitive to the presence of sulfate and chloride ions of sufficient concentration. The results are discussed in connection with the mechanism of action of other  $XO_4^{n-}$  particles previously investigated and the nature of passive potentials.

In previous papers<sup>2-6</sup> it was indicated that fur-

(1) Operated by Union Carbide Nuclear Company for the U. S. Atomic Energy Commission.

(6) R. F. Sympson and G. H. Cartledge, ibid., 60, 1037 (1956).

ther understanding of the mechanism of the inhibition of corrosion might be obtained from a comparison of the action of various ions or molecules of the general formula  $XO_4^{n-}$ . The present paper presents the results obtained by the use of osmium-(VIII) oxide, which was found to have interesting properties in this connection. As previously re-

<sup>(2)</sup> G. H. Cartledge, Corrosion, 11, 335t (1955).

<sup>(3)</sup> G. H. Cartledge, THIS JOURNAL, 59, 979 (1955).

<sup>(4)</sup> G. H. Cartledge, ibid., 60, 28 (1956).

<sup>(5)</sup> G. H. Cartledge, ibid., 60, 32 (1956).

ported,<sup>2</sup> ruthenium(VIII) oxide is reduced and the iron corrodes very rapidly in corresponding experiments. The oxidizing power of an 0.04 f solution of osmium(VIII) oxide at a pH of 6 is just slightly lower than that of a chromate solution at the same concentration and acidity, the calculation being made on the assumption that the reduction products are hydrated osmium(IV) oxide and chromium-(III) oxide, respectively.<sup>7</sup> It may be anticipated that any film arising from reaction between iron and the oxidizing agent will have different properties in the two cases, however, owing to the differences in composition and structure of the resulting products. On account of the volatility of osmium-(VIII) oxide, experiments could not be continued in the neighborhood of 100° for such long times as were used in the previous work. Nevertheless, the experiments showed that the oxide is capable of inducing passivity which is very stable at room temperature and persists even up to  $95^{\circ}$  so long as sufficient osmium remains in solution.

Passivation Experiments.—In the first demonstration of the passivating action of osmium(VIII) oxide, strips of mild steel (0.097% carbon) were dipped for a few seconds into an aqueous solution containing one gram of the oxide per hundred ml. (0.039 f). The strips were then rinsed carefully and transferred to a very dilute cupric sulfate solution. In repeated tests there was no *immediate* reaction with the cupric sulfate unless the specimens were activated in some way. The experiments behaved exactly as in similar demonstrations of the passivating action of concentrated nitric acid. It was quite apparent, however, that the passivity produced by osmium(VIII) oxide is sensitive to activation not only by mechanical or chemical means, but also by foreign ions of sufficient concentration. By contrast, attempts to produce passivity by dipping steel specimens into solutions of potassium pertechnetate always failed.

Passivation experiments were conducted at temperatures as high as  $95^{\circ}$  by using reaction tubes made from waterjacketed, standard-taper joints to diminish the loss of osmium(VIII) oxide vapor. Before use, the specimens were abraded with 2/0 emery and degreased with acetone. It was found that a 0.2% solution of the passivator generally failed to prevent corrosion of the mild steel, the osmium compound being rapidly and completely reduced to the dioxide. When 0.5-1.0% solutions were used, the metal slowly became covered with a rather uniform, brassy film. The film increased in depth of color for a few hours at  $95^{\circ}$ and then remained unchanged so long as the solution still contained a sufficient concentration of osmic acid.

The film existing under these conditions was very sensitive to a variety of conditions that caused breakdown. If this occurred a few black mushroom-like growths developed over small pits while the greater part of the surface film remained unchanged in appearance. Prior to breakdown, the specimens (4 cm.<sup>2</sup> area) suffered essentially no change in weight, while control specimens similarly treated in distilled water alone were losing up to 12 mg. The brassy films were shown to contain osmium by activation analysis.<sup>8</sup> The film was shown to be electrically conducting and cathodic to the pits by immersing pitted specimens for about 30 seconds in a solution containing 0.25 g. of CuSO<sub>4</sub>·5H<sub>2</sub>O, 1.7 g. of Na<sub>2</sub>SO<sub>7</sub>·10H<sub>2</sub>O and 3 drops of 1.0 N H<sub>2</sub>SO<sub>4</sub> in 100 ml. The film possessed adequate conductivity for local action to deposit copper rapidly over the entire film, while the pits remained bright.

Tests were made to determine the minimum concentration of osmic acid required for continuing prevention of corrosion at room temperature. The specimens were again mild steel which were abraded and degreased as before. Osmium solutions that were  $2 \times 10^{-2}$ ,  $8 \times 10^{-3}$  and  $4 \times 10^{-3} f$ prevented corrosion for the three weeks during which observations were continued. Faint brown films formed after several days in these tests. In a solution that was  $2 \times 10^{-3} f$ , spotting was observed after some hours and corrosion progressed steadily until the osmic acid was completely reduced.

Since it was evident that the passivation was accompanied by the formation of a film of mixed oxides by an oxidationreduction process, experiments were made to determine whether such processes would be altered by the action of a mixture of osmic acid and potassium pertechnetate. The pertechnetate was present at inhibiting concentrations,<sup>2</sup> and it was found that there is definitely a synergistic action of the two substances. This was manifested, first, in that the formation of the brassy film was very considerably retarded by the presence of potassium pertechnetate and, second, in that the  $\beta$ -activity due to reduced forms of technetium on the specimen was very much diminished by the presence of osmic acid. Thus, in an experiment with 0.016 f osmic acid in which the temperature was alternated between 24 and 95°, the technetium activity was not detectably above background count after 9.5 hours at  $95^{\circ}$  and 107 hours at room temperature. Similar specimens after such treatment in the pertechnetate solution alone normally had beta counts corresponding to at least 2000 disintegrations min.<sup>-1</sup> cm.<sup>-2</sup>. Electrode Potentials.—The electrode potential of very

Electrode Potentials.—The electrode potential of very pure electrolytic iron in osmic acid was determined at 24.5° in the presence of potassium sulfate as supporting electrolyte. The metal used was sample number 1 of reference 2. The measurements were made as indicated in reference 4, except that a motor-driven stirrer was used in the cell, since the volatility of osmium(VIII) oxide precluded the passage of a gas stream through the solution. In a preliminary experiment it was apparent that the potential approached the approximately known thermodynamic value for the OsO<sub>2</sub>– OsO<sub>4</sub> couple under the prevailing conditions. The electrolytic iron electrode became passive with no visible change in appearance, and the e.m.f. of the cell attained a stable and reproducible value in an hour or less, as a rule.

Bonhoeffer and his associates<sup>9,10</sup> consider the passive iron electrode to function as an indicator electrode for the oxidation-reduction system effective in the electrolyte, except that the iron potential falls below the potential of a platinum electrode in the same solution because continuing corrosion of the iron produces some cathodic polarization. This polarization was shown by Vetter<sup>10</sup> to amount to 300 mv. or more in different cases in acid solution. In connection with the present work it was found possible to determine the reversible potential of the couple (Pt)Os(OH)<sub>4</sub>(ppt)-OsO<sub>4</sub>(aq), the  $E^{\circ}$  value being -0.964 v.<sup>7</sup> Hence it was feasible to make a direct comparison of the iron potential with that of a platinum electrode cathodically coated with hydrated osmium(IV) oxide.

The platinum wires were coated by electrolysis of an alkaline solution of osmium(VIII) oxide as previously described.<sup>7</sup> The potentials of two such electrodes and an electrolytic iron electrode were measured with the results shown in Figs. 1 and 2. It will be seen from Fig. 1 that the iron potential duplicated that of the osmium couple both in magnitude and in its variation with acidity. To demonstrate the independence of the three electrodes in the cell, in the second experiment (Fig. 2) the platinum electrodes were polarized in opposite directions by passage of a current of approximately 1 ma. for 5 seconds without removing the iron electrode. The results demonstrate that the passivation of iron by osmic acid in the *p*H range shown is so complete that no anodic polarization is required to bring the iron potential up to the thermodynamically reversible value. The view of the Bonhoeffer group is thus well verified by these measurements.

Other measurements of electrode potentials were made to determine whether the nobility induced by osmic acid is sensitive to the presence of foreign electrolytes, as was found to be the case in experiments with  $XO_4^{u-1}$  inhibitors reported previously.<sup>6</sup> Because of the volatility of osmium (VIII) oxide, these experiments were conducted at 24° and with mechanical stirring in cells exposed to the atmosphere. The results are therefore only qualitatively comparable to those carried out at 57.5°.

In the first experiment, two electrolytic iron electrodes were immersed in 0.039 f osmic acid in  $5 \times 10^{-4}$  f potassium

<sup>(7)</sup> G. H. Cartledge, This Journal, 60, 1468 (1956).

<sup>(8)</sup> The author is indebted to Mr. G. W. Leddicotte of the Analytical Chemistry Division for making this examination.

 <sup>(9)</sup> H. Beinert and K. F. Bonhoeffer, Z. Elektrochem., 47, 536 (1941).
 (10) K. J. Vetter, *ibid.*, 55, 274 (1951).

sulfate. The electrodes quickly came to the same potential (within 1 mv.) and were very stable. Addition of potassium chloride in several portions did not alter the potential initially and induced instability only when its concentration reached  $8 \times 10^{-3} f$ . When the solution was siphoned off and replaced by  $5 \times 10^{-4} f$  potassium sulfate alone, the potentials began falling rapidly and rusting soon followed. In a similar experiment, potassium sulfate was added after the potential had become stabilized at the thermodynamic value in  $5 \times 10^{-4} f$  potassium sulfate. Instability of the potential was noted when the concentration reached  $4 \times 10^{-3} f$  and pitting followed. It was found impossible to reach the thermodynamic potential when freshly abraded electrodes were immersed in 0.039 f osmic acid containing  $5 \times 10^{-3} f$  potassium sulfate at a pH of about 6; thermodynamic potentials were attained, however, when the potassium sulfate concentration was only 1 or  $2 \times 10^{-3} f$ . A specimen of mild steel has been preserved for over two months without corrosion in a 1% osmic acid containing copper(II) sulfate at about  $10^{-3} f$ .

### Discussion

The experiments at 95° quickly produced visible films, the failure of which at weak spots or flaws in the metal led to a pitting type of corrosion. This film breakdown was greatly increased both in frequency of occurrence and in rate when low concentrations of potassium sulfate were present. Even at  $24^{\circ}$ , a faintly visible film formed after a few days. It is evident, therefore, that, in the osmium experiments, a film of reaction products is produced in the passivation process, though a noble electrode potential may be achieved without visible film. From a consideration of the appropriate electrode potentials it may be seen that osmium(VIII) oxide is able to oxidize either metallic iron or ferrous ions to the ferric state. The observed electrode potential clearly showed that such oxidation does not have to proceed very far, however, before its rate is reduced to a very low value. The experiments demonstrated, further, that the film, though protective against oxygen or osmic acid while maintained in its noble state, yet has an electronic conductivity that is adequate for rapid cathodic processes, such as the reduction of cupric ions or the equilibration of the  $Os(OH)_4$ -OsO<sub>4</sub> couple.

The maintenance of the noble potential, with the associated low corrosion rate, appears to be contingent upon the adsorption of osmium(VIII) oxide, however, since the debasing caused by sulfate ions could hardly arise from their direct participation in an oxidation-reduction process. This conclusion is supported by the necessity for some minimum concentration of dissolved osmic acid and by the rapid debasing that occurs when it is removed. The film is therefore not inherently stable and protective; it becomes stable only in the presence of inhibiting molecules or ions. It is unimportant, however, whether the inhibition be provided by osmic acid or by the pertechnetate ion, for example.

In comparison with the ions  $TcO_4^-$ ,  $CrO_4^-$ ,  $MoO_4^-$  and  $WO_4^-$  previously studied, the action of osmium(VIII) oxide appears to differ only in detail. Because of its strong oxidizing power and rapid reaction rate it differs from the more weakly oxidizing pertechnetate ion and the more sluggish chromate ion in forming a visible film rather quickly. In all cases, however, the sensitivity to electrolytes suggests that competitive adsorption of the unreduced inhibitor particles is a prerequisite to the formation of a stable film. With the very



Fig. 1.—Iron and coated platinum electrodes in 0.039  $OsO_4$  containing 5  $\times$  10<sup>-4</sup> f K<sub>2</sub>SO<sub>4</sub> vs. S.C.E. at various acidities.



Fig. 2.—Iron and costed platinum electrodes in 0.039 f OsO<sub>4</sub> containing  $2 \times 10^{-3}$  f  $_{\rm SO_4}$  vs. S.C.E. The iron was stabilized in an osmic acid solution of higher concentration than that used in the measurements. The drop in the potentials (ca. 2 mv.) upon polarization of the two platinum electrodes was probably associated with the formation of a little colloidal Os(OH)<sub>4</sub> during the electrolysis. Such material always lowered the potentials very slightly.

stable molybdate and tungstate ions the production of passive potentials is achieved only in presence of oxygen.<sup>6</sup> The primary function of the inhibitor particle therefore appears to be to stifle the liberation of hydrogen so that the building of a coherent oxide film may proceed by consumption of either oxygen or oxidizing inhibitor in accordance with the relative rates of the available reactions. The rapid attainment of steady potentials in osmic acid demonstrates how little reaction has to occur in this case before passivation is essentially complete. The uniqueness of osmic acid in this group of inhibitors clearly is associated chiefly with the rapidity with which the polarized couple returns to its stable value, as shown in Fig. 2.

The fact that the ircn electrode reached the thermodynamic potential of the  $Os(OH)_4$ -OsO<sub>4</sub> couple is of special significance. An iron electrode in a passivating solution has several possible electrode processes available by which the potential may be determined. In the present case, four such processes are

- (a)  $2c^- + FeO + 2H^- \longrightarrow Fe + H_2O; E^\circ = -0.05 v.$ (inner interface)
- (b)  $2e^- + "FeO_2"(outer) + 2H^+ \swarrow "FeO"(inner) + H_2O; E^\circ = 0.58 v. (within the film)$
- (c)  $4e^- + OsO_4 + 4H^+ \rightleftharpoons Os(OH)_4$ ;  $E^\circ = 0.96 v$ . (outer interface)
- (d)  $4e^- + O_2 + 4H^+ \longrightarrow 2H_2O$ ;  $E^\circ = 1.23 v$ . (outer interface)

For half-reaction (a), the normal potential is approximately -0.05 v. for any of the known bulk oxides of iron. Equation (b) represents schematically a reversible process to account for the Flade potential.<sup>11</sup> This was shown by Weil<sup>12</sup> and by Vetter<sup>13</sup> to be an equilibrium potential when no current is passing through the film and no oxidation-reduction system is accessible in the electrolyte. The potential has the value +0.58-0.058 pH at 20°. The formulas within the quotation marks in this equation are, for the moment, intended only to represent oxides of different oxidation state and free-energy content so formulated as to correspond to the known magnitude and pH dependence of the Flade potential. Half-reactions (c) and (d) show the two oxidation-reduction processes which may use the filmed iron only as an indicating electrode.

With several reaction paths available, the potential as measured will depend upon the relative rates and corresponding degrees of polarization of the different half-reactions. The observation that the potential of the iron electrode corresponds to the reversible potential of the Os(OH)<sub>4</sub>-OsO<sub>4</sub> couple shows that reactions (a), (b) and (d) are too slow under the existing conditions to lead to any detectable polarization of half-reaction (c): the iron is, in fact, merely an indicating electrode for the osmium couple. So far as is known, the pertechnetate ion and osmic acid are the only substances that have been observed to produce such essentially complete passivation of iron in neutral or acidic media as to give thermodynamic oxidation-reduction potentials.<sup>14</sup> As shown previously,<sup>4</sup> the TcO<sub>2</sub>-TcO<sub>4</sub>couple is so sluggish that reaction (d) affects the measured potential appreciably unless air is excluded.

With respect to the nature of the surface state with which the Flade potential and passivity are associated, it may be suggested that it is not necessary to postulate the existence of an energy-rich unknown oxide of iron. This was done, for example, by Bancroft and Porter,<sup>15</sup> Bonhoeffer<sup>9,16</sup> and, on the basis of experiments with the ferrate ion, FeO<sub>4</sub><sup>=</sup>, by Uhlig and O'Connor.<sup>17</sup> The essential condition to be satisfied is that, when no current is passing and no oxidation-reduction process is available between the metal and the electrolyte, there shall be a process involving two or more components of the film itself that will have a normal potential of 0.58 v. positive to the hydrogen electrode, together with the observed pH dependence. From the demonstration of a thermodynamic potential for the  $Os(OH)_4$ -OsO<sub>4</sub> couple with iron electrodes, both the essential inactivity of the metal and the

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(17) H. H. Uhlig and T. L. O'Connor, J. Electrochem. Soc., 102, 562 (1955). The well-known formation of ferrate ions by anodic polarization of iron in strongly alkaline solutions cannot be considered a proof of their formation during passivation in acidic media, where the stability is far lower. electronic conductivity of the film are established. It may then be assumed that the metallic iron does not enter into the process by which the Flade potential is determined; that is, the reaction Fe +  $H_2O \rightarrow FeO + H_2$  is not involved. The 0.58-v. normal potential, with its known pH dependence, may then be assigned to the equilibrium between two oxidized products within the film, as symbolized provisionally in equation (b).

The elimination of iron from consideration in the potential-determining processes is justified also by the behavior of the inhibited carbon-steel specimens T-28 and T-29 that have been under observation for more than 3.5 years.<sup>2,3</sup> No iron oxidation product is visually detectable, and the  $\beta$ -activity of the technetium dioxide on the specimens has remained constant within the accuracy of the measurements since a stable value was reached early in the experiment. These results demonstrate that, if any continuing corrosion of iron is occurring, the equivalent local-action current must have averaged considerably less than  $10^{-9}$  amp. per cm.<sup>2</sup>, whereas corrosion currents of  $10^{-5}$  to  $10^{-6}$  amp. per cm.<sup>2</sup> have been reported for iron passivated anodically or by nitric acid.<sup>12,18</sup>

It seems reasonable to assume that the oxygen bound immediately at the metal surface is held more firmly than that in any bulk oxide of iron. Such a condition would correspond to the layer of oxygen on tungsten, as investigated by Langmuir.<sup>19</sup> This means that the free energy of such a two-dimensional "inner" oxide, "FeOi," is substantially more negative than that of the common bulk oxides of iron. To account for the magnitude of the Flade potential and its pH dependence, it is necessary to have a free-energy change of 13.35 kcal. per equivalent, or a  $\Delta F^0$  of -26.7 kcal. for equation (b) above. Since films on passivated iron have been shown<sup>20,21</sup> to contain Fe<sub>2</sub>O<sub>3</sub> and FeO(OH) ( $\alpha$  or  $\gamma$ depending upon conditions), it will be assumed that the more highly oxidized component in equation (b) is  $Fe_2O_3$ . The less highly oxidized component may be described as an "abnormal FeO" or "FeO<sub>1</sub>." The equation for the potential-determining electrode process in the film then becomes

(e) 
$$2e^- + Fe_2O_3 + 2H^+ \swarrow 2^{\prime\prime}FeO_i^{\prime\prime} + H_2O;$$
  
 $\Delta F^\circ = -26.7$  kcal

From this equation and the free energies of formation of Fe<sub>2</sub>O<sub>3</sub> and H<sub>2</sub>O(l)<sup>22</sup> one may calculate that the inner iron oxide has a  $\Delta F_{\rm f}^0$  of -73.6 kcal. mole.<sup>-1</sup> This value seems reasonable for a surface film; it may be compared with the following free energies of formation of bulk oxides: FeO, -58.4; ZnO, -76.05; MnO, -86.8 kcal. mole.<sup>-1</sup>.

The application of a positive potential exceeding the Flade potential should be expected first to produce the passive film at the equilibrium potential and then to polarize it to the higher value. When the potential falls below the Flade potential by

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(22) W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc.. New York, N. Y., Second Ed., 1952. cathodic polarization or local activation, the higher oxide is necessarily reduced according to equation (e) and a thermodynamic calculation shows that the reaction

"FcO<sub>i</sub>" + 2H<sup>+</sup> 
$$\longrightarrow$$
 Fe<sup>++</sup>(aq) + H<sub>2</sub>O(l);  
 $\Delta F^{\circ} = -3.4$  kcal

must proceed unless the ratio  $[Fe^{++}]/[H^+]^2$  exceeds 310. In short, the inner oxide cannot exist alone in distinctly acidic solutions. Its existence necessarily depends upon maintenance of the higher oxide and the correspondingly high potential.

To summarize: the osmium and technetium experiments demonstrated that it is possible to block the metallic iron so effectively that its reaction does not disturb the oxidation-reduction system in the electrolyte. The film is sufficiently conductive for electrons, however, for the thermodynamic potential of the system to be indicated. These facts justify the conclusion that iron may be excluded as one of the reactants in the process by which the Flade potential, as an equilibrium value, is established. The present assumption of an "abnormal" lower oxide may be compared thermodynamically with the earlier assumption of an unknown higher oxide by means of the following tabulation of the freeenergy values involved in the alternative interpretations

$\Delta F^{\circ}$ (kcal.)	Difference
0	Fe, H <sub>2</sub> , H <sup>+</sup>
-30.0	1/3 "FeO <sub>3</sub> " (+ H <sub>2</sub> )) 26.7
-56.7	$H_2O(+ 1/_3Fe)$ }
-58.4	FeO
-59.0	$1/_{8}\mathbb{F}e_{2}O_{3}$
-73.6	''FeOi''
-177.1	$Fe_2O_3(+H_2)$ ) 26.7
-203.8	$2^{4}$ FeO <sub>i</sub> " + H <sub>2</sub> O $\int 20.7$

It may be pointed out that the rather large negative free-energy value of "FeO<sub>3</sub>" required to satisfy the Flade potential by a postulated reaction  $6e^- +$ "FeO<sub>3</sub>" +  $6H^+ \rightleftharpoons$  Fe -  $3H_2O$  is irreconcilable with the powerful oxidizing power of the ferrate ion in acid solution. This is another argument against the assumption of its presence in the passive film,<sup>17</sup> since the energy of adsorption could hardly be sufficient to stabilize it to the requisite degree. This is not to say, however, that adsorption of ferrate ions may not provide the inhibition and oxidation required for the formation and stabilization of the passive film in alkaline solutions.

# DYNAMIC MECHANICAL PROPERTIES OF CONCENTRATED SOLUTIONS OF SODIUM DESOXYRIBONUCLEATE<sup>1</sup>

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Dynamic mechanical properties of salt-free aqueous solutions of sodium desoxyribonucleate have been studied in the concentration range from 0.38 to  $18.3 \times 10^{-3}$  g./ml., and at temperatures from 5 to 35°, by the wave propagation and forced vibration torsion pendulum methods. The real parts of the dynamic rigidity and viscosity measured at different temperatures superposed when reduced to  $25^{\circ}$  at each concentration. The same quantities when reduced to unit concentration and viscosity (including some data in the presence of 0.2 *M* sodium chloride at  $10 \times 10^{-3}$  g./ml. polymer) superposed except for a region corresponding to the center of the plateau of the relaxation spectrum. Calculation of the spectrum from both rigidity and viscosity provided values in good agreement. The shape of the relaxation spectrum was similar to that of a high molecular weight polyisobutylene or cellulose tributyrate in a higher concentration range, except that the plateau level was unusually low (order of  $5 \times 10^3$  dyn/cm.<sup>2</sup>, reduced to unit concentration). The terminal zone of the spectrum was near the location predicted by the Rouse theory; the width of the plateau was 3.3 decades at a concentration of  $12 \times 10^{-3}$  g./ml. It is concluded that the viscoelastic properties are associated with intramolecular configuration changes just as in the case of the more familiar flexible polymers, and that such motions involve coupling with neighboring molecules, though of a somewhat different character from that observed in other polymers.

### Introduction

Earlier measurements of the viscoelastic properties of several vinyl polymers<sup>3-5</sup> and cellulose derivatives<sup>6,7</sup> have delineated the relaxation spectra of these systems in their plateau and terminal zones; their dependence on temperature and concentration has been described with reduced variables, and

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deviations from the theoretical spectrum of Rouse<sup>8</sup> have been discussed in terms of molecular entanglements.<sup>3,9</sup> We now report similar information for a very different polymer—the sodium salt of desoxyribonucleic acid (SDNA)—which exhibits marked viscoelastic effects at quite low concentrations.

Some earlier rigidity measurements on solutions of SDNA in 0.2 M sodium chloride in the concentration range from 5 to 20  $\times$  10<sup>-3</sup> g./ml. have been published,<sup>10</sup> but it is now apparent<sup>11</sup> that the material (sample I) had undergone some degradation. The present measurements, on a new preparation (sample II), cover a concentration range

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Fig. 1.—Dynamic rigidity reduced to 25°, plotted logarithmically against frequency (from wave propagation). Concentrations in ascending order 0.38, 0.75, 1.5, 3.0, 5.9, 11.8 and 18.3  $\times$  10<sup>-3</sup> g./ml. Pip right, measurements at 5°; successive 90° rotations clockwise, 15, 25 and 35°.



Fig. 2.—Dynamic rigidity from wave propagation reduced to reference state of unit concentration and viscosity. Pip right,  $0.38 \times 10^{-3}$  g./ml.; successive 90° rotations clockwise, increasing concentrations as listed under Fig. 1. Black circles,  $10.0 \times 10^{-3}$  g./ml. in 0.2 *M* sodium chloride.

from 0.38 to  $18 \times 10^{-3}$  g./ml. in salt-free solution, with additional data at  $10 \times 10^{-3}$  g./ml. in 0.2 *M* sodium chloride.

#### Materials and Methods

The preparation and characterization of the SDNA have been described.<sup>11</sup> Its molecular weight and radius of gyration were  $5.8 \times 10^6$  and 2170 Å., respectively, comparing well with current preparations in other laboratories.<sup>12</sup> Solutions were prepared as described previously.<sup>11</sup> Their *p*H was always between 6.45 and 7.0, usually near 6.75; the mechanical properties are expected to be insensitive to *p*H in this range.

The dynamic rigidities, G', and dynamic viscosities,  $\eta'$ , were measured over the entire concentration range in

water at frequencies between 8 and 400 cycles/sec. and temperatures 5, 15, 25 and 35°, by the method of transverse wave propagation.<sup>13,14</sup> Some of the measurements were made with an improved apparatus constructed by Mr. D. J. Plazek. Data were also obtained in 0.2 M sodium chloride at 10.0  $\times 10^{-3}$  g./ml., from 5 to 35°.

At two SDNA concentrations in water, 3 and  $12 \times 10^{-3}$  g./ml., G' and  $\eta'$  were measured at 5 and 25° over a wide range of low frequencies—from 6 × 10<sup>-4</sup> to 0.6 cycles/sec.—by the forced vibration torsion pendulum of Morrisson, Zapas and DeWitt.<sup>15</sup>

### Results

Values of G' from wave propagation measurements at different temperatures were reduced to  $2^{\circ}$ by the formula<sup>16</sup>  $G'_{\rm p} = G'T_0c_{\rm C}/T_c$  and are plotted in Fig. 1 against the reduced frequency  $\omega \eta T_0 c_0 / \eta_0 T c.$  Here  $T_0 = 298^{\circ} \text{K}$ ;  $c, c_0, \eta$  and  $\eta_0$  are the concentrations (differing from each other due only to thermal expansion) and the steady flow viscosities at temperatures T and  $T_0$ , respectively. The ratio  $\eta/\eta_0$  was obtained from measured values extrapolated to zero shear rate<sup>11</sup> or for the more dilute solutions calculated from interpolated values of the apparent activation energy for viscous flow (Fig. 2, ref. 11). At each con-centration all the  $G'_p$  values superpose within experimental error, showing that all the viscoelastic mechanisms concerned have the same temperature dependence. Earlier data of Katz<sup>10</sup> on sample I fall below the present data by an order of magnitude or more, supporting the conclusion<sup>11</sup> that sample I was partially degraded when the mechanical properties were measured.

The data of Fig. 1 after further reduction to a reference state of unit viscosity and concentration<sup>16</sup> are plotted in Fig. 2, where  $G'_r =$  $G'T_0/Tc$  and  $\omega_r = \omega_\eta T_0/Tc$ . The points fall reasonably on a single

curve, indicating that in this range the mechanisms all have the same concentration dependence. A similar plot for the reduced dynamic viscosity,  $\eta'_r$ , was also somewhat scattered but could be represented within experimental error by  $\eta'_r = 0.20$  $G'_r/\omega_r$ , corresponding to an approximately constant damping index over the whole range,  $\lambda/x_0 = 0.63$ .

Values of G' and  $\eta'$  from torsion pendulum measurements at 5° were reduced to 25° and combined with measurements at 25° as shown in Fig. 3.

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The coincidence of these more precise data shows clearly the identity of temperature dependence for mechanisms extending over a range of time scale of three logarithmic decades. Although the two types of measurements do not overlap, a reasonable interpolation provides curves extending over six decades for these two SDNA concentrations. Their shapes are qualitatively similar to those of cellulose derivatives<sup>6,7</sup> and polyisobutylene<sup>3</sup> of high molecular weight in a considerably higher concentration range of 50 to 250  $\times$  10<sup>-3</sup> g./ml.

In Fig. 3 are also shown plots of the non-Newtonian apparent viscosity in steady flow,  $\eta_a$ , against rate of shear, from measurements at the Mellon Institute quoted in an earlier paper.<sup>11</sup> These lie quite close to the corresponding curves of  $\eta'(\omega)$ , as would be expected from the theory of De-Witt<sup>17</sup>; they are, however, somewhat to the right of the corresponding dynamic viscosities, as found also by DeWitt for polyisobutylene solutions.<sup>5</sup>

Relaxation Distribution Functions.—The logarithmic relaxation spectrum,  $\Phi_{\rm p}$ , was calculated from the data of Fig. 3 by the usual second approximation formulas<sup>18</sup> for both concentrations, and the results are plotted in Fig. 4. The agreement between the calculations from G' and  $\eta'$  is excellent except for the shortest time at the higher concentration (wave propagation data) where the result from G' is probably more reliable.

These spectra show the three zones characteristic of linear polymers of high molecular weight in concentrated solution—the beginning of a transition at the left, a broad plateau, and a terminal region at the right. In contrast to a number of other polymers, however, the shapes are not quite the same at different concentrations; at  $3 \times 10^{-3}$ g./ml. the plateau is flat as observed especially in cellulose derivatives,<sup>6</sup> while at  $12 \times 10^{-3}$  there is a minimum and maximum as observed in undiluted polyisobutylene<sup>19</sup> and polyvinyl acetate.<sup>20</sup>

For reduction to unit concentration and viscosity, the curves of Fig. 4 were shifted by plotting log  $\Phi_{\rm r}$  (*i.e.*, log  $\Phi/c$ ) against log  $\tau c/\eta$ . Here log  $\eta$ at 25° was estimated by extrapolating  $\eta'$  to zero frequency, giving 2.25 and 3.91, respectively, though the former is somewhat higher than that reported previously<sup>11</sup> from direct measurement. As seen in Fig. 5, the terminal zones now coincide exactly, showing that the slowest relaxation mechanisms have the same concentration dependence,<sup>4</sup> and the curves approach again at the

(18) M. L. Williams and J. D. Ferry, J. Polymer Sci., 11, 169 (1953).

(19) R. S. Marvin, Proc. 2nd Intern. Congress Rheology, 1954, p. 156.



Witt<sup>17</sup>; they are, however, somewhat to the right of the corresponding dynamic viscosities, as found also by DeWitt for polyisototale are produced to 25°, plotted ogarithmically against circular frequency. Circles from torsion pendulum, open at 25°, black at 5°; solid curves at right from wave propagation. Dashed curves (5, 6) denote apparent viscosity as a function of rate of shear (reference 11). Concentrations: 1, 3, 5 are  $3.0 \times 10^{-3}$  g./ml.; 2, 4, 6 are  $12.0 \times 10^{-3}$ .

left end of the plateau, though they diverge in the center. This lack of superposition is not inconsistent with the successful superposition of  $G'_r$  shown in Fig. 2. Values of  $\Phi_r$  calculated from the latter, as well as from the associated plot of  $\eta'_r$ , are also shown in Fig. 5 as vertical lines (the top and bottom of each line representing the calculation from G' and  $\eta'$ , respectively). At the right, where  $G'_r$  is obtained from wave data on dilute solutions,  $\Phi_r$  derived therefrom agrees with curve 1, from torsion pendulum data on a dilute solution. Since there are no wave data on concentrated solutions in this region cf reduced time scale, the superposition failure is not apparent from the wave data alone.<sup>21</sup>

#### Discussion

Comparison with Rouse Theory.—According to the theory of Rouse,<sup>8</sup> the relaxation spectrum of a flexible linear polymer depends on coöperative modes of Brownian motion of the polymer chain and not on details of structure; if, in concentrated solutions, the interlacing with other molecules retards all such motions to the same extent,<sup>3</sup> then only the molecular weight is needed for an explicit calculation of the reduced spectrum  $\Phi_r$ . The function calculated in this manner<sup>23</sup> is compared

<sup>(17)</sup> T. W. DeWitt, J. Applied Phys. 26, 889 (1955).

<sup>(20)</sup> K. Ninomiya and H. Fujita, J. Colloid Sci., in press.

<sup>(21)</sup> The divergence between the two curves at different concentrations cannot be removed by subst tuting  $c^2$  for c in the reduced variables, as introduced by Hatfield<sup>22</sup> and DeWitt<sup>5</sup> for synthetic polymers at high concentrations. In such a plot, the maximum divergence in the center of the plot is over-corrected.

<sup>(22)</sup> M. R. Hatfield and G. B. Rathmann, J. Applied Phys., 25, 1082 (1954).

<sup>(23)</sup> The theory actually predicts a discrete terminal relaxation time,  $\tau_r = 6M/\pi^2 RT$ . The tail of the spectrum shown at the right is a fictitious continuous curve which would be calculated by our approximation methods<sup>18</sup> from dynamic v.scosity.



Fig. 4.—Relaxation spectra at 25° calculated from Fig. 3. Curve 1, 3.0 × 10<sup>-3</sup> g./ml., 2, 12.0 × 10<sup>-3</sup>. Circles top black calculated from G', bottom black from  $\eta'$ .



Fig. 5.—Relaxation spectra reduced to reference state of unit concentration and viscosity. Curves 1 and 2 correspond to those in Fig. 4. Vertical lines denote calculations from  $G'_r$  in Fig. 2 (top bar) and corresponding reduced dynamic viscosity data (bottom bar) from wave propagation measurements. ROUSE, Rouse theory for  $M = 5.8 \times 10^6$ .

with the experimental result in Fig. 5. The location of the terminal zone where  $\Phi$  drops steeply is predicted rather successfully, as it is for vinyl polymers<sup>3,6</sup> and cellulose derivatives.<sup>6,7</sup> The divergence at shorter times is also seen in other polymers of high molecular weight, and its origin is discussed below. The close similarity of SDNA to other polymers in these respects is strong evidence that the viscoelastic properties, like the non-Newtonian flow,<sup>11</sup> are governed in these concentrated solutions by configurational rearrangements of the molecules. Even though in very dilute solution the SDNA molecule is rather stiff, it evidently possesses some flexibility; and when interlaced with its neighbors the rate of its rearrangements is determined primarily by the resistance of its environment rather than its own internal stiffness.

Plateau of the Relaxation Spectrum.—The existence of a plateau, diverging from the linear portion of the theoretical spectrum with a slope of  $-\frac{1}{2}$  on a logarithmic plot, has been attributed in other polymers to coupling of neighboring molecules by some sort of occasional entanglements which severely retard the slow relaxation mechanisms without affecting the rapid ones.<sup>9,24</sup> Though

(24) J. D. Ferry, R. F. Landel and M. L. Williams, J. Applied Phys., 26, 359 (1955).

there is evidence for such entanglements from several sources,<sup>25,26</sup> their nature is only vaguely understood. It is remarkable that SDNA with its far greater extension and stiff structure, which could hardly be expected to kink by doubling back on itself, for example, manifests much the same coupling behavior as the more flexible polymers.

Of course, this appears at much smaller concentrations than usual; at  $3 \times 10^{-3}$  g./ml., for example, polystyrene of the same molecular weight shows no evidence of coupling at all,<sup>27</sup> the entanglement probability corresponding to fewer than two coupling points per molecule.<sup>9</sup> Moreover, the level of the plateau for SDNA is lower by an order of magnitude than the usual range of 0.6 to  $3.0 \times 10^5$  dyn/cm.<sup>2</sup> (reduced to unit concentration). The level is not related directly to the number of entanglements, but is believed to depend on their distribution and the nature of the coupling process.

The width of the plateau is approximately related to the distance between entanglements by the formula<sup>24</sup>  $\Delta = (B - 1) \log (M/2M_e)$ , where B is the exponent describing the dependence of viscosity on molecular weight, and  $M_e$  the average molecular weight between entanglements. As measured from the theoretical Rouse line with a slope of  $-\frac{1}{2}$  to the corresponding rise in the experimental curve for  $12 \times 10^{-3}$  g./ml. with the same slope at the left,  $\Delta = 3.3$  decades. If B is 3.4, as it is for many synthetic polymers,<sup>28</sup>  $M_e = 1.2 \times 10^5$  at this concentration.

**Terminal Zone of the Spectrum.**—The tail of the spectrum at the right drops much less steeply and extends to longer times than it should for a linear polymer homogeneous with respect to molecular weight. Similar behavior in other polymers<sup>3,6,7</sup> has been attributed to molecular weight heterogeneity, but this does not seem so likely in the case of SDNA. The relaxation mechanisms in this region reflect coöperative motions of groups of molecules coupled by entanglements. Even if the molecules are all of the same length, the gradual decrease in coupling through sequences of entanglements<sup>24</sup> should broaden the spectrum. Further examination of the terminal zone may clarify the nature of the entanglement coupling.

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- (20) P. Bueene, J. Chem. Phys., 20, 1959 (1952).
   (27) P. E. Rouse, Jr., and K. Sittel, J. Applied Phys., 24, 690
- (1953).
  - (28) T. G. Fox and S. Loshaek, *ibid.*, 26, 1080 (1955).

<sup>(25)</sup> A. V. Tobolsky and E. Catsiff, J. Polymer Sci., 19, 111 (1956).
(26) F. Bueche, J. Chem. Phys., 20, 1959 (1952).
# NOTES

# DIPOLAR IONS IN NON-AQUEOUS SOLVENTS. I. DIELECTRIC INCREMENTS AS SUPPORTING EVIDENCE FOR THE DIPOLAR STRUCTURE OF SULFAMIC ACID<sup>1</sup>

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The existence of sulfamic acid in the solid state as a dipolar ion (or zwitterion) was suggested initially by Baumgarten<sup>2</sup> in 1929. Experimental verification was provided in 1951 when Kanda and King<sup>3</sup> showed by X-ray diffraction methods that sulfamic acid has a crystalline structure which is characteristic of a dipolar ion. Nevertheless, support for this structure of sulfamic acid in any solution has remained lacking. Little evidence for the dipolar nature of sulfamic acid is obtainable from aqueous solution in which it is almost completely dissociated<sup>4</sup> into sulfamate ions and solvated protons owing to the greater basicity of water in comparison to that of the sulfamate ion. Furthermore, sulfamic acid is practically insoluble or reacts readily with the majority of non-aqueous solvents<sup>5,6</sup> to form substituted ammonium salts or other products. Recently in this Laboratory it has been fortuitously observed, however, that sulfamic acid dissolves readily (in dimethyl sul-foxide, in N,N-dimethylacetamide and in N,N-dimethylpropionamide) forming stable, low-conducting solutions which have dielectric properties which indicate that sulfamic acid remains in the dipolar form after dissolution.

#### Experimental

1. Solutes.-Sulfamic acid which was obtained from the G. Frederick Smith Chemical Company having a purity assay of 99.98% was dried in a desiccator over anhydrous magnesium perchlorate prior to using without further purification.

Glycine (Eastman Kodak Co. grade) was recrystallized several times from aqueous solution by adding ethanol. The final product was dried to constant weight in a vacuum oven at 50°

Aminoiminomethanesulfinic acid (Eastman Kodak Co. grade) was dried over anhydrous magnesium perchlorate and used without further purification.

2. Solvents -- Distilled water of good quality was available from a departmental supply.

Dimethyl sulfoxide was rendered anhydrous by refluxing it for several hours in contact with calcium oxide. Two fractional distillations at reduced pressure yielded a product having the following physical properties at 25°: density, 1.0958 g./ml.; viscosity, 0.0196 poise; dielectric constant,

46.7. N,N-Dimethylacetamide and N,N-dimethylpropionamide were synthesized similarly from the proper acid and dimethylamine as described in a previous paper.<sup>7</sup> The

(1) This research was supported in part by a contract with the Office of Ordnance Research.

(2) P. Baumgarten, Ber., 62, 820 (1929).
(3) F. A. Kanda and A. J. King, J. Am. Chem. Soc., 73, 2315 (1951)

(4) E. G. Taylor, R. P. Desch and A. J. Catotti, ibid., 73, 74 (1951).

(5) M. E. Cuprey, Ind. Eng. Chem., 30, 627 (1938).

(7) G. R. Lester, T. A. Gover and P. G. Sears, This JOURNAL, 60, 3076 (1956).

physical properties of the retained products were as follows for N,N-dimethylacetamide and N,N-dimethylpropion-amide, respectively, at 25°: densities, 0.9366 and 0.9205 g./ml.; viscosities, 0.00919 and 0.00935 poise; dielectric constants, 37.8 and 32.9.

3. Apparatus and Procedure.—The bridge, cells, temperature control and principal aspects of the calibration and measuring procedures have been described in detail previously by Leader.<sup>8</sup>

The standard media which were used to calibrate the dielectric constant cells were air and water. The values used for the dielectric constants of these at 25° were unity and 78.54°,<sup>9</sup> respectively. All measurements were made at ten megacycles. The estimated uncertainty associated with any experimental dielectric value did not exceed 0.1 of a dielectric unit.

Solutions were prepared on a weight basis with all transfers except those for the aqueous glycine solutions being made in a dry box. Necessary buoyancy corrections were applied. Suitable density data were available<sup>10,11</sup> for the conversion of molalities to molarities.

#### **Results and Discussion**

Extensive tabulation of corresponding values of the dielectric constant,  $\epsilon$ , and the concentration, C has been omitted from this paper<sup>12</sup> inasmuch as for each system the dielectric constant is a linear function of the molar concentration of solute. The data in each case can be described by an equation of the type

$$\epsilon = \epsilon_4 + \delta C \tag{1}$$

where  $\epsilon$  is the dielectric constant of the solution,  $\epsilon_0$  is the dielectric constant of the solvent,  $\delta$  is the dielectric increment per mole of solute per liter of solution, and C is the molar concentration. The results are summarized in Table I.

The results for the aqueous glycine solutions agree within experimental error with the widely accepted research of Wyman and McMeekin<sup>13</sup> and

#### TABLE I

VALUES OF CONSTANTS FOR PLOTS OF EQUATION 1 FOR SOLU-TIONS OF DIPOLAR SOLUTES IN SEVERAL SOLVENTS AT 25°

Solvent	Solute	€0	δ
Water	Glycine	78.54	22.5
N,N-Dimethylacet- amide	Sulfamic acid	37.8	15.6
N,N-Dimethylpro- pionamide	Sulfamic acid	32.9	15.3
Dimethyl sulfoxide	Sulfamic acid	46.7	7.6
Dimethyl sulfoxide	Aminoiminometh- anesulfinic acid	46.7	14.5

(8) G. R. Leader, J. Am. Chem. Soc., 73, 856 (1951).

(9) J. Wyman, Phys. Rev., 35, 623 (1930)

(10) F. T. Gucker, W. F. Ford and C. E. Moser, THIS JOURNAL, 43, 153 (1939).

(11) R. K. Wolford, unpublished data, University of Kentucky, 1956.

(12) Material supplementary to this article has been deposited as Document number 5045 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by siting the Document number and by remitting in advance \$1.25 for photoprints, or \$1.25 for 35 mm. microfilm, by check or money order payable to: Chief, Photoduplication Service, Library of Congress

(13) J. Wyman and T. L. McMeekin, J. Am. Chem. Soc., 55, 908 (1933).

<sup>(6)</sup> L. F. Audrieth, M. Sveda, H. H. Sisler and M. J. Butler, J. Am. Chem. Soc., 26, 49 (1940).

As may be noted from the values of  $\delta$  in Table I, the dielectric increment of sulfamic acid in each of the two amides is approximately twice that for it in dimethyl sulfoxide. Although the smaller increment for sulfamic acid in dimethyl sulfoxide perhaps can be attributed partially to the greater dielectric constant of pure dimethyl sulfoxide as compared to those of the amides, it is probably reduced principally by some type of solute-solvent interaction. Data are not included for N,N-dimethylformamide solutions because sulfamic acid interacts with the formyl group of that solvent to produce a conducting species.

A direct comparison of the dielectric properties of solutions of sulfamic acid with those of some of the  $\alpha$ -aminocarboxylic acids, such as glycine, cannot be made inasmuch as the latter are insoluble in the non-aqueous solvents. The increment for sulfamic acid in any of the non-aqueous solvents is less than the increment of 22.6 dielectric units per mole per liter of solution for the  $\alpha$ -aminocarboxylic acids in water; however, this might be expected as calculations show a smaller separation of charges on the basis of free rotation for sulfamic acid<sup>3</sup> as compared to a substance such as glycine.<sup>14</sup>

Taurine ( $H_2NCH_2CH_2SO_3H$ ) was found to be insoluble in the nonaqueous solvents. However, aminoiminomethanesulfinic acid ( $HN_2:NHSO_2H$ ) is soluble to about 0.2 M in dimethyl sulfoxide although it is insoluble in the amides. The value of  $\delta$  for aminoiminomethanesulfinic acid in dimethyl sulfoxide was found to be 14.5 at 25° and is probably greater than that for sulfamic acid in the same solvent partially as a result of a greater separation of charges.

Acknowledgment.—The authors wish to express their appreciation to the Stepan Chemical Company for donating the dimethyl sulfoxide which was used in this research.

(14) G. Albrecht and R. Corey, J. Am. Chem. Soc., 61, 1087 (1939).

## SMALL ANGLE X-RAY SCATTERING BY ALUMINUM HYDROXIDE GEL<sup>1</sup>

By Paul W. Schmidt, Jan Krogh-Moe<sup>2</sup> and Harold D. Bale

## Physics Department, University of Missouri, Columbia, Missouri Received May 25, 1956

The small angle X-ray scattering by aluminum hydroxide gel has been studied on a collimation system of design similar to the one used by Beeman,<sup>3</sup> using balanced filters, copper  $K_{\alpha}$  radiation and a Geiger tube detector. The collimator slits were  $1/4 \times 10$  mm., with 50 cm. between neighboring slits. No attempt was made to correct for collimation errors, since these are not likely to affect the conclusions drawn from the data. The gel was precipitated from a solution of Al<sup>+++</sup> ions in water

(1) Work supported by the Research Corporation.

(2) Research fellowship from the International Cooperation Administration.

(3) A. Guinier and G. Fournet, "Small Angle Scattering of X-Rays," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 95. by adding 3 M ammonium hydroxide solution in an amount corresponding to approximately pH 8 for the final mother liquid. The gel was separated from the mother liquid by filtering and sealed in an aluminum sample holder with "Saran Wrap" windows.

Figure 1 shows the scattering obtained for a precipitate from a 0.25 M solution of aluminum ni-The initial curve, made immediately after trate. preparation, has a larger slope than the next, made 24 hours later on the same sample stored at room temperature. The aging effect appears to be completed within this period, since no additional change in the intensity curve was noticed in tests made after this time. Work was also done on gel that was left in the mother liquid for 48 hours before filtering. These curves indicate the same aging had occurred in the mother liquid that took place in the sample holder in the first case. The direction of the change of slope with aging is unexpected, since according to the conventional interpretation the observed aging effect would correspond to a decrease of particle size with time. A powder sample, made by air drying the freshly prepared gel, appeared to have approximately the same slope as the fresh gel and showed no aging effect.

Preliminary experiments on gels prepared from 0.125 M aluminum sulfate solution (the same  $Al^{+++}$  ion concentration as in the previous experiment) indicates a larger slope for the scattering curve than in the aluminum nitrate case. A small aging effect corresponding to a decrease in particle size was noticeable. A gel precipitated from 0.0125 M aluminum sulfate showed a smaller slope for the scattering curve than the gel precipitated from the more concentrated sulfate. The aging effect here was small, perhaps within the experimental error, and seemed to go in the opposite direction to the aging effect found for the nitrate data.

Weiser<sup>4</sup> has made a study of the crystallite size of aluminum hydroxide gel using the X-ray diffraction line broadening method. His results indicate the crystal size changes in a different direction than the parameter determined from the small angle scattering data; the crystallites grow larger with age and the crystals precipitated from dilute solutions are larger than those precipitated from concentrated. He also found that crystallites precipitated from aluminum sulfate were smaller than those precipitated from aluminum nitrate. These disagreements between the line broadening method and small angle scattering seem to indicate that the small angle scattering is not a measure of the size of the crystallites. It is questionable whether the small angle scattering results can be interpreted in terms of average particle sizes, since the exact nature of the gel is not known. It is entirely possible that the scattering could be caused by holes or regions of lower density in a continuous liquid-like structure rather than by individual particles. Hence a decrease in the slope of the scattering curve on aging could be caused either by a decrease

(4) H. B. Weiser and W. O. Milligan, "Advances in Colloid Science," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1942, p. 228-233. in particle size or by a decrease in size of the pores. Also the establishment of a new phase could be a cause for the observed effect.

Van Nordstrand and co-workers<sup>5</sup> have found that at very large angles of the small angle scattering region the scattering from alumina catalysts varies as the inverse fourth power of the scattering angle. This angular dependence, which has been predicted by Porod,<sup>6</sup> was not found in the present scattering experiment, since the measurements were taken at angles smaller than obtainable with the apparatus used by Van Nordstrand. The theoretical curves used below to fit the scattering data predict that the observed scattering will not vary with the inverse fourth power of the angle.

The data can probably best be interpreted by Fourier transform methods. All information obtainable from scattering experiments is contained in the characteristic function  $\gamma(r)$ , given by

$$\gamma(r) = (C/r) \int_0^\infty sI(s) \sin sr \, ds$$

where C is a constant, I(s) is the observed intensity,  $\theta$  is the scattering angle,  $\lambda$  is the wave length of the radiation, and

 $s = (4\pi\theta)/\lambda$ 

The characteristic function  $\gamma(r)$  is discussed in the book by Guinier and Fournet.<sup>7</sup> It represents an average value of correlations in electron density fluctuations between regions separated by a distance r. The function has been applied to light scattering by Debye and Bueche.<sup>8</sup> Porod<sup>6</sup> has investigated  $\gamma(r)$  for samples composed of randomly distributed matter of uniform electron density. His work has been extended by Debye<sup>9</sup> and applied to solid porous catalysts. Debye found that his data could be fitted by a characteristic function of the form

$$\gamma(r) = A \exp(-r/a) + (1 - A) \exp(-r^2/2b^2)$$

where a, b and A are adjustable parameters. The corresponding scattered intensity I(s) will be, where B is a constant

$$I(s) = B[2a^{3}A(1 + a^{2}s^{2})^{-2} + (\pi/2)^{1/2}b^{3}(1 - A) \exp((-b^{2}s^{2}/2))]$$

A reasonably good fit of the data of Fig. 1 was obtained with A, a and b equal to 0.9504, 18.91 and 99.3 Å., respectively, for the freshly prepared sample. For the aged sample the corresponding values were, respectively, 0.9854, 18.61 and 103.9 Å. The curves in Fig. 1 are drawn with these parameters. The fit at the smallest angles could be improved by adding another gaussian term to the equation for I(s). However, as the data at 0.0018 radians are somewhat likely to be in error, a better fit possibly should not be expected.

One can calculate  $\gamma(r)$  by direct numerical integration of the scattering data, assuming that the scattering outside the experimental range makes a

(5) R. A. Van Nordstrand and K. M. Hack, paper presented at ACS meeting, Chicago, Sept., 1953; R. A. Van Nordstrand and M. F. L. Johnson, paper presented at ACS meeting, New York, Sept., 1954.

(8) P. Debye and A. M. Bucche, J. Appl. Phys., 20, 518 (1949).
(9) P. Debye, Report distributed to members of the American Petroleum Institute.



Fig. 1.—Gel precipitated from  $0.25 \ M$  aluminum nitrate. Scattered intensity plotted against scattering angle, with the experimental points fitted to Debye s theoretical scattering curve: A, freshly prepared sample; B, same sample 24 hours after preparation.



Fig. 2.—Gel precipitated from 0.25 M aluminum nitrate. Plot of  $r^2\gamma(r)$  against distance, r, in A.: A, freshly prepared sample; B, same sample 24 hours after preparation.

negligible contribution to the integral. Figure 2 shows the result of such an integration for the gels for which the scattering is shown in Fig. 1. The maximum of the curve of  $r^2\gamma(r)$  can be taken as a measure of the size of the regions of inhomogeneity giving rise to the scattering. This definition would appear reasonable since it gives very nearly the correct result for spherical particles, for which the diameter equals approximately twice the distance at which the maximum of  $r^2\gamma(r)$  occurs.

With a relatively smooth intensity curve, as encountered in this kind of work, the Fourier transform can be performed rapidly by expanding the intensity curve in the first few terms of a power

<sup>(6)</sup> G. Porod, Kolloid Z., 124, 83 (1951).

<sup>(7)</sup> A. Guinier and G. Fournet, ref. 3, p. 75-82.

series and doing the transform analytically. A further investigation will be made of this method of analyzing the small angle scattering data from these gels.

The function  $r^2\gamma(r)$  determined by numerical integration agreed only qualitatively with the function  $r^2\gamma(r)$  corresponding to the scattering function which was fitted to the data. Close agreement probably cannot be expected, however, since the two characteristic functions are obtained by making different assumptions about the scattering outside the range of experimental observation.

## THE HEAT OF COMBUSTION OF ERBIUM<sup>1</sup>

By Elmer J. Huber, Jr., Earl L. Head and Charles E. Holley, Jr.

Contribution from the University of California, Los Alamos Scientific Laboratory

#### Received June 4, 1956

The rare earth metals and their compounds are of increasing interest to chemists and technologists as they become more available and more is known about them. During the past few years we have measured the heats of combustion of a number of the rare earth metals and this paper is the seventh of the series<sup>2-7</sup> reporting the results of the measurements. The method, involving the determination of the heat evolved from the combustion of a weighed sample of the metal in a bomb calorimeter at a known initial pressure of oxygen, has been described.<sup>6</sup> The same units and conventions are used here.

Erbium Metal.—The erbium metal was analyzed and found to have the following per cent. impurities: C, 0.009; H, 0.014; N, 0.001; O, 0.011; Mg, 0.005. No other metallic impurities were detected.

The metal thus contained about 0.1% impurities. If it is assumed that the non-metallic impurities are combined with the erbium as the carbide, hydride, nitride and oxide, the erbium is 98.69 mole %metal (atomic weight Er = 167.27).

An X-ray pattern of the erbium showed a two atom hexagonal close-packed unit cell and a calculated density of 9.05 g./cc.

**Combustion of Erbium.**—The erbium was burned on sintered discs of erbium oxide in oxygen at 25 atmospheres pressure. The oxide was approximately 99.9% pure. The metal showed no increase in weight when exposed to  $O_2$  at 25 atm. pressure for one hour. Combustion varied from 99.73 to 100.00% of completion. The average initial temperature for the runs was 25.2°. The results are listed in Table I. This average value of 5657.3  $\pm$ 3.8 joules/g. must be corrected for the impurities present.

Correction for Impurities.—The calculated percentage composition of the erbium by weight is Er

(2) E. J. Huber, Jr., and C. E. Holley, Jr., J. Am. Chem. Soc., 74, 5530 (1952).

(4) E. J. Huber, Jr., and C. E. Holley, Jr., ibid., 75, 5645 (1953).

(5) E. J. Huber, Jr., and C. E. Holley, Jr., *ibid.*, **77**, 1444 (1955).

(6) E. J. Huber, Jr., C. O. Matthews and C. E. Holley, Jr., *ibid.*, 77, 6493 (1955).

(7) E. J. Huber, Jr., E. L. Head and C. E. Holley, Jr., THIS JOURNAL 60, 1457 (1956).

TABLE I

THE HEAT OF COMBUSTION OF ERBIUM

Mass Er burned,	Wt. Mg,	$\operatorname{Wt.}_{\mathfrak{s}_2\mathcal{O}_{\mathfrak{s}_1}}$	Joules/ deg.,	$\Delta T$ , °K	Energy Firing,	from Er,	Dev. from
		6.	10001		1.	J./ 6.	
2.2573	6.89	42.6	10031.0	1.2922	10.2	5662.5	5.2
2.1177	7.88	48.9	10032.6	1.2144	9.1	5657.1	. 2
2.1534	7.19	35.6	10029.2	1.2338	12.0	5658.3	1.0
2.1637	6.9 <b>6</b>	32.1	10028.2	1.2401	13.5	5662.0	4.7
2.1 <b>78</b> 1	7.12	33.8	10028.7	1.2462	13.2	5651.3	6.0
2.1280	7.21	31.3	10028.0	1.2183	11.0	5652.4	4.9
					Av	. 5657.3	3.7
					Sta	and. Dev	. 1.9

metal 98.71; ErH<sub>2</sub>, 1.18; Er<sub>2</sub>O<sub>3</sub>, 0.088; ErN, 0.013; C, 0.009; Mg, 0.005. The carbon is probably present as  $\text{ErC}_2$  but its heat of formation is not known and is probably small. The heat of combustion of Er metal corrected<sup>6</sup> for impurities is 5,660.2 j./g. The correction due to impurities amounts to 0.05% of the uncorrected value.<sup>9</sup>

Calculation of the Uncertainty.—The uncertainty to be attached to the corrected value includes the uncertainty in the energy equivalent which is 0.04%, the uncertainty in the calorimetric measurements which is 3.8 j./g. or 0.07% and the uncertainty introduced in the correction for the impurities,<sup>6</sup> which is estimated to be 0.06%.

The combined uncertainty is 5.7 joules/g. The value for the heat of combustion gives for the reaction in the bomb a value of  $\Delta E_{25\cdot0^2} = -1893.6 \pm 1.9 \text{ kj./mole.}$ 

**Composition of the Erbium Oxide.**—The oxide formed was pink in color. An X-ray pattern showed it to be the C-type sesquioxide. Analysis by the method of Barthauer and Pierce<sup>10</sup> showed no oxygen above that necessary for the sesquioxide.

Heat of Formation of  $\text{Er}_2\text{O}_3$ .—Using methods of calculation reported elsewhere<sup>6</sup> the heat of formation of  $\text{Er}_2\text{O}_3$ ,  $\Delta H_{25}^\circ = -1897.8 \pm 1.9$  kj./mole. In defined calories this is  $-453.59 \pm 0.45$  kcal./mole. No literature values are available for comparison. It is interesting to note that this value is even greater than the value reported for  $\text{Dy}_2\text{O}_3^7$  which seemed high when compared with the heats of formation reported for  $\text{Gd}_2\text{O}_3$ ,<sup>5</sup>  $\text{Sm}_2\text{O}_3^6$  and  $\text{Yb}_2\text{O}_3^7$ .

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They also appreciate the courtesy of Dr. F. H. Spedding of the Ames Laboratory, A.E.C., through whom the metal and oxide were obtained.

(8) The specific heat of  $Er_2O_3$  is estimated to be 0.26 joule/g./°. The specific heat of Pt is taken as 0.136 joule/g./° and the specific heat of  $O_2$  as 0.651 joule/g./°. The amount of MgO formed is so small that its contribution to the energy equivalent of the calorimeter may be neglected.

(10) G. L. Barthauer and D. W. Pierce, Ind. Eng. Chem., 18 (1946).

<sup>(1)</sup> This work was done under the auspices of the A. E. C.

<sup>(3)</sup> E. J. Huber, Jr., and C. E. Holley, Jr., ibid., 75, 3594 (1953).

<sup>(9)</sup> The heat of formation of  $ErH_2$  is taken as -57 kcal./mole from the unpublished work of R. N. R. Mulford of this Laboratory. The heat of formation of ErN is estimated at -75 kcal./mole from the published values of LaN and CeN. See Selected Values of Chemical Thermodynamic Properties, N.B.S. Circular 500, 1952, pp. 350, 354. The heats of combustion of graphite (to  $CO_2$ ), and magnesium (to MgO) are taken as 33,000 and 24,670 j./g., respectively. The heats of formation of  $H_2O(g)$  and  $NO_2$  are taken as -58 and +8 kcal./ mole.

## THE EFFECT OF PICOLINES ON MALONIC ACID

## By Louis Watts Clark

#### Contribution from the Department of Chemistry, Saint Joseph College, Emmitsburg, Maryland Received May 18, 1966

Kinetic studies previously have been reported on the decomposition of malonic acid in several aromatic amines including aniline, quinoline and pyridine.<sup>1-3</sup> In these solvents smooth decarboxylation of malonic acid takes place by a first-order reaction. While the mechanism of the reaction has not been completely elucidated infrared measurements by Fraenkel and co-workers2 indicated strong interaction between malonic acid and amines. These workers suggested that an intermediate compound is formed between malonic acid and amine due to solvation of the carboxyl carbon atom. It was believed that valuable information on the mechanism of this reaction might be obtained by studying the effect on the rate of decomposition of malonic acid produced by slight variations in the structure of the solvent molecules. The simplest case that could be imagined was the addition of a single methyl group to pyridine in each of the three available positions. Rate studies were carefully conducted using reagent malonic acid in high purity picolines. The results of this investigation are reported herein.

#### Experimental

**Reagents.**—The reagents used were: (1) malonic acid, reagent grade, 100% assay; (2) 2-methylpyridine, purified, b.p. 127-130°, sp. gr. 0.950 at 15°; (3) 3-methylpyridine (98%), b.p. 142-144°; (4) 4-methylpyridine, purity 98% minimum, water content 0.2% maximum, b.p. 142-144°, f.p. 2.4° min.

## Results and Discussion

The specific reaction velocity constants at the various temperatures studied for the three picolines (calculated from the slopes of the lines formed by plotting log (a - x) vs. t) were as follows: (1) 2-picoline: 113.4°, 0.00175 sec.<sup>-1</sup>; 120.7°, 0.00295; 129.9°, 0.0056; (2) 3-picoline: 113.4°, 0.00208; 120.7°, 0.00384; 129.9°, 0.0075; (3) 4-picoline: 110.0°, 0.00182; 116.6°, 0.00315; 126.8°, 0.0074.

When log k was plotted against 1/T according to the Arrhenius equation straight lines resulted from which the activation energies and frequency factors were calculated. The enthalpies, entropies and free energies of activation at 110° were calculated from the Eyring equation. The data thus obtained, as well as the values of the specific reaction velocity constants for the reaction in each solvent at 110°, are shown in Table I, which includes also for comparison corresponding data for pyridine.<sup>3</sup>

In the case of 2-picoline the +I effect of the methyl group would be expected to increase the basicity of the nitrogen with respect to pyridine and thereby lower the amount of energy required to form the activated complex (assuming that malonic acid does form an unstable intermediate compound with the amine). On the other hand the steric factor would be expected to diminish the probability of the formation of the activated complex. Since methyl is a relatively small group it would be expected that the +I effect would outweigh the steric effect resulting in an increase in rate. These predictions are borne out by the results. By comparing lines (1) and (2) of Table I we see that the methyl group in the 2-position has considerably lowered the heat of activation as compared with pyridine and has also brought about a large de-

	Malonic Acid in Picolines, Kinetic Data							
	System	$E^*$ (cal.)	(sec1)	Temp. coeff.	$\Delta H$ <sup>‡</sup> (cal.)	$\Delta S^{\ddagger}$ (e.u.)	$\Delta F^{\ddagger_{110}}$ (cal.)	$k_{110^0}$ (sec. <sup>-1</sup> )
1.	Malonic a <b>c</b> id plus pyridine	26,600	$1.59 \times 10^{12}$	2.75	<b>2</b> 6,000	+ 7.2	23,240	0.0009
2.	Malonic acid plus 2-picoline	21,750	$3.84 \times 10^{9}$	2.0	<b>20</b> ,900	-17.35	27,550	0.00133
3.	Malonic acid plus 3-picoline	22,600	$1.5 \times 10^{10}$	2.0	21,900	-14.24	27,350	0.001685
4.	Malonic acid plus 4-picoline	25,650	$9.1 \times 10^{11}$	2.3	25,210	- 5.6	27,350	0.00182

TABLE I

Apparatus and Technique.—The apparatus and technique in this study were the same as those used in studying the decomposition of malonic acid in triethyl phosphate.<sup>4</sup> Kinetic Studies.—Samples of malonic acid weighing 0.1857 g. (sufficient to yield 40.0 ml. of CO<sub>2</sub> at S.T.P. on complete

Kinetic Studies.—Samples of malonic acid weighing 0.1857 g. (sufficient to yield 40.0 ml. of  $CO_2$  at S.T.P. on complete reaction) were introduced into 100 ml. of picoline (saturated with dry  $CO_2$  gas) in the reaction flask in the thermostat oilbath in the manner previously described. The evolved carbon dioxide was measured at constant pressure. The experiment was carried out at three different temperatures between 110–130° in each picoline. In every experiment the total volume of gas produced was 100% of the theoretical yield within the limit of error of the experiment. crease in the entropy of activation. This means that less energy is required for activation (due to the increase in basicity caused by the +1 effect of the methyl group), but the steric effect decreases the probability of the formation of the activated complex. Of these two opposing effects the change in enthalpy predominates resulting in a slight increase in the rate at  $110^{\circ}$ .

When the methyl group is in the 3-position we would expect little steric hindrance and at the same time a smaller effect upon the basicity because of the greater distance between the methyl group and the nitrogen in the ring. Again the results completely confirm these expectations. Examining line (3) we see that the enthalpy of activation is lowered by 3-picoline but not to the extent that it

<sup>(1)</sup> Y. Ogata and R. Oda, Bull. Inst. Phys. Chem. Res. (Tokyo), Chem. Ed., 23, 217 (1944); C.A., 43, 7904 (1949).

<sup>(2)</sup> G. Fraenkel, R. L. Belford and P. E. Yankwich, J. Am. Chem. Soc., 76, 15 (1954).

<sup>(3)</sup> L. W. Clark, This Journal, 60, 1340 (1956).

<sup>(4)</sup> L. W. Clark, ibid., 60, 1150 (1956).

is by 2-picoline. The entropy of activation is higher for 3-picoline than for 2-picoline indicating less interference by the methyl group in the formation of the activated complex. The rate of decomposition of malonic acid in 3-picoline at  $110^{\circ}$  is slightly higher than in 2-picoline.

Since the methyl group in 4-picoline is so far removed from the nitrogen atom we would expect very little interference with the formation of the activated complex. On the other hand we would not expect the +I effect of the methyl group to be very pronounced at such a remote distance. Nevertheless we would expect some increase in basicity resulting in an increase in rate. The actual results are in accord with this interpretation. If we examine line (4) of Table I we see that there is a slight decrease in the enthalpy of activation of 4-picoline as compared with pyridine (due, undoubtedly, to the greater basicity of the 4-picoline as compared with pyridine, showing that methyl in the 4-position still exerts a perceptible +I effect upon the electronegative nitrogen atom), and also there is only a very small adverse change in the entropy of activation ( this might be attributed to the bulkyness of the molecule of 4-picoline as compared with pyridine). The rate of decomposition of malonic acid in 4-picoline at 110° is slightly larger than in 3-picoline and is twice as great as in pyridine.

These results lend support to the suggestion that malonic acid forms an unstable intermediate compound with non-aqueous basic solvents. Further work on the problem is contemplated.

# THE DIELECTRIC PROPERTIES OF SOLID NITRODICHLORO-*o*-XYLENES<sup>1</sup>

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Received June 6, 1956

Several years ago McMahon reported<sup>2</sup> that some polar wax-like substances have significantly higher dielectric constants in the solid state when the molten substances are solidified under an electric field (steady or alternating) than they do when solidified without an impressed field. More recently he has published<sup>3</sup> more data on this phenomenon and has reported an analogous effect of magnetic fields. The substance which he found to show the most marked effect was Nitrowax, which is a mixture mainly of nitrodichloro-oxylenes.

The investigation being reported in this note was a study of the electric field effect on the individual isomers 3-nitro-4,5-dichloro-o-xylene (I) and 4nitro-3,6-dichloro-o-xylene (II), and on certain mixtures of them.

## Experimental

The isomers I and II were synthesized by previously

(3) Ref. 2, 1955, p. 47.

reported procedures.<sup>4,5</sup> Dielectric constants were measured with the heterodyne-beat apparatus of Wallis and Wood<sup>6</sup> together with a dielectric constant measuring cell adapted from a 6H6 vacuum tube,<sup>7</sup> the cathode-to-plate capacitance serving as a measure of the dielectric constant of the intervening dielectric. All of the terminal connections of the 6H6 were grounded except the heaters and cathodes. The cell was surrounded by a jacket and was thermostated at 25° by water, at 100° by steam or at 138° by *n*-amyl alcohol vapor. The apparatus was calibrated by measurements with air and with purified benzene in the cell. The isomers and their mixtures were introduced into the cell by melting them and sucking the liquid in through copper tubes soldered into the 6H6.

For experiments involving solidifications under an electric field, an alternating potential was supplied from the line through a variable transformer to the cathode-plate terminals of the 6H6. In all the experiments reported here the potential was 120 volts. Since these electrodes approximate concentric cylinders with an annular spacing of about 0.04 cm. and an inner radius of about 0.06 cm., the resulting electric field would be very roughly uniform and of the order of 3000 volts per centimeter.

#### Results

The Pure Isomers.—The dielectric constant of molten I at 138° was 12.6 and that of molten II at 100° was 14.0. The compounds solidified under no field had dielectric constants at 25° which were not significantly different from that of the compounds solidified under the field, namely, about 2.7 in each case. Neither I nor II appeared to pass through waxy states prior to melting nor upon refreezing.

Mixtures of the Isomers.—A liquefied mixture of 1 part I with 10 parts of II passed through a waxy transition state on cooling although it became hard and brittle at room temperature. The dielectric constant of the molten mixture at  $100^{\circ}$ was 13. When solidified under no field, the dielectric constant at  $25^{\circ}$  was 3.0, a value which did not differ significantly from that for the mixture solidified under the field.

A liquefied mixture of 1 part I with 2 parts II had a melting point of  $77.5-78.5^{\circ}$  and passed through a waxy transition state on cooling. At room temperature it was still waxy, but became hard and brittle on standing overnight. This mixture showed a substantial though somewhat erratic increase in dielectric constant when solidified under the field as compared to its dielectric constant when solidified under no field. The erratic fluctuations may be attributed at least in part to the formation of cracks and gas pockets during solidification.<sup>8</sup> The dielectric constant of the waxy form was found to be much higher than that of the hard, brittle form. The data are summarized in Table I. The rate of change of dielectric constant as the waxy form changed to the hard form was measured in one instance and the data are plotted in Fig. 1.

#### Discussion

McMahon explained the effect of the electric field applied during solidification as due to an

(4) C. Boyars, J. Am. Chem. Soc., 75, 1989 (1953).

(5) L. E. Hinkel, E. E. Ayling and L. C. Bevan, J. Chem. Soc., 1874 (1928).

(6) R. G. Dickinson, R. F. Wallis and R. E. Wood, J. Am. Chem. Soc., 71, 1238 (1949).

(7) R. E. Wood, Science, 116, 358 (1952).

(8) Cf. S. E. Kamerling and C. P. Smyth, J. Am. Chem. Soc., 55, 462 (1933).

Based on a portion of the M.S. Thesis of Carl Boyars, May, 1952.
 W. McMahon, "Annual Report, Conference on Electrical Insulation of the Division of Engineering and Industrial Research," National Research Council, 1948, p. 84.

### TABLE [

DIELECTRIC CONSTANTS OF A 1:2 MIXTURE OF 3-NITRO-4,5-DICHLORO-0-XYLENE AND 4-NITRO-3,6-DICHLORO-0-XYLENE

State and history of mixture	Av. dielectric constant	meas- ure- ments	Av. dev.	
Liquid, 100°	13.4	43	0.29	
Wax, 25°. Frozen under no field and measured shortly after freez- ing	14.8	1.1	54	
Brittle solid, 25°. Frozen under no	14.0	14	.01	
field and allowed to stand at least 1 day before measurement	3.4	7	.29	
Wax, 25°. Frozen under a field of about 3000 v./cm. and measured		••	00	
shortly after freezing Brittle solid, 25°. Frozen under a	16.5	18	.89	
field of about 3000 v./cm. and al- lowed to stand at least 1 day be-				
fore measurement	3.6	5	.04	

orientation of crystallites of the wax in the direction of higher polarizability. The molecules are presumed to have a disc-like shape with dipoles in the plane of the disc and to be capable of rotating readily in the solid state only about an axis per-pendicular to the plane of the disc. Orienting effects of electric fields on waxes have been reported by Ewing,<sup>9</sup> Bennett,<sup>10</sup> and Müller and coworkers.<sup>11</sup> White, Biggs and Morgan<sup>12</sup> have reported 10tation to occur only in the plane of the benzene ring in solid penta- and hexa-substituted benzenes in which the substituents are chlorine, nitro and methyl groups. These authors found that 3-nitro-4,5-dichloro-o-xylene showed no molecular rotation in the crystal. They reported that its isomer, 5-nitro-3,4-dichloro-o-xylenc, showed a transition to a waxy, translucent state; above the transition temperature molecular rotation in the solid was found. However, the melting point they reported for the latter compound leads to the conclusion that its purity and identity are in doubt.

The low dielectric constants we have found for the solid 3-nitro-4,5-dichloro-o-xylene and 4-nitro-3,6-dichloro-o-xylene indicate that orientation of the molecular dipoles does not take place in the electric field applied for measuring dielectric constant. When these two compounds are mixed in proportions which give a waxy solid, the high dielectric constant of the resulting wax suggests that molecular rotation is occurring. Molecules in a wax are not held as rigidly as molecules in an ordinary crystal lattice. The increase in dielectric constant due to solidification in an applied electric field also appears to be a characteristic of the waxy state. The explanation of this increase as being due to the orienting effect of the field on the wax crystallites as they are forming seems logical.

The shape of the graph in Fig. 1 indicates that the transition from the waxy to the brittle solid is a

(9) M. Ewing, Phys. Rev., 36, 378 (1930).

(10) R. D. Bennett, *ibid.*, **37**, 103 (1931), J. Franklin Inst., **211**, 481 (1931).

(12) A. II. White, B. S. Biggs and S. O. Morgan, J. Am. Chem. Soc., 62, 16 (1940).



Fig. 1 - 1:2 mixture of 3-nitro-4,5-dichloro-*o*-xylene with 4-nitro-3,5-dichloro-*o*-xylene. This graph shows the rate of change of dielectric constant as the mixture changes from the waxy to the brittle form.

heterogeneous process propagating itself at the boundary surface between the two phases. It is like the freezing of a supercooled liquid or the crystallization of a supersaturated solution. In fact there is a marked similarity between the shape of this curve and one of those plotted by Collins and Leineweber<sup>13</sup> to represent their data on the rate of precipitation of barium sulfate from supersaturated solutions. Nitrowax appears to retain its waxy character indefinitely at ordinary temperatures. Whether there are temperature ranges in which the waxy states of the mixtures we studied are indefinitely stable has not been determined.<sup>14</sup>

(13) F. C. Collins and J. P. Leineweber, This Journal,  ${\bf 60},~393~(1956).$ 

(14) Since this note was submitted, a further publication by W. McMahon, J. Am. Chem. Soc., **78**, 3290 (1956), has appeared, giving many more experimental details than are found in ref. 2 and 3. It is asserted that the increase in dielectric constant which accompanies solidification under an electric field is isotropic.

# DIPOLE MOMENTS OF CYCLOHEXYL AZIDE, CYCLOPENTYL AZIDE AND 3-BROMOCYCLOHEXENE<sup>1</sup>

BY ROY L. BENNETT AND J. M. SCOTT

Contribution from the Richardson Chemical Laboratory, Tulane University, New Orleans, Louisiana Received June 5, 1956

A study<sup>2</sup> of the azido group moments in certain aromatic and aliphatic compounds gave values of 1.55 and 2.12 debyes, respectively. This work extends the study to cyclohexyl and cyclopentyl azides and indicates the effect of ring closure on the dipole moment. The dipole moment of 3-bromocyclohexene shows a small increase, 0.21 D, over that of cyclohexyl bromide and shows the effect of the adjacent double bond in the ring.

### Experimental

Materials.—C.P. benzene was tested with an isatin solution to ensure the absence of thiophene and purified by freezing and discarding the portion which melted first. The remaining liquid was distilled from, collected and stored over sodium wire,  $n^{30}$ D 1.4946.

<sup>(11)</sup> A. Müller, Proc. Roy. Soc. (London), A120, 437 (1928); A. Müller and W. B. Saville, J. Chem. Soc., 127, 599 (1925).

<sup>(1)</sup> Taken from a thesis submitted for the M.S. degree by Roy L. Bennett, now in military service.

<sup>(2)</sup> H. O. Spauschus and J. M. Scott, J. Am. Chem. Soc., 73, 210 (1951).

### Notes

## TABLE I

Compound	α	β	$E_1$	$V_1$ (ml./g.)	Мт	P <sub>2</sub> °	$P_0$	$\begin{array}{c} \mu \times 10^{18}, \\ \text{e.s.u.} \end{array}$
Cyclohexyl azide	4.9550	-0.10449	2.2735	1.1462	35.37	155.65	118.51	$2.37 \pm 0.03$
Cyclopentyl azide	4.9827	-0.10487	2.2769	1.1464	31, 18	138.69	105.95	$2.27 \pm 0.03$
3-Bromocyclo-								
hexene	4.1901	-0.32672	2,2741	1.1461	35.92	166. <b>2</b> 9	128.57	$2.51 \pm 0.04$

Cyclohexyl and cyclopentyl azides were prepared by the method reported by Boyer,<sup>3</sup> from the corresponding bromides by refluxing with an alcohol-water solution of sodium azide. After extraction with ether and removal of the latter by distillation, the azide was distilled in an atmosphere of nitrogen under reduced pressure. Cyclohexyl azide distilled at 64-65° at 21 mm.;  $d^{25}_4$  0.98546;  $n^{25}_D$  1.4690. Cyclopentyl azide distilled at 51-52° at 20 mm.;  $d^{25}_4$  0.9789;  $n^{25}_D$  1.4615. An indication of purity was obtained by the constancy of refractive indices of successive distillation fractions.

Cyclohexene was brominated by refluxing with N-bromosuccinimide in carbon tetrachloride<sup>4</sup> to give 3-bromocyclohexene. After removal of the succinimide by filtration, the carbon tetrachloride and excess cyclohexene were distilled off. The 3-bromocyclohexene was distilled under reduced pressure; b.p. 56-57° at 11 mm.,<sup>5</sup> d<sup>25</sup><sub>4</sub> 1.3767; n<sup>25</sup>D 1.5265. The 3-bromocyclohexene decomposed so readily that it was necessary to redistil the compound, make the solutions and measure their dielectric constants and densities immediately and in rapid succession.

Density.—The densities of the benzene solutions were measured at  $25.00 \pm 0.02^{\circ}$  with calibrated 25-ml. Weld type specific gravity bottles. Smaller pycnometers were used for the pure substances.

Dielectric Constants.—The dielectric constants of the benzene solutions of the compounds were measured at  $25.00 \pm 0.05^{\circ}$  with the heterodyne beat apparatus and the cell described previously.<sup>6</sup>

#### **Results and Calculations**

The total polarization at infinite dilution,  $P_2^0$ , of each compound was calculated by the method of Halverstadt and Kumler' using their equation

$$P_2^{\circ} = (E_1 - 1)/(E_1 + 2)(M_2V_1 + M_1\beta) + 3\alpha V_1M_1(E_1 + 2)^2$$

in which  $E_1$  and  $V_1$  represent the dielectric constant and specific volume of the pure solvent while  $M_1$ and  $M_2$  are the molecular weights of solvent and solute, respectively. The constants  $\alpha$  and  $\beta$ ,  $E_1$ and  $V_1$  in the empirical equations were evaluated by the application of the method of least squares to the experimental data. The orientation polarization,  $P_0$ , was obtained in the usual manner, using a correction of 5% for atomic polarization. The dipole moment was determined by the use of the equation

$$\mu = 0.01273 (P_0 T)^{1/2} \times 10^{-18} \text{ e.s.u.}$$

The constants, other data and the dipole moments calculated are listed in Table I.

A comparison of the dipole moments of cyclohexyl bromide,<sup>8</sup> 2.3 D, and cyclopentyl bromide,<sup>9</sup> 2.20 D, with the analogous azides shows that the bromo and azido moments are nearly identical. However, *n*-butyl bromide,<sup>10</sup> 1.85 D, sec-butyl

- (3) J. H. Boyer, University of Michigan Engineering Research Institute Reports, October, 1951.
- (4) K. Ziegler, A. Späth, E. Schaef, W. Schumann and E. Winkelmann, Ann., 551, 80 (1942).
- (5) A. T. Blomquist and J. Kwiatek, J. Am. Chem. Soc., 73, 2098 (1951), reported b.p. 68-70.5° at 26 mm.
- (6) H. O. Spauschus, A. P. Mills, J. M. Scott and C. A. MacKenzie, ibid., 72, 1377 (1950).
- (7) I. F. Halverstadt and W. D. Kumler, ibid., 64, 2988 (1942).
- (8) J. W. Williams, *ibid.*, **32**, 1831 (1930).
- (9) M. T. Rogers and J. D. Roberts, *ibid.*, 68, 843 (1946).
- (10) A. Parts, Z. physik. Chem., B7, 327 (1930).

bromide,<sup>10</sup> 2.12 *D*, and *t*-butyl bromide,<sup>10</sup> 2.21 *D*, show an increase in the moment as the branching in the compound increases within the sphere of induction. This work indicates that the dipole moment of a cyclic compound is closer to that of a branched chain than to a straight chain compound. Since cyclohexene itself has a dipole moment of 0.75 D,<sup>11</sup> the moment of 3-bromocyclohexene would be expected to be greater than that of either cyclohexyl azide or bromide.

(11) M. Puchalik, Acta Phys. Polon., 4, 145 (1935).

# THERMAL EFFECTS IN THE CHEMISORP-TION OF OXYGEN ON NICKEL: A COM-PARATIVE INVESTIGATION USING POW-DERS AND EVAPORATED FILMS

BY R. M. DELL, <sup>1a</sup> D. F. KLEMPERER<sup>1b</sup> AND F. S. STONE

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A comparative study has been made of the behavior of nickel powder and nickel film toward oxygen chemisorption. It becomes evident that, besides cleanliness, other less commonly emphasized factors contribute markedly to the observed differences in behavior.

Nickel powder, prepared from the oxalate, was reduced with hydrogen and outgassed.<sup>2</sup> When Specimen I (wt. 5.66 g., S.A. 9.65 m.<sup>2</sup>) was exposed to 1.5 mm. pressure of oxygen at  $-183^{\circ}$ , very rapid adsorption of 4.54 cm.<sup>3</sup> (S.T.P.) occurred. On warming to 20°, a further 1.07 cm.<sup>3</sup> was adsorbed. Assuming equal areas of the three main planes to be present, a 1:1 atomic monolayer of oxygen on nickel requires 0.284 cm.<sup>3</sup>/m.<sup>2</sup>. Adopting this as a standard for comparisons, Specimen I adsorbed 1.66 atoms of O per Ni at  $-183^{\circ}$ , rising to 2.05 at 20°.

Studies with other specimens, however, showed that the limits of the uptake are strongly dependent upon factors other than temperature. Pressure and porosity, for example, both have an influence upon the uptake limit. The controlling factor is evidently the dissipation of the heat of adsorption. At the moment of contact with oxygen, there is an intense local disturbance in the surface layers, and unless the heat can be distributed rapidly, incorporation of adsorbed oxygen as oxide will be encouraged. New sites are then generated and in this way a number of layers of oxygen can be taken up by the solid. Under sufficiently extreme conditions, the effect appears as the well-known pyrophoric property—Specimen I, for instance, was py-

<sup>(1) (</sup>a) Admiralty Research Laboratory, Teddington, England; (b) Division of Tribophysics, C.S.I.R.O., Melbourne, Australia.

<sup>(2)</sup> R. M. Dell and F. S. Stone, Trans. Faraday Soc., 50, 501 (1954).

rophoric when exposed to 50 mm. pressure of oxygen at 20°—but the significance of inadequate heat dissipation has seldom been considered in orthodox adsorption studies. Evaporated films may also be expected to show the effect (see below), especially when a thick film is deposited on a thin glass base. The high uptake limits for oxygen chemisorption on nickel and iron films reported by Beeck<sup>3</sup> are probably to be attributed to this cause.

When coupled with poor heat dissipation, the high heat of oxygen adsorption ( $\sim 100 \text{ kcal./mole}$ ) makes for difficulties in adsorption calorimetry. A *direct* determination of the heat of adsorption of oxygen on nickel powder is liable to a substantial error for this reason. The tendency is for hot spots to develop in the region of the specimen first encountered by the gas. Some improvement may be obtained by using oxygen-helium mixtures.<sup>4</sup> In the present case, however, the problem has been overcome by using nitrous oxide. N<sub>2</sub>O decomposes very slowly on nickel at  $20^{\circ}$  yielding chemi-sorbed oxygen, but N<sub>2</sub>O itself and N<sub>2</sub> are negligibly chemisorbed at low pressures. Using this method,<sup>5</sup> Specimen II (11.4 g., 43.5 m.<sup>2</sup>) gave the results shown in Fig. 1. (In contrast to copper,<sup>5</sup> the whole of the nickel surface was active toward N<sub>2</sub>O decomposition.) Less accurate results, obtained using  $O_2$ -He mixtures, are also included. Each heat determination with  $N_2O$  increased the coverage by only 0.2%; the coverage range between determinations was traversed by admitting charges of oxygen. Bearing in mind the high heat and the irreversibility of the chemisorption, the constancy of the heat is attributable to a "layering effect." Due to the slow speed of reaction, the small amount of oxygen produced by  $N_2O$  decomposition during a heat measurement is probably chemisorbed randomly on the adsorbent. On the other hand, the much larger charges of oxygen admitted between heat measurements are likely to be adsorbed preferentially on the first portion of bare surface which they encounter.<sup>3</sup> Each fresh increment of gas (whether oxygen or nitrous oxide) is therefore adsorbed upon a sparsely covered surface, with the result that the observed heat of chemisorption remains constant. As complete saturation is approached, the conditions change abruptly to the other extreme: the heat then falls steeply to a value characteristic of the heat of adsorption of oxygen on nickel oxide.<sup>2</sup> For Specimen II, saturation at  $20^{\circ}$  corresponded to 2.96 layers. The use of N<sub>2</sub>O throughout would presumably have given a lower uptake limit, but the very slow rate of decomposition rendered this experiment impracticable.

As the work on evaporated films will be described in detail elsewhere,<sup>6</sup> only certain salient features will be reported here. Specimen III (0.020 g., 0.632 m.<sup>2</sup>), an evaporated film, was exposed to oxygen at 20° and 0.5 mm. pressure. 0.187 cm.<sup>3</sup> was adsorbed immediately, corresponding (q.v.) to 1.04 layers. Specimen IV (0.017 g., 0.540 m.<sup>2</sup>)



Fig. 1.—Heat of adsorption of oxygen on reduced nickel powder (wt. 11.4 g., S.A.  $43.5 \text{ m}^2$ ) at 20° using a Garner-Veal<sup>4</sup> calorimeter: O, determined with nitrous oxide, allowance having been made for the heat of formation of N<sub>2</sub>O; I, determined with an oxygen-helium mixture. The adsorption limit at 36.61 cm.<sup>3</sup> corresponds to 2.96 atoms of oxygen per nickel in the original surface.



Fig. 2.—Heat of adsorption of oxygen on evaporated nickel film (wt. 0.050 g., S.A. 1.57 m.<sup>2</sup>) at 20°, using a Beeck-type calorimeter.<sup>3</sup> In the absence of a conventional surface area measurement, the area in this case has been assessed on the assumption that the adsorption limit at 0.474 cm.<sup>3</sup> corresponds to a monolayer (see text).

gave a rapid adsorption of 0.179 cm.<sup>3</sup>, corresponding to 1.17 layers. These values, which approximate to a monolayer, are substantially smaller than those observed with the powdered nickel specimens (e.g., 2.05 and 2.96), a result which we attribute to the much easier dissipation of heat in the films and their support. The heat of adsorption, however, is apparently not without effect. With Specimen IV the surface area was measured both before and after the chemisorption of the oxygen. It was found that the krypton  $v_m$  decreased by 30% following the chemisorption of the cxygen layer. Our tentative interpretation is that the local mobility conferred upon the nickel by the high heat of adsorption has caused sintering.

To complete the comparison, the heat of adsorption on films has been measured. In view of the better heat dissipation, direct measurement with oxygen could be made in this case. Some results are shown in Fig. 2. Fifteen admissions, each of  $0.036 \text{ cm.}^3$ , were made and residual oxygen pressures only appeared in the last two increments. The constancy of the heat as a function of coverage is again attributable to a layering effect (q.v.). Compared

<sup>(3)</sup> O. Beeck, "Advances in Catalysis," Vol. II, Academic Press, New York, N. Y., 1950.

<sup>(4)</sup> W. E. Garner and F. J. Vcal, J. Chem. Soc., 1436 (1935).

<sup>(5)</sup> R. M. Dell, F. S. Stone and P. F. Tiley, Trans. Faraday Soc., 49 195 (1953).

<sup>(( )</sup> D. F. Klemperer and F. S. Stone, to be published.

with the powder, the high heats in Fig. 2 are to be expected. Aside from considerations of cleanliness, the condensed film is a very imperfect porous material with a high degree of heterogeneity. These heats must also contain a contribution from strain energy, for if the chemisorption confers upon the surface the ability to sinter, it must also relieve strain. Better values of heat of adsorption (and catalytic parameters) can obviously be obtained by using annealed films, but, as is well known, their small areas introduce new limitations. It is in these respects that parallel work with powders assumes its proper perspective and value.

## DENSITY OF LIQUID DEUTERIUM **BROMIDE**<sup>1</sup>

#### By M. GOLDBLATT AND E. S. ROBINSON

Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico Received May 31, 1956

The density of liquid deuterium bromide has been determined over a temperature range of 0 to Within this temperature range, the density 25°. of liquid deuterium bromide under an atmosphere in the presence of a heated platinum catalyst. As a source of deuterium, tank stock of 99.6% deuterium content was used with no attempt at further purification. The bromine, which was of analytical grade, was stored over P2O, to ensure that the halogen be dry. A deuterium bromide free of bromine and water was obtained by allowing the material to flow through a trap cooled by carbon dioxide and trichloroethylene and be condensed in a trap cooled by liquid nitrogen.

Introgen. In order to measure the density of liquid DBr, a micro-pycnometer made of straight glass capillary tubing was used—much in the manner of J. M. Furter.<sup>2</sup> The mean radius of the capillary to be used was determined by the mercury method outlined by Mann and Purdie.<sup>3</sup> The deuterium bromide gas was transferred into the pycnometer by cooling the capillary tubing with liquid nitrogen. By sealing off the tubing at a short distance above the level of the solid DBr, the vapor volume above the deuterium bromide, when it became liquid, was minimized. The pycnometer was clamped in a vertical position so that a cathetometer could be used to read both the height of the liquid column and the length of the vapor space. Mixtures of ice and water were used to give bath temperatures ranging from 0 to 25°. The bath container was a dewar, which had been evacuated but not silvered, allowing the liquid height to be measured through the dewar walls. Linearity of the index marks on the capillary made it possible to tell that there was no optical distortion.

After the run, the weight of the DBr was ascertained by weighing the pycnometer before and after breaking it, and allowing the gas to escape. Then the density was calcu-



of deuterium bromide gas can be found from the relation

lated for each temperature from the relation

$$d_{\mathfrak{r}}\circ = \frac{M-\mathfrak{r}}{HA}$$

Experimental Methods.-The synthesis of DBr was accomplished by the direct union of the elements,  $D_2$  and  $Br_2$ ,

 $D = 1.961 - 5.981 \times 10^{-3}t + 3.503 \times 10^{-8}t^2$ 

where M is the total weight of DBr, m is the calculated weight of material in the vapor phase, H is the height of the

(2) J. M. Furter, Helv. Chim. Acta, 21, 1666 (1938).

(3) F. G. Mann and D. Purdie, J. Chem. Soc., 59, 13 (1937).

liquid column, and A is the average cross-sectional area of the tube. Vapor pressure data for HBr were used to make the estimation of the weight of gas in the vapor phase,<sup>4</sup> because deuterium bromide vapor pressure data could not be found for the temperature range of interest. The maximum correction for weight of bromide in the vapor space was about one per cent. of the total weight of material being measured.

**Results.**—Three runs were made on the density of liquid deuterium bromide over the temperature range of 0 to  $25^{\circ}$  with three separate pycnometers. Figure 1 shows the experimental data with a curve derived from an averaging of the data. The maximum deviation of an individual measurement from this curve was 0.007 g. per cubic centimeter, and the standard deviation of the data was  $\pm 0.005$  g. per cubic centimeter. A least-squares treatment of the data was used to derive equation 1.

(4) N. A. Lange, "Handbook of Chemistry," Handbook Publishers, Inc., Sandusky, Ohio, 1946, p. 1412.

# A PRELIMINARY STUDY OF THE PHOTOLYSIS OF PENTABORANE VAPOR<sup>1</sup>

#### By Herman Burwasser and Robert N. Pease

Contribution from the Frick Chemical Laboratory, Princeton University, Princeton, N. J.

#### Received June 13, 1956

Although there have been a number of kinetic studies of thermal reactions of the boron hydrides,<sup>2</sup> the only photochemical investigations to be found in the literature are some early experiments by Stock<sup>3</sup> on the effects of long exposures of diborane and tetraborane to the radiation from a mercury vapor lamp. In the hope of adding somewhat to the meager data available, we have made a pre-liminary investigation of the results of exposing pentaborane vapor to a hydrogen arc through a thin silica window. It was hoped in this way to make use of radiation of wave lengths below 2000 Å, since Platt and co-workers<sup>4</sup> have found that a hexane solution of pentaborane only absorbs appreciably below 2050 Å.

#### Experimental

A Hanovia hydrogen discharge tube was used as a light source. The reaction cell was a quartz tube with a volume of approximately 100 cc., connected directly to the discharge tube via a quartz ground joint, the window of the tube being common to both lamp and cell. The window itself extended in a concave form approximately 2 cm. into the reaction cell and was 0.5 mm. thick. The joint was covered with glyptal enamel to ensure a vacuum seal. A mercury cut-off, functioning also as a manometer, separated the cell from the analytical system. Liquid pentaborane was stored in a tube connected to a 1 liter mixing bulb and a mercury manometer by a Hoke bellows valve, series 480, and was vaporized as needed.

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(2) For a recent review of boron hydride chemistry, see F. G. A. Stone, Quart. Revs. (London), 9, 174 (1955).

(3) A. Stock, Ber., 46, 1959, 3353 (1913).

(4) J. R. Platt, H. B. Klevens and G. W. Schaeffer, J. Chem. Phys., 15, 598 (1947). The analytical system consisted of a McLeod gage, liquid nitrogen trap, Toepler pump and a gas buret. Analyses of the gaseous mixtures were made with a Perkin-Elmer model 21 infrared spectrometer, and a Consolidated Engineering Corporation mass spectrometer model 21-620 (for hydrogendeuterium analysis). The procedure utilized for the infrared determination of boron hydrides had been developed by McCarty and co-workers.<sup>6</sup>

The pentaborane was subjected to the vacuum purification techniques and the purity of the sample was checked at various intervals by observing the infrared spectrum. Hydrogen and deuterium, pur:fied by diffusion through palladium, were provided by Dr. P. M. Gundry of this Laboratory.

The experimental procedure was as follows: after the system had been evacuated to  $10^{-6}$  mm., pentaborane vapor was admitted to the mixing bulb at the desired pressure and kept there while the lamp was turned on and allowed to warm to full intensity. In the runs with H<sub>2</sub> and D<sub>2</sub>, the pentaborane was frozen out with liquid nitrogen and the desired amount of H<sub>2</sub> or D<sub>2</sub> added. The mixture was then allowed to warm to room temperature and the final pressure noted. The gas or gases were then admitted to the illuminated reaction cell through another bellows valve, and the time and initial pressure noted. At the conclusion of the run, the mercury in the cut-off was lowered and the gaseous mixture was transferred quantitatively by means of the Toepler pump to the gas buret. The mixture was sometimes fractionated at liquid nitrogen temperatures although it was found that small quantities of diborane could not be quantitatively removed from the non-condensable fraction at these temperatures. All experiments were performed at room temperature.

Pentaborane vapor was used to calibrate the volumes of the reaction cell and infrared cell relative to the gas buret.

The amount of pentaborane decomposed was calculated by taking the difference between the initial pressure of pentaborane in the reaction cell and the amount of pentaborane left as determined by the infrared absorption. Hydrogen was determined by taking the difference between the final pressure of the gaseous mixture, as measured in the gas buret, and the total amount of boron hydrides (B<sub>5</sub>H<sub>9</sub> and B<sub>2</sub>H<sub>6</sub>) as determined from the infrared. Diborane was measured directly from the infrared and is therefore the most accurately determined quantity in the experiment.

Due to the deposition of a solid, it was necessary to clean the window between the lump and reaction cell by rinsing with nitric acid after each run.

## **Results and Discussion**

The results of this work are summarized in Table I. As will be seen from the table, increasing the exposure time beyond a half hour only moderately increased the extent of reaction. This might have been due to reversibility and to some extent this seems to be the case as shown by the experiments with hydrogen added (see bottom of table), but in the main it is probably the result of solid

TABLE I

	Рнот	OLYSIS OF	Pentabo	RANE	
Time, hr.	Initi H2	al BaHa	Pressure for: II2	e in mm. med BiH6	Reacted B <sub>5</sub> H <sub>9</sub>
$0^a$		17.0	0	0ª	
0.5		17.0	1.0	0.20	1.3
1.0		16.2	1.4	.24	1.4
1.5		17.0	1.5	.27	1.4
1.0		4.0	1.4	0.24	1.2
1.0		9.7	1.5	. 23	1.4
1.0		22.5	1.5	.24	1.3
1.0	77.7	8.9		0.25	0.8
1.0	109.0	9.3		. 22	(1.7)
1.0	94.0	14.6		. 24	1.1
1.0	95.0	15.0		. 25	0.9

º Blank run.

(5) L. V. McCarty, G. C. Smith and R. S. McDonald, Anal. Chem., 26, 1027 (1954).

deposition on the cell window. With respect to the effect of concentration, it will be noted that an increase in the partial pressure of pentaborane from 4 to 22 mm. had little, if any, effect on yield. This is presumably due in part to deposition of solid but may also be the result of strong or substantially complete absorption.<sup>4</sup>

Some further observations were made on the solid product. On rinsing with water, the material seemed to consist of small white crystals which slowly went into solution. The characteristically strong odor of boron hydrides could be detected. The freshly prepared solution was also found to reduce permanganate solution partially. The presence of borate ion was confirmed by a fluorescence test involving an alcoholic benzoic solution complex with borate ion.<sup>6</sup>

Attempts to remove the solid by hydrogenation (irradiation in the presence of hydrogen for one hour) were unsuccessful, *i.e.*, no volatile boron hydrides could be detected. The solid seemed in part to be subject to sublimation. This fact together with a rough material balance might indicate the presence of decaborane  $(B_{10}H_{14})$ .

To gain some information as to the nature of the primary process, experiments with deuterium were undertaken. It was assumed that if no hydrogen deuteride was formed, the primary reaction could not have involved free hydrogen atoms. However it was found that 11 mm. each of deuterium and pentaborane irradiated for one hour produced a mixture of hydrogen, deuterium and hydrogen deuteride in approximately equilibrium concentrations (determined by mass spectrometric analysis). There is thus extensive exchange. As was to be expected, mixtures of hydrogen and deuterium on irradiation showed no exchange. It was also shown that there was no dark reaction between pentaborane and deuterium nor between deuterium and the products of the irradiation.

These results suggest that perhaps the primary process is the separation of a hydrogen atom

$$B_{5}H_{9} + h\nu \longrightarrow H + B_{5}H$$

In the presence of deuterium, exchange occurs H.

$$+ D_2 \longrightarrow HD + D$$

The process is completed by reaction of D or H with another molecule of  $B_5H_9$ 

H (or D) +  $B_5H_9 \longrightarrow B_5H_{8'} + H_2$  (or HD)

The steps leading to the conversion of the assumed  $B_{5}H_{8}$  radical into diborane and into solid product are not clear.

(6) C. E. White, A. Weissler and D. Busker, Anal Chem., 19, 802 (1947).

# SOLUTIONS OF EUROPIUM AND YTTERBIUM METALS IN LIQUID AMMONIA

By JAMES C. WARF AND WILLIAM L. KORST

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## Received June 25, 1956

It is well known that samarium, europium and ytterbium, unlike the other rare earth elements, form a number of compounds in which the oxida-

tion number of the metal is two, and that in this state there are certain resemblances to the alkaline earth elements. We have recently shown, for example, that europium and ytterbium form dihydrides isostructural with the alkaline earth hydrides.<sup>1</sup> On the further basis of structure, density and the volatility of europium and ytterbium, in which respects a certain similarity to calcium, strontium and barium exists, it was considered that, like the alkaline earth metals, these rare earth metals may dissolve in liquid ammonia.

Calcium, strontium, barium, europium and ytterbium are all either face-centered or body-centered cubic, but density considerations are more pertinent, as europium and ytterbium are distinctly less dense than their neighbors. Pauling<sup>2</sup> has shown the relation of the metallic radii of europium and vtterbium to that of barium. Europium and ytterbium are much more volatile than the other rare earth metals.<sup>3</sup> The evidence suggests that in metallic europium and ytterbium, each atom contributes two electrons to the mobile lattice electrons, as in the alkaline earth metals, while in the other rare earth metals, three electrons per atom are contributed.

#### Experimental

Solutions of Europium and Ytterbium in Liquid Ammonia. -A simple apparatus attached to the vacuum line was used, in which ammonia could be distilled from sodium and condensed on the metal. The ytterbium and samarium metals were kindly supplied by Dr. F. H. Spedding, who also reduced europium salts, obtained through the courtesy of Mrs. Herbert N. McCoy; this metal had been cast in a tentalize supplied. tantalum crucible.

Both europium and ytterbium were found to dissolve in liquid ammonia at  $-78^{\circ}$ , forming solutions having the characteristic deep blue color of metals in ammonia. Europium appeared to be the more soluble. While no solubility measurements were made, europium solutions 1.14f and ytter-bium solutions 0.25 f were prepared. Samarium was appar-ently insoluble. Evaporation of ammonia from europium and ytterbium solutions left golden metallic crystals, pre-sumably the metal basammoniates. sumably the metal hexammoniates

Ytterbium in Ammonia via Electrolysis - Efforts were made to show that ytterbium(II) salts in ammonia could be electrolyzed, yielding solutions of ytterbium. A solution of ytterbium(II) iodide in liquid ammonia, approximately 0.005 f, was prepared by adding the stoichiometric amount of ammonium iodide to ytterbium in ammonia. An electrolytic cell with platinum clectrodes was employed. The yellow YbI<sub>2</sub> solution was electrolyzed, and after an initial period of gas evolution, a deep blue color appeared around the cathode. The color was not stable; on diffusing out-ward, it disappeared with the formation of an unidentified

precipitate, conceivably Yb(NH<sub>2</sub>)<sub>2</sub>. Europium(II) Amide.—An attempt was made to prepare europium amide by catalytic decomposition of the ammonia solution. Europium was leached with liquid ammonia from a fragment of the tantalum crucible in which it was cast, and filtered through a sintered glass disk into a vessel holding a few milligrams of iron(III) oxide. After standing approximately an hour, the ammonia was removed, leaving the amide and the lustrous bronze-colored metal ammoniate; the latter was decomposed, as judged by the disappearance of the golden color, by evacuation at room temperature. The gray-brown residue was analyzed for nitrogen and for europium. This gave an N/Eu ratio of 0.484, corresponding to 27.9% Eu(NH<sub>2</sub>)<sub>2</sub>. Presumably the pure amide could be prepared by more effective decomposipure amide could be prepared by more effective decomposition of the ammonia solution of the metal.

Attempted Preparation of Europium Solutions in Am-monia by Leaching Europium Oxide Reduction Products.—

(1) W. L. Korst and J. C. Warf, Acta Cryst., 9, 452 (1956).

(2) L. Pauling, J. Am. Chem. Soc., 69, 542 (1947).

(3) (a) A. H. Daane, D. H. Dennison and F. H. Spedding, ibid., 75, 2272 (1953); (b) E. I. Onstott, ibid., 77, 812 (1955)

Daane, et al.,<sup>3a</sup> have shown that ytterbium and samarium oxides may be reduced by lanthanum at 1450°. We thought that it may not be necessary actually to distil the ytterbium (or europium) metal away, but that mere leaching of the reaction product would serve to yield liquid ammonia solutions. Accordingly, a mixture of europium oxide and lanthanum, the former in 10% excess over the amount demanded by the equation  $Eu_2O_3 + 2La = 2Eu + La_2O_3$ , was fired in a sealed molybdenum crucible under 300 mm. of helium pressure in an induction furnace. The temperature was maintained at  $1450-1460^\circ$  for 25 minutes. After cooling, the reaction product was leached with liquid ammonia, but not a trace of blue color formed. The experiment was repeated under much the same conditions, except that aluminum was substituted for lanthanum; the result was the same. The reduction reaction is evidently rapidly reversible, the reactants being favored at lower temperatures.

## Discussion

The heat of solution of europium in liquid ammonia was estimated at -26 kcal./g. atom by the difference of two energy-cycle equations for europium and calcium. This was based on the heats of sublimation of the metals,<sup>4,5</sup> the first two ionization potentials of the metals,<sup>6</sup> and the difference between the heat of ammoniation of the gaseous ions, interpolating Coulter's<sup>7</sup> data at the ionic radius of Eu<sup>++</sup> (1.10 Å.).

Finally, the possibility that americium metal is soluble in liquid ammonia should be noted, since the position of this element in the actinide series corresponds to that of europium in the lanthanide series. Evidence supporting such a conjecture lies in the distinctly low density of americium<sup>8</sup> compared to neighboring elements and in its somewhat low heat of vaporization.<sup>9</sup> But lack of definite evidence of americium(II) compounds and the existence of a hydride in which the H/Am ratio is approximately 2.7<sup>8</sup> would indicate insolubility of the metal in ammonia. The conclusion of Graf, *et al.*,<sup>10</sup> that in metallic americium there are three valence electrons per atom also indicates insolubility in ammonia.

This work was carried out in part under the auspices of the Office of Naval Research.

(4) A tentative value of 40 kcal./g.-atom for europium was supplied by Dr. Adrian Daane.

(5) National Bureau of Standards, Circular 500, "Selected Values of Chemical Thermodynamic Properties," U. S. Govt. Printing Office, Washington, D. C., 1952.

(6) C. E. Moore, "Atomic Energy Levels," Vol. I, Natl. Bur. Standards, Circular 467, 1949; H. N. Russell, W. Albertson and D. N. Davis, *Phys. Rev.*, **60**, 641 (1941).

(7) L. V. Coulter, This Journal, 57, 553 (1953).

(8) E. F. Westrum, Jr., and L. Eyring, J. Am. Chem. Soc., 73, 3396 (1951).

(9) S. C. Carniglia and B. B. Cunningham, *ibid.*, **77**, 1502 (1955).
(10) P. Graf, *et al.*, *ibid.*, **78**, 2340 (1956).

# SOME PROPERTIES OF THE SYSTEMS DIOXANE-BUTYL ALCOHOLS<sup>1</sup>

By R. I. Rush, D. C. Ames, R. W. Horst and J. R. MacKay

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Especially because of its excellent solvent properties 1,4-dioxane has been of considerable interest to many investigators in recent times. Binary mixtures of dioxane and water, methyl alcohol and

(1) This investigation was made possible by a grant from the Carnegie Research Fund of Centre College.

ethyl alcohol have been studied with respect to certain physical properties such as density, index of refraction, viscosity, surface tension and vapor pressure.<sup>2-5</sup> Several ternary systems have also been investigated.<sup>6,7</sup> However, data relating to the physical properties of mixtures of dioxane and various other substances are not too abundant. Consequently, it seemed desirable to begin a study of some of the physical properties of binary mixtures of dioxane and organic hydroxy compounds. This paper deals with the densities, refractive indices and viscosities of the systems dioxane and each of the four butyl alcohols at  $25.00 \pm 0.05^{\circ}$ .

## **Purification of Materials**

**Dioxane**.—1,4-Dioxane (Eastman Kodak No. 2144) was further purified by a modification of the method of Eigenberger.<sup>8</sup> Each time before distilling as needed the product was refluxed with metallic sodium for one hour or until a fraction was obtained, on distillation, which had a refractive index of 1.4200 at 25.00°, which value agrees well with those reported in the literature cited.<sup>2-7</sup>

*n*-Butyl Alcohol.—Eastman Kodak No. 50 *n*-butyl alcohol was fractionally distilled as needed, each sample used having a refractive index of 1.3974 at 25.00°. This agrees with determinations reported in the literature.<sup>9</sup> sec-Butyl Alcohol.—Eastman Kodak No. 943 sec-butyl

sec-Butyl Alcohol.—Eastman Kodak No. 943 sec-butyl alcohol was found to have a refractive index of 1.3950 at 25.00°. Since this was in good agreement with values found in the literature,<sup>9</sup> no further purification was carried out.

Isobutyl Alcohol.—I: was found necessary to purify Eastman Kodak No. 303 isobutyl alcohol. This was accomplished by a modification of a method described in Beilstein.<sup>10</sup> That portion of the distillate having a refractive index of 1.3939-1.3940 at 25.00° was collected for use.

*t*-Butyl Alcohol.—Eastman Kodak No. 820 *t*-butyl alcohol, without further purification, was found to have a refractive index of 1.3849 at  $25.00^{\circ}$ , which compares favorably with values obtained by other investigators.<sup>11-14</sup>

#### Experimental

Constant Temperature Water-bath.—Throughout the work a constant temperature water-bath was employed, the temperature being controlled by a thermoregulator. The variations in temperature were observed by the use of a Beckmann differential thermometer which was checked against a thermometer certified by the National Bureau of Standards in order to determine the reading at 25.00°. At no time was the deviation from this temperature greater that  $\pm 0.05^{\circ}$ .

**Preparation of Solutions**.—All solutions were prepared by the direct weighing of both components in a small flask having a standard taper glass stopper. The size of the flask was such that the solutions nearly filled it.

Density Determinations — The pycnometers with the solutions contained therein were allowed to remain in a constant temperature water-bath at  $25.00 \pm 0.05^{\circ}$  for at least 30 minutes in order to reach equilibrium. Each value obtained was the result of two or more determinations.

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(4) L. W. Oholm, Finska Kemistsamfundets Medd., 48, 19 (1939).

(5) (a) R. N. Hopkins, E. S. Yerger and C. C. Lynch, J. Am. Chem. Soc., 61, 2460 (1939); (b) W. A. Amis, A. R. Chopin and F. L. Padgitt, *ibid.*, 64, 1207 (1942).

(6) C. H. Schneider and C. C. Lynch, *ibid.*, **65**, 1063 (1943).

(7) R. J. Berndt and C. C. Lynch, *ibid.*, **66**, 282 (1944).

(8) E. Eigenberger, J. pwakt. Chem., 130, 75 (1931).

(9) R. F. Brunel, J. L. Crenshaw and E. Tobin, J. Am. Chem. Soc.,

43, 561 (1921).
(10) Beilstein, "Handbuch der Organischen Chemie," 4th ed. Vol. I.
1918, p. 374.

(11) "Beilstein," Vol. I, 1st Supp., Berlin, 1928, p. 192.

(12) H. Adkins and W. E. Broderick, J. Am. Chem. Soc., 50, 499 (1928).

(13) D. R. Simmons and E. R. Washburn, ibid., 68, 235 (1946).

(14) D. R. Dreisbach and R. A. Martin, Ind. Eng. Chem., 41, 2875 (1949).







Fig. 2.—Index of refraction: O, *n*-butyl alcohol-dioxane system;  $\Theta$ , isobutyl alcohol-dioxane system;  $\Phi$ , sec-butyl alcohol-dioxane system;  $\Phi$ , *t*-butyl alcohol-dioxane system.



Fig. 3.—Viscosity: O, *n*-butyl alcohol-dioxane system;  $\bigcirc$ , isobutyl alcohol-dioxane system;  $\bigcirc$ , *sec*-butyl alcohol-dioxane system.

Refractive Index Determinations.—An Abbe refractometer having an accuracy of  $\pm 0.0001$  was used in making all measurements. By means of a small pump water from a constant temperature bath was circulated around the cell of the refractometer. The temperature of the water was maintained at  $25.00 \pm 0.05^{\circ}$ . All values reported are the mean of at least six determinations. Viscosity Measurements.—In all viscosity determinations

Viscosity Measurements.—In all viscosity determinations the Ostwald–Fenske pipet was employed, each pipet being calibrated by using a standard viscosity sample obtained from the National Bureau of Standards. Before measuring the viscosity the pipet and its contents were allowed to remain in the constant temperature water-bath at  $25.00 \pm$  $0.05^{\circ}$  for 30 minutes, the solutions or pure liquids being protected from moisture of the atmosphere by drying tubes. In each case a 5-ml, sample was used and a one-tenth second stopwatch was employed to determine the time of flow, the variations on any one sample usually being not more than twoor three-tenths of a second. Each value reported is the mean of at least six determinations.

#### Results

Summaries of the experimental data obtained are given in Tables I, II, III and IV.<sup>15</sup> In order to show the extent to which the systems deviate from the ideal, graphs were made plotting the mole fraction of the alcohol against the ratio

measured a						
$d(alc.) \cdot X(alc.)$	$+ d(dioxane) \cdot X(dioxane)$					

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*n***-BUTYL ALCOHOL-DIOXANE SYSTEM** 

Mole fraction alcohol	Mole fraction dioxane	Density (g./ml.)	Refractive index (np)	Viscosity (mpoises)
0.0000	1.0000	1.0286	1.4200	11.65
.0528	0.9472	1.0148	1.4180	11.26
. 1148	.8852	0.9990	1.4161	10.91
. 1998	. 8002	.9790	1.4140	10.78
.2320	. 7680	.9720	1.4131	10.73
.2877	.7123	.9580	1.4120	10.70
.3274	. 6726	. 9490	1.4108	10.74
. 4083	. 5917	.9308	1.4090	10.99
. 5280	. 4720	.9042	1.4060	11.69
. 6722	.3278	.8731	1.4032	13.28
.7606	.2394	.8545	1.4016	14.90
. 8730	. 1270	.8314	1.3994	18.06
.9654	.0346	.8128	1.3980	22.64
1.0000	.0000	.8060	1.3974	24.14

TABLE II

SOBUTYL ALCOHOL-DIOXANE SYSTEM

	ISOBULL AL	COHOL-DIO	CANE DISTRU	
Mole fraction alcohol	Mole fraction dioxane	Density (g./ml.)	Refractive index (nD)	Viscosity (mpoises)
0.0000	1.0000	1.0286	1.4200	11.65
.0581	0.9419	1.0127	1.4180	11.31
. 1155	. 8845	0.9985	1.4160	11.09
. 1680	. 8320	.9852	1.4144	10.99
.2141	. 7859	. 9740	1.4130	11.07
. 2589	.7411	. 9629	1.4117	10.98
. 2859	.7141	. 9567	1.4110	11.07
. 4212	. 5788	.9241	1.4072	11.44
. 4 <b>244</b>	. 5756	. 9240	1.4073	11.53
. 4934	.5066	. 9069	1.4054	12.06
.5261	. 4739	. 9003	1.4047	12.31
. 5835	. 4165	.8874	1.4031	12.96
. 6896	. 3104	.8643	1.4008	14.89
.7646	. 2354	. 8480	1.3990	16.68
. 8750	. 1250	. 8244	1.3966	21.40
. 9584	. 0416	. 8066	1.3949	27.87
1.0000	. 0000	. 7980	1.3940	32.95

(15) Data for the index of refraction of the *t*-butyl alcohol-dioxane system were checked by the following undergraduate students working under a National Coöperative Undergraduate Chemical Research Program project directed by the senior author of this paper; Dan Schulte, under the immediate supervision of Prof. B. Kenneth Lewis, Department of Chemistry, Phillips University, Enid, Oklahoma; Phyllis Ann Raymond, under the immediate supervisior of Prof. Lester A. Michel, Department of Chemistry, Colorado College, Colorado Springs, Colorado; and Ernie N. Hart, under the immediate supervision of the senior author of this paper. where d is density and X is mole fraction. Corresponding ratios were used for index of refraction and viscosity. The resulting curves are given in Figs. 1, 2 and 3.

	Sec-BUTYL AI	COHOL-DIO	XANE SYSTEM	[
Mole fraction alcohol	Mole fraction dioxane	Density (g./ml.)	Refractive index(np)	Viscosity (mpoises)
0.0000	1.0000	1.0286	1.4200	11.65
.0577	0.9423	1.0125	1.4171	11.19
. 1569	. 8431	0.9874	1.4143	10.71
. 2587	.7413	. 9621	1.4112	10.46
. 4084	. 5916	.9270	1.4070	10.61
. 4794	.5207	.9106	1.4050	10.92
. 5825	. 4175	. 8881	1.4026	11.73
. 6958	.3042	. 8635	1.2001	13.24
. 7640	. 2360	. 8494	1.3988	14.74
.8744	. 1256	.8272	1.3969	18.80
.9587	.0413	.8106	1.3955	24.70
1.0000	.0000	.8031	1.3950	29.34

## TABLE III

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# TABLE IV

t-BUTYL ALCOHOL-DIOXANE SYSTEM

Mole fraction alcohol	Mole fraction dioxane	Density (g./ml.)	Refractive index (np)	Viscosity (mpoises)
0.0000	1.0000	1.0286	1.4200	11.65
. 1214	0.8786	0.9935	1.4142	11.18
. 1476	.8424	. 9828	1.4128	11.10
. 2090	.7910	. 9689	1.4106	11.11
.2222	.7778	. 9648	1.4098	11.14
. 3341	.6659	. 9350	1.4054	11.34
.4290	.5710	.9105	1.4019	11.97
.5305	. 4695	.8854	1.4980	13.04
. 6353	. 3647	.8605	1.3948	14.96
.7283	.2717	.8391	1.3920	17.73
.8224	. 1776	.8180	1.3892	21.79
.9122	.0878	.7988	1.3870	<b>29</b> , $41$
1.0000	. 0000	.7806	1.3849	49.99

## SWELLING OF PROTEIN MOLECULES IN SOLUTION. II

#### By TERRELL L. HILL

Naval Medical Research Institute, Bethesda, Md. Received July 16, 1956

In an earlier paper<sup>1</sup> it was shown that, from a theoretical point of view, an  $\alpha - \beta$  transformation in the peptide chains could account for the swelling of bovine serum albumin in the pH range 2-4. In the present note, which is essentially a supplement to I, we examine an alternative possibility, namely, that the swelling results from (1) the extension of flexible, cross-linked polypeptide chains and (2)the breakage of some of the cross-links<sup>2</sup> in the network. This model also proves to be adequate, qualitatively, as we shall see below.

The equations are based for the most part on earlier papers<sup>1,3</sup> so we can omit many details. In the present model, we picture a protein molecule as

(1) T. L. Hill, THIS JOURNAL, 60, 358 (1956). Referred to below as I.

(2) As suggested by C. Tanford, J. G. Buzzell, D. G. Rands and S. A. Swanson, J. Am. Chem. Soc., 77, 6421 (1955).

(3) T. L. Hill, J. Chem. Phys., 20, 1259 (1952). Referred to as P below.

The free energy of a protein molecule, in the presence of electrolyte with Debye-Hückel parameter  $\kappa$ , swollen to a volume V, with N protons bound on B possible sites, and  $\hat{M}$  of the  $\hat{M}_0$  weak cross-links formed, is then<sup>1,3</sup>

$$A(M,N,V,\kappa) = A_0 + \Delta A'(M) + \Delta A_1(V,M) + \Delta A_2(N) + \Delta A_3(N,V,\kappa)$$
(1)

where

 $A_0 =$  free energy in reference state (unswollen, un-charged, N = 0, M = 0)  $\Delta A' =$  free energy of cross-links  $\Delta A_1 =$  mixing and deformation free energy  $\Delta A_2 =$  binding free energy  $\Delta A_3 =$  electrostatic free energy

For a given  $\kappa$  and hydrogen ion concentration c in solution, the equilibrium values of M, N and V are found from

$$\partial A / \partial M = 0 \tag{2}$$

$$\partial A/\partial V = 0 \tag{3}$$

$$\partial A/\partial N = \mu = \mu^{\circ} + kT \ln c$$
 (4)

where  $\mu$  is the chemical potential of hydrogen ions. The cross-link free energy is

$$\Delta A' = -kT \ln \frac{M_0!}{M!(M_0 - M)!} e^{-MW/kT}$$
  
=  $-kT[M_0 \ln M_0 - M \ln M - (M_0 - M) \ln (M_0 - M)] + MW$  (5)

From eq. P19

$$\Delta A_{1} = B' V_{0}(1-v) + kT Z_{\nu}(v^{-1}-1) \ln (1-v) - \nu kT \left[ \frac{3}{2} (1-v^{-2/3}) - \frac{1}{2} \ln v \right]$$
(6)

where B' is a heat of mixing constant,  $V_0$  is the reference volume (no swelling) of the protein molecule,  $v = V_0/V$ , v is the number of polypeptide chains (between cross-links) in the network, and Z is the number of statistical units in each chain. The product  $Z\nu$  is a constant but  $\nu = 2(M_s + M)$ and  $\hat{Z}$  is proportional to  $(M_s + M)^{-1}$ .

The binding free energy  $\Delta A_2$  is given by eq. I6 and the electrostatic free energy by eq. I19.

From eq. 2 we then find for the equilibrium number of weak cross-links

$$\frac{M}{M_0} = \left[1 + v e^{W/kT} e^{3(v-2/3 - 1)}\right]^{-1}$$
(7)

Equation 3, for the equilibrium extent of swelling, leads to (at zero ionic strength)

$$D = \frac{K}{2} v^{2} + \ln (1 - v) + v + \frac{1}{Z(M)} \left( v^{1/3} - \frac{v}{2} \right) - \left[ \frac{\epsilon^{2} \beta v_{0}}{30(3/4\pi)^{1/3} Dk T V_{0}^{4/3}} \right] (n + N)^{2} \frac{v^{4/3}}{(1 - v)^{2}} (6 - 8v + 5v^{2})$$
(8)

where the heat of mixing parameter  $K = 2B'v_0$  $\beta/kT$ ,  $v_0$  is the molecular volume of the solvent (water),  $\beta v_0$  is the volume of a statistical unit, D is the dielectric constant of the solvent,  $\epsilon$  is the charge on a proton and  $n\epsilon$  is the charge on the protein 1594



Fig. 1.—Swelling of protein as a function of pH + constant. The constant f is defined in I.



Fig. 2.—Titration curve and weak cross-link breakage curve of protein as functions of pH + constant.

molecule when N = 0. The titration curve, which follows from eq. 4, is the same as eq. 121.

In numerical calculations, for a given value of v, one calculates M from eq. 7 and hence Z (M), then  $n \pm N$  from eq. 8, and finally c from eq. 121.

Because of the approximate nature of the model and theory, and uncertainty as to the actual mechanism of swelling, our object here is merely to show that swelling by a factor of the order of ten, over a few pH units, as observed experimentally, can be obtained from choices of parameters which are not unreasonable.

We make calculations for zero ionic strength only, using the parameters of I for bovine serum albumin: B = 106, n = -6,  $T = 298.2^{\circ}$ K., D =78.54,  $V_0 = 9.137 \times 10^{-20}$  cc./molecule. Also, we take  $M_s = 16$  (S-S links),  $M_0 = 16$  (as a guess),  $\beta$ = 9.4, Z = 10 when M = 0, and -W = 1.302kcal./mole (so that, arbitrarily,  $M/M_0 = 0.90$  at  $V = V_0$ ). Figure 1 shows swelling (1/v) as a function of pH + constant in two cases: (1) K = 2.626 so that v = 0.85 at zero charge (n + N = 0); and (2) K = 1.422 so that v = 0.65 at zero charge. It is seen that the higher value of K leads to a "phase transition." The critical value for this transition is about K = 1.9. From Rowen and Simha's<sup>4</sup> analysis of the sorption of water vapor by various proteins, one would estimate K = 1.8 for bovine serum albumin. Qualitatively, then, the swelling behavior in Fig. 1 is satisfactory.

Figure 2 shows the titration curve and the crosslink breakage curve for the case K = 1.422. As in I, the titration curve is not steep enough.

It should be emphasized that in the present model the really essential feature involved in the swelling of the protein molecule is the extensibility of the chains rather than the breakage of crosslinks. Thus, the maximum swelling (from n + N= 0 to 100) in the K = 1.422 case above is by a factor of 11.4, while with the same model and parameters except that weak cross-links are assumed not to exist (M = 0, Z = 10), the maximum swelling factor is almost as large, namely, 9.9.

We have also examined a model in which we have a cross-linked network of inflexible chains of constant length, but again with both permanent and weak cross-links. In this case one can show that V is proportional to  $(M + M_s)^{-2}$  if all chains are assumed, as an approximation, to be average chains.  $\Delta A_1$  is missing here and A is a function of M, N and  $\kappa$  or V, N and  $\kappa$ . This model proves to be unsatisfactory because (1)  $M_0$  must be of the order of 30 or 40 to obtain sufficient expansion and (2) -W must be unreasonably large in order to provide adequate resistance to the expansion sought by the electrostatic forces.

(4) J. W. Rowen and R. Simha, THIS JOURNAL, 53, 921 (1949).

# NUCLEAR MAGNETIC RESONANCE CHEMICAL SHIFT DETERMINATIONS BY MEANS OF A CONCENTRIC CYLINDER SAMPLE CELL

By M. Garcia Morin, Grover Paulett and Marcus E. Hobbs

Department of Chemistry, Duke University, Durham, N. C. Received July 28, 1947

A sample cell apparently similar to ones used by Reilly, *et al.*,<sup>1</sup> and Bothner-By and Glick<sup>2</sup> with two concentric compartments in one of which a reference substance can be kept separate from the sample to be studied has been found useful for measurements of nuclear magnetic resonance (NMR) chemical shifts. Precision in measurement of the chemical shift,<sup>3</sup>  $\delta$ , of the order of  $\pm 0.002$  is obtained. A number of types of sample cells used for NMR measurements have been reviewed by Wertz<sup>4</sup>

(4) J. E. Wertz, Chem. Revs., 55, 829 (1955).

<sup>(1)</sup> C. A. Reilly, H. M. McConnell and R. G. Meisenheimer, *Phys. Rev.*, **98**, 264A (1955).

<sup>(2)</sup> A. A. Bothner-By and R. E. Glick, J. Am. Chem. Soc., 78, 1071 (1956).

<sup>(3)</sup> L. H. Meyer and H. S. Gutowsky, THIS JOURNAL, 57, 481 (1953).

and recently Broersma<sup>5</sup> has used stationary concentric test-tubes for magnetic relaxation measurements. The type of cell described below has been used successfully with the spinner type probe of the Model V-4300B Varian High Resolution Spectrometer in our investigations and those reported by Bothner-By and Glick.<sup>2</sup> In principle the cell could be used in non-spinner type probes but in this case complications are introduced which seriously limit its usefulness for chemical shift measurements. Although a similar type cell or variations of it is in use in some other laborato-

ries, a published description of details of construction, the limits of usefulness and the precision of measurements that may be obtained does not seem to be available. Figure 1 shows the construction of the cell. The outside compartment is made from a 14 cm. length of 5 mm. o.d. Pyrex tubing, as straight and uniform as practicable.

Pyrex tubing, as straight and uniform as practicable. The inside compartment is a piece of straight, uniform, thin walled capillary about 1 mm. in diameter made by heat drawing a piece of 12 mm. o.d. Pyrex tubing. In fabricating the cell, the capillary and the outside tube

In fabricating the cell, the capillary and the outside tube are sealed together at one end using two simply constructed accessories to assist in maintaining the two tubes essentially concentric. One accessory is a thin walled brass tube approximately 4 cm. long sized to fit snugly inside the 5 mm. tube and bored to fit the capillary tube. A steel wire, of diameter slightly smaller than the wall thickness of the brass tube, is hard soldered to one end of the tube and serves as a convenient means of removing the brass tube after the center capillary is sealed to the closed end of the 5 mm. Pyrex tubing. The closure process and sealing of the capillary is carried out simultaneously and during this process the brass tube is placed about 1 cm. from the end being sealed. The other accessory is a small brass plug with a hole sized to fit the capillary and with a slot to allow the steel wire to pass through the plug. It is used at the upper end of the assembly during the sealing operation to assist in keeping the capillary centered.

After sealing, the brass plug and tube are removed. At this stage of the assembly, the capillary extends approximately 2 cm. beyond the open end of the 5 mm. Pyrex tube. A Teflon cap with a center hole bored to fit the capillary and with the inside machined to make a snug fit on the outside of the 5 mm. tube is used as a closure for the assembled sample tube as well as a centering device for the upper end of the capillary. The Teflon cap is shown in cross section in Fig. 1.

With the cell so assembled any convenient reference liquid may be placed in the capillary by means of a very small diameter capillary pipet and the reference capillary tube sealed off at about i cm. above the open end of the 5 mm. Pyrex tupe. Any liquid sample may then be placed in the annular space between the capillary and the outer 5 mm. Pyrex tube by means of a capillary pipet.

The simple geometry of the system allows one to readily calculate bulk magnetic susceptibility corrections. The necessary field equations are obtained, by application of appropriate boundary conditions for each cell boundry, using the general solution of Laplace's equation for the case of symmetry along the z-axis.<sup>6</sup> With the spinning probe the cavity field<sup>7</sup> in the direction of the external field that a molecule experiences,  $H_{\rm m}$ , in both the capillary and annulus is given by  $H_{\rm m} = H_0(1 - \frac{2}{3}\pi\kappa_{\rm m})$  where  $H_0$  is the external field and  $\kappa_{\rm m}$  is the bulk magnetic susceptibility per cc. of the material in the capillary or in the annulus.

If the sample is stationary, the cavity field in the

(6) W. R. Smythe, "Static and Dynamic Electricity," McGraw-Hill Book Co., New York, N. Y., 2nd Edition, 1950, p. 63.

(7) C. F. J. Böttcher, "Theory of Dielectric Polarization," Elsevier Press, New York, N. Y., 1952, p. 52.



Fig. 1.—Cross-section of sample cell.

direction of the external field that molecules in the capillary experience is given by the same expression as above, but in the annulus the cavity field,  $H_{\rm a}$ , is given by

$$H_{a} = H_{0} \left\{ 1 - \frac{2}{3} \pi \kappa_{a} + 2\pi \left[ (\kappa_{g} - \kappa_{a}) \frac{c^{2}}{r^{2}} + (\kappa_{1} - \kappa_{g}) \frac{d^{2}}{r^{2}} \right] (2 \cos^{2}\theta - 1) \right\}$$

The above expression is the general form of the equation for the field in the annulus from which the equation given by Reilly, *et al.*,<sup>1</sup> follows if one takes the difference in  $H_a$  for maximum and minimum values of the  $(2\cos^2\theta - 1)$  term. In the expression for  $H_a$ , a refers to the material in the annulus, g to glass, i to material in the capillary, *c* and *d* are the external and internal radii of the capillary, *r* is the geometric mean radius of the annulus and  $\theta$  is the angle between the radius vector and the external field in the plane perpendicular to the long axis of the tube, the latter being perpendicular to the direction of the external field. Terms of the order of  $10^{-10}$  or less have been neglected in deriving the above expressions.

A number of cells have been constructed as above by selection from ordinary stock tubing and by hand drawing and selection of the necessary capillaries. Undoubtedly the cells could be improved by use of true bore tubing and machine drawn capillaries, but the results obtained thus far indicate that a quite satisfactory product can be obtained without these refinements.

The equipment used to test a number of sample cells consisted essentially of a Varian High Resolution Spectrometer, the Varian sample spinning probe, a Sanborn recorder and a 5076 gauss permanent magnet which has a sufficiently homogenous field in certain volume elements of the gap to allow precise observations. Instrumental errors attributable to small temperature drifts during sweep intervals, small changes in the magnitude of the sweep signal not accounted for by calibration<sup>8</sup> and to the precision with which one can read the absorption maxima is estimated to be about 0.1 milligauss. In a number of comparison measurements, using a constant reference substance and sample material, cells showing deviations from average values of more than 0.1 milligauss probably should be discarded. (See Series B of Table I.)

The results of a series of measurements of several samples of sulfuric acid solutions using water as a reference liquid are recorded in Table I. These results are in the reasonably dilute region insofar as resonance shifts are concerned and without a satisfactory internal reference standard, such as the water in the capillary of the sample tube, the observed shifts would be quite difficult to determine with the precision indicated. Cells similar to the one described are being used in the dilute sulfuric acid region to determine the precise slopes of the plot of

(8) J. T. Arnold and M. E. Packard, J. Chem. Phys., 19, 1608 (1951).

<sup>(5)</sup> S. Broersma, J. Chem. Phys., 24, 153 (1956).

chemical shift,  $\delta$ , versus mole fraction of acid using water as a reference substance. Details of this investigation will be reported later.

In Table I, the shifts recorded under series A were obtained using a single cell with four to six different placements of the indicated sample cell in the turbine spinner. The deviations, d, recorded in this series of measurements are the average deviation of a single observation for the several values recorded for the chemical shift as the indicated cell was consecutively repositioned in the turbine spinner. In series B, the same solution was placed in the annulus of each of the indicated cells and the recorded shifts are the average of several measurements with the cell in the same position in the turbine spinner.

#### TABLE I

CHEMICAL SHIFTS<sup>a</sup> OF SULFURIC ACID SOLUTIONS IN TERMS OF MILLIGAUSS AND  $\delta = 10^{5} (H_r - H_c)/H_r$  Using Concen-

Mole					
of H <sub>2</sub> SO <sub>4</sub>	Cell				
$\times 10^{3}$	no.	$\Delta H$	$d_{\Delta H}$	δ	$d_{\delta}$
			Series A		
2.38	5	0.68	$\pm 0$ 05	0.013	$\pm 0.001$
	6	0.72	$\pm$ .03	.014	± .001
4.79	5	0.96	$\pm$ .05	.019	$\pm$ .001
	6	0.84	$\pm$ .08	.017	$\pm$ .002
6.87	<b>5</b>	1.23	$\pm$ .04	. 024	$\pm$ .001
	6	1.30	$\pm .04$	.026	$\pm$ .001
9.85	<b>5</b>	1.63	± .07	.032	$\pm$ .001
	6	1.40	± .08	. 028	$\pm$ .002
			Series B		
29.5	1	4.54	$+0.12^{b}$	0.0894	+0.002
	5	4.47	+ .08	.0880	+ .001
	7	4.44	+ .02	.0875	+ .001
	8	4.29	$13^{b}$	.0845	002
	9	4.34	08	.0855	001
	10	4.42	.00	.0871	. 000
	11	4.39	03	.0865	001
	12	4.44	+ .02	.0875	+ .001
Av.		4.42	$\pm$ .06	.0870	± .001

<sup>a</sup>  $H_r$  is the magnetic field intensity necessary to obtain resonance absorption at a fixed frequency for the reference compound, namely, water.  $H_c$  is the field intensity required for observing resonance absorption in the system under investigation, namely, sulfuric acid solutions. <sup>b</sup> These cells might be discarded, but are included in the table to indicate the maximum deviations observed.

# THE DISTRIBUTION OF SOME PHOSPHONOFLUORIDATES BETWEEN ORGANIC SOLVENTS AND WATER

#### BY ROBERT W. ROSENTHAL, REUBEN PROPER AND JOSEPH Epstein

Chemical Warfare Laboratories, Army Chemical Center, Maryland Received July 23, 1956

In connection with other work carried out in these laboratories, it was considered desirable to determine the distribution of some phosphonofluoridates (I-IV)<sup>1</sup> between organic solvents and water. The four compounds studied had the formula

(1) These compounds are sufficiently toxic that one should observe extreme care in working with them.



where

$\mathbf{R}$	$\mathbf{R}^{1}$	
Methyl	isopropyl	( I)
Methyl	pinacolyl	(II)
Ethyl	isopropyl	(III)
Methyl	cyclohexyl	(IV)

Some of the physical properties of I and III have been reported.2

In the work described herein, the distribution of the compounds I-IV between water and various solvents was determined at room temperature  $(25-29^{\circ}).$ 

### Experimental

Reagents.-The phosphonofluoridates were synthesized by the Organic Branch and analyzed by the Analytical Research Branch of the Chemical Warfare Laboratories. Elemental analysis indicated that the compounds were of high purity, i.e. >95%. Stock solutions of the phosphonofluoridates were made up daily either in distilled water and the pH of the solution adjusted to 5.5–5.7 to minimize hydrolysis<sup>3</sup> or in one of the organic solvents to be tested.

The organic solvents used herein were purified according to standard procedures.<sup>4</sup> Water-saturated organic solvents and organic solvent-saturated water were used in the distribution studies to minimize errors due to volume changes. The preparation of the solvents was accomplished by agitation of mixtures of water and the solvent for approximately one hour on a Burrell-Wrist-Action shaker, centrifugation and separation.

The following reagents were used for analytical determinations.

a. Phosphate buffer, 0.05 M pH 8.7: prepared by mixing 100 ml. of 1 M KH<sub>2</sub>PO<sub>4</sub>, 100 ml. of 1 M NaOH and 1 liter of distilled water, adjusting to pH 8.7 with saturated NaOH solution, and diluting to 2 liters with distilled water.
b. o-Tolidine reagent: 1% aqueous solution of o-tolidine dibudeableride (stored under refirerention and used at any

dihydrochloride (stored under refrigeration and used at any temperature up to room temperature.) c. Sodium perborate reagent: 1.25% aqueous solution

of sodium perborate (prepared daily).

B. Procedure.-Known volumes of solvent and water were pipetted into a glass-stoppered graduated cylinder. A very small volume of solution containing the phosphono-fluoridate was pipetted into the cylinder. The solutions were shaken vigorously for at least one minute (preliminary work showed that equilibrium was established in 15 seconds) and allowed to separate. Aliquots of the two phases were withdrawn and analyzed for phosphonofluoridate concentration colorimetrically by a modification of the o-tolidine perborate method for estimation of phosphonofluoridates.<sup>3</sup> The modification allowed us to use one standard curve to determine the concentration of the phosphonofluoridate for either the organic or aqueous phase. A description of a typical experiment on one solvent pair will illustrate the technique.

Calibration Curve.-Known quantities of the phosphonofluoridate, varying from zero to 536 mg. (in either water or chloroform), were added to a series of glass-stoppered graduated cylinders, each containing 40 ml. of acetone, 4 ml. of buffer, 2 ml. of o-tolidine reagent and sufficient chloroform or water so that the final solution contained 3 ml. of chloroform and 10 ml. of water exclusive of water from the aqueous reagents (these latter volumes were varied from solvent pair to solvent pair). A homogeneous solution resulted. Three ml. of perborate solution was then added to each cylinder and the intensity of color measured after 20 minutes in a Klett–Summerson photoelectric with a

TRIC CYLINDER SAMPLE CELLS

<sup>(2)</sup> C. E. Redemann, et al., J. Am. Chem. Soc., 70, 3604 (1948).

<sup>(3)</sup> J. Epstein and V. E. Bauer, Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, February 27-March 2, 1956.

<sup>(4)</sup> L. Fieser, "Experiments in Organic Chemistry," 2nd Edition, D. C. Heath and Company, New York, N. Y., 1941.

No. 42 filter. The colorimetric readings (corrected for blanks) were plotted against mg. of phosphonofluoridate.

Analyses.—In the analysis for phosphonofluoridate in the chloroform phase, one ml. of this phase was added to a cylinder containing 40 ml. of acctone, 4 ml. of buffer, 2 ml. of o-tolidine reagent, 2 ml. of chloroform and 10 ml. of water. For the aqueous phase, 10 ml. was added to a cylinder containing 40 ml. of acetone, 4 ml. of buffer, 2 ml. of o-tolidine and 3 ml. of chloroform. The concentration in each phase was determined by comparison of the net colorimetric readings with the calibration curve.

### Results

The results of a typical experiment, viz, the determination of the distribution coefficient (solvent/water) of I between chloroform and water, are given in Table I.

## TABLE I

DATA FOR THE DETERMINATION OF THE DISTRIBUTION OF I BETWEEN CHLOROFORM AND WATER

		Vol. ratio	Phosp fluoridate	hono- recovered		
Run	Total (I), µg.	CHCl <sub>3</sub> / H <sub>2</sub> O	CHCla, µg.	H2O, μg.	Recovery,	K
1	4474	1:10	3346	1070	98.6	31.4
<b>2</b>	4474	1:7	3890	823	105.4	33.0
3	4474	1:5	3890	636	101.0	30.6
4	8948	1:7	7550	1670	103.0	31.7
5	8948	1:5	8150	1350	105.8	30.2
6	8948	1:10	6860	2230	101.5	30.7
					Av	31.2

Per cent. recovery  $(100 \times \text{wt. phosphonofluori-date found by analysis/nominal weight phosphono-fluoridate) was calculated for each experiment and values of <math>100 \pm 5\%$  were usually obtained. A summary of the K's obtained is given in Table II,

#### TABLE II

Distribution Coefficients of Phosphonofluoridates between Organic Solvents and Water ( $T = 25-29^{\circ}$ )

No

Com- pound	Solvent	of runs	Distribution coefficient	Stand dev.
I	Chloroform	6	31.2	0.61
	sym-Tetrachloroethane	<b>2</b>	17.6	1.5
	1-Nitropropane <sup>a</sup>	6	4.70	0.29
	1,4-Dichlorobutane	5	2.68	. 06
	Nitrobenzene <sup>a</sup>	<b>6</b>	2.51	.28
	1,2-Dibromoethane	<b>5</b>	2.25	. 12
	Benzene	6	2.08	.04
	Chlorobenzene	4	1.95	. 12
	Tributyl phosphate	6	1.82	. 04
	Carbon tetrachloride	<b>6</b>	0.84	.06
	<i>n</i> -Heptane	3	0.20	.01
	Perfluorodimethyl-			
	cyclohexane	6	$<\!\!1$	
	Perfluoromethylcyclo-			
	hexane	6	<0.1	
II	sym-Tetrachloroethane	4	382	44.7
	Benzene	6	41.1	0.7
	<i>n</i> -Heptane	6	5.34	0.27
III	sym-Tctrachloroethane	6	71.8	13.9
	Benzene	7	7.36	0.30
	<i>n</i> -Heptane	6	0.49	0.02
ΙV	sym-Tetrachloroethane	4	508.1	75.4
	Chloroform	4	474	75
	Benzene	<b>2</b>	42.2	0.6
	<i>n</i> -Heptane	5	2.35	0.16
	1 - 11 - 11 ff + modt	had (	muchlished	\ \

<sup>a</sup> Analyzed by a different method (unpublished)

#### Discussion

An attempt was made to correlate the distribution coefficients between I and various organic solvents with Hildebrand and Scott's "solubility parameter."<sup>5</sup> (This quantity,  $\partial$ , which has been identified with the internal pressure of a liquid has been useful in predicting the solubility of one liquid in another.) In general the closer the  $\partial$ -values of two liquids, the greater the mutual solubility.<sup>6</sup> The  $\partial$  of I was calculated to be 9.04 from the equation

$$\partial = \left(\frac{\Delta H_{\rm v} - RT}{V_{\rm e}}\right)^{1/2}$$

where  $H_V$  is the heat of vaporization of  $25^{\circ.7}$   $V_{\rm I}$  was calculated from the molecular weight and density of I at  $25^{\circ.7}$  A comparison of the differences between values of  $\partial_{\rm solvent}$  (using Hildebrand's values<sup>6</sup> or calculated from literature values of  $\Delta H$ ) and  $\partial_{\rm I}$  with the K's of I between eight of these solvents and water shown in Table III.

#### TABLE III

Solubility Parameters (d) of Various Organic Solvents and Distribution Coefficients (K) of  $I^a$  between These Solvents and Water

Solvent	$\partial_{solvent}$	$\delta_1 \stackrel{\pm}{-} \Delta_{solvent}^{\Delta \partial_1}$	K
Benzene	9.15	0.11	2.08
Carbon tetrachloride	8.60	0.44	0.84
<i>n</i> -Heptane	7.00	2.04	0.20
Chlorobenzene	9.50	0.46	1.94
Nitrobenzene	10.0	0.96	2.51
1-Nitropropane	10.45	1.41	4.70
Chloroform	9.30	0.26	31.2
sym-Tetrachloroethane	8.23	0.81	17.6

<sup>a</sup>  $\partial_x = 9.04$ .

For the non-polar liquids shown in Table III, (i.e., benzene, carbon tetrachloride and n-heptane) there is qualitative agreement between the prediction of distribution and the observed coefficient, *i.e.*, K increases as  $\Delta \partial$  decreases. Large deviations are found for sym-tetrachloroethane and chloroform, two materials capable of hydrogen bonding. A comparison of the K values for the  $CCl_4$  and CHCl<sub>3</sub>-water systems suggests that hydrogen bonding may be an important factor in determining the solubility of I in organic solvents. Moreover, a comparison of coefficients of I between halogenated hydrocarbons and the water shows that Kdecreases as the organic solvents' power to hydrogen bond decreases (as might be derived from a consideration of the inductive effects of groups directly attached to the carbon bound to the hydrogen) i.e.,  $HCCl_3 > Cl_2CH-CHCl_2 > Cl-(CH_2)_4$  $Cl > Br-(CH_2)_2-Br$  (Table II). Subsequent studics of absorption in the infrared region of the spec-

(6) J. II. Hildebrand and H. Eenesi, J. Am. Chem. Soc., 70, 3980 (1948).

(7) A. W. H. Wardrop and P. J. R. Bryant, personal communication.

<sup>(5)</sup> J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes," 3rd Edition, Reinhold Publ. Corp., New York, N. Y. 1950, p. 129 and 435.

tra on solutions of I in CHCl<sub>3</sub> indicated stretching of the phosphoryl bond, which was attributable to hydrogen bonding.<sup>8</sup>

The high solubility of I in chlorobenzene, relative to its solubility parameter in Table III, is likewise attributed to a hydrogen bonding capacity, albeit small. The higher solubility of I in nitropropane as as compared to nitrobenzene and in nitrobenzene as compared to chlorobenzene may be correlated with the electron densities of the bonding hydrogens as influenced by the inductive effects of the electronegative groups and the distance of these groups from the bonding hydrogen.

The K's for I, II, III and IV between sym-tetrachloroethane and water show an increase in solubility of the solute in the organic solvent with increasing molecular weight of the phosphonofluoridate. Approximately the same proportional increase in K is found with the benzene-water pair.

(8) G. F. Svatos and J. Goldenson, Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, February 27-March 2, 1956. This may be seen from Table IV, where K between I and the organic solvent is assigned a value of unity.

### TABLE IV

RATIO OF DISTRIBUTION COEFFICIENTS (BENZENE TO WATER AND sym-Tetrachloroethane to Water) of Phosphonofluoridates

	Phosphonofluoridates			
Solvent pair	IV	III	11	Ι
Benzene/H <sub>2</sub> O	21:	19.7:	3.5:	1
sym-Tetracbloroethane/H <sub>2</sub> O	28.2:	21.6:	4.1:	1

Since there is little or no possibility for hydrogen bonding in the benzene-water system, the increase in K is attributed for the most part to an increase in the size of the alkyl groups on the phosphonofluoridate, (thus increasing the lipoid solubility and decreasing the water solubility of the phosphonofluoridate) rather than to a variation in electron density on the various phosphoryl oxygen atoms.

**Acknowledgment.**—The authors wish to thank Corporal Robert Gelberg for technical assistance.

# COMMUNICATIONS TO THE EDITOR

# MAGNETIC PROPERTIES OF ZINC SULFIDE PHOSPHORS WITH MANGANESE ACTIVATOR

## Sir:

Investigations have been carried out from 77 to  $300^{\circ}$ K. on the magnetic properties of unexcited cubic ZnS:Mn phosphors, prepared mainly with chloride-activator. The phosphor preparative procedure and magnetic measuring technique have been described in a previous article.<sup>1</sup>

It was found in the present investigation that appreciable loss of manganese occurred through reaction with the chloride coactivator, with loss of MnCl<sub>2</sub> at the crystallization temperatures used. Incorporated manganese was therefore determined by chemical (colorimetric) analysis in all of the samples measured.<sup>2</sup> The results for cubic ZnS: Mn phosphors are summarized in Table I.

#### TABLE I

Summary of Magnetic Effects: Amounts in Columns 1 and 3 Are Given in Per Cent. by Weight

1 Mn Added	2 NaCl	3 Mn Found	Bohr Magne- tons	5 Weiss Constant
0.1%	Yes	0.08%	5.75	$\sim 0$
1.0	Yes	0.49	5.81	13.8
10.0	Yes	1.64	5.71	28.3
10.0	No	9.0	4.62	93.0

In comparing the properties of manganese in an oxygen-dominated lattice<sup>3</sup> with the sulfur-dominated lattice, it is found that the moments of man-

(1) S. Larach and J. Turkevich, Phys. Rev., 98, 1015 (1955).

(3) S. Larach and J. Turkevich, Phys. Rev., 89, 1060 (1953).

ganese in ZnS are in good agreement with those in Zn<sub>2</sub>SiO<sub>4</sub>. The Weiss constants for manganese in sulfides are greater than for manganese in silicates, indicating that interaction probably occurs to a greater extent in the cubic zinc sulfide lattice than in the rhombohedral zinc orthosilicate lattice. Schneider and England<sup>4</sup> have indicated that spin-spin interaction occurs in ZnS:Mn phosphors, by paramagnetic resonance investigations.

It would be of interest to investigate the magnetic properties of ZnS: Mn phosphors which contain quenching amounts of paramagnetic transition element poisons.<sup>5</sup>

## RCA LABORATORIES

Radio Corporation of AmericaSimon LarachPrinceton UniversityJohn TurkevichPrinceton, New JerseyJohn Turkevich

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(4) E. E. Schneider and T. S. England, Physica, 17, 221 (1951).

(5) R. H. Bube, S. Larach and R. E. Shrader, *Phys. Rev.*, **92**, 1135 (1953).

# THE KINETICS OF NUCLEATION IN TURBULENT JETS

#### Sir:

The rapid mixing which occurs when a turbulent jet of vapor issues into a relatively stationary cooler gas provides a means of quenching for studies of the kinetics of nucleation. An analysis of the rate of production of condensation nuclei in such a system enables a comparison of experimentally observed rates with theory.

Figure 1 is a cross-section of a turbulent jet. The region in which mixing occurs may be characterized by n, the mass ratio of cooling gas to nozzle gas in a

<sup>(2)</sup> Analyses by Dr. M. C. Gardels.

given volume element dv. It is known how the mean values of n depend upon the coördinates,<sup>2</sup> and that the redistribution of mass and heat by mixing in turbulent jets is rapid compared to ordinary diffusion or heat conduction.<sup>3</sup> Then the jet temperature T and the vapor concentration may be expressed as functions of the coördinates and experimental parameters. For the case of self-nucleation, the rate of production of nuclei, J, cc.<sup>-1</sup> sec.<sup>-1</sup>, may be written as a function of T and the supersaturation S. In a steady state, the total number I of nuclei produced per second is given by

$$I = \int J(S, T) dv \tag{1}$$

where the integral is taken over all elements of volume in which nuclei are being formed. The rate J may be written in the form<sup>4</sup>

$$J = A \exp\left\{-\Delta\phi^*/kT\right\}$$
(2)

where  $\Delta \phi^*$  is the free energy of formation of a critical nucleus from supersaturated vapor. Expressions for  $\Delta \phi^*$  and A have been obtained by application of macroscopic concepts<sup>4,5,6</sup>; these can be tested by comparison of values of *I* computed from equation (1) with experimental results.

Fortunately, experimental conditions may be so arranged that the region of production of nuclei at significant rates is limited, since the initial quenching may be overcome by dilution, for as  $n \to \infty$ ,  $T \rightarrow T_2$ . This accounts, e.g., for the disappearance of condensation trails from jet planes under certain conditions. The region of nucleus production may be followed by a region of growth, and I may be experimentally determined by photoelectric counting of the aerosol particles in a downstream sample. The high sensitivity of modern light scattering instruments' facilitates experiments with low vapor pressure materials under conditions such that the heat of condensation and the vapor depletion are negligible. Employing a nucleation apparatus especially designed for such studies, experiments have been conducted with dibutyl phthalate, octadecane, triethylene glycol, phenanthrene, and sulfur, chosen as representatives of classes of molecules in which the intermolecular forces are of different types. The data have been treated as indicated above, and by somewhat simpler approximate methods, among them one due to Amelin.<sup>8</sup> The results, which are available in preliminary form,<sup>9</sup> indicate significant departures from the simple theory based on the liquid drop model of the critical

(2) T. Baron and L. E. Alexander, Chem. Eng. Progress, 47, 181 (1951); T. Baron, ibid., 50, 73 (1954).

(3) H. C. Hottel, (a) Fourth Symposium on Combustion, Williams and Wilkins Co., Baltimore, Md., 1953, Paper No. 9; (b) OSRD Report No. 468, Jan. 12, 1942.

(4) M. Volmer, "Kinetik der Phasenbildung," Edwards Bros., Ann Arbor, Mich., 1945.

(5) R. Becker and W. Doring, Ann. Physik, 24, 719 (1935).

(6) J. Frenkel, "Kinetic Theory of Liquids," Dover Pub., Inc., New York, N. Y., 1955, Ch. 7.

 (7) C. T. O'Konski and G. J. Doyle, Anal. Chem., 27, 694 (1955);
 C. T. O'Konski, M. D. Bitron and W. I. Higuchi, ONR Tech. Report No. 3, Contract ONR 222-12, Project No. NR 051-302, Sept. 1, 1956, to be published.

(8) A. G. Amelin, Kolloid. Zhur., 10, 169 (1948).

(9) (a) W. I. Higuchi, Thesis, University of California, September, 1956; (b) C. T. O'Konski, Final Report, Contract ONR 222-12, Project No. NR 051-302, to be published.



Fig. 1.—Cross section of a turbulent jet illustrating nucleus production and aerosol formation.

nucleus. The deviations depend upon the molecular type, and are in the direction of higher than predicted nucleation rates.

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W. I. HIGUCHI

RECEIVED SEPTEMBER 17, 1956

## THE ANOMALOUS ENTROPY OF POTASSIUM NITRITE

#### Sir:

Bridgman<sup>1</sup> observed that a commercial sample of potassium nitrite of about 85% purity undergoes a transition involving an enthalpy change of about 1200 cal./mole under high pressure. The authors have confirmed this observation by a time-temperature cooling curve on a sample of high purity. The transition takes place at  $-13 \pm 2^{\circ}$  under atmospheric pressure and involves  $1200 \pm 200$  cal./ mole.

The existence of such a transition, which is tentatively believed to involve complete order-disorder of the nitrite ion, led the authors to investigate its effect on the standard entropy of potassium nitrite crystals.

(1) P. W. Bridgman, Proc. Amer. Acad. Sci., 51, 81 (1915).

v	APOR PRESSU	RE OF SOLUTIONS OF	NITRITES OF	MOLALITY $m$ Rel	ATIVE TO THA	T OF PURE WATE	R.
LiN	IO2	LiNO2		NaNC	)2	KNO	2
m	$p/p_0$	m	$p/p_0$	m	$p/p_0$	m	$p/p_0$
0.3315	0.9895	15.10	0.432	0.3082	0.9903	0.2345	0.9928
0.432	. 986 <b>2</b>	17.82	. 369	. 4320	.9858	. 4690	. 9853
1.133	. 9608	19.77	.331	.651	.9792	. 470	. 9815
1.343	. 9518	20.5 (satd.)	.317	1.418	.9544	. 939	.9714
2.74	.897	$LiNO_2.H_2O$		$2_{-}955$	.9051	1.997	.9424
4.76	. 809	$LiNO_2.^1/_2H_2O$	. 163	6.800	. 7865	4.640	.8740
5.79	.763	$LiNO_2$ . <sup>1</sup> / <sub>2</sub> H <sub>2</sub> O		12.34	6426	9.576	. 7650
7.53	. 688	LiNO <sub>2</sub>	. 106	12.38 (satd.)		19.95	. 6116
8.76	. 638					31.18	. 5197
1 <b>2</b> .78	. 497					34.3 (satd.)	

TABLE I

The nitrites were prepared by reaction of the respective C.P. chlorides with silver nitrite. Analysis for nitrite was carried out by permanganate titration as confirmed by the weight increase of nitrite samples after conversion to the nitrates by means of nitric acid. All samples were better than 99.9% pure.

Vapor pressure measurements of solutions of lithium, sodium and potassium nitrites were made with an apparatus very similar to that of Gibson and Adams.<sup>2</sup> The vapor pressure data are recorded in Table I. Values of the activity coefficients of the saturated solutions,  $\gamma_{\pm}$ , were evaluated by the method of Randall and White<sup>3</sup> and found to be 2.60, 0.552 and 0.181 for lithium, sodium and potassium nitrites, respectively. These activity coefficients were combined with the heats of solution given by Bureau,<sup>4</sup> the entropy of lithium ion given by Johnston and Bauer,<sup>5</sup> and the entropies of the

(2) R. E. Gibson and L. H. Adams, J. Am. Chem. Soc., 55, 2679 (1933).

(3) M. Randall and A. M. White, J. Am. Chem. Soc., 48, 2514 (1926).

(4) J. Bureau, Ann. Chim., 8, 5 (1937).

other ions in dilute solution given by Latimer<sup>6</sup> to yield by means of the Gibbs-Helmholtz equation,  $S^0$  LiNO<sub>2</sub> 22.8 (21.3),  $S^0$  NaNO<sub>2</sub> 24.7 (25.3),  $S^0$ KNO<sub>2</sub> 35.0 (28). Comparison with values in parentheses predicted by Latimer<sup>6</sup> on the assumption that the entropies in this series should be logarithmically dependent on the molecular weight of the cation shows the anomalously high value for potassium nitrite.

The above data indicate that caution should be observed in prediction of entropies of compounds in which order-disorder transitions characteristic of ions such as  $NO_2^-$ ,  $CN^-$ ,  $N_3^-$ , etc., can occur. The effect may be quite as large as that encountered in a paramagnetic salt.

(5) H. L. Johnston and T. W. Bauer, J. Am. Chem. Soc., 73, 1119 (1951).

(6) W. M. Latimer, "The Oxidation States of the Elements and their Potentials in Aqueous Solutions," Prentice-Hall, Inc., New York, N. Y., 1952.

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