# THE JOURNAL OF PHYSICAL CHEMISTRY

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## THE JOURNAL OF PHYSICAL CHEMISTRY

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# THE JOURNAL OF PHYSICAL CHEMISTRY

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## FREE VOLUMES AND FREE ROTATION IN SIMPLE LIQUIDS AND LIQUID SATURATED HYDROCARBONS<sup>1</sup>

By A. Bondi

Shell Development Company, Emeryville, California Received September 8, 1953

The term "free volume" has been applied indiscriminately to several essentially different concepts. In order to avoid the resulting confusion each of these is here separately defined and a terminology is proposed. The difference between the observed volume and the volume at 0°K. has been renamed the expansion volume  $V_E$ . The empty space in a liquid  $V - V_w$  (where  $V_w =$  van der Waals volume of the molecule, calculated from thermal collision cross-sections and from X-ray diffraction patterns of crystals) is called the empty volume  $V_t$ . The volume swept out by the center of gravity of the thermally vibrating molecule (called "free volume" by the proponents of the cage model theory of liquids) has been renamed the fluctuation volume  $\mathcal{V}$ . Rigorously, the fluctuation volume can only be calculated from the thermodynamic properties of a liquid. It is shown in this paper that an approximate fluctuation volume  $\mathcal{V}_0$  can be calculated by the simple relation  $\mathcal{V}_0 = (4\pi/3) \cdot (V_t/A)$ ,<sup>3</sup> when A is the surface area per mole of molecules. The relation of  $\mathcal{V}_0$  to other approximate calculations of  $\mathcal{V}$  is illustrated with data on monatomic and diatomic liquids. The upper and lower bounds of validity of  $\mathcal{V}_0$  are established as approximately the melting point and the atmospheric boiling point of simple liquids by comparison of the observed entropy of vaporization  $\Delta S_1 = [\Delta S_v \text{ (obsd.)} - \Delta S_1^*]_{P/T}$  is then a measure of restriction of external molecule rotation in the liquid. Comparison of the empty volume available in the liquid with that required to permit external rotation in the liquid. Comparison of the entry  $V_v$ , (where L and w are the length and width, respectively, of the molecule in question), could be correlated for a large number of representative normal, isomeric and cyclic paraffins with  $\Delta S_1$ . The physical reality of this excess entropy of vaporization has been established by comparison with that calculated from  $\mathcal{V}_0$ . (gas). For a number of long chain paraffins both sets

1.1 Introduction.—The common use of the free volume theories<sup>2-4</sup> of liquids in the calculation of the equilibrium and the transport properties of liquids has been retarded by two basic uncertainties, namely, the degree of approximation involved in the theory itself, and the mode of computation of the "free volume" from the known physical properties of liquids. The first of these uncertainties recently has been clarified by Kirkwood,<sup>5</sup> who showed that the free volume theory can be considered as a first approximation to a rigorous molec-

(1) Presented before the Division of Physical and Inorganic Chemistry, Mesting of the American Chemical Society, September, 1953.

 (2) J. H. Hildebrand and R. L. Scott. "Solubility of Non-Electrolytes," Reinhold Publ. Corp., New York, N. Y., 1951, p. 70-76.

(3) (a) J. O. Hirschfelder, D. P. Stevenson and H. Eyring, J. Chem.
 Phys., 5, 896 (1937); (b) J. F. Kincaid and H. Eyring, *ibid.*, 6, 620 (1938).

(4) J. E. Lennard-Jones and A. F. Devonshire, Proc. Roy. Soc. (London), A163, 53 (1937); A165, 1 (1938).

(5) J. G. Kirkwood, J. Chem. Phys., 18, 830 (1950).

ular theory of the liquid state. It is the purpose of this paper to deal with a method of its computation and to delineate the area of applicability of the free volume concept to calculations of the properties of liquids.

Since it is not always entirely clear which of the various free volume functions has to be employed in a given case, it appeared worthwhile to restate the definitions of the different free volumes, to introduce a nomenclature and to illustrate their physical significance in terms of their numerical values for simple substances in Part I. Part II will deal with the application of the method to the calculation of some of the equilibrium properties of hydrocarbons.

## I. Free Volumes of Simple Liquids

**1.2 Nomenclature.**—The following definitions are proposed for free volumes: (1) The empty



Fig. 1.—Ratic of the solid-like fluctuation volume  $\mathcal{V}_0$  to the fluctuation volume  $\mathcal{V}_0$  as a function of the degree of expansion.

volume (per mole)  $V_{\rm f} = V_{\rm T} - V_{\rm w}$ , where  $V_{\rm T} =$  macroscopic volume (cm.<sup>3</sup>/mole) at temperature T,  $V_{\rm w} =$  volume per mole (or gram atoms) of substance as calculated from the "van der Waals" dimensions obtained by X-ray diffraction methods or from gas kinetic collision cross sections. Typical data on  $V_{\rm w}$  are given in Table I.

(2) The expansion volume<sup>6</sup> (per mole)  $V_{\rm E} = V_{\rm T} - V_0$ , where  $V_0 =$  volume (cm.<sup>3</sup>/mole) of substance at 0°K. (in the crystalline state).

(3) The fluctuation volume<sup>6</sup> (per mole)  $\mathcal{U} = N_A v_{\varphi_1}$  where  $v_{\varphi}$  is the volume swept out by the center of gravity of the molecule as a result of its thermal vibration. (This fluctuation volume has been called "Free Volume" by Eyring and by Lennard-Jones.<sup>3a,4</sup>) The new name has been proposed in order to reduce the possibility of confusion with the empty volume.

#### TABLE I

VOLUME PROPERTIES OF SEVERAL SIMPLE SUBSTANCES (All in Cm.<sup>3</sup>/Mole)

Sub- stance	<i>T</i> , °	$V\mathbf{T}$	$V_0^{a}$	Vwb	Vkc
А	84	28.1	<b>23</b> . $4$	17.4	12.5
	87 <sup>d</sup>	28.5			
$N_2$	63.3	31.9	<b>27</b> . $4$	13.25	12.65
	$77.4^d$	34.8			
$CH_4$	90.5	35.0	30.65	16.8	17.2
	$112^d$	38.0			
$\mathrm{CCl}_4$	293	96.5	74.6	61	57°

<sup>o</sup> Zero point volumes from ref. 11 and from W. Biltz and A. Sapper, Z. ancrg. allgem. Chem., 203, 277 (1932). Other data from "Lancolt-Börnstein Tabellen." <sup>b</sup>van der Waals radii from ref. 10. <sup>o</sup> Collision diameters from J. A. Beattie and W. H. Stockmayer in Taylor-Glasstone "Treatise on Physical Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1951, and J. O. Hirschfelder, R. B. Bird and E. L. Spotz, Chem. Revs., 44, 205 (1949). <sup>d</sup> Boiling temperature. <sup>e</sup> Average of values ranging from 50.3 to 64 depending upon the method of determination of the collision diameter.

2.0 The Fluctuation Volume.—Several methods have been proposed in the past to calculate the fluctuation volume.<sup>2,3</sup> They were either restricted

(6) These expressions have been coined by Prof. Joel H. Hildebrand.

to spherical molecules<sup>3a</sup> or required the knowledge of physical properties which are not always available.<sup>3b</sup> It is here proposed to estimate the fluctuation volume from the density and the van der Waals volume on the basis of the assumption that all of the empty volume is accessible to the thermal motions of the molecules in the liquid state.

With this assumption one can easily see that as long as the "free path" is small compared with the molecule diameter, the fluctuation volume  $U_0$  is given by

$$U_0 = \frac{4\pi}{3} \left( \frac{V_f}{A} \right)^3 \times N_A \tag{3}$$

where A = area per mole of molecules. It is apparent that  $2V_f/A$  is the average amplitude Y of the thermal oscillations of the molecules in the liquid, since the empty space per unit surface area of a molecule defines the radius of the cage within which it moves. For the case of atoms equation 3 becomes<sup>7</sup>

$$\mathcal{U}_0 = V_{\rm f}^3 / 27 V_{\rm w}^2 \tag{3a}$$

while for polyatomic molecules both  $V_{\rm w}$  and A have to be calculated from the known bond distances and from van der Waals radii. The justification for the assumption of communal accessibility of the empty volume in liquids has been given by Eyring<sup>3a</sup> and by others.<sup>4</sup> The fluctuation volume of a liquid, where the atoms have fixed lattice positions and therefore provide only solid-like accessibility of the empty volume to the thermal vibrations of the atoms, has been calculated by Hirschfelder and co-workers.<sup>8</sup> A comparison of this "solid-like" fluctuation volume  $U_{\rm s}$  with  $U_{\rm 0}$ , as a function of the degree of expansion  $V_{\rm T}/V_{\rm w}$  is shown in Fig. 1. The vast majority of liquids composed of spherical molecules is already at the melting point expanded to  $V_{\rm T}/V_{\rm w} \sim 2$  whence  $U_{\rm s}/U_{\rm 0} \sim 1$ . The assumption of communal accessibility of the empty volume is therefore important only for liquid metals for which  $V_{\rm T}/V_{\rm w}$  is often quite small.

The exact determination of  $\mathcal{V}_0$  requires the knowledge of  $V_{w}$ , the van der Waals volume. For monatomic substances  $V_w$  is identical with the gas kinetic collision volume  $V_{\mathbf{k}} = (\pi/6) r_0^3 N_{\mathbf{A}}$  where  $r_0 =$ collision diameter obtained from gas viscosity, second virial coefficients, etc. For polyatomic molecules the calculations were based on Pauling's bond distances and van der Waals radii, and for liquid metals on his metallic radii (derived from Xray diffraction pattern of the metals in the crys-The densities are from recent data talline state). collections. All of these data, especially the X-ray derived van der Waals radii, are undoubtedly only approximations. This must be taken into consideration in the evaluation of the  $\mathcal{V}_0$  data. The relative magnitudes of the volume parameters employed are apparent from the data of Table I.

2.1 Comparison with Other Fluctuation Volume Data.—A comparison of the fluctuation volumes calculated by different methods is given in Tables II and III. Here  $U_1$  is the fluctuation volume calculated from vapor pressure data,<sup>2,3b</sup>  $U_2$  that de-

<sup>(7)</sup> An expression similar to (3a) had been proposed by Kittel but containing  $V_{\rm T}$  instead of  $V_{\rm W}$ .

<sup>(8)</sup> R. J. Buehler, R. H. Wentorf, C. F. Curtiss and J. O. Hirschfelder, J. Chem. Phys., 19, 60 (1951).

rived from sound velocity,<sup>35</sup> and  $U_3$  is that computed from p-v-t data.<sup>3a</sup> We find generally good agreement between  $U_0$  and  $U_1$ . The other two are usually somewhat smaller.

## TABLE II

EMPTY VOLUMES AND FLUCTUATION VOLUMES OF SIMPLE LIQUIDS

Substance	T	$V_{t}$	$V_{\mathbf{w}}$	$V_{\rm f}$	Vo	$\mathbb{U}_1^a$	$\mathbb{U}_2^a$	Usa
Argon	84	28.1	12.5	15.6	0.80		0.223	0.9
	87	28.5		16.0	.97	0.85	.261 <sup>b</sup>	
Xenon	165	43	21	22	. 90	1.3		
$N_2$	63. <b>3</b>	31.9	13.25	18.65		0.405	.352 <sup>c</sup>	
CH	90.5	35.0	17.0	18.0	. 59	0.53	.18°	
$CF_4$	145	45.0	24.0	21.0	. 435	0.41		
CCl₄	293	96.5	55.0	41.5	.42	0.24	.28	0.16
<sup>a</sup> Defining equations for fluctuation volumes								

$$\mathcal{U}_1 = V_{\text{gas}} \exp\{-\Delta S_v/R\} = (RT/p) \exp\{-\Delta H_v/RT\}$$

$$(7)_2 = V_{\star} (u_{\pi}/u_{\rm I})^3 = V_{\star} (xRT/M)^{3/2}/u_{\rm I}$$

 $\mathcal{U}_3 = (4\pi\gamma/3 V^2)(R\beta/\alpha)^3$ 

where p = vapor pressure,  $\Delta H_{\nu} =$  heat of vaporization,  $u_g, u_L =$  sound velocity of vapor and of liquid resp.,  $x = C_p/C_{\nu}$ ,  $\beta =$  compressibility,  $\alpha =$  thermal expansion coefficient,  $\gamma =$  geometrical packing factor. <sup>b</sup> Sound velocity data from A. Van Itterbeek, *et al.*, *Physica*, 15, 624 1949). <sup>c</sup> Sound velocity data from L. Bergmann, "Der Ultraschall," Zürich, 1949.

## TABLE III

EMPTY VOLUMES AND FLUCTUATION VOLUMES OF LIQUID METALS (CM.<sup>3</sup>/MOLE)

Metal	°K.	$V_{\mathbf{T}}^{a}$	$V_w^b$	$V_{\rm f}$	$\mathbb{U}_0^c$	$\mathbb{U}_1^d$	$\mathcal{U}_2^e$
Hg	300	14.81	8.52	6.29	0.13	0.08 <sup>f</sup> to	0.014
						.152	
	573	15.60		7.08	. 19	.24 to	
						.45	
Zn	<b>693</b>	9.45	5.68	3.77	.06	.04	0.025
	1179	10.0		4.32	. 09 <b>3</b>	. 2	
Cd	603	14.0	8.43	5.57	.09	.04	0.025
	873	14.5		6.07	.12	.103	
Ga	1250	12.60	6.22	6.38	.25	. 30	(0.15-0.2

<sup>a</sup> Density data from "Liquid Metals Handbook," U. S. AEC, 1952. <sup>b</sup> Calculated from metallic radii, L. Pauling, "Nature of the Chemical Bonds," Cornell University Press, Ithaca, N. Y., p. 409-10. <sup>c</sup> Calculated from  $\mathcal{V}_0 = V^3 t/27 V^2 w$ . <sup>d</sup> Calculated from vapor pressure data by Ditchburn and Gilmoure, *Rev. Mod. Phys.*, 13, 310 (1941). <sup>e</sup> Calculated from sound velocity data by O. J. Kleppa, J. *Chem. Phys.*, 17, 668 (1949); 18, 1331 (1950). <sup>f</sup> Range represents scatter of vapor pressure data in the literature. <sup>e</sup> Uncertain due to rather long range extrapolation.

This result suggests that the numerical value of  $\mathcal{U}_0$  is identical with the fluctuation volume appearing in the cage model theory, since in the defining equation of  $\mathcal{U}_1$ 

$$\Delta S_{\rm vap}/R = \ln \left( V_{\rm gas}/\mathcal{V}_1 \right) \tag{4}$$

where  $\Delta S_{\text{vap}}$  = entropy of vaporization, the right hand side represents the logarithm of the ratio of the partition function of the gas to the partition function proposed by the cage model theory for the liquid. We shall therefore define the region of usefulness of  $\mathcal{V}_0$  in terms of the region, where for spherically shaped molecules it is numerically identical with  $\mathcal{V}_1$ . An analysis of the differences between the various fluctuation volumes of simple substances is beyond the scope of this paper.

2.2 Fluctuation Volume and Intermolecular Forces.—The degree of expansion of a liquid, the ratio  $V_t/V_w$ , and therefore  $V_f$  as well as  $\mathcal{O}_0$ , are determined by the three variables  $r_0$ , the collision

diameter (or the van der Waals dimensions),  $\epsilon_0$ , the potential of average force between a pair of molecules, and the absolute temperature T. On the basis of various equations of state that have been proposed for liquids, the ratio  $\mathcal{V}_0/V_w$  should be a unique function of  $\epsilon_0/kT$  at low pressures (such that  $pV_{\rm T} << RT$ ).

The experimental points of Fig. 2, a plot of  $\mathcal{V}_0/V_w$  vs.  $\epsilon_0/kT$  (from gas kinetic data) appear to straddle a single line, indeed. The relation of this line to the equations of state of Lennard-Jones and Devonshire and of the appropriately modified Hirschfelder, Stevenson and Eyring equation<sup>9</sup> is indicated by comparison with curves 2 and 5. Curves 3 and 4 have been calculated from the thermal vibration amplitude of a molecule in the field of its neighbors, such that

$$\mathbb{U}_{4} = N_{A}(\pi/6)r_{0}^{3} \left[ \left( \frac{3}{2} \ z\epsilon_{a}/kT \right)^{1/2} - 1 \right]^{-3} \quad (5)$$

where z = number of nearest neighbors,  $\epsilon_a =$  attractive component of the Lennard-Jones potential function. The empirical measure of the fluctuation volume,  $\mathcal{V}_0$ , therefore appears to fit into the general pattern predicted by the existing theories of the liquid state. Its magnitude is in agreement with that predicted by the Lennard-Jones and Devonshire theory at values of  $\epsilon_0/kT > 1.3$ , *i.e.*, at high densities. We shall see below that this conclusion holds quite generally.



Fig. 2.—Relation of fluctuation volume  $\mathcal{V}_0$  to molecule dimensions  $(V\mathbf{w})$  and intermolecular potential  $\epsilon_0$ , according to experiment (Curve 1), Lennard-Jones and Devonshire theory (Curve 2) for Z = 10, Equation 5 with Z = 10 (Curve 3), with Z = 6 (Curve 4), and modified Hirschfelder, Stevenson and Eyring theory, with Z = 6 (Curve 5).

3.1 The Change of Entropy with Volume.— As long as no other change takes place, any iso-

(9) Namely  $\bigcup_1 = N_A \times ro^3 [(z\epsilon/kT)^{-1/2}]^{-3}$ ; and for  $\bigcup_2$  one obtains:  $\bigcup_2 = V_\ell (\sqrt{2\kappa kT/3} z\epsilon_b)^{-3/2}$ , if the sound velocity in a liquid is given as  $u_L = (3z\epsilon_a/\sqrt{2}m)^{1/2}$ ,  $\kappa = C_p/C_v$ . thermal change in the fluctuation volume of a liquid is accompanied by a change in entropy

$$S_2 - S_1 = R \ln \left( \mathcal{V}_{0(2)} / \mathcal{V}_{0(1)} \right)$$
(6)

where the numbers 1 and 2 refer to the initial and the final state, respectively. We have seen above that for the case  $\mathcal{V}_{0(1)} = \mathcal{V}_0, \mathcal{V}_{0(2)} = V_{gas}$  (the evapora-tion),  $\Delta S = \Delta S_{vap}$ . The close proximity of the values of  $\mathcal{V}_0$  and  $\mathcal{V}_1$  for most of the examples cited in Tables II and III permits the inference that the entropy of vaporization of simple liquids can indeed be calculated for  $\mathcal{V}_0$  with fair accuracy. The error is given by  $R \ln(\mathcal{U}_1/\mathcal{U}_0)$ , and hence is but 1.4 e.u. if  $\mathcal{U}_0$  differs from  $\mathcal{U}_1$  by as much as a factor of two.

If the process involved is the compression of the liquid by the amount  $\Delta V$  then we have

$$\Delta S = \Delta V (\partial S / \partial V)_{\rm T} = R \ln \left( \mathcal{V}_{0(2)} / \mathcal{V}_{0(1)} \right)$$

Since  $(\partial S/\partial V)_{T} = (\partial P/\partial T)_{v}$ , the validity of this rule can be checked easily by means of the available p-v-t data of suitable liquids. Typical results are given on Table IV.

## TABLE IV

## ENTROPY OF COMPRESSION IN SIMPLE LIQUIDS

Substance	<i>t</i> , °K.	<i>P</i> , kg. cm2	∆S,ª e.u.	ΔSobs, e.u.	∆Si, e.u.
Neopentane	398	250 - 500	0.83	1.10 <sup>b</sup>	0.27
Carbon disulfide	293	1 - 500	0.46	0.89°	. 43
<i>i</i> -Pentane	298	1 - 500	1.0	$1.52^a$	.52

<sup>a</sup> Calculated from fluctuation volume data by means of equation 6. <sup>b</sup> Calculated from data by Van Wijk and Seeder, *Physica*, 7, 40 (1940). <sup>c</sup> Calculated from data by P. W. Bridgman, "The Physics of High Pressure," G. Bell and Sons, 1949.

Deviations of the observed entropy change from the value computed by means of equation (6) are usually ascribed to hindered molecular rotation in the case of evaporation and to configuration changes in the case of compression of the liquid. The meaning of these deviations will be discussed in detail in Part II.

3.2 The Limits of Applicability of the Fluctuation Volume.—The fluctuation volume,  $U_0$ , has inherent lower and upper limits of applicability. The lower limit is that volume at which the motion of a molecule is so restricted that its thermal oscillations do not sweep out all of the available empty volume. In many instances this point will be identical with the melting point. Those spherically symmetrical molecules which rotate relatively freely in the solid state may be exceptional and their thermodynamic properties might be described by the fluctuation volume down to the first order transition temperature at which rotation ceases.

The upper bound of the fluctuation volume concept is at that degree of expansion at which  $v/r_0^3 \ge 2$ (equivalent to  $V/V_w \ge 12/\pi$ ) because at that point a molecule can pass through the cage formed by its nearest neighbors without activation energy.<sup>8</sup> It is conceivable that the "rigidity" of the cage formed by the nearest neighbors becomes insuffificient to permit description of the average thermal motions by the fluctuation volume at a much lower degree of expansion. One might guess that such be the case at a temperature where  $\epsilon_0/kT \sim 1$ . Empirically it is found that  $U_0$  ceases to predict the entropy of vaporization correctly at  $V_{\rm T}/V_{\rm w} \sim$ 

2.3  $\pm$  0.1 (equivalent to  $v/r_0^3 \sim 1.2 \pm 0.05$ ), a point usually just above the atmospheric boiling temperature.

In principle one should expect that beyond  $v/r_0^3$ = 2 the entropy of vaporization is given by  $\Delta S_{\rm v}$  =  $R \ln (V_g/V_f)$ . This supposition cannot be tested very well because the liquid is usually within a few degrees of its critical temperature at that degree of expansion. From the few available entropy of vaporization data in this range one computes a reference free volume of the order of  $0.5V_{\rm f}$  at  $V_{\rm T}/V_{\rm w}$ ~  $12/\pi$ . It can be shown that the entropy of vaporization of low molecular weight gases out of their solutions is indeed dependent on  $\overline{V}_{\rm f}$  if  $\overline{V}/V_{\rm w}$  is of the order of  $12/\pi$ , where  $\overline{V}$  and  $\overline{V}_{f}$  are the partial molal volume and empty volume of the dissolved gas, respectively.

One may say, therefore, that the (empirical) fluctuation volume  $\mathcal{U}_0$  describes the location of the center of gravity of the molecules in a liquid adequately between the freezing point and the atmospheric boiling point. The empty volume appears to describe the location of the center of gravity of molecules in a fluid at volumes in excess of the critical. The range between the atmospheric boiling point and the critical temperature is probably not describable by a simple cage model theory of the liquid stage.

## II. Free Volumes and Free Rotation of Saturated Hydrocarbons

4.1 Van der Waals Volume of Hydrocarbons.— The van der Waals volume of polyatomic substances is only rarely expressible in terms of thermal collision diameters. It must, instead, be computed from the X-ray diffraction patterns, i.e., from the bond distances, bond angles and van der Waals radii.<sup>10</sup> In the case of hydrocarbons even the latter course does not lead to unambiguous answers, since there is some latitude in the choice of van der Waals radii compatible with known crystal structure and densities.

The over-all radius of the methyl group having been given by Pauling as 2.0 Å., the hydrogen radius as 1.20 Å., the carbon radius was selected such that the van der Waals volume of methane be identical with the gas kinetic collision volume, namely, as 1.7 A. Table V contains the resulting group incre-

## TABLE V

VOLUME FORMULAS FOR *n*-PARAFFINS (ALL IN CM.<sup>3</sup>/MOLE) N = Number of carbon atoms per chain

(1) van der Waals volume (using r(H) = 1.2 Å., r(C) =1.7 Å.)  $V_{w}(CH_{3})$ : 13.5 cm.<sup>3</sup>,  $V_{w}(CH_{2})$ : 10.2 cm.<sup>3</sup>,  $V_{w}(CH)$ : 6.8 cm<sup>3</sup>,  $V_{w}(-C)$ : 3.3 cm.<sup>3</sup>

$$V_{\rm w} = 6.6 + 10.2N$$

- (2)Zero point volume (at 0°K.) (from ref. 11)  $V_0 = 12.89 + 13.685N$
- Volume at 20° (from Calingaert, et al., Ind. Eng. Chem., (3)33, 103 (1941))  $V_{293} = 30.392 + 16.375N + 74.44/N^2$

ments for  $V_{\rm w}$ , while Table VI presents a comparison of  $V_{\rm w}$  with the various gas kinetic collision volumes.

(10) L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940.

The agreement between  $V_{\rm w}$  and  $V_{\rm k}$  extends over a far greater range than one had any reason to expect for asymmetric molecules (for *n*-pentane the axial ratio is about 1.7). The agreement between  $V_{\rm w}$  and the kinetic volume computed from Lennard-Jones' approximation  $r_0 = 0.833 V_{\rm c}^{1/a}$  (A) (where  $V_{\rm c}$  = critical molal volume) up to cetane simply means that the critical volume is a nearly constant multiple of  $V_{\rm w}$  for the saturated hydrocarbons.

#### TABLE VI

Comparison of the Calculated van der Waals Volume of Hydrocarbons,  $V_w$ , with the Collision Volumes Calculated from Gas Viscosity  $V_k(\eta)$ , from Critical Volume  $V_{k(v_c)}$ , and from Second Virial Coefficients  $V_{k(w_c)}$  (All in Cm<sup>3</sup>/Mole)

,	K(D) (1100 II		,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	
	$V_{\mathbf{w}}$	$V_{k(\eta)}^{a}$	$V_{\mathbf{k}}(\mathbf{v_c})^{\mathbf{b}}$	$V_{\mathbf{k}(\mathbf{B})}^{c}$
CH₄	17.0	17.2	18.3	17.1
$C_2H_6$	<b>27.0</b>	<b>27</b> . 1	26.2	39.2
C3H	37.2	40.7		55.3
$n-C_4H_{10}$	47.4	48.0		73.1
$n-C_5H_{12}$	57.6	60.6	57.0	
$n-C_6H_{14}$	67.8	65.5	68.0	
$n-C_8H_{18}$	88.2	130.6	89.0	
$n-C_9H_{20}$	98.4	190.2	101.0	
n-C16H34	170.0	$230^{d}$	$187.2^{\circ}$	
Cyclohexane	61.2	71.0	57	

<sup>a,b</sup> From data of J. O. Hirschfelder, R. B. Bird and E. L. Spotz, *Chem. Revs.*, **44**, 205 (1949), except where noted. <sup>c</sup> From data of J. A. Beattie and W. H. Stockmayer, in Taylor-Glasstone, "Treatise on Physical Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1951. <sup>d</sup> From diffusion constant data of R. S. Bradley, *et al.*, *Proc. Roy. Soc. (London)*, A198, 226, 239 (1949); A206, 65 (1951). <sup>e</sup> From critical volume data in M. P. Doss, "Physical Constants of the Principal Hydrocarbons," N. Y., 1943.

4.2 The Empty Volume and the Zero-point Volume of Hydrocarbons.-The empty volume  $V_{\rm f}$  of the saturated hydrocarbons at their atmospheric boiling points constitutes about 50% of their molal volume at that temperature. Only for methane it is a somewhat larger fraction (56%) as is apparent from the data of Table VII. At their critical temperature  $V_{\rm T}/V_{\rm w}$  varies from 4.9 for *n*-octane to 5.9 for methane on the one hand and to 5.8 for *n*-hexadecane on the other, hence  $V_{\rm f}$  constitutes about 80 to 84% of the critical molal volume. At room temperature  $V_{\rm f}$  decreases from 48.5% for *n*-pentane to about 35% for  $(\rm CH_2)_{\infty}$ , while  $V_0/V_{\rm w}$ varies from 1.8 for methane to 1.36 for cetane, and  $V_{\rm f}/V_0$  correspondingly from 44 to 26.5%. The paraffin hydrocarbons are thus seen to be only approximately in corresponding states at their critical temperatures and at their atmospheric boiling points. At equal temperatures the degree of expansion is governed by the concentration of methyl groups in the system since the CH<sub>3</sub>-CH<sub>3</sub> and the CH<sub>3</sub>-CH<sub>2</sub> interaction potentials are significantly smaller than all other group interactions in these liquids. The comparison of the volume properties of isomeric and normal paraffins brings this out (see Tables VII and XI).

The peculiar alternation effect in the zero-point volume  $V_0$  as one ascends the *n*-paraffin series (Table VIII), already noted by Biltz<sup>11</sup> as probably

TABLE V	II
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VOLUME PROPE	RTIES (	of Vario	dus Paf	RAFFIN	Hydroc	RBONS
Substance	°K.	VT,ª cm.³/ mole	Ví. cm. <sup>8</sup> / mole	$V_{ m f}/V_{ m T}$	Va,b cm.³/ mole	$V_{\rm E}/V_{\rm T}$
CH4	90.5 112 <sup>c</sup> 191 <sup>d</sup>	35 38 98.6	18.0 21.0 81.6	0.51 .55 .83	30.65	0.124 .193
C <sub>2</sub> H <sub>6</sub>	184 <sup>e</sup>	55	28	.49	40.0	. 272
CaH8	231° 298	76 89	38.8 51.8	.51 .58	54.6	.282 .387
n-C4H10	273 <sup>c</sup> 298 423 <sup>d</sup>	96 101 258	48.8 53.6 210.6	. 506 . 53 . 81	66.4	. 308 . 343
$n-C_{\delta}H_{12}$	293° 309°	116 118	58.4 60.4	. 503 . 51	81.7	. 297 . 307
neo-C <sub>6</sub> H <sub>13</sub>	283 <sup>e</sup>	120	62.4	. 52		
n-C6H14	293 342° 508 <sup>d</sup>	131.3 139.5 367	63.5 71.7 299.2	.48 .515 .815	94.6	.279 .323
n-C1H18	293 371° 540 <sup>d</sup>	146.2 162 415	68.2 84.0 337	.466 .518 .81	109.9	. 258 . 321
n-C <sub>8</sub> H <sub>18</sub>	293 399° 569 <sup>d</sup>	162 185.5 448	73.8 97.3 360	.456 .525 .80	120.8	. 254 . 349
2,2,4-Trimethyl- pentane	293 372	$\begin{array}{c} 165 \\ 184 \end{array}$	77.5 96.5	.47 .525		
<i>n</i> -C <sub>9</sub> H <sub>20</sub>	293 424	178 210	79.6 111.6	. 447 . 531	136.1	. 236 . 352
n-C18H54	293 559° 734 <sup>d</sup>	292 391° 1025	122.0 221.0 855	.417 .565 .835	(231.4)	. 211
a Data from		of Tabl		h Data	f	. 11

<sup>a</sup> Data from ref. *e* of Table VI. <sup>b</sup> Data from ref. 11. <sup>c</sup> Boiling point. <sup>d</sup> Critical temperature. <sup>e</sup> G. W. Nederbragt and J. W. M. Boelhouwer, *Physica*, 13, 305 (1947).

due to crystal structure alternations is almost exactly compensated by the melting point expansion, as shown by the last two columns of Table VIII.

TABLE VIII

RELATION	OF ALTERNATION	Effec	rs to Crystai	LIZATION
Substance	Voa	Δ	$V_0 + \Delta V_i b$	Δ
$C_1$	30.65		33.3	
		9.35		11.8
$C_2$	40.0		45.1	
	1	4.6		
$C_3$	54.6			
	J	1.8		
n-C <sub>4</sub>	66.4		73.3	
	1	5.3		16.8
n-C <sub>5</sub>	81.7		90.1	
	1	2.9		16.4
$n-C_6$	94.6		106.5	
	1	5.3		16.8
$n-C_7$	109.9		123.2	
	1	0.9		16.8
n-C <sub>8</sub>	120.8		140	
	1	5.3		
n - C	136 1			

<sup>a</sup> Zero point volumes from Biltz, et al.<sup>11</sup> <sup>b</sup> Freezing point contractions from H. Sackmann and F. Sauerwald, Z. physik. Chem., A195, 295 (1950).

This result suggests very strongly that volume alternations should not be found in the liquid state as one ascends the *n*-paraffin series. The expansion volume  $V_{\rm E} = V_{\rm T} - V_0$ , which is occasionally found in the literature as measure of the free space in liquids,<sup>12</sup> contains the alternation effect and is

(12) A. K. Doolittle, J. Appl. Phys., 22, 1031, 1471 (1951); 23, 236 (1952).

<sup>(11)</sup> W. Biltz, et al., Z. physik. Chem., 151, 13 (1930).

therefore hardly a good property to use for the correlation with other properties of liquids.

The change of  $V_{\rm f}$  with temperature is given by the (empirical) thermal expansion formula

$$V_{\rm f}(T) = V_{\rm f}(T^0) + V_{\rm L}[\alpha_{\rm I}(T - T^0) + \alpha_{\rm 2}(T - T^0)^2] \quad (7)$$

where  $\alpha$  are the conventional expansion coefficients,  $T^0$  is a reference temperature. Since  $\alpha_1$ , the dominant factor, is related to the density  $\rho$  by the relation  $\alpha_1 = A_1/\rho$ , where  $A_1$ , the temperature coefficient of density, is a function of the molecular weight only,<sup>13</sup> it is apparent that the isomer with the lower density not only exhibits a larger empty volume  $V_f$  than the member of the normal paraffin series, but for it  $V_f$  also increases more rapidly with temperature.

The change of  $V_{\rm f}$  with pressure is demonstrated by some of Bridgman's recent data<sup>14</sup> on Fig. 3,





where the fractional change in volume with pressure  $\Delta V_{(p)}$  at room temperature relative to the free volume  $V_{\rm f}$  at that temperature has been plotted vs. the pressure (P) and vs. log P. Neither curve exhibits any singularity at the point corresponding to the zero point volume. The location of the freezing contraction is a function of temperature only and is unrelated to the location of the  $V_0$ intersection. The curves beyond the freezing point are direct continuations of the initial curves and can be added to them without break. The  $\Delta V_{(p)}$  vs. P curve demonstrates the continual decrease of compressibility with increasing degree of compression. However, even at 40,000 atmospheres the compressibility of *n*-heptane is still of the order of  $5 \times 10^{-12}$ , far above the  $10^{-14}$  to be ex-

(13) M. R. Lipkin and S. S. Kurtz, Ind. Eng. Chem., Anal. Ed., 13, 291 (1941).

(14) P. W. Bridgman, Proc. Am. Acad. Arts Sci., 77, 115 (1949).

pected if deformation of chemical bonds (or angles) were the source of compression. Extrapolation of the logarithmic curve predicts squeezing out of all of the empty volume at 65,000 atmospheres. The interval from the point corresponding to  $V_0$  to the intersection with the line  $\Delta V_{(p)}/V_f = 1$  must represent sufficient deformation of the van der Waals interaction field to lead to the equivalent of complete packing of the usually empty space. The smoothness of the volume vs. pressure curve is good evidence for the "softness" of the low energy collision diameter upon which our calculations had been based.

5.1 The Fluctuation Volume.—A simple consideration of the geometry of the average motion of a molecule in the average (uniform) field of force of its neighbors leads to the conclusion that the volume swept out by the center of gravity of a molecule is of nearly spherical shape regardless how complex the shape of the molecule and can therefore be adequately described by equation 3. The area per mole of saturated hydrocarbon molecules can be computed from the increments (in units of 10<sup>9</sup> cm.<sup>2</sup>/mole):  $-CH_3 = 2.14$ ,  $>CH_2 = 1.36$ , >CH =0.58. The slightly negative contribution of the quaternary carbon atom can be neglected.

Typical fluctuation volume data of hydrocarbons have been accumulated in Table IX. For the lower members of the series there is reasonable agreement between  $\mathcal{O}_0$  and  $\mathcal{O}_1$  at temperatures below the at-

TABLE IX

FLUCTUATION VOLUMES OF VARIOUS PARAFFIN HYDROCAR-BONS

	<b>()</b>	0, cm.³∕	<b>U</b> 1,	U2,
Substance	<i>T</i> , <sup>o</sup> K.	mole	cm. <sup>3</sup> /mole	cm. <sup>3</sup> /mol
	90.J	0.39	0.50	0.177
C <sub>2</sub> H <sub>6</sub>	148	0.71	1.01	
$C_3H_8$	231"	0.84	$1.08^{a}$	
$n-C_4H_{10}$	$273^{h}$	0.87	$1.16(?)^{a}$	
$n-C_5H_{12}$	293	0.87	0.89 <sup>1</sup>	0.734°
	$309^{h}$	0.95	$1.09^{a}$	1.07
$neo-C_5H_{12}$	$283^{h}$	0.98	1.38°	1.35
n-C6H11	293	0.705	0.39 <sup>1</sup>	0.517°
	342 <sup>h</sup>	1.01	1.03ª	(1.39)
$n-C_7H_{16}$	<b>2</b> 93	0.53	0.15'	0.377°
	371 <sup>h</sup>	1.11	0.91ª	(1.85)
$n-C_8H_{18}$	293	0.53	0.076'	0.31°
	$399^{h}$	1.20	0.86 <sup>a</sup>	(2.47)
2,2,4-Trimethyl-	293	0.58	0.29'	$0.42^{d}$
pentane	37 <b>2</b>	1.11	1.31ª	
$n-C_9H_{20}$	293	0.49	0.043 <sup>1</sup>	0.26°
		1.36	$0.75^{a}$	
n-C16H54	293	0.36	$8  imes 10^{-59}$	0.095 <sup>e</sup>
	$559^{h}$	2.14	0.27ª	

<sup>a</sup> Heat of vaporization data from F. D. Rossini, et al., API Project 44, Tables Properties of Pure Hydrocarbons. <sup>b</sup> Sound velocity data from ref. b, Table III. <sup>c</sup> Sound velocity data from ref. c Table II. <sup>d</sup> Sound velocity data from "Landolt-Bornstein Tabellen." <sup>c</sup> Sound velocity data from "Landolt-Bornstein Tabellen." <sup>c</sup> Sound velocity data from N. Utter and R. Kling, Compt. rend., 227, 41 (1948). <sup>f</sup> Heat of vaporization data from N. S. Osborne and D. C. Ginnings, J. Res. Natl. Bur. Standards, 39, 453 (1947). <sup>e</sup> Vapor pressure data from G. S. Parks and G. E. Moore, J. Chem. Phys., 17, 1151 (1949). <sup>h</sup> Boiling point. mospheric boiling point. At the boiling point and above  $\mathcal{U}_0 < \mathcal{U}_1$  for the spherical or nearly spherical molecules. Small adjustments in the van der Waals radii might make the agreement somewhat better, but could not detract from the fact that the cage model theory loses its applicability somewhere near the expansion characteristic of the boiling point in the case of these hydrocarbons.

The fluctuation volume data computed from sound velocity  $(\mathcal{V}_2)$  are smaller than  $\mathcal{V}_0$ , just as we had seen with the simple substances (Table II). Because of the arbitrariness in the assignment of the packing factor one cannot make any good comparisons with  $\mathcal{V}_3$ . The  $\mathcal{V}_3$  data of Table X indicate that  $(\partial \mathcal{V}_3/\partial T)_v$  is a small number. The approximation  $(\partial \mathcal{V}/\partial T)_v = 0$ , made implicitly in the use of  $\mathcal{V}_0$  as expression for the fluctuation volume, is therefore not likely to be seriously in error.

## TABLE X

## Comparison of Fluctuation Volumes at Equal Degrees of Expansion<sup>4</sup>

	$V_{ m T}/V_{ m W}$	<i>T</i> , ⁰K.	P,b atm.	U3, cm. <sup>3</sup> / mcle	$V_{\rm T}/V_{\rm w}$	°K.	$P,^a$ atm.	U3, cm. <sup>3</sup> / mole
n-Pentane	1.62 1.62	$175 \\ 298$	1 2200	0.085	1.77 1.77	$252 \\ 298$	1 800	0.34
	1.62	346	3000	.11	1.77	346	1200	.67
n-Octane	1,62 1,62 1,62	216 298 346	1 1100 2000	.08 .06 .0 <b>7</b> 5	1.77 1.77 1.77	293 298 346	1 50 700	.31 .25 .23

<sup>a</sup> Computed from data by P. W. Bridgman, *Proc. Am.* Acad. Arts Sci., 66, 185 (1931). <sup>b</sup> Pressure data given are only approximate interpolations, since the  $\mathcal{V}_3$  data were obtained from  $\mathcal{V}_3 vs. Vr$  plots.

5.2 Effect of Molecule Sizes and of Molecular Structure.—Reflecting the trend already noted in the discussion of the empty volume, a glance down the data of Table IX shows a steady decrease in fluctuation volume  $\mathcal{U}_0$  at a given temperature with increasing molecular weight, reaching an asymptotic limiting value for  $(CH_2)_{\infty}$ , which can easily be estimated from the data given.

For chain molecules which are so long that their thermal motions are carried out segmentally, the physical meaning of the fluctuation volume is not easily visualized. Here the average amplitude of the thermal vibrations of the chain  $Y = 2V_{\rm f}/A$  is perhaps a more directly recognizable measure of the molecular motions.

The careful Fourier analysis of the X-ray diffraction data of liquid heptane by Pierce<sup>15</sup> provides an opportunity to compare the amplitude Y with the difference  $r_{\rm T} - \bar{r}_0$ , where  $r_{\rm T}$  = average side spacing at temperature T and  $\bar{r}_0$  = weighted average crosssectional diameter of a polymethylene chain, taken as 4.3 Å. Then one obtains

	at $-50^{\circ}$	$at + 65^{\circ}$
Y, Å.	1.03	1.41
$r_{\rm T} - \bar{r}_0$ , Å.	$1.1 \pm 0.15$	1.45

a surprisingly close agreement.<sup>16</sup> The oscillation amplitudes calculated from sound velocity are always somewhat smaller than Y, even if corrected for segmental motions of the long chain mole-

(15) W. C. Pierce, J. Chem. Phys., 3, 252 (1935).

(16) The data obtained by application of Bragg's law to the X-ray diffraction patterns of liquids are undoubtedly incorrect and cannot be used for legitimate comparisons.

cules.<sup>17</sup> The peculiar decrease of  $\mathcal{V}_1$  with increasing chain length of the *n*-paraffins, and especially the correspondingly growing discrepancy between  $\mathcal{V}_0$  and  $\mathcal{V}_1$  will be discussed in detail in section 6.2. Suffice it to say here that the ratio of  $\mathcal{V}_0/\mathcal{V}_1^{18}$  is a measure of the hindrance to external molecular rotation in the liquid.

The ease of close packing of complex bodies is difficult to predict from first principles. As the molecular forces between methyl groups are smaller than those between methylene groups it is a fair guess—not always a correct one—that branching should increase  $V_{\rm f}$ . Since branching changes the magnitude of A only slightly (often raising it a bit) there should be a general parallelism between  $U_0$ and  $V_{\rm T}$ , which is found indeed.

Since both branching, especially at the center, and cyclization increase the spherical symmetry of the molecule, both of these forms of isomerization make for increasingly free rotation in the liquid even at low temperature, as is evident from the ratio  $\mathcal{V}_0/\mathcal{V}_1$  among the data of Table XI. Correspondingly  $V_f$ ,  $\mathcal{V}_0$  and  $\mathcal{V}_1$  increase with the number of methyl groups per molecule. A more detailed discussion of structural effects appears to be premature until more data have become available.

### TABLE XI

EFFECT OF BRANCHING AND RING CLOSURE ON EMPTY VOLUMES AND FLUCTUATION VOLUMES (CM.<sup>3</sup>/MOLE)

							V0
Substance	<i>T</i> , ⁰K.	$V_{\mathrm{T}}$	$V_{f}$	$\mathfrak{V}_0$	$\mathbb{U}_2$	$\mathbb{U}_1$	$\mathbb{U}_1$
n-Hexane	<b>2</b> 9 <b>3</b>	131.3	63.3	0.733	0.517	0.39	1.9
2,2-Dimethyl-							
butane	293	133	65.5	.726	. 56 <b>7</b>	0.885	0.8
Cyclohexane	293	108	46.8	.48	. 27	. 39	1.2
	$354^a$	116	54.8	.8		1.04	0.8
<i>n</i> -Heptane	293	146.2	68.0	. 53	.38	0.15	3.5
2,2-Dimethyl-							
pentane	293	148.4	70.7	. 62	.48	. 39	1.6
Methylcyclohexane	293	129.7	57.5	. 55	. 28	.32	1.7
	3 <b>74</b> <sup>a</sup>	141	68.8	. 97		1.10	0.9
n-Octane	293	162.5	70.4	. 53	. 31	0.08	6.6
2,2,4-Trimethyl-	293	165	73.4	. 58	. 42	.29	2.0
pentane	$372^a$	184	92.4	1.11		1.31	0.8
Hexamethylethane	374	173.8	86.2	0.77		0.82	.9
<sup>a</sup> Boiling point							

5.3 Mixture Law for the Fluctuation Volume.— A rule for the change of fluctuation volume on mixing can be derived from the defining equation 3. This rule can also be based on the assumption that the effective vibration amplitude is the average of the amplitudes of the components

$$Y_{(12)} = x_1 Y_{(1)} + x_2 Y_{(2)} \text{ or } \mathbb{U}_{(12)^{1/3}} = x_1 \mathbb{U}_{(1)^{1/3}} + x_2 \mathbb{U}_{(2)}^{1/3}$$
(8)

where  $x_i$  are mole fractions of the components. Figure 4 shows that—at least for hydrocarbon mixtures—such a law is well obeyed. The mixture law  $U_{12} = U_1^{x_1} \times U_2^{x_2}$  proposed by Hirschfelder, et al.,<sup>3a</sup> does not give as satisfactory agreement with experiment, as is evident from the plot of log  $U_2$  vs.  $x_2$  on Fig. 4.

While equation 8 can be expected to hold for ideal mixtures of low molecular weight compounds,

- (17) A. Bondi, J. Chem. Phys., 19, 128 (1951).
- (18) Called "free angle ratio" by Kincaid and Eyring.<sup>3b</sup>

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Fig. 4.—Fluctuation volumes  $\mathcal{V}_2$  and vibration amplitudes Y of mixtures of neohexane and *n*-butylbenzene;  $x_1 =$  mole fraction of neohexane (sound velocity data from Utter and Kling).

replacement of the mole fraction by volume fractions is likely to give better agreement with experiment for mixtures of heterosized components, *i.e.*, for mixtures, the entropy of mixing of which is given by the Flory-Huggins formula. The application of the volume fraction additivity of the fluctuation volume is illustrated by the curve for the system *n*-heptane-*n*-hexadecane on Fig. 5.

6.1 The Problem of Free Rotation in the Liquid.—For an infinitely long methylene chain the ratio of the volume at onset of free rotation (around the long axis) to its own volume should be equal to the ratio of the area of the circle circumscribing the rectangle cepicting the cross section of the *n*-paraffin chain to the area of this rectangle. Using the accepted values of the dimensions of the *n*-paraffin chain this ratio is 1.6. Experimentally observed values for the ratio of the molal volume at the melting point to the van der Waals volume  $V_w$  are for

in all cases very close to the theoretical value required for free rotation around the long axis. Actually, however, these molecules are not infinitely long chains. Hence part of the free volume is spent for the space between the end groups. The resulting volume deficiency is easily gained by the statistical density fluctuations around any given molecules. These fluctuations of the communal free space are of the order of  $e^{-1/2}$  times the average density and travel through the system with the velocity of sound, *i.e.*, at a rate of  $10^5$  cm. sec.<sup>-1</sup> =



Fig. 5.—Thermal vibration amplitude  $(Y_2)$  of mixtures of *n*-heptane and *n*-hexadecane;  $\phi_1$  = volume fraction of *n*-heptane (sound velocity data from Utter and Kling).

 $10^{13}$  Å. sec.<sup>-1</sup>. The angular velocity of rotation of the chain is

$$2\pi\nu = (kT/I)^{1/2}$$
 (9)

where I is the moment of inertia of the chain crosssection. For *n*-heptane  $2\pi\nu = 0.67 \times 10^{12}$  sec.<sup>-1</sup>, hence the circumferential velocity is about 16  $\times$  $10^{12}$  Å, sec.<sup>-1</sup>. Since only a fraction of a full density fluctuation is required to enable the rotation to take place, it is apparent that enough emptiness can be at required spots in time to permit free rotation for most of the molecules present. For tumbling rotation there is, of course, not nearly enough space. One may guess the fraction of molecules that has enough space to carry out such tumbling rotation as  $e^{-\Delta S^{j}_{v}/R}$  where  $\Delta S^{j}_{v}$  is the excess entropy of vaporization, defined in section 6.2. For *n*-heptane at  $20^{\circ}$  this fraction is 0.29 and at the boiling point 0.71. The circumferential velocity of the tumbling motion is also about  $1.9 \times 10^{12}$  Å./ sec. However, the amount of extra volume needed is about two times more than the fluctuations from the communal use of free space will supply (even at the boiling point). Hence the deficiency in the tumbling population even at the boiling point. It is easy to see that this deficiency must increase as the chains increase in length, although it may be somewhat alleviated by the tendency of the longer chains to coil up.

6.2 Restricted Rotation of Higher Molecular Weight Hydrocarbons in the Liquid State.— The restriction of rotation of long chain compounds around their short axis must make an increasingly important contribution to their physical properties as the chain length is increased. A simple measure of the degree of restriction to be expected is the ratio of the empty volume required for free rotation around the short axis  $V_f(rot)$  to the available empty volume  $V_f$  at the temperature and pressure under consideration. For sake of simplicity one might set

$$V_{\rm f}(\rm rot) = \frac{\pi}{4} L^2 w N_{\rm A} - V_{\rm w} \tag{10}$$

where L = length, w = width of molecule. The maximum degree of restriction  $\Re = V_{\rm f}(\text{rot})/V_{\rm f}$  differs somewhat from the similar expression proposed by Halford,<sup>19</sup>  $N_{\rm A}(4\pi/3)r^3_{\rm max}/V_{\rm T}$ , where  $r_{\rm max} = \text{maximum}$  distance of any point from the center of

(19) R. S. Halford, J. Chem. Phys., 8, 496 (1940).



Fig. 6.—Free energy of the equilibrium: chains parallel stretched out  $\rightleftharpoons$  chains coiled randomly, in several *n*-paraffins according to Equation 8.

gravity of the molecule. The latter expression does not take into account the wide variation of empty volume between different liquids nor of the differences in swept volume between branched and straight chains of equal leng-hs.

The length L of the flexible chains must now be determined. The most probable configuration of chain molecules in the gaseous state can be calculated if one knows bond lengths, bond angles and the magnitude and shape of the potential restricting rotation around the bonds.<sup>20</sup> The coiling is counteracted in the condensed phases by the preference for parallel arrangement of the chains owing to the anisotropy of polarizability, which determines the magnitude of attractive forces between molecules. The increase in potential energy of the system as one changes from parallel to random arrangement of the chain molecules can be estimated from London's theory<sup>21</sup> and Müller's data<sup>22</sup> to be of the order of 1/4 of the energy of vaporization. The gain in entropy due to coiling of the molecules, on the other hand, is given by the well known formula of the kinetic theory of rubber elasticity as  $\Delta S = R(L^2/L^2)$  $\langle L^2 \rangle$ , where L = length of stretched out molecules,  $\langle L^2 \rangle$  = average square end-to-end distance of the coiled molecules. Hence the equilibrium between coiled and parallel stretched molecules can be estimated by

$$\frac{\Delta F(\text{coiling})}{RT} = \frac{\Delta H_v}{4RT} - \frac{L^2}{\langle L^2 \rangle}$$
(11)

Using Taylor's formulas for the calculation of  $\langle L^2 \rangle$ ,  $\Delta F$  has been computed as function of temperature for several normal paraffins. The results are shown in Fig. 6. For the *n*-paraffins up to C<sub>10</sub> at low temperatures one finds but a very small degree of coiling even in the gaseous state. The longchain molecules, up to C<sub>40</sub>, begin to coil up in their own melts<sup>23</sup> to an appreciable extent only at temperatures in excess of 200°.

We are therefore justified in using the simple stretched out length of the *n*-paraffins over most of

- (20) F. W. Taylor, J. Chem. Phys., 16, 257 (1948).
- (21) F. London, THIS JOURNAL, 46. 305 (1942).
- (22) A. Müller, Proc. Roy. Soc. (London), A154, 624 (1936).

(23) In dilute solutions, where  $\Delta H_v$  applies to the solvent, these molecules are appreciably coiled at much lower temperatures. This subject will be discussed elsewhere.

the temperature range of interest, viz.,  $L = 1.27 \times (N - 1) + 2r(CH_3)$ , where  $r(CH_3) =$  van der Waals radius of the methyl group (2.0Å. according to Pauling<sup>10</sup>). Under conditions where coiling is prevalent, the maximum swept volume is  $V(rot) = (\pi/6)N_L < L^2 >^{1/2}$ .

The entropy of vaporization of a condensed phase is determined by the increase in volume accompanying the process of vaporization and by configurational contributions arising from the loss of order and from the acquisition of rotational degrees of freedom frozen in or restricted in the condensed phase. By comparison of the observed entropy of vaporization of a liquid with its "ideal" entropy one can therefore obtain the contribution of restricted rotation to the entropy of vaporization at any given vapor volume. The "ideal" entropy of vaporization can be defined as

$$\Delta S_{\mathbf{v}}^* = R \ln(V_{\text{gas}}/\mathcal{V}_0) = R \ln \left(RT/p\mathcal{V}_0\right)$$

where  $\mathcal{U}_0$  is computed from density and X-ray diffraction data as described above.<sup>24</sup> Then an "excess" entropy of vaporization can be defined as

$$S_{\mathbf{v}}^{\mathbf{j}} = [\Delta S_{\mathbf{v}} \text{ (sample)} - \Delta S_{\mathbf{v}}^{*}]_{p/T}$$
(12)

If the proposed concept of the degree of restriction  $\mathfrak{R}$  is correct then there should be a simple correlation between  $\Delta S_{\nu}^{5}$  and  $\mathfrak{R}$ . The curve of Fig. 7 shows that the hydrocarbons, for which data are available, fit very well into such a correlation. It is interesting to note that, at least at low temperatures, the maximum degree of restricted rotation imposed by geometry upon hydrocarbons in the liquid is far greater than that imposed by hydrogen bonds in the typically "associated" liquids, water or methyl alcohol; only glycerol with  $\Delta S_{\nu}^{i} = 11.5$  at  $55^{\circ}$  approaches the large values obtained with some of the long chain hydrocarbons. The excess entropy of vaporization of perhydrofluorene turned out to be far too low when  $\mathfrak{R}$  was computed from the dimensions of a planar molecule. Assumption of

(26) R. H. Busey and W. F. Giauque, ibid., 75, 806 (1953).

<sup>(24)</sup> If one does not have the requisite data for the calculation of  $\bigcup a$  one may use  $\Delta S_{\nu}$  of mercury, a monatomic liquid of relatively ideal behavior in place of  $\Delta S_{\nu}^*$  at the same value of p/T, as recently proposed by Brown.<sup>25</sup> Using the vapor pressure and heat of vaporization data of mercury by Busey and Giauque<sup>26</sup> one finds  $\Delta S_{\nu}(Hg)$  and  $\Delta S_{\nu}^*$  to agree generally to within 2 e.u.

<sup>(25)</sup> O. L. I. Brown, J. Am. Chem. Soc., 74, 6096 (1952).



Fig. 7.—Relation between degree of restriction  $\Re$  and the excess entropy of vaporization of various saturated hydrocarbons calculated from data in part from R. W. Schiessler, et al., API Project 42, synthesis and properties of higher molecular weight hydrocarbons.

a "chair" configuration brought perhydrofluorene right into the general correlation curve of Fig. 7. A Fisher-Hirschfelder model of this hydrocarbon demonstrated that it can indeed exist only in bent, chair-like configurations.

Which and how many degrees of freedom of the flexible molecules are restricted at any given value of R might be estimated from a comparison of  $\Delta S^{j}_{v}$ with  $\Delta C_{\mathbf{v}}$ , the difference in heat capacity at constant volume between the liquid and the ideal gas state. The latter can be calculated from statistical data by means of the method of Pitzer<sup>27,28</sup> and  $C_{v}(liq)$  is obtained from the measured values of  $C_p$  and the sound velocity, etc., to determine  $C_p/C_v$ . The data of Table XII have been obtained in this way. The last column, the rotational contribution to  $C_{\mathbf{y}}$ was obtained by subtracting 3 units for the solidlike contribution of the potential energy to  $C_{\mathbf{v}}$ , which is exhibited even by argon and mercury.<sup>3b</sup> The restriction of rotation of the large molecules is probably best understood in terms of the rotation of individual methylene groups. The heat capacity contribution of this mode is about 2.6 units per methylene group and the entropy contribution about 6.1 e.u. per methylene group at  $25^{\circ}$ . In the case of cetane at 25° one estimates from both data equally about 2.6 restricted methylene groups per molecule and for the tridecylmethane about 8 to 10

(28) G. C. Pimentel and W. B. Person, J. Am. Chem. Soc., 76, 528 (1953).

such groups. The constancy of the ratio  $\Delta S^{i}_{\nu}/\Delta C_{\nu}(\text{rot})$  for this series of paraffin chain compounds may be taken as an independent confirmation of the physical meaning of  $\Delta S^{i}_{\nu}$  and of the method of its determination.

## TABLE XII

Comparison of Excess Entropy of Vaporization  $\Delta S^i_v$ with the Excess Heat Capacity at Constant Volume  $\Delta C_v = C_v (\text{liquid})^{\rho} - C_v (\text{gas})^k$ 

Substance	<i>T</i> , °K.	Uo, cm. <sup>3</sup> / mole	$\Delta S^{j_v}$ , e.u.	$\Delta C_{\mathbf{v}},$ cal./°K. mole	(rot), <sup>a</sup> cal./°K. mole	
Long cha	in comp	ounds a	at room t	temperat	ure	
<i>n</i> -Heptane	298	0.65	2.9	$4.0^{e}$	1.0	
n-Hexadecane	298	. 36	16.0	$9.7^{e}$	6.7	
Tri-( <i>n</i> -decyl)- methane	<b>2</b> 98	. 27	54.3	23.6 <sup>ef</sup>	20.6	
Short ch	ain com	pounds	at low te	emperatu	res	
Methane	90.5	0.59	0.3	3.20	0.20	
Propane	100	.20	$(7.4)^{b}$	$(5.1)^{c}$	$(2.1)^{c}$	
	150	.37	3.6	$(5.4)^{c}$	$(2.4)^{c}$	
<i>n</i> -Pentane	<b>200</b>	. 37	7.9	$(4.5)^{d}$	$(1.5)^{d}$	
	250	. 55	1.5	$(3.3)^{d}$	$(0.3)^{d}$	
	298	.87	0	3.0	0	

 $^{a}\Delta C_{\mathbf{v}}(\operatorname{rot}) = \Delta C_{\mathbf{v}} - 3.0.$  <sup>b</sup> From rather far extrapolated vapor pressure data.  $^{c}C_{p} - C_{v}$  was obtained from  $(\partial E/\partial V)_{r}(\partial V/\partial T)_{p}$ , where  $(\partial E/\partial V)_{T}$  was approximated as  $\Delta E_{vap}/V_{T}$ . <sup>d</sup>  $C_{p}/C_{v}$  was calculated from extrapolated sound velocity data. <sup>e</sup> Gaseous heat capacity calculated by Pitzer's method. <sup>f</sup> Liquid heat capacity from F. B. Fischl, et al., J. Am. Chem. Soc., 67, 2075 (1945). <sup>a</sup> Most liquid heat capacity data from Timmermans, "Physical Constants of Organic Substances." <sup>h</sup> Most gaseous heat capacity data from API Project 44.

At low temperatures where the internal rotations of the chains are practically frozen into torsional oscillations, restricted external rotation of the entire molecule would be responsible for the excess entropy of vaporization and for the excess heat capacity, leading to a ratio  $\Delta S^{i}_{v}/\Delta C_{v}(rot)$  which varies according to the molecular weight and geometry of the substance in question and may be very different from the ratio observed where internal rotation is restricted by external restraints. The data for *n*-pentane and propane at low temperatures confirm this supposition.

Restriction of rotation must have a strong effect on the entropy of fusion  $\Delta S_f$ . Hirschfelder, Stevenson and Eyring<sup>3a</sup> showed that for small rigid molecules

$$\Delta S_{\rm f} = R + (S_{\rm r} - S_{\rm e}) \tag{13}$$

where  $S_r$  = rotational contribution to the entropy and  $S_e$  = entropy contribution of oscillations in the solid corresponding to the rotations in the liquid. If the rotations in the liquid are not free, the entropy of fusion must be smaller, most likely by the amount of  $\Delta S_v$  at the fusion temperature, or

$$\Delta S_{\rm f} = R + (S_{\rm r} - S_{\rm e}) - \Delta S^{\rm j}{}_{\rm v} \qquad (14)$$

The data for benzene, shown in Table XIII, are in reasonable agreement with this equation. The calculation of  $S_r$  of flexible molecules must take into consideration the rotation around the skeletal bonds. This can be done most easily by the method of Pitzer.<sup>27,28</sup> In the absence of spectroscopic data regarding the rotational oscillations of

<sup>(27)</sup> K. S. Pitzer, J. Chem. Phys., 8, 711 (1940).

the molecule and its component parts in the crystal one can only guess the value of  $S_e$ . The corresponding data are collected in Table XIII. But even without the speculative estimate of the details it is apparent from a comparison of the entropy of fusion per methylene group of the *n*-paraffins (~3 e.u.) with that of the exceedingly restricted tri-(*n*decyl)-methane (~1.8 e.u. per methylene group) how strongly restriction cf external rotation in the liquid state influences the entropy of fusion.

## TABLE XIII

Calculation of the Entropy of Fusion of Various Hydrocaebons

		S	8	. ai	ΔSf,	e.u.
Substance	Model	e.u.	e.u.	ΔS <sup>*</sup> v, e.u.	Calcd.ª	served
Benzene	Rigid rotator	$20.6^b$ $20.6^b$	12.6° 10.8°	$egin{array}{c} 1.2^d\ 2.2^d \end{array}$	7.8 9.6	8.43 8.43
Ethane	Rigid rotator	13.7°	7.5 <sup>1</sup>	Small	8.20	<b>7</b> .60°
n-Heptane	Flexible rotator	$29.2^h$	8.61	4 <sup>g</sup>	18.6	18.39
n-Hexadecane	Flexible rotator	86.4 <sup>h</sup>	$28.8^i$	$16.5^{l}$	<b>43</b> .1	44.3
Tri-(n-decvl)-	Flexible	$181.6^{h}$	$62.4^{m}$	$60^{n}$	61.2	$60.27^{p}$

<sup>a</sup> By means of equation 14. <sup>b</sup> (Calculated) from data by R. C. Lord and D. J. Andrews, THIS JOURNAL, 41, 149 (1937). <sup>c</sup> Calculated from Raman frequencies of crystal given by I. Ichishima and S. Mizushima, J. Chem. Phys., 18, 1686 (1950). The two sets of values are given corresponding to somewhat different assignments of frequencies to torsional oscillations in the crystal. <sup>d</sup> Calculated from data cited in Timmermans, ref. g, Table XII. <sup>e</sup> Calculated from moments of inertia cited by Herzberg, "Infrared and Raman Spectra," p. 437. <sup>f</sup> An average frequency of 50 cm.<sup>-1</sup> was used for the three torsional oscillations of the molecule. <sup>e</sup> Estimated from data by Timmermans, ref. g in Table XII. <sup>h</sup> Calculated by the method of Pitzer (for all but the  $F_0(T)$  and the vibrational contributions) using the recent data by Pimentel. <sup>i</sup> Calculated for one torsional oscillation of the entire molecule (50) cm.<sup>-1</sup>, and for (n - 1)torsional oscillations of the methyl and methylene groups (275 cm.<sup>-1</sup>) according to Herzberg, ref. e, p. 343). <sup>l</sup> Calculated from the vapor pressure data of Parks and Moore, ref. g in Table IX. <sup>m</sup> Calculated for three torsional oscillations of the three decyl groups (50 cm.<sup>-1</sup>) and (n - 1)torsional oscillations of the methyl and methylene groups (275 cm.<sup>-1</sup>). <sup>n</sup> Calculated from vapor pressure data of Bradley, et al., ref. d of Table VI. <sup>e</sup> From API Project 44 Tables on the Properties of Hydrocarbons. <sup>p</sup> From ref. f of Table XII.

#### Conclusions

Central to the calculation of the empty volume as well as of the fluctuation volume of any liquid is the determination of the van der Waals volume, *i.e.*, the volume from which other but the reference molecule are excluded in thermal collisions. This is most easily done for atoms or spherical molecules, since their thermal collision cross sections and crystal X-ray diffraction data are easily evaluated. The dimensions of more complicated molecules are rarely defined unequivocally. The saturated hydrocarbons are particularly suitable since they consist of simple repeating units, the dimensions of which could be selected from among the various available data by combining those which are consistent with the X-ray diffraction data and the thermal gas kinetic collision cross-sections of the lowest members of the series. The numerical equality of the fluctuation volume data computed from the same dimensions with the fluctuation volume data calculated from the entropy of vaporization of the lower members of the series must be considered as further confirmation of the correctness of the choice of the van der Waals volumes of these hydrocarbons.

At lower temperatures, especially for the higher hydrocarbons, there is no agreement between  $U_0$  and the fluctuation volume calculated from vapor pressure, sound velocity or compressibility, although the latter usually deviate less than the former from "actual" fluctuation volume  $U_0$ . One must therefore conclude that the fluctuation volume data of more complicated molecules estimated by these indirect methods must always be viewed with suspicion even if consistent with each other unless they are also consistent with density and related information.

Calculation of the exact van der Waals volume of the paraffin molecules leads to the conclusion that the normal paraffins have sufficient free volume in the liquid state to rotate around their long axis throughout the liquid range, beginning at the melting point. Different views suggesting this kind of rotation of the *n*-paraffin to be restricted are based on larger values for the van der Waals volume than have been used here.<sup>29</sup>

Rotation around the small axis, on the other hand, proves to be severely restricted, the more so the longer the molecule and the greater its length/ diameter ratio. Comparison of the entropy gain due to coiling with the potential energy gain of the system due to the random instead of parallel arrangement of the methylene chains leads to the conclusion that in most of the temperature range of interest (0 to 200°) the *n*-paraffins from  $C_7$  to  $C_{40}$ exist in the liquid state primarily in the plane, stretched out form. Consequently the maximum degree of restriction could be expressed in terms of the ratio of the amount of empty volume required to permit complete rotation of the stretched out molecule to the actual amount of free volume at any given temperature. The correlation between the degree of restriction, as defined, and the excess entropy of vaporization proved to be quite general, i.e., independent of the geometry of the saturated hydrocarbons. The excess entropy of vaporization was also found to be a measure of the amount by which the entropy of fusion of hydrocarbons is reduced by the restriction of rotation in the liquid state.

Acknowledgment.—The writer is indebted to Prof. Joel H. Hildebrand for the stimulation and encouragement to do this work and to Drs. Otto Redlich and Dale J. Meier for valuable discussions.

<sup>(29)</sup> R. J. Moore, P. Gibbs and H. Eyring, This Journal, 57, 172 (1953).

Note.—After completion of this manuscript a series of papers by Bertil Jacobson (*Acta Chim. Scand.*, **6**, 1485 (1952); **7**, 51, 58, 705 (1953)) came to the author's attention which derived the average amplitude of thermal oscillations from density data in a manner similar to that proposed in this report.

## THE CRYSTAL STRUCTURE OF YTTRIUM TRICHLORIDE AND SIMILAR COMPOUNDS

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The crystal structure of yttrium trichloride has been determined from single crystal X-ray diffraction data. It is found to have a structure like that of aluminum chloride; monoclinic, space group C2/m, with lattice dimensions a = 6.92 Å, b = 11.94, c = 6.44, and  $\beta = 111.0^{\circ}$ . Atomic parameters have been determined by Fourier methods. The structure can be described as a slightly distorted sodium chloride type with two-thirds of the metal atoms omitted. Lattice dimensions determined from rowder data are reported for dysprosium trichloride, holmium trichloride, erbium trichloride, thulium trichloride, ytterbium trichloride, lutetium trichloride, thallium trichloride and indium trichloride, all of which have this same structure.

## Introduction

Our knowledge of the crystal chemistry of rare earth compounds is extensive for the elements near lanthanum, but quite sparse for those higher in the rare earth series. Because of the regular gradation of ionic radius in these elements, it is possible to learn the effects of ionic size on structures with minimum interference from other factors. They are also of interest because of the similarity between their structures and those of corresponding compounds of the new synthetic actinide elements. For these reasons we have been studying structures of a number of these compounds. This paper describes the structures of some trichlorides.

Bommer and Hohmann<sup>1</sup> observed from powder diagrams that trichlorides of the rare earth elements from lanthanum to gadolinium are isostructural, that those of terbium and dysprosium have a second structure, and that those of the elements holmium to lutetium, as well as a second form of dysprosium trichloride, are isostructural with yttrium trichlorice. Zachariasen<sup>2</sup> solved the struc-ture of uranium trichloride and showed that it is the same as that of lanthanum chloride and its isomorphs. The terbium trichloride structure is still unknown. Because our supply of yttrium is much greater than of these rare earths, we chose the yttrium compound for single crystal work to solve the third structure. The resulting data allowed the interpretation of powder data for the corresponding rare earth chlorides as well as thallium and indium trichlorides.

## Experimental

Yttrium Trichloride.—Polycrystalline yttrium trichloride was prepared by passing dry hydrogen chloride gas over a few milligrams of pure yttrium oxide in a platinum boat at 550° for six hours. To obtain single crystals, this product was heated a few degrees above the melting point, estimated as 680°, and cooled over a period of one to two hours. Since yttrium trichloride is extremely deliquescent, the platinum boat still inside the original fused quartz tube was quickly transferred to a dry-box. The atmosphere of this box was broken up into tiny anhedral fragments or cleavage flakes. Selected fragments were sealed in glass capillaries as diffraction specimens. After many trials, a few suitable single crystals more or less spherical in shape were obtained. The cleavage flakes were discarded because of the strong variation in X-ray absorption for different reflections. Powder specimens were transferred to capillaries in the same dry-box.

Other Trichlorides.—Samples of trichlorides of many of the rare earths and of thallium and indium were prepared from the corresponding oxides by the method described above for yttrium trichloride. Most of these preparations were carried out by Dr. C. W. Koch. Our best sample of indium trichloride was prepared by Mr. E. S. Clark by the reaction of chlorine gas with indium metal at 200°.

reaction of chlorine gas with indium metal at 200°. **X-Ray Methods.**—Equi-inclination Weissenberg photographs were taken for rotation about each of the three principal axes with Cu K $\alpha$  radiation. The calculations reported here are based on a set of observations with [100] as the rotation axis. Multiple-film technique and visual comparison were used to estimate the intensities.

The data from each Weissenberg layer were normalized to give the best fit with the calculated intensities. In this way the absorption effect of the glass capillary, which is greater at greater angles of inclination, is taken partly into account. Since the capillary was not exactly coaxial with the camera, some error remains. This capillary absorption was found to cause the third layer to be weaker by about a factor of three relative to the zero layer, in agreement with approximate calculations based on the thickness of the relatively poor capillary.

relatively poor capillary. Unit cell dimensions for yttrium trichloride were obtained from the Weissenberg photographs and checked with the powder patterns. For the other compounds, unit cell dimensions were obtained from powder patterns, indexed with the aid of the single crystal data. The powder patterns were obtained in cameras of radius 4.5 cm. with Cu K $\alpha$  ( $\lambda =$ 1.5418 Å.) and Cr K $\alpha$  ( $\lambda =$  2.2909 Å.) radiation. Data for yttrium and lutetium trichlorides are listed in Tables IV and V, respectively, in the Appendix.

## Crystal Structure of Yttrium Trichloride

Unit Cell and Space Group.—Yttrium trichloride was found to be monoclinic with unit cell dimensions:  $a = 6.92 \pm 0.02$  Å.,  $b = 11.94 \pm 0.04$  Å.,  $c = 6.44 \pm 0.02$  Å.,  $\beta = 111.0 \pm 0.5^{\circ}$ . Diffraction was observed only if h + k = 2n, with no additional systematic extinctions. Thus the space group is C2/m, Cm or C2. A satisfactory structure was found for C2/m, and atomic packing requires that deviations from this symmetry be small. Therefore, Cm and C2 were not considered further.

The density measured by flotation in mixtures of bromoform and *n*-butyl phthalate is 2.55 g./cm.<sup>3</sup>. Calculated from the unit cell dimensions with four molecules of yttrium trichloride per unit cell the density is 2.61 g./cm.<sup>3</sup>.

Atomic Positions.—If it is assumed that the distances between yttrium atoms are as great as possible, only two reasonable arrangements of these atoms are found that are consistent with any of the three possible space groups. One of these, with two atoms in the *ac* face, leads to disagreement with the observed intensities. The other, with all four yttrium atoms in the *ab* face at y = 1/6, 2/6, 4/6 and 5/6, and x = 0 or 1/2, is satisfactory. The fact that 060 and 0,12,0 are so strong compared to other 0k0 reflections suggests that the chlorine atoms are also

<sup>(1)</sup> H. Bommer and E. Hohmann, Z. anorg. allgem. Chem., 248, 373 (1941).

<sup>(2)</sup> W. H. Zachariasen, J. Chem. Phys., 16, 254 (1948).

in layers at intervals of 1/6 of the b axis. It is easy to find such an arrangement, with conventional ionic radii, as described elsewhere.<sup>3</sup> We were not able to find any other reasonable arrangement that differed significantly from this one. Structure factors calculated for this trial structure are in rather good agreement with the observed ones. The atomic positions were refined by three-dimensional Fourier calculations which resulted in few changes of sign. The electron density was sampled by appropriate plane and line sections to locate the maxima. The final maxima, after addition of backshift corrections, correspond to the following atomic coordinates

Space group C2/m  $(0, 0, 0; \frac{1}{2}, \frac{1}{2}, 0) +$ Y in 4(g):  $\pm$  (0,y,0) with y = 0.166; Cl in 4(i):  $\pm$  (x,0,z) with x = 0.211, z = 0.247; Cl in 8(j):  $\pm (x, y, z; x, \overline{y}, z)$  with x = 0.229, y = 0.179and z = 0.760

The observed values of |F| and those calculated for atomic positions not greatly different from these are tabulated in Table III which is found in the Appendix.

The backshift corrections for termination of the series were 0.000, -0.003, +0.001, -0.009, +0.001and -0.001 in the order in which the atomic parameters are listed above. The standard deviations of the parameters due to random errors in the observed intensities, calculated from  $F_0 - F_c$  by the method of Cruikshank,<sup>4</sup> are 0.001, 0.003, 0.004, 0.003, 0.002 and 0.004 in the same order.<sup>6</sup>

Discussion of the Structure.—The chloride ions are arranged approximately in cubic close packing. The yttrium ions are located in octahedral holes between alternate pairs of close packed layers of chloride ions. The coordination octahedra are linked by shared edges into pseudo-hexagonal sheets parallel to (001), of the type found also in the chromic chloride<sup>6</sup> and ferric chloride<sup>7</sup> type structures. If the anion close packing were perfect the structure could be considered as sodium chloride type with two-thirds of the cations omitted as shown in Fig. 1. The ideal structure illustrated in this figure corresponds to a monoclinic unit cell with the dimensions: a = 6.67 Å., b = 11.67 Å., c = 6.67 Å.,  $\beta = 109.5^{\circ}$ , if the volume is assumed to be the same as that of the unit cell observed for yttrium trichloride.

The six chloride neighbors of each yttrium ion are two each at the distances 2.58, 2.63 and 2.69 A. The chloride-chloride distances within the coordination octahedron are 3.45 (2), 3.46 (1), 3.71 (2), 3.83 (2), 3.85 (2), 3.86 (2) and 3.91 (1). The numbers in parentheses are the number of times each distance occurs. The three shortest distances correspond to the shared edges of the coordination octahedra, as is to be expected for an ionic struc-The chloride-chloride distances between ture.<sup>8</sup>

(3) G. F. Carter, Ph.D. Thesis, University of California, 1952.

(4) D. W. J. Cruikshank, Acta Cryst., 2, 65 (1949).

(5) These values would be reduced slightly if a temperature factor were included in the calculation of  $P_c$ .

(6) N. Wooster, Z. Krist., 74, 363 (1930).

(7) N. Wooster, *ibid.*, 83, 35 (1932).
(8) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1945, p. 400.



Fig. 1.-Idealized trichloride structure, showing relation to sodium chloride structure. The broken lines outline two of the monoclinic unit cells; several atoms are missing from one of them.

layers are 3.69, 3.86, 3.87 and 4.16 Å. Between octahedra in the same layer they are 4.27 and 4.42. These distances show how within the layer the anions tend to crowd around the cations. All these distances have probable errors of about 0.03 Å.

The cleavage is observed to be parallel to (001), as is to be expected for this layer structure.

#### Isostructural Compounds

Inspection of the powder diffraction patterns indicated that the structure of yttrium trichloride is similar to the structures of the trichlorides of dysprosium, holmium, erbium, thulium, ytterbium, lutetium, indium and thallium. The lattice constants found for these compounds are listed in Table I. In most cases these dimensions may be in

$\mathbf{T}$	BLE	εI

LATTICE	DIMENSION	IS OF	Monoclinic	TRICHLO	ORIDES
	a. Å.	b. Å.	c. Å.	в	V. Å.

	<i>u</i> , <i>n</i> .	0, A.	<i>c</i> , <i>n</i> .	ρ	· , A.
YCl <sub>2</sub>	6.92	11.94	6.44	111.0°	497
DyCl <sub>3</sub>	6.91	11.97	6.40	111.2	494
HoCl <sub>3</sub>	6.85	11.85	6.39	110.8	485
ErCla	6.80	11.79	6.39	110.7	479
TmCl <sub>3</sub>	6.75	11.73	6.39	110.6	474
YbCl₃	6.73	11.65	6.38	110.4	468
LuCl₃	6.72	11.60	6.39	110.4	467
TlCl <sub>3</sub>	6.54	11.33	6.32	110.2	440
InCl <sub>3</sub>	6.41	11.10	6.31	109.8	422
AlCl <sub>3</sub> <sup>a</sup>	5.93	10.24	6.17	108	357

<sup>a</sup> Ketelaar, MacGillavry and Renes, reference 9.

error by a few hundredths of an angström unit because they are based on lines at relatively small angles. In the cases of the lutetium and indium compounds, for which better patterns were obtained,

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the errors are believed to be less than 0.01 and 0.005 Å., respectively. The accuracy is difficult to judge because of the large number of coincidences or near coincidences of powder lines.

The data for the lutetium compound are listed in Table V of the Appendix. In this case the cations are rather dominant in determining the intensities, and powder lines are observed in general only if k = 6n and  $h + l \neq 4m + 2$  or if k = 6n + 3 and  $h + l \neq 4m$ . The 00l reflections are stronger than they should be in a random powder, but just these reflections are favored if cleavage flakes tend to be oriented parallel to the walls of the capillary.

Ketelaar, MacGillavry and Renes<sup>9</sup> have determined the structure of aluminum chloride and found it to be the same as the structure we describe here. Because we were misled by the earlier incorrect report<sup>10</sup> of the aluminum chloride structure, the more recent work escaped our attention until after our parameters were determined (except for the backshift correction). The parameters, compared in Table II, are as similar as can be expected considering the difference in cell dimensions. In the yttrium case the metal atoms are dominant in determining the intensities while in the aluminum case they are relatively unimportant. This effect is so great that there is no obvious resemblance between the respective powder patterns.

### TABLE II

ATOMIC COÖRDINATES IN YTTRIUM TRICHLORIDE AND ALUMINUM CHLORIDE

	YCl3	AlClaa
y (M)	0.166	0.167
x (4Cl)	.211	. 226
z (4Cl)	. 247	.219
x (8Cl)	.229	. 250
y (8Cl)	. 179	. 175
z (8Cl)	.760	.781

<sup>a</sup> Ketelaar, MacGillavry and Renes, reference 9.

Comparison of the interatomic distances in the two crystals is interesting. For aluminum chloride the cation-anion distances are 2.29, 2.33 and 2.32 A., considerably less than for the yttrium compound. The octahedron edges, of course, are also less, being 3.11 and 3.16 Å for the shared edges and 3.34, 3.28, 3.34, 3.33 and 3.34 Å. for the unshared edges. The interlayer distances are 3.80, 3.79, 3.90 and 3.80 Å., hardly less on the average than for yttrium chloride. The distances between octahedra of the same layer are 3.58 and 3.33 Å. These distances are listed in the same order as the corresponding distances for yttrium chloride listed above. The obvious features of these data are that for the aluminum compound the anions within a layer are much closer together and are also more perfectly packed, though the shared edges remain shorter than the others, and that the distances between layers are almost independent of the cation size.

It is surprising that aluminum chloride and yttrium trichloride are isostructural, while scandium chloride has the rhombohedral ferric chloride-type

(9) J. A. A. Ketelaar, C. H. MacGillavry and P. A. Renes, Rec. trav. chim. Pays-Bas, 66, 501 (1947).

structure.<sup>11</sup> However, the latter structure involves the same kind of octahedral layers, and the only difference in the structures is in the stacking of these layers. Also, it is possible that polymorphism occurs, since it has been observed in the case of dysprosium trichloride.<sup>1</sup>

There is a trend in the relative values of the cell dimensions of these trichlorides as the cell volume increases. The angle  $\beta$  increases, and a and b increase at a greater rate than c. Thus the interatomic distances probably vary smoothly between the extremes represented by the aluminum and yttrium compounds.

On the basis of these results, one would say that the yttrium ion is slightly larger than the dysprosium ion, whereas in the oxychloride<sup>12</sup> and oxide<sup>13</sup> it is between dysprosium and holmium, and in the fluoride<sup>14</sup> it is between holmium and erbium. This variation in relative radii amounts to only about 0.03 Å. The dimensions observed for thallium trichloride and indium trichloride correspond to cationic radii<sup>15</sup> of about 0.77 and 0.72 Å., respectively, compared with 0.89 and 0.80 which can be estimated from data for the oxides,<sup>13</sup> and 0.73 for indium by comparison of indium and scandium hydroxides.<sup>16</sup> This variation illustrates the difficulty of assigning unique radii to the transition elements.

We thank Dr. Koch for preparing many of the compounds and for help in the chemical procedures, Mr. Clark for preparing the indium chloride, Mrs. Carol H. Dauben for performing some of the computations and checking many others and for much help in preparing the manuscript, Mrs. Helena W. Ruben for taking most of the powder photographs, and Professor Leo Brewer for the use of his dry-box. This research was done under the auspices of the U.S. Atomic Energy Commission.

## Appendix

In Table III are listed structure factors derived from Weissenberg photographs of the zero, first, second and third layers for rotation about the aThese values, labeled "F obsd.," were normaxis. alized as described above.

The "F calcd." values were calculated by using the following equation (for values of hkl permitted by the space group)

$$F = f_{Y}^{+3} \cos 2\pi (0.167k) + f_{Cl}^{-1} [\cos 2\pi (0.215h + 0.244l) + \cos 2\pi (0.762h + 0.176k + 0.239l) + \cos 2\pi (0.762h - 0.176k + 0.239l)]$$

where  $f_{\mathbf{Y}}^{+3}$  is the scattering power of the yttrium ion estimated in an arbitrary way from the Thomas-Fermi scattering factors for the yttrium atom listed in "Internationale Tabellen,"<sup>17</sup> and  $f_{Cl}$  is the Har-

(11) W. Klemm and E. Krose, Z. anorg. Chem., 253, 218 (1947).

(12) D. H. Templeton and C. H. Dauben, J. Am. Chem. Soc., 75, 4560 (1953)

(13) V. M. Goldschmidt, F. Ulrich, T. Barth and G. Lunde, Strukturbericht, 1, 261 (1931).

(14) A. Zalkin and D. H. Templeton, J. Am. Chem. Soc., 75, 2453 (1953).

(15) These radii correspond to a scale on which  $Al^{+++} = 0.51$ , Sc + + + = 0.72 and  $Y^{+++} = 0.90$  Å.

(16) K. Schubert and A. Seitz, Z. anorg. Chem., 256, 226 (1948).

(17) "Internationale Tabellen zur Bestimmung von Kristallstrukturen," Vol. II, Edwards Brothers, Ann Arbor, Michigan, 1944, p. 571-572.

<sup>(10)</sup> J. A. A. Ketelaar, Z. Krist., 90, 237 (1935).

## CRYSTAL STRUCTURE OF YTTRIUM TRICHLORIDE

		Т	able III				$20\overline{7}$	+24.5	0	310	+ 4.8	7.7
CALCULAT	ED AND	Obse	RVED STR	UCTURE	Factors	OF	<b>220</b>	-11.3	14.9	311	+21.5	14.8
		YTTRIU	M TRICHLO	RIDE			221	-20.0	24.7	311	+14.3	0
h <b>kl</b>	Caled.	Obsd.	hkl	Calcd.	Obsd.		$22\overline{1}$	- 6.6	7.7	312	+17.8	19.5
001	+37.1	37.1	136	-24.9	12.9		222	-15.7	17.7	$31\overline{2}$	+22.6	24.9
002	- 8.7	10.3	$13\overline{6}$	-11.9	13.6		$22\overline{2}$	-16'0	23	313	+11.8	15.6
003	+21.1	21.2	137	-35.4	12.7		223	- 7.4	0	$31\overline{3}$	+13.0	10.4
004	+47.5	43.5	150	+17.4	24.2		$22\overline{3}$	-20.6	22.2	314	+ 4.4	0
005	+26.9	22.3	151	+18.4	22.3		224	- 6.4	0	$31\overline{4}$	+3.6	0
006	- 8.9	0	151	+ 87	10		224	-10.5	Ō	315	+ 6.6	Õ
007	+ 9	Ő	152	+10.2	11.6		225	-11.4	Õ	315	+ 9.3	ň
020	-20.3	30.8	152	+85	11.2		225	- 3.8	Õ	316	$\pm 16.4$	0
021	-17 1	19 1	153	+69	0		226	-11.0	Õ	217	+ 10. 4	0
021	-12.1	12.7	153	+15.4	17.3		226	- 9.5	Ő	220	+10.5	20 1
022	-11.6	13.8	154	+10.6	0		227	-14.6	Ő	330	-27.5	32.1
020	-12.6	13.8	154	+15.5	12.8		228	- 8 2	Õ	331	- 0.9	50 0
024	-11 7	11 1	155	+12.7	12.0		240	-17.2	26 4	331	-53.9	58.9
020	- 8	0	155	+12.1 +12.1	Ő		241	-18 1	22.8	332	-18.0	20.5
020	- 9.5	9.6	156	+ 9 0	Ő		241	-82	11 1	332	-24.3	37.8
040	<u> </u>	10 1	156	+ 4.2	Ő		242	- 9 1	0	333	-41.1	41.6
049	-14.4 -91.1	19.1 99.2	170	$\pm 14$ 1	15.2		242	- 8.8	97	333	+ 0.1	0
042	- 12	11 1	170	+14.1 1 5 9	10.2		242	- 63	0	334	-24.7	24.7
043	-12	0	171	T 0.2	21.7		240	-17.0	17.8	$33\overline{4}$	-19.2	15.5
044	- 0.2	11 7	171	- 9 4	19 /		210	_11.0	13.0	335	- 1.9	0
040	- 9.0	71 1	172	- 0.4	12.4		244	-11.0	16	335	-40.2	28.5
000	+00.0	11.1 21 Q	172	+ 9.0	16.1		244	-10.0	10	336	- 5.9	0
060	+21.9	01.0	173	+10.0	10.1		245	-12.0	0	336	-23.6	16.4
062	- 2.3	17	173	+ 4.4	0		240	- 6.8	0	337	- 1 1	0
003	+10.0	24	174	+10.7	0		240	-57	0	350	+34	Õ
004	+41.9	04 15 4	174	+10.7	0		240	- 0.7	0	351	+5.6	0
000	+24.7	10.4	175	+ 4.1	0		200	- 1,4 	25 7	351	$\pm 17.4$	22 6
080	-17.1	19.1	175	+11.7	0		201	T20.0	20.1	359	+17.4 +17.1	22.0
081	-11.9	11.7	1/0		20.2		201	+44.0	10 0	357	$\pm 91.3$	22.0
082	- 0.3	0	190	-20.0	20.2		202	T44.0	40.0	252	$\pm 15.9$	18 5
083	- 8.3	10 7	191	-42.3	40.0		202	+47.9	47.4	252	-1.7.9	10.0
084	-14.0	12.7	191	- 0.9	0		203	+20.1	24.1	254	$\pm 1.0$	0
0, 10, 0	- 1.4	10 0	192	-22.9	21.0		203	+23.2	20	254		0
0, 10, 1	- 9.5	13.8	192	-18.0	21		204	- 1.0	0	255		0
0, 10, 2	-18.0	18	193	+ 1.5			204	- 0.7	0	255	$\pm 10.1$	16 /
0, 10, 3	- 9.9	0	193	-39.3	30.9		200	+ 9.0	10 7	256	+10.1	10.4
0, 12, 0	+36.5	24.4	194	-11.8	10 5		205	+14.2	12.7	330	+10.9	15 5
0, 12, 1	+19.2	15.9	194	-21.6	12.5		200	+32.8	13.0	350	+10.0	10.0
0, 12, 2	- 1.0	0	195	-34.3	17.5		200	+35.8	17.1	270	+ 1.3	0
110	+20.6	25	195	+1.5	0		207	+22.7	9.5	370	+ 4.0	17.9
111	+14.8	17.4	196	-11.2	0		280	- 4.0	10 1	371	+22.7	17.2
111	+18.3	20.9	1, 11, 0	+12.0	12.5		281	-15.5	19.1	371	+ 5.9	16 7
112	+11.4	13.8	1, 11, 1	+15.8	14.7		281	-4.0	0	372	+10.0	10.7
112	+10.8	8.6	1, 11, 1	+3.3	0		282	-10.2	10.4	372	+10.1	21.0
113	+14.3	17.7	1, 11, 2	+ 9.9	0		282	-10.4	17	272	+ 0.0	21 4
113	+12	10.3	1, 11, 2	+ 4.9	0		283	- 0.3	15	273	+10.0	21.4
114	+12.4	0	1, 11, 3	+14.3	0		283	-17.3	15	274	+ 5.1	0
114	+15.1	11.8	1, 11, 3	+13.8	0		284	- 2.1	0	074	T J.J	0
115	+ 9.2	0	1, 13, 0	+9.3	0		284	- 5.3	0	200	+ 4.0	94 5
115	+11.6	0	1, 13, 1	+18.6	11.5		285	-13.0	10	390	-21.1	24.0
116	+8	0	200	+7.6	8.6		2, 10, 0	-17.3	18	201	- 0.2	41 7
116	+ 6.4	0	201	+24.8	29.8		2, 10, 1	-12.7	0	391	-38.4	41.7
117	+ 8.3	0			does not	t,	2, 10, 1	- 7.0	0	392	-13.3	10 5
130	-30.1	41.7	201	+28.8	appear on f	lim	2, 10, 2	-2.1	U	392	- 19.9	01 0
131	-65.3	69.4	202	+54.2	63.2		2, 10, 2	- 1.7	U	393	- 34.1	<u>41.9</u>
131	- 8.9	11.9	202	+63.4	57.4		2, 10, 3	- 5.2	U	393 204	- 14.2	02 ⊭
132	-31.0	37.8	203	+28.3	37.7		2, 10, 3	- 6.8	0	394	- 20.7	43.0 16 4
132	-25.1	29.6	203	+30.6	23		2, 10, 4	- 16.5	15.0	394	- 14.7	10.4
133	+ 2.0	0	204	- 1.8	0		2, 10, 5	- 7.3	0	395	- 33.5	19
$13\overline{3}$	-54.4	48.7	$20\overline{4}$	- 0.8	0		2, 12, 0	- 0 4	0	3, 11, 0	+ 1.1	U
134	-15.0	15.5	205	+7.3	0		2, 12, 1	+17.4	22.9	3, 11, 1	+ 0.9	0
134	-18.8	22.2	205	+14.3	14.4		2, 12, 2	+33.6	21.5	3, 11, 1	+15.0	U
135	-39.3	34	<b>206</b>	+35.7	<b>23</b> . $2$		2, 12, 2	+34.3	22 1	3, 11, 2	+13.5	0
135	- 1.9	0	$20\overline{6}$	+38.2	<b>24</b> . $2$		<b>2</b> , 12, 3	+20.5	12.5	3, 11, 2	+16.7	0

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tree scattering factor for the chloride ion.<sup>17</sup> No temperature factor is included in these data.

In Table IV are listed the powder intensity data for yttrium trichloride. The intensities were calculated according to the formula

$$I = F^2 p \times \frac{1 + \cos^2 2\theta}{\sin^2 \theta \, \cos \, \theta}$$

## TABLE IV

## Observed and Calculated Powder Pattern Intensities for Yttrium Trichloride

Cu Ka Radiation<sup>a</sup>

	aint	A		7	ι
hkl	Calci.	Obad.	Calcd.	Obsd.	C
001	0.0134	0.0165	172		1
020	.0137 j	0.0105	52 J	Va	2
110	.0134	.0205	98	w	2
111	.0239	.0234	54	w	1
021	.0331	.0331	34	vw	-
111	.0458	.0455	18	vw	2
201	.0515 ]	0514	30 ]		1
130	.0518	.0514	65	m	1
200	.0570 โ	0505	2		2
131	.0572 🕺	.0567	5	vw	0
$11\overline{2}$	.0622		7		3
002	.0638		2		0
040	.0667		2		о 0
$22\overline{1}$	.0681		2		
220	.0736		6		1
$20\overline{2}$	.0788 ]		88 ]		3
131	.0792	.0787	196	9	3
022	.0824		7		0
041	.0831	.0845	10	w	2
201	.0953 ]		11)		4
132	.0956	0948	23	m	2
$22\overline{2}$	.0955		9		4
112	1061		4		ר ר
221	.1120	. 1100	12	w	-
$31\overline{1}$	.1159		5		U
241	.1182		2		2
150	.1184		9		]
240	.1237	.1215	8	vvw	2
$15\overline{1}$	.1240	•••••	2		0
310	1323		1)		4
$31\overline{2}$	. 1323		13		2
042	. 1325		11		
$11\overline{3}$	. 1335	.1350	3	mw-br	1
$20\bar{3}$	. 1391		11		2
132	. 1395		23		5
$24\overline{2}$	.1456	1440	2)		4
151	. 1459	.1449	7 1	w	1
003	.1480		5		5
$33\overline{1}$	.1492	1500	64		4
060	. 1500 ∫	.1502	33	m	1
$22\overline{3}$	. 1558		8		5
241	.1621		6		0
$15\overline{2}$	.1623		1		3
023	.1646 )		3		3
$33\overline{2}$	. 1656		11		0
330	. 1657	1671	14	_	0 0
061	.1665	.10/1	15	ms	4
202	.16€6		28		4
$13\overline{3}$	.1668 )		56		v =
° (Cu Ka,	$\lambda = 1.5418$	Å.).			plied

where F is the structure factor, p is the permutation factor and  $\theta$  is the Bragg angle. In Table V are listed the powder data for lutetium trichloride. The intensities of all the isostructural rare earth trichlorides are very similar to those of lutetium trichloride.

		TAB	le V		
Powder	DIFFRACTION	Data	FOR	LUTETIUM	TRICHLORIDE
	Cr	Ka R	adiat	lionª	

	eint	A	T
hkl	Calcd.ª	Obsd.	Obsd. b
001	0.0366	0.0371	ma
020	.0390	0.0011	
130	.1204	1209	ms
201	.1208 J	. 1200	
$20\overline{2}$	.1816	1818	8
131	. 1817 )		5
201	.2176	2182	m
132	.2186 ]		
132	.3159	.3159	m-
203	.3161 )	10200	
003	.3295	.3305	w
$33\overline{1}$	.3493 )	3503	a
060	.3508 )	.0000	6
202	.3760 \	3782	m
133	.3774 )		
330	.3856		
332	.3862	.3879	m
061	.3874 )		
261	.4712	.4723	w
400	.5296	.5331	w
262	.5324 }		
403	.5675	.5684	vw
261	.5684 J		
004	. 5860	.5858	ms
203	.6077	6087	m
134	.6094 J		
263	.6669	.6674	<b>w</b> ~
063	. 6803	.6803	w
$40\overline{4}$	.7266 )	7970	m
262	.7268 )	.1215	- m
134	.8038 }	8047	W-
205	.8046 )		
532	.8186		
461	.8198 }	. 8202	w
190	.8224)		
533	.8802		
400	.8804	.8822	m
191	. 8633 )		
53U 005	.9152	.9153°	m-
222	0000 )		
335	0363	0366	m(a-)
064	.9366	. 9900	ша(рг)
263	9583		
405	.9588	.9581°	w

 $^{a}\lambda = 2.2909$  Å.  $^{b}s = strong, m = medium, w = weak, v = very, br = broad. <sup>c</sup>Observed value for <math>K\alpha_1$  multiplied by 1.0011.

## SPREADING OF HYDROCARBONS AND RELATED COMPOUNDS ON WATER

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The tendencies of several alkyl benzenes, isoöctane and tetralin to spread on water have been investigated by two methods. Surface and interfacial tensions have been measured and the corresponding initial spreading coefficients have been calculated. With the exception of the tetralin, all of the materials have positive spreading coefficients. Spreading pressures for the spreading liquids have been measured with the hydrophile balance. The spreading pressures and initial spreading coefficients are nearly the same for these liquids. Evidence is presented which indicates that the spreading ability acquired by aged tetralin is due chiefly to the formation of tetralin hydroperoxide.

The relative abilities of different liquids to spread on water as duplex films may be predicted from initial spreading coefficients which are related to surface and interfacial tensions by an equation formulated by Harkins.<sup>2</sup> Harkins considered that duplex films must be at least two molecules in thickness and probably are three or more molecules in thickness. He stated that the lower hydrocarbons may spread on water as duplex films which later change to non-duplex films or monolayers. Langmuir<sup>3</sup> considered that monolayers containing long hydrocarbon chains behaved essentially as duplex films. It appears that unless a monolayer acts as a duplex film the concept of spreading coefficient, depending upon interfacial tension, is without significance for lens and monolayer type of spreading. Miller<sup>4</sup> concluded that the spreading pressures for liquids which spread from lenses as monolayers should differ from initial spreading coefficients by the forces necessary to orientate and pack molecules in the films.

The possibilities suggested by these viewpoints have made it seem worthwhile to carry out an experimental study of the spreading behavior of hydrocarbons including alkyl benzenes having different length and complexity of side chains.

One of the hydrocarbons, tetralin (1,2,3,4-tetrahydronaphthalene), was observed to be non-spreading in the pure form. A considerable spreading ability was acquired by tetralin which was allowed to age for some time after purification. Robertson and Waters<sup>5</sup> have studied the autoxidation of tetralin and the decomposition of tetralin hydroperoxide. They have identified many of the products of these reactions and have determined the relative amounts in which some of them are formed. The chief products are tetralin hydroperoxide,  $\alpha$ -tetralone and  $\alpha$ tetralol. It was decided to determine the surface activity of each of these materials in the pure form and in solution in tetralin and to determine which is the chief contributor to the spreading ability of aged tetralin. The kinetics of the oxidation has been further studied by Woodward and Mesrobian.6

Materials.-The hydrocarbons, ethylbenzene, normal and isopropylbenzenes, n-, sec- and t-butylbenzenes, and

isoöctane (2,2,4-trimethylpentane) were of the best grade obtainable from Eastman Kodak Co. When necessary they were purified by fractional distillations until satisfacfor density, refractive index and surface tension, or until constant values unchanged by further purification were obtained. An analytical grade of benzene was recrystallized until nine-tenths of the liquid solidified within the range 5.54 to  $5.52^{\circ}$ . A technical grade of tetralin was purified by treatment with sodium followed by repeated fractional distillations until satisfactory constants were obtained. Interfacial tensions with water probably provide the best indication of purity for such materials at least as far as surface active impurities are concerned. These values have not been previously determined for more than half of the hydrocarbons investigated and agreement with those that have been recorded was not as close as with the other con-stants. It was our practice to extract surface active im-purities from the hydrocarbons with water until interfacial tensions were reproducible and constant. Measured constants are recorded in Table I.

Carefully redistilled water with a surface tension of 72.10 + 0.04 dynes/cm. at  $25.0^{\circ}$  was used in all critical parts of the work.

Tetralin hydroperoxide was synthesized by the method of Hock and Susemihl<sup>7</sup> from purified tetralin. The final product, after several recrystallizations from petroleum ether (30-60°), melted at 56.0°. The freshly purified hydroper-oxide showed no surface activity when placed on pure water. The white, dry and nearly odorless crystals were stored in an atmosphere of nitrogen in a laboratory desk. After several months, during which time they were exposed only intermittently to diffuse light, they became yellow, sticky and very surface active. Because of this change it was necessary to recrystallize the material shortly before using.

 $\alpha$ -Tetralone was synthesized from  $\gamma$ -phenylbutyric acid as described in "Organic Syntheses."<sup>8</sup> The material was a pale yellow oil having an odor resembling that of pepper-mint, and boiling at 104° under 2 mm. of mercury pressure. Its refractive index was 1.5669 and its density 1.0919 g./ cm.<sup>3</sup> at 25.0°. Its spreading pressure, measured with a hydrophile balance, was 14.0 dynes per cm. This value did not change during a month of aging, in a laboratory desk, even though the oil darkened slightly.

The  $\alpha$ -tetralol was prepared from  $\alpha$ -tetralone by the Meer-wein—Ponndorf—Verley method of reduction. The  $\alpha$ -tetralol produced was a light yellow oil which distilled at 107° under two mm. of mercury pressure. Its spreading pressure was 19.4 dynes/cm. while its refractive index and density at 25.0° were 1.5613 and 1.0750 g./cm.<sup>3</sup>, respec-tively. It dealered slightly upon aging for accurate mode It darkened slightly upon aging for several weeks, tivelv in a laboratory desk, but showed no measurable change in surface activity during this time. Methods.—The surface and interfacial tensions necessary

for the calculation of spreading coefficients were measured by capillary rise methods. The instruments and methods of operation have been described.<sup>9</sup> Spreading pressures were measured with a hydrophile balance mounted in a con-stant temperature cabinet. The barriers were moved along the tray of this balance by means of a motor driven mechanism mounted outside the cabinet. A small iron rod

<sup>(1)</sup> E. I. du Pont de Nemours and Company Fellow 1949-1950; Standard Oil Company (Indiana) Fellow 1950-1951; present address: Standard Oil Development Co., Linden, N. J.

<sup>(2)</sup> W. D. Harkins, J. Chem. Phys., 9, 552 (1941).

<sup>(3)</sup> I. Langmuir, ibid., 1, 756 (1933).

<sup>(4)</sup> N. F. Miller, This Journal, 45, 1025 (1941).

<sup>(5)</sup> A. Robertson and W. A. Waters, J. Chem. Soc., 1574, 1578 (1948).

<sup>(6)</sup> A. E. Woodward and R. B. Mesrobian, J. Am. Chem. Soc., 75, 6189 (1953).

<sup>(7)</sup> H. Hock and W. Susemihl, Ber., 66, 61 (1933).
(8) E. L. Martin and L. F. Fieser, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., p. 569.

<sup>(9)</sup> L. F. Transue, E. R. Washburn and F. H. Kahler, J. Am. Chem. Soc., 64, 274 (1942).

TABLE I

			· -			
	Р	ROPERTIES MEAS	URED AT $25.0^{\circ}$			
Material	Density, g./cm. <sup>3</sup>	Refractive index, <i>n</i> D	Surface tension, dynes/cm.	Interfacial tension, dynes/cm.	Spreading coefficient, dynes/cm.	Spreading pressure, dynes/cm.
Benzene	0.8734	1.4979	28.23	34.0	9.9	9.8
Toluene <sup>9</sup>	. 86 <b>2</b> 3		27.94	35.7	8.5	8.8
Ethylbenzene	.8625	1.4931	28.43	37.4	<b>6</b> . <b>2</b>	6.0
n-Propylbenzene	.8579	1.4895	28.49	38.5	5.1	5.1
Isopropylbenzene	.8577	1.4889	27.71	38.7	5.7	6.0
n-Butylbenzene	.8560	1.4873	28.73	39.6	3.8	3.6
sec-Butylbenzene	8577	1.4877	28.20	39.2	4.7	4.7
t-Butylbenzene	.8627	1.4902	27.63	39.3	5.2	5.3
Isoöctane	.6880	1.3890	18.44	49.3	4.4	4.4
Tetralin	.9659	1.5393	36.02	38.6	-2.5	0.0

with a pointed hydrophobic tip was permanently mounted to the tray to serve as a reference point in filling the tray so that depth of liquid might be reproduced. The experimental techniques have been described.<sup>10</sup>

Dean and Li<sup>11</sup> recognized the possibility that sorption of vapors from the spreading liquid by the surrounding stearic acid monolayer might interfere with the direct measurement of spreading pressure of volatile liquids with the hydrophile balance. They concluded, however, that the area of monolayer exposed to saturated vapor is too small to produce a detectable change in spreading pressure. The criterion would seem to be whether or not all the spreading liquid becomes compressed into a lens by the expanded monolayer. In this investigation care was taken to avoid such excessive compression.

**Results.**—Many measurements, twenty to thirty or more, of surface tension and interfacial tension were made on each of from three to eight different portions of the most carefully purified sample of each material. Between measurements the relative positions of the surfaces or interfaces were altered. This was done in several ways, by tilting the instrument, by altering the pressure on the liquid in the wide tube, or by altering the amount of liquid in the instrument. For the interfacial tensions the water and organic liquids were mutually saturated. The mutual solubility of the hydrocarbons and water was so slight that the densities of the pure liquids and of the liquids saturated with water did not differ by more than 0.0003 g./cm.<sup>3</sup> The individual determinations of surface tension did not differ from the recorded average values by more than 0.05dyne/cm. The deviations were somewhat larger with interfacial tensions but the great majority of the individual measurements agreed with the recorded average within 0.1 dyne/cm. Average values are recorded in Table I.

Different samples, even of the same liquid, did not always display the same pattern of spreading. Sometimes the added liquid seemed to spread as a layer of uniform thickness until stopped by the film pressure built up in the surrounding stearic acid monolayer. These broad lenses or layers would sometimes break up into many small lenses separated from each other by an invisible film. Some samples of each liquid studied, except tetralin, formed a lens, or a cluster of small lenses, surrounded by a very thin film which made no visible angle of contact along its outer boundary with the surrounding stearic acid. There was no measurable difference in the spreading pressures which

(10) E. R. Washburn and C. P. Keim, J. Am. Chem. Soc., 62, 1747 (1940).

could be identified with the pattern of spreading shown by samples of the same material of equal purity. The deviations among a great many individual determinations of spreading pressures from the recorded averages were not greater than 0.2 dyne/cm. These values were obtained by adding dry hydrocarbons to the stearic acid film covered water surface. The values obtained with hydrocarbons saturated with water were not measurably different.

The spreading pressures as measured with the hydrophile balance are direct measures of the tendencies of the hydrocarbons to spread on water in contact with air. Exactly, they are the minimum film pressures necessary to prevent the hydrocarbons from spreading from a lens as a thin layer. This is shown by the following development. The initial spreading coefficient for a hydrocarbon, b upon water, a, according to Harkins,<sup>2</sup> is represented by

$$S_{b/a} = \gamma_a - (\gamma_b + \gamma_a'_b') \tag{1}$$

In a similar manner the tendency for a hydrocarbon to spread upon water initially covered with a monolayer of stearic acid a\* is given by the relation

$$S_{b/a^*} = \gamma_{a^*} - (\gamma_b + \gamma_{a'b'}) \tag{2}$$

and spreading will occur if this difference is greater than zero. The surface tension of the film covered water  $\gamma_{a^*}$  may be represented by

$$\gamma_{a}* = \gamma_{a} - \pi \tag{3}$$

where  $\pi$  is the film pressure. A combination of these equations results in

$$S_{b/a^*} = S_{b/a} - \pi \tag{4}$$

which indicates that the spreading of the hydrocarbon as a duplex film will stop when the film pressure of the stearic acid becomes equal to the initial spreading coefficient of the hydrocarbon.

These spreading pressures should not be confused with the equilibrium film pressures of Harkins<sup>2</sup> although in some cases they are not much different in magnitude. Harkins' equilibrium film pressures were measured in an atmosphere saturated with vapors of the spreading liquid, a condition not easily attained when the organic liquid is added to an open surface of water. The spreading pressures are definite quantities easily reproducible to within a few tenths of a dyne per centimeter. The fact that the measured spreading pressures for the hydrocarbons studied in this investigation agree closely with initial spreading coefficients may indicate that these liquids spread on an open water

<sup>(11)</sup> R. B. Dean and F. S. Li, ibid., 72, 3979 (1950).

surface as films which are either polymolecular in thickness or if monomolecular they are at least duplex in character. That is, they possess independent liquid-air and liquid-water boundary tensions. In any case the findings of this research neither confirm nor do they contradict the conclusion of Miller<sup>4</sup> that the spreading pressure is greater than the initial spreading coefficient. Several of the liquids studied by Miller gave differences which are no larger than the experimental error.

The difference between the spreading pressures of benzene and toluene is 1.0 while for toluene and ethylbenzene the difference is 2.8, almost three times as large. For ethylbenzene and n-propylbenzene the difference is 0.9 while for *n*-propylbenzene to n-butylbenzene a larger difference, 1.5, is again noted. This alternation of relative change in spreading pressure is so much larger than experimental error that it seems significant. The values for ethylbenzene and isopropylbenzene are identical and more nearly like that of the compact t-butylbenzene than any of the other alkyl benzenes. It is possible that these relationships are determined by ease and efficiency of packing the molecules in the surface layer or in the film. A fairly straight line is obtained when spreading pressures of the straight chain alkyl benzenes are plotted vs. number of carbon atoms in the chain. This line, when extrapolated, indicates that alkyl benzenes with straight chains containing more than seven carbon atoms should not spread upon water.

A phenomenon which may be related to packing or molecular arrangement was encountered. When small amounts of benzene, toluene or isoöctane were dropped on a stearic acid monolayer under an initial pressure somewhat less than the spreading pressure of the added liquid the pressure would increase instantly to the spreading pressure and remain there until the added liquid had nearly disappeared by evaporation. With the alkyl benzenes from ethylbenzene through the butylbenzenes the behavior was different. Shortly after the additions of these liquids, and while a large proportion of the added liquid still remained as a lens surrounded by a large film, the pressure began to decrease slowly but steadily. Simultaneously with this decrease the lenses of the alkyl benzenes began to break up into smaller lenses, slowly at first, then more rapidly as the pressure decreased. Subdivision and surface activity were very pronounced but could be greatly reduced or stopped altogether by stirring of the lens with a fine, freshly cleaned, glass rod or platinum wire or by adding new drops of spreading liquid. The stirring was associated with an increase of surface pressure to substantially the same value as that observed immediately after the initial addition of the drop. This rise was very rapid, often being complete after two or three gentle strokes of the rod through the lens. Sometimes more vigorous agitation was necessary to cause a return to the initial high value. If allowed to remain undisturbed the pressure would again decrease and stirring or the addition of fresh liquid would again bring it back to the original value. With the less volatile liquids several such pressure rises could be

produced during the existence of a single addition of spreading liquid.

When drops of freshly purified tetralin were placed on a water surface covered with a continuous film of stearic acid under as low a film pressure as it was possible to measure with a hydrophile balance there was no detectable increase in film pressure due to the added tetralin. Upon aging in contact with a limited amount of air and exposed to laboratory light for a few days the tetralin developed a slight spreading pressure, too small to be measured with the film balance but indicated by the appearance of a drop of the liquid on the film covered water surface. The lens was much flatter than with freshly purified tetralin. Upon further aging measurable spreading pressures developed which, in a period of 120 days, appeared to reach a limiting value of about 21 dynes per cm. The rate of increase was greatly increased by placing the clear glass container of the tetralin in direct sunlight and greatly decreased by keeping the tetralin in a dark place. A sample of freshly purified tetralin, from which air was displaced with nitrogen, was sealed in a glass tube in a nitrogen atmosphere. No spreading ability was acquired in a month's time although the tube and contents were exposed to direct sunlight when possible during the month. Preliminary measurements were made with aging at 40 and 55°. Although spreading ability increased somewhat more rapidly at the elevated temperatures than at room temperature, the increases were small. This may indicate that a photochemical reaction, nearly independent of temperature, is important.

The spreading behavior during the life of a drop deserves some mention. When a sample of aged tetralin was added to a water surface covered with a stearic acid film under low initial pressure, the drop would spread rapidly to a maximum pressure, depending on the age of the sample, then the pressure would decrease until it became essentially the initial film pressure. The maximum pressure was usually reached within 10 or 15 seconds after the addition of the drop while 15 minutes might be necessary for the return to the initial low pressure. Agitation of the tetralin layer during the slow decrease had little or no influence on the spreading pressure. The added tetralin drop contracted into a deep lens with almost no spreading ability. It seemed that water had extracted or destroyed the material which caused the aged tetralin to spread.

Solutions of different concentrations of each of the oxidation products of tetralin were prepared in tetralin. The spreading pressures were measured immediately after the preparation and again after the solutions had aged for different periods of time. The results of typical experiments are recorded in Table II. The pure tetralin, the values for which are recorded in the first horizontal line of Table II, was stored in a 25-ml. glass-stoppered flask with greater exposure to more air than the solutions which were in small weighing bottles. This probably accounts for the relatively rapid increase in spreading pressure shown by the initially pure tetralin.

The tetralin hydroperoxide causes the greatest increase in spreading ability while the  $\alpha$ -tetralone

TABLE II
Spreading Pressures of Tetralin and of Solutions of Oxidation Products in Tetralia
Solute, tetralin hydroperoxide

vt. %	Initial		Values o	htd. after the indi	cated no. of days.	dvnes/cm.	
peroxide	values	$D_{ays} \rightarrow 16$	25	35	60	94	119
0.000	0.0	6.8	10.4	13.0	17.6	20.7	20.9
. 104	0.7	5.6	8.2	10.4	15.9	19.6	<b>20</b> . $2$
. 227	1.3	6.6	9.2	11.1	16.3	19.6	20.2
. 456	2.7	8.5	10.8	12.9	17.5	20.0	20.3
.570	3.4	8.6	11.1	13.3	17.6	20.1	20.3
1.399	7.7						
5.160	14.6						
	Solute, a	-tetralone			Solute, a	-tetralol	
Wt. % solute	Initial values	29 days	67 days	Wt. % solute	Initial values	21 days	58 days
0.208	0.3	13.3	19.6	2.124	4.4	9.8	15.8
.832	.3	12.7	18.8	4.538	10.2	11.7	15.8
2.756	1.5	12.4	18.9	6.196	12.5	13.1	15.6
3.554	2.5	11.4	18.4	9.108	13.7	14.2	16.3
6.009	3.2	11.8	18.3	10.19	14.1	14.2	15.9
13.44	6.1	11.1	17.4				

has the least influence. The spreading abilities of all the solutions increase with age and seem to approach a common limiting value of somewhat above 20 dynes/cm. under the conditions of the experiments. The fact that the more concentrated solutions of  $\alpha$ -tetralone show a slower rate of increase in spreading pressure than the more dilute solutions suggests that this material, especially in high concentrations, may retard the formation of compounds which increase the spreading ability of tetralin as it ages.

It is possible to determine the concentration of  $\alpha$ tetralone in tetralin by a study of light absorption with a spectrophotometer. The optimum wave length is 330 m $\mu$ . The solutions closely follow Beer's law. This analysis was used to provide further indication of the relative influence of the different materials on the spreading of aged tetralin. A sample of aged tetralin which had a spreading pressure of 6.2 dynes/cm. was found to contain 0.19 wt. %  $\alpha$ -tetralone. Robertson and Waters<sup>5</sup> observed that the concentration of  $\alpha$ -tetralol formed by the decomposition of the hydroperoxide in tetralin was about one third less than the concentration of  $\alpha$ -tetralone formed at the same time. This would indicate a concentration of about 0.14 wt.  $\frac{97}{20}$  $\alpha$ -tetralol in the aged tetralin sample. From graphs of spreading pressure vs. concentration it was determined that the 0.19 wt. %  $\alpha$ -tetralone corresponds to a spreading pressure of 0.2 dyne/cm. while the 0.14 wt. %  $\alpha$ -tetralol corresponds to 0.4 dynes/cm. If these spreading pressures are additive the sum, 0.6 dyne/cm., leaves 5.6 dynes/cm. as the contribution of the hydroperoxide to the spreading pressure of 6.2 dynes/cm. for the original sample. Thus it seems that the hydroperoxide is the major contributor to the spreading ability possessed by aged tetralin.

## THE AMPHOTERIC PROPERTIES OF TELLURIUM DIOXIDE

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Tellurium dioxide behaves as an ampholyte with an isoelectric point, corresponding to the minimum solubility, occurring at pH 3.8. The solubility of TeO<sub>2</sub> in the various solutions used is small, amounting in maximum to  $1.02 \times 10^{-2}$  mole/l., in 1 N HCl at 25°. The solubility of the dioxide does not, accordingly, affect appreciably the pH of the solutions except above pH 7. From solubility and pH measurements  $K_a'$  of tellurous acid was calculated to be  $1.4-4.3 \times 10^{-6}$  and  $K_b'$ to be  $3.1 \times 10^{-11}$ .

It is fairly well established that an ampholyte possesses equal opportunities to dissociate, within the isoelectric zone, either as an acid or as a base. Outside that zone any one of the two processes may prevail, the acid dissociation above the isoelectric point and the basic dissociation below it. Above the isoelectric point the acid remains practically undissociated until a pH of the same magnitude as its  $pK_*$  value is reached when it loses its identity owing to the incidence of acid-base reaction. Similarly, below that point the base remains undissociated until a pH equal to  $pK_{Ca}$  of the corresponding conjugate acid which is equal to  $pK_w - pK_b$ .

The pH, at which complete precipitation of tellurium dioxide takes place, corresponding to its isoelectric point was found by Haissinsky and Cottin<sup>1</sup> to lie at pH 4.2. This latter value appears thus to contradict the above picture interrelating the isoelectric point with the dissociation constant

(1) M. Haissinsky and M. Cottin, Anal. Chim. Acta, 3, 226 (1949)

of tellurous acid, as the former lies at a higher pH than the  $pK_{\rm a}$  of this acid which amounts according to Blanc<sup>2</sup> to 2.699.

We tried therefore to find out the cause of this contradiction by redetermining the position of the isoelectric point and the dissociation constants of tellurous acid from solubility measurements.

## Experimental

Preparation of Tellurium Dioxide.—A sample of TeOs was prepared from powdered tellurium following the procedure recommended by Schuman<sup>3</sup> and which is supposed to yield a pure product containing not less than 99.84%TeO<sub>2</sub> but the purity may rise up to 99.96%. Solubility of Tellurium Dioxide in Hydrochloric Acid

Solubility of Tellurium Dioxide in Hydrochloric Acid and in Buffer Solutions.—Hydrochloric acid solutions of various concentrations ranging from  $1-10^{-4}$  N were prepared from the constant boiling acid by accurate dilution. Their pH values were determined using the quinhydrone electrode. Clark and Lubs buffer solutions<sup>4</sup> covering the pH range 1-10 were prepared as recommended by the authors and their pH values measured by the hydrogen electrode. Samples of the oxide were introduced together with 150 ml. of the hydrochloric acid or buffer solutions into wellsteamed flasks having a capacity of 250 ml. each. These were sealed off, placed in a thermostat adjusted at 25° and shaken strongly for a period of 170 hours which was found to be quite sufficient for the attainment of saturation.<sup>3</sup> After that period the solutions were left to stand at 25° for a sufficient time to allow any suspended particles to settle down. The tellurium content of the saturated solutions was potentiometrically determined by the aid of potassium permanganate in weakly alkaline solutions.<sup>6</sup> This method was found suitable for the accurate determination of small amounts of tellurium (IV). Portions of the solutions were potentiometrically titrated with 9.9  $\times 10^{-3}$  or 9.9  $\times 10^{-4}$ N KMnO<sub>4</sub> after adjusting the alkalinity of the solutions

TABLE	T
TUDDE	-

Solubility	OF	Tellurium	DIOXIDE IN	Hydrochloric
		ACID SC	LUTIONS	
HCl,		Original pH	pH at saturation	Solubility, mole/l. × 10
1		0.092	0.092	102
0.5		0.41	0.41	39.1
0.1		1.11	1.11	7.70
0.05		1.38	1.38	4.207
0.01		2.05	2.05	1.638
0.005		2.47	2.47	0.99
0.001		3.17	3.17	0.2574
0.0005		3.40	3.40	0.1485
0.0001		4.07	4.07	0.1326
water		6.5	6.45	0.375

$\mathbf{T}_{\mathbf{A}}$	BLE	Π

SOLUBILITY OF TEL	LURIUM DIOXIDE IN	BUFFER SOLUTIONS
Original pH	pH at saturation	Solubility, mole/l. × 104
1.11	1.11	7.70
2.39	2.39	2.03
3.05	3.05	0.544
4.2	4.2	0.297
4.96	4.93	0.544
6.03	5.99	0.9405
7.07	7.02	1.46
8.0	7.93	3.613
9.0	8.9	
9.95	9.6	

(2) E. Blanc, J. chim. phys., 18, 28 (1920).

(3) R. Schumann, J. Am. Chem. Soc., 47, 356 (1925).

(4) W. M. Clark and H. A. Lubs, J. Biochem., 25, 479 (1916), cited in H. T. S. Britton, "Hydrogen Ions," Vol. I, 3rd Ed., Chapman and Hall, London, 1942, pp. 301-310.

(5) I. M. Issa and S. A. Awad, Analyst, 78, 487 (1953).

to 0.08 N in respect to NaOH. In order to prove that the saturated solutions were free from dispersed TeO<sub>2</sub>, solutions in 0.1 and 1 N HCl were subjected to ultrafiltration using a high pressure filtering apparatus supplied by the Membrangsellschaft, gottingen and cellophane filters impermeable to congo red. The pressure used was 5 atmospheres and three drops were obtained per minute. The concentration of TeO<sub>2</sub> in the filtrates did not deviate from its concentration in the original solutions.

The pH values of the HCl and buffer solutions before and after saturation with  $TeO_2$  were also redetermined with the aid of a glass electrode using a Marconi-EKO pH-meter accurate to  $\pm 0.02$  pH unit. The potentiometer was calibrated by the aid of well-checked buffer solutions. The results are shown in Tables I and II.

## **Results and Discussion**

Tables I and II contain typical pH and solubility data in the hydrochloric acid (1 to  $10^{-4} N$ ) and buffer solutions (pH 1 to 10). From these results it is apparent that the solubility of tellurium dioxide does not affect the pH of solutions ranging from 0.1– 4.2. Above this latter pH till the neutral point the oxide levels down, although only to a small extent, the pH of the solution. Above pH 7 the levelling down of pH becomes somewhat apparent and becomes only pronounced above pH 9. The smallness of the magnitude of the levelling down effect in solutions of  $pH \sim 4$ , up to pH 7 is apparently due to the smallness of the solubility of TeO<sub>2</sub> in these solutions (compare Table II).

On plotting the solubility of  $\text{TeO}_2$  in hydrochloric acid and in buffer solutions against their pH values, before or after saturation with  $\text{TeO}_2$ , the curves shown in Figs. 1 and 2, respectively, were obtained. From these curves it is apparent that the solubility passes through a minimum within the pH range 3.5-4.2. The point of minimum solubility corresponding to the isoelectric point as obtained by extending the two branches of the V-shaped curves occurs at  $\sim p$ H 3.8. This point although corresponding to a lower pH than 4.2 due to Haissinsky and Cottin<sup>1</sup> yet it confirms the location of the isoelectric zone in the region of pH 4.





The Dissociation Constants of Tellurous Acid.— The above data can be made use of in determining  $K_a'$  and  $K_b'$  which represent the magnitude of the acid and basic dissociation constants of tellurous acid, using relations due to Krebs and Speakman.<sup>6</sup> Thus

$$\log\left(S/S^{\circ}-1\right) = pH - pK_{a}$$
 (1)

and

$$\log (S/S^{\circ} - 1) = (pK_{w} - pK_{b'}) - pH \qquad (2)$$

In these equations S represents the solubility at the respective pH at saturation and  $S^{\circ}$  the solubility in strongly acid solutions. The latter value which could be evaluated by plotting log S against pHand extrapolating to pH 0, and better by the method of least squares using data obtained at pH4.2, 4.93, 5.99 and 7.02 was found to amount to  $3.2 \times 10^{-6}$  mo.e/liter. In Tables IIIa and IIIb are listed the log  $(S/S^{\circ} - 1)$  values together with  $pK_{\rm a}'$  and  $pK_{\rm b}'$  values calculated by the use of re-lations 1 and 2. By plotting the log  $(S/S^{\circ} - 1)$ values against pH a V-shaped curve (see Fig. 3) approximately similar to the S - pH plots (Figs. 1 and 2) is obtained which also passes through a minimum at the isoelectric point, viz, at pH 3.8. From the results shown in Table IIIa the most probable values for  $pK_{a}'$  are those computed at pH 7 and 8, as these latter pH values are far removed from the isoelectric point. These correspond to  $K_{a}$  values ranging from  $1.4-4.3 \times 10^{-6}$ . Similarly from the results shown in Table IIIb the most probable values of  $pK_{\rm b}'$  are those obtained at 0.05 to 0.5 N HCl within which range the compound dissociates as a monoacid base (see below). These correspond to  $K_{\rm b}'$  values amounting to  $\sim 3.1 \times 10^{-11}$ .

These values do not represent, however, the true dissociation constants unless the acid is monobasic or the base monoacid. For a polybasic acid or a



polyacid base they represent the mean values of the different dissociation constants unless the first constant is the predominating one and the other constants are small in comparison. The values of  $K_{a}'$  obtained above are however much smaller than that reported by Blanc,<sup>2</sup> amounting to  $2 \times 10^{-3}$ .

	TABL	E IIIA	
	BUFFER S	Solutions	
pH at saturation	$(S/S^2)$	pg 2 − 1)	$pK_{\mathbf{a}}'$
2.39	1.	79	
3.05	1.	20	
4.2	0	.92	
4.93	1.	20	3.73
5.99	1.	45	4.54
7.02	1	.65	5.37
7.93	2	.09	5.84
	TABL	e IIIb	
	HCl So	LUTIONS	
HCl, N	pH at saturation	$(S/S^{\circ}-1)$	$pK_{b}'$
1	0.092	3.50	10.41
0.5	0.41	3.09	10.5
0.1	1.11	2.38	10.51
0.05	1.38	2.11	10.51
0.01	2.05	1.70	10.25
0.005	2.47	1.48	10.05

 $K_{a}'$  also can be calculated from the relation

[H]

$$= \sqrt{K_{a}K_{w}/K_{b}}$$
(3)

in which  $[H^+]$  corresponds to the  $H^+$  ion activity at the isoelectric point.<sup>7</sup>

Taking  $[H^+] = 1.5 \times 10^{-4}$ ,  $K_w = 10^{-14}$  and  $K_b = 10^{-12}$  s the value of  $K_s$ ' as calculated from relation 3 amounts to  $2.51 \times 10^{-6}$  which is comparable with the values obtained above from solubility measurements, and applying the relations of Krebs and Speakman.<sup>6</sup>

Schumann<sup>3</sup> from solubility measurements concluded from the constancy of the  $S/[H^+]$  values that TeO<sub>2</sub> behaves as a monoacid base within the

(7) Cited in H. T. S. Britton, ref. 4, p. 215, 216.
(8) W. M. Latimer, "Oxidation Potentials," 2nd edition, Prentice-Hall, Inc., New York, N. Y., 1952, p. 86.

<sup>(6)</sup> H. A. Krebs and J. C. Speakman, J. Chem. Soc., 593 (1945).

## Adsorption of Nitriles on Hydrogen Electrodes

acid range 0.1-0.73 N HClO<sub>4</sub>. Kasarnowsky<sup>9</sup> on the other hand considered tellurous acid as a weak base which he represented as  $Te(OH)_4$  and gave for  $K_{\rm b}$  the value  $10^{-46}$ . It must, however, be taken into consideration that a weak polyacid base like a weak polybasic acid must dissociate in steps, the first of which, as in the case under consideration can be represented as

 $Te(OH)_4 - H_2O \longrightarrow TeO_2HOH \longrightarrow TeO_2H^+ + OH^-$ 

The findings of Schumann were substantiated by the following data from which it is apparent that  $S/[H^+]$  is approximately constant between 0.05-0.5 N HCl, thus

(9) J. Kasarnowsky, Z. physik. Chem., 109, 287 (1924).

[H *]	S, mole/l.	$S/[{ m H^{+}}] imes10^3$
0.8091	$10.20 \times 10^{-3}$	12.6
.3892	$3.91 \times 10^{-3}$	10.02
.0776	$0.77 \times 10^{-3}$	9.92
.0417	$0.42 \times 10^{-3}$	10.08
. 0090	$0.164 \times 10^{-3}$	18.2

The value of  $K_{\rm b}'$  amounting to 3.1  $\times$  10<sup>-11</sup> as computed from the data shown in Table IIIb is undoubtedly higher than that given by Latimer.<sup>8</sup> However, by determining  $K_b'$  from the results obtained by Schumann<sup>3</sup> and applying our  $S^{\circ}$  value,  $3.2 \times 10^{-6}$  mole/l., the values obtained varied from  $2.4-2.8 \times 10^{-11}$  which compares well with our  $K_{\rm b}$ value.

## THE COMPETITIVE ADSORPTION FROM AQUEOUS SOLUTIONS OF HYDROGEN AND NITRILES ON PLATINIZED PLATINUM

## BY THOMAS C. FRANKLIN\* AND RAY D. SOTHERN

Contribution from the Department of Chemistry of the University of Richmond, Richmond, Virginia Received December 17, 1953

The adsorption of a series of nitriles on the hydrogen electrode has been investigated coulometrically. The amount of hydrogen adsorbed and the potential of the electrode were determined for various concentrations of nitrile. The adsorption of the nitrile was found to follow the Freundlich equation. The potential of the cell is proportional to the logarithm of the amount of adsorbed hydrogen. A comparison of the poisoning effect of various nitriles indicated that the poisoning ability is primarily related to the size of the molecule.

Since it is known that the presence of poisons such as arsenic, mercury and sulfur compounds causes the hydrogen electrode to become erratic, an investigation has been initiated into the adsorption of foreign materials on the hydrogen electrode and their effect upon the potential of the electrode. Poisons as strong as those just mentioned almost completely replace the hydrogen adsorbed on the electrode; therefore a series of weaker poisons, the nitriles, was selected for this study.

The system used in these experiments consisted of platinum black as the adsorbent, 2 N sulfuric acid as the solvent, and hydrogen and the nitrile as competitive adsorbates.

The competitive equilibria may be expressed as shown in the equations

$$\begin{array}{l} H_2 \mbox{ (soln.)} + H_2 O \mbox{ (ads.)} = 2 H \mbox{ (ads.)} + H_2 O \mbox{ (soln.)} \\ RCN \mbox{ (soln.)} + H_2 O \mbox{ (ads.)} = RCN \mbox{ (ads.)} + H_2 O \mbox{ (soln.)} \end{array}$$

The quantity of water in solution as well as the amount of dissolved  $H_2$  may be assumed to be constant. The amount of nitrile in solution is considered to be the amount added. Of the three remaining quantities: H, RCN and  $H_2O$  adsorbed, only the first lends itself to direct measurement, this by a coulometric method. A similar investigation has been made on the adsorption of acetic acid

## Experimental

by Oikawa and Mukaibo.1

Equipment and Reagents.-The apparatus consisted of a small platinized platinum wire, immersed in a solution of 2 N sulfuric acid. This solution was connected by a saturated ammonium sulfate-agar bridge to a saturated calomel half-cell, which served as a non-polarizable electrode. The cell was connected through switches to a Sargent Model XXI Polarograph and to a Fisher Type S Potentiometer.

The electrodes were made by cutting 20 gage platinum wire into 2 cm. lengths which were then sealed into glass tubing. These electrodes were then platinized for three minutes in a 3% solution of chloroplatinic acid containing a trace of lead acetate, using an applied potential of 3 volts. The electrodes were then washed briefly in distilled water and in concentrated sulfuric acid and were aged several hours in 2N sulfuric acid. Just prior to use these electrodes were anodically polarized at oxygen evolution for 20 to 30 minutes.

To determine the effect of pressure, a more elaborate cell was required. This cell consisted of two 200-ml. round bottom flasks as electrode compartments connected by means of a salt bridge compartment. The hydrogen halfcell was connected through a ballast tank to a water aspirator. A mercury manometer was used to measure the pres-

The temperature of the cell was controlled by using a Sargent Model S-84805 constant temperature bath. The nitriles used were the best grade available from the Eastman Kodak Company.<sup>2</sup> Drocedure — Hydrogen was bubbled over the electrode

Procedure.—Hydrogen was bubbled over the electrode until a steady potential was attained, as indicated by the potentiometer. The flow of hydrogen was stopped and sufficient time was allowed for equilibrium to be established between the hydrogen dissolved in solution and that ad-sorbed on the electrode. The adsorbed hydrogen was then removed by electrolytic oxidation with the pen recorder of the polarograph recording a current-time curve for this oxidation. The number of coulombs passed was determined from the area under this curve.

A measured quantity of poison was then added and the process repeated. The decrease in area under the curve was taken as a measure of the amount of poison adsorbed. This procedure was repeated for each poison studied at several different concentrations of poison.

<sup>\*</sup> Chemistry Department, Baylor University, Waco, Texas.

<sup>(1)</sup> M. Oikawa and T. Mukaibo, J. Electrochem. Soc. Japan, 20, 568 (1952).

<sup>(2)</sup> In order to check for the possible effect of impurities Mr. Philip Oglesby made a series of runs, first on the commercially available nitrile, then on the redistilled nitrile. There was no difference in the results.

The areas under the curves were measured by a planimeter, the quantity of electricity measured being between 6 and 2000 microcoulombs.

In order to obtain reproducible results the current-time curves were taken with the voltage increasing over a short span, 0.6 v., rather than at a constant applied potential.

This voltage span, chosen from previously run currentvoltage curves, was chosen to take in the oxidation peak of hydrogen without taking in subsequent oxidation processes.

## Data and Results

The data can be put into two groups: (1) The effect of the nitrile on the amount of hydrogen adjacent to the electrode. (2) The resultant effect on the potential of the hydrogen electrode.

Figure 1 shows the effect of propionitrile on the





amount of hydrogen adjacent to the electrode. Plotted along one axis is the logarithm of the milligrams of propionitrile in 140 milliliters of solvent. Along the other axis is plotted the logarithm  $(A_0 A)/A_0$ .  $A_0$  is the area under the current time curve when  $H_2$  alone is adsorbed. A is the area under the current-time curve when both H<sub>2</sub> and the nitrile are adsorbed.  $A_0 - A$  therefore corresponds to the amount of hydrogen displaced by the nitrile.  $A_0$  is a measure of the adsorbing area of the electrode. Therefore  $(A_0 - A)/A_0$  can be pictured as representing the amount of nitrile adsorbed per unit area of adsorbent. This graph then corresponds to a log-log plot of the Freundlich equation and the resultant straight line confirms the applicability of the Freundlich equation.

The other phase of the problem was the measurement of the resultant effect on the potential of the



Fig. 2.-Variation of potential with amount of adsorbed hydrogen (acetonitrile).

hydrogen electrode. Figure 2 indicates a linear relationship between the logarithm of the amount of hydrogen adsorbed (as measured by the area under the current time curve) and the e.m.f. of the cell. As will be noticed there is a good deal of scatter to the data. All of the e.m.f. data exhibited the same sort of scatter. This scatter is probably due to failure of the system to reach final equilibrium since potential measurements were made with hydrogen bubbling over the electrode.<sup>3</sup>

The Nernst equation for the hydrogen electrode shows a linear relationship between the e.m.f. and the logarithm of the pressure of the hydrogen. Therefore it follows that there should be a linear relationship between the amount of adsorbed hydrogen and the pressure. This relationship was found to be true and is shown in Fig. 3.



Fig. 3.-Variation of amount of adsorbed hydrogen with pressure.

Similar experiments were run on butyro-, ncapro-, isocapro- and phenylacetonitriles and the results were similar to those just described.

In trying to draw some correlation between molecular structure and poisoning, a plot (Fig. 4) was



Fig. 4.-Effect of molecular weight on poisoning ability.

made of molecular weight against millimoles of nitrile added to produce the same degree of poisoning as taken from graphs similar to Fig. 1. In view of the scatter of the original data the regularity of the curve was a great surprise and indicates that

<sup>(3)</sup> That this explanation is true is shown by a series of recent runs by Mr. Phillip Oglesby in this Laboratory. He measured the e.m.f. in a hydrogen saturated solution with no hydrogen bubbling over the electrode. These runs showed the same type relationship with practically no scatter. The slope of his graphs was 0.059 in agreement with the theoretical slope for the Nernst equation.

size is probably the primary factor in the nitrile series in blocking the electrode surface.

In summary it can be said that: (1) The effect of the nitriles on the potential of the hydrogen electrode seems to be due to a displacement of the hydrogen adsorbed on the surface. The potential of the hydrogen electrode is governed by the concentration of adsorbed hydrogen not by the pressure of hydrogen above the solution. (2) The displacement ability of the nitrile seems to be primarily a function of its size.

We wish to take this opportunity to express our thanks to the Research Corporation for the financial assistance which they are furnishing for this project and to Mr. Samuel L. Cooke, Jr., for his aid in preparing this article for publication.

## MOLECULAR WEIGHT, MOLECULAR WEIGHT DISTRIBUTION AND MOLECULAR SIZE OF A NATIVE DEXTRAN

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Native dextran, as produced by a subculture of *Leuconostoc mesenteroides* NRRL B-512, was separated into a number of fractions. The fractions were characterized as to their molecular weight and size by means of light scattering and intrinsic viscosity in aqueous solutions, and their degree of branching, in terms of 1-6/non 1-6 linkages, by periodate oxidations. The molecular weights ranged from 12 to 600 million. The intrinsic viscosities were fairly low due to the high degree of branching. Flory's viscosity theory did not satisfactorily explain the experimental data. This discrepancy is probably due to the highly branched nature of the dextran molecular inhomogeneity of the fractions. Using a recent theoretical development by Benoit, the molecular inhomogeneity of the fractions and the deviation of their radii of gyration from the radius of a hypothetical linear molecule of the same molecular weight were estimated from the angular dependence of scattered light.

The polyglucose dextran can be produced by Leuconostoc mesenteroides using sucrose as starting material. We felt that it would be of interest to investigate the molecular weight and molecular weight distribution of this polymer more intensively than has been done in the past.<sup>1</sup> The structures, however, of several types of dextran have been the subject of previous study.<sup>2</sup> Therefore, it also seemed worthwhile to attempt a correlation of the structure (degree of branching) of native dextrans and its fractions with their molecular weight and size.

## Experimental

Fractionation.—A sample of native dextran produced by the so-called whole culture method with Leuconostoc mesenteroides (NRRL B-512) was obtained from the Dextran Corporation. The dextran is produced by massive inoculation of a medium containing approximately 10% sucrose plus cornsteep liquor and mineral salts as nutrients. The population of Leuconostoc reaches a maximum of about 1 billion per milliliter. The culture is kept as sterile as possible in order to keep out other organisms as for instance molds. An approximately 1% solution (pH 7.6), which proved to be quite hazy, was used in the fractionation.

proved to be quite nazy, was used in the fractionation. The solution was centrifuged (approximately 20,000 × gravity) for 50, 90 and 145 minutes. A pellet-like sediment of 2.4% (based on total solids) was obtained, independent of the time of centrifugation. This sediment, apparently an insoluble carbohydrate polymer, was not further investigated (the very low Kjeldahl,  $N \leq 0.12\%^3$  ruled out the possibility of a proteinic composition). The centrifuged solution was used for fractionate along conventional lines. Evidently the molecular weights are so large that there are only very small differences in the solubility of the various species. However, it was possible to prepare five main fractions by carefully adding methanol and varving the temperature. These fractions were further divided into 10

(1) F. R. Senti and N. N. Hellman, Report of Working Conference on Dextran, July, 1951.

(2) I. Levi, W. L. Hawkins and H. Hibbert, J. Am. Chem. Soc., 64, 1959 (1942).

(3) Performed in the laboratory of the Dextran Corporation.

subfractions. In Table I the precipitation conditions for the 5 main fractions are given.

## TABLE I

PRECIPITATION CONDITIONS OF THE FIVE MAIN FRACTIONS

action	Methanol (vol. %)	Temp., °C.	Yield, %
Α	42.5	36.6	20.0
в	42.5	35.5	15.6
С	42.5	34.6	13.4
D	42.6	32.3	24.3
$\mathbf{E}$	43.3	5.0	20.8

In addition to fractions A-E, fraction 11 was separated by concentrating the supernatant of fraction E and adding a very large excess of methanol. Fraction 12 was obtained by evaporation of the final supernatant. The latter two fractions seem to be of an irregular character: 11 is very small and shows an extremely large intrinsic viscosity (Table II)<sup>4</sup>; 12 seems to contain essentially low molecular weight contaminants. The original native dextran contained 0.028% N, 0.14% of reducing sugars in terms of glucose, and lost approximately 10% on dialysis through Visking cellulose casing. Some of the low molecular weight comtaminants were probably occluded in fractions 1-10. The actual yields of the fractions are given in Table II (second column). In the third column the weight fractions are adjusted for losses and for the neglect of the centrifuged sediment and of fractions 11 and 12.

sediment and of fractions 11 and 12. (B) Viscosity.—Viscosities of aqueous solutions were measured in an Ubbelohde dilution viscosimeter at 32.7°. In all cases 4 or 5 dilutions were made and  $\eta_{sp}/c$  was extrapolated to  $c \rightarrow 0$ . The intrinsic viscosities are given in Table II.

(C) Light Scattering.—Optical clarification of the polymer solutions proved to be difficult. The customary methods of filtration and centrifugation both failed. (Filtration using Selas 04 and ultrafine glassinter resulted in clogging of the filters; centrifugation led to partial molecular sedimentation of the very large molecules in the comparatively high centrifugal field.) The following procedure was found to be satisfactory: clear water was prepared by distillation and consecutive double filtration (Selas 04 filter). Comparatively concentrated dextran solutions were used as master solutions and were filtered (medium glassinter) in small increments directly into the clear water. The dilu-

(4) The reason for this irregularity is unknown.

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Fraction	Yield, %	Adjusted yield, %	$[\eta],$ cm. <sup>8</sup> g. <sup>-1</sup>	$(Kc/R_0) = 0$ × 10 <sup>9</sup>	$\overline{M}_{W} \times 10^{-7}$	$B  imes 10^{5}$	$(\overline{R_z^2})^{1/2},$ Å.	$\frac{1-6}{\text{non } 1-6}$
1	9.0	9.6	198	1.7	60	1.0	2930	6
2	11.8	12.7	180	3.35	30	2.7	2520	
3	10.5	11.2	170	4.0	<b>25</b>	1.8	2445	
4	4.4	4.7	140	10.0	10	2.0	1835	
5	7.9	8.5	143	10.5	9,5	1.8	1770	18
6	6.8	7.3	130	16.3	6.1	4.2	1360	
7	3.3	3.5	115	18.8	5.3	3.0	1255	
8	4.7	5.1	118	22.8	4.4	3.5	1080	
9	17.5	18.7	105	32.5	3.05	<b>4</b> . <b>2</b>	850	
10	17.5	18.7	86	79.0	1.26		570	35
11	0.4		318					
12	3.0							
Total	96.8	100						
	+2.4 (se	ediment, ren	noved by ce	entrifugation	n)			
Parent polymer		,	151	7.0	14.3 15.5°	1.5	2720	15

TABLE II

<sup>a</sup> Calculated by combination of the molecular weight of the fractions, neglecting 11 and 12.

tions were ordinarily 50-100-fold; hence, the dust concentration was negligible. Concentrations were followed gravimetrically as well as interferometrically (refractive index increment dn/dc = 0.151 at 546 m $\mu$ ). A Phoenix B.S. photometer<sup>5</sup> equipped with a cylindrical cell having 2 flat faces<sup>6</sup> was used. The incident light was vertically polarized; in all cases parallel readings at 436 and 546 m $\mu$  were



Fig. 1.—Reciprocal intensity plot for fraction 1: 0, 436 m $\mu$ ; •, 546 m $\mu$ .

(5) B. A. Brice, M. Halver and R. Speiser, J. Opt. Soc. Am., 40, 768 (1950)

(6) L. P. Witnauer and H. J. Scherr, Rev. Sci. Instr., 23, 99 (1952).

taken. Depolarization was determined at 90°. The angular dependence of scattered light was measured between 20 and 135° with particular emphasis on the low angles. Reciprocal intensity plots  $(kc/R\theta, vs. \sin^2 \theta/2 + kc)$  were drawn.<sup>7</sup> Recently a correction factor for the angular dependence has been proposed which is caused by the reflection of the incident beam.<sup>8</sup> This correction is immaterial for our solutions because the angular dependence has essentially been measured in the forward scattering range (20-90°). Only in the case of fractions 9 and 10 which are of a comparatively small size has the angular range been extended to 135°. As a typical example, the plot for fraction 1 is given in Fig. 1. The final results are tabulated in Table II.

(D) Periodate Oxidations.<sup>9</sup>—Oxidations were made on fractions 1, 5 and 10, and on the original sample. Fraction 1 was sufficiently pure due to repeated precipitations in the course of fractionation. Fractions 5 and 10 and the parent polymer were purified by dialysis. The results are given in terms of 1-6/non 1-6 linkages in Table II.

(E) Cumulative Methanol Precipitation.—The precipitation was conducted at 32.7° in conically shaped tubes. Increments of water-diluted methanol were added to a known volume of solution by means of a microburet. Some of the results are given in Table III.

## TABLE III

## METHANOL PRECIPITATION

Vol. %						
MeOH	40.20	40.31	40.40	40.60	40.84	41.10
Wt. %	Haze	30. <b>2</b>	46.0	62.4	72.5	76.0
precip.	point					

## Results

All experimental results are summarized in Table II. A cumulative molecular weight distribution function has been established in the usual manner based on the yields and molecular weights of the different fractions (Fig. 2).<sup>10</sup>

Because of the lack of sharpness of the fractions (resulting from the experimental difficulty of the fractionation), the distribution function must be considered rather crude. Qualitatively, however, it can be seen that native dextran is very inhomogeneous and, hence, that the distribution is extremely

(7) B. H. Zimm, J. Chem. Phys., 16, 1099 (1948).

(8) H. Sheffer and J. C. Hyde, Can. J. Chem., 30, 817 (1952).

(9) A. Jeanes and C. O. William, J. Am. Chem. Soc., 72, 2655 (1950).

(10) As mentioned above, the sediment and fractions 11 and 12 were not taken into account.



Fig. 2.—Cumulative molecular weight distribution of native dextran.

widespread. Also included in Table II is the hypothetical molecular weight of the original polymer as it results from the combination of the molecular weights of fractions 1–10. Agreement between the calculated and the experimental molecular weight is fairly good. The steepness of the cumulative precipitation (Table III) illustrates again the difficulty of separating different species, *i.e.*, the extremely small dependence of solubility on molecular weight in the extremely high molecular weight range.

The molecular weights are obtained using the customary double extrapolation of  $c \rightarrow 0$  and  $\sin^2\theta/_2 \rightarrow 0$  (Fig. 1). Those values, particularly those of the top fractions, are somewhat uncertain  $(\pm 15\%)$ .

Results at the two wave lengths are in good agreement  $(\pm 5\%)$  and are therefore averaged. (This was also done with the virial coefficient *B* and the root mean square radius of gyration  $(\overline{R^2})^{1/2}$ . To our knowledge, the molecular weight of fraction 1 (600 million) is the highest that has been observed for any polymeric material. However, similarly high molecular weights have been reported lately for other carbohydrate polymers.<sup>11,12</sup>

The virial coefficients B are calculated for  $\sin^2\Theta/_2 \rightarrow 0$  according to the equation

$$Kc/R_0 = 1/M_w + 2Bc$$
 (1)

The radii are obtained (for  $c \rightarrow 0$ ) according to the equation

$$16\pi^2 R^2 / 3\lambda^2 M = \text{(initial slope)} \tag{2}$$

As pointed out by Zimm<sup>13</sup> the thus calculated radii represent a so-called Z-average. In view of the relative inhomogeneity of the fractions, the latter is appreciably higher than the corresponding weight average.

The virial coefficients are all relatively small (of the order of  $1-5 \times 10^{-5}$ ) in comparison, for instance, with the values for polystyrene in butanone (ca.  $1-2 \times 10^{-4}$ ).

The periodate oxidations show an increasing degree of branching with increasing molecular weight. The lowest fraction (10) is considerably more linear than the higher fractions.

## Discussion

Similar investigations have been carried out pre-

(11) B. H. Zimm and C. D. Thurmond, J. Am. Chem. Soc., 74, 1111 (1952).

(12) L. P. Witnauer and F. R. Senti, J. Chem. Phys., 20, 1978 (1952).

(13) P. Outer, C. I. Carr and B. H. Zimm, ibid., 18, 830 (1950).

viously on branched dextran<sup>14</sup> and slightly crosslinked polystyrene.<sup>15</sup> In the first case the degree of branching in terms of 1–6/non 1–6 linkages was independent of molecular weight, which is equivalent to stating that the number of branch points increases proportionally with the molecular weight.

M. Wales<sup>14</sup> has used the viscosity theory of P. Flory<sup>16</sup> in a modified form for branched dextran molecules. According to the equation

$$[\eta]^{2/i}/M^{1/i} = gK^{2/i} + 2C'_{\rm m}\psi_1[1 - (\Theta/T)](M/[\eta])K^{6/i}g^{i/2}$$
(3)

one can plot  $[\eta]^{2/s}/M^{1/s}$  versus  $M/[\eta]$ . As the molecular weight approaches zero the number of branch units per molecule approaches zero and the factor g approaches unity. Hence

$$\lim_{M/[\eta] \to 0} [\eta]^{2/3} / M^{1/3} = K^{2/3}$$
(4)

Wales obtained  $K^{2/3}$  equal  $1 \times 10^{-2}$ , using (100 cm.<sup>3</sup> g.<sup>-1</sup>) as units of intrinsic viscosity. In order to make our results comparable we employ the same units. In our case (Fig. 3) the extrapolation is rather uncertain. However, the possible range of  $K^{2/3}$  appears to be  $5-7 \times 10^{-3}$ . It is important to note that Wales used viscosity average molecular weights, whereas in this study the molecular weights are weight averages. If the molecular weight distribution is relatively wide, which is undoubtedly the case with our fractions, there will be a considerable difference between the two averages. Using the lower viscosity average would increase the intercept and would give a better numerical agreement with Wales' results.



Fig. 3.—Flory-Schaefgen plot: •, fractions; O, parent polymer.

Plotting intrinsic viscosity vs. molecular weight on the customary double logarithmic plot (Fig. 4) gives a curved line with an initial slope of 0.29 and a final one of 0.13. In order to compare our results with previous work,<sup>14</sup> it should be kept in mind that if the curve could be extended to a lower molecular weight range, a considerably steeper slope would most probably be obtained. The decreasing slope (at higher molecular weights) is evidently caused by the increase in the degree of branching which, in turn, decreases the effective volume of the molecules.

From the basic assumption  $[\eta] \propto (\overline{R^2})^{3/2}/M$  Flory<sup>16</sup>

$$\Phi = [\eta] \times M/(\overline{L^2})^{3/2} \tag{5}$$

<sup>(14)</sup> M. Wales, P. A. Marshall and S. G. Weissberg, J. Polymer Sci., 10, 229 (1953).

<sup>(15)</sup> C. D. Thurmond and B. H. Zimm, ibid., 8, 477 (1952).

<sup>(16)</sup> P. J. Flory and T. G. Fox, Jr., J. Am. Chem. Soc., 73, 1904 (1951).

•



 $\log \overline{M}_{w}$ . Fig. 4.—Intrinsic viscosity versus molecular weight: fractions; O, parent polymer.

has derived a universal constant where L is the end-to-end distance for linear molecules. The radius of gyration R can be substituted for L in this case

$$\Phi' = [\eta] \times M/(\overline{R^2})^{3/2} \tag{6}$$

where  $\Phi' = 6^{3/2} \times \Phi = 14.7 \Phi$ . In this form the equation can also be tested for branched dextran molecules. By substituting numerical values for  $\overline{R}^2$  as determined by light scattering, the following results for  $\Phi'$  are obtained (Table IV).

	Тав	le IV				
VALUES FOR FRACTIONS AND PARENT POLYMER						
Fraction	$\Phi' \times 10^{-21}$	Fraction	$\Phi \times 10^{-21}$			
0	21.5	6	31.5			
1	47	7	31			
2	33.5	8	41			
3	29	9	52			
4	22	10	65			
5	24.5					

The numerical value of  $\Phi$  is given by Flory as  $2.1 \times 10^{21}$  which corresponds to  $\Phi' = 31 \times 10^{21}$ . From Table IV it can be seen that  $\Phi'$  varies and differs from the value given by Flory, especially in the case of the extreme fractions. All numerical values of Table IV are affected by the fact that the experimentally determined radii are z-averages. This means that for inhomogeneous fractions the Rvalues will be too large. Hence,  $\Phi'$  will be smaller than it would be if ideally sharp fractions were used. This is illustrated by the low  $\Phi'$  for the unfractionated (most inhomogeneous) sample 0. In a later section of this paper it will be shown that a rough estimate of the inhomogeneity of the fractions, as expressed by the ratio of the z-average to the weight average molecular weight, is of the order of 1.8. If this is taken into account, the  $\overline{R^2}_{z^-}$ values, as obtained from light scattering, can be reduced to a weight average  $R^2$ 

 $\overline{R_z^2} = 1.8 \times \overline{R^2}$ 

Under these conditions, all  $\Phi'$  values given in Table IV would have to be multiplied by a factor of  $1.8^{3/2} = 2.4$ .

It seems to us that the results of Table IV can be interpreted in two different ways.

First, one could assume all the fractions to be comparable with respect to their molecular inhomogeneity. In this case  $\Phi'$  will not be a constant but a function of the molecular weight as it appears to be in Table IV. However, this assumption is certainly not true quantitatively. (The actual differences in the molecular weight distributions of the fractions would be extremely difficult to determine experimentally.) A second approach would be to assume a greater numerical value for Flory's  $\Phi'$  for this particular system and to ascribe all variations of  $\Phi'$  for this particular system and to ascribe all variations of  $\Phi'$  to differences of molecular inhomogeneity. This explanation alone does not seem to be sufficient in view of the fact that whereas the molecular weights of the parent polymer and fractions 3 or 4 are comparable, the inhomogeneity obviously differs appreciably; however,  $\Phi'$  is not affected very greatly. This fact suggests that any difference in the degree of homogeneity between the fractions (which is certainly less than that between the parent polymer and any given fraction) is not likely to cause variations of  $\Phi'$  such as have been observed.

Very probably the variation of  $\Phi'$  is caused by both effects, *i.e.*, by differences of molecular inhomogeneity together with a real dependence of  $\Phi'$ on the molecular weight of those highly branched and extremely large molecules.

Turning to  $R_z^2$  as a function of  $\overline{M}_w$ , we find (Fig. 5) that initially  $\overline{R_z^2}$  appears to increase slightly more than linearly with  $\overline{M}_w$  but tends to level off with increasing degree of branching. This effect in a "non-ideal" solvent is in contrast with previous results of Zimm<sup>15</sup> on branched polystyrene in butanone which were explained in terms of the dependence of R on the virial coefficient. It seems that in our case water is a more nearly ideal solvent for dextran than butanone for polystyrene. Another important fact seems to be the very much stronger increase of the degree of branching with increasing molecular weight in our system.



Fig. 5.—Mean square radius versus molecular weight;  $\bullet$ , fractions;  $\bigcirc$ , parent polymer;  $\bullet$ , hypothetical linear fractions.

It has to be emphasized again that the R-values in Fig. 5 are z-averages. The importance of this is illustrated by the single point representing the parent polymer; since the latter is less homogeneous than are the fractions, this point falls off the curve.

From the preceding discussion it is quite evident that it would be very desirable to be able to estimate the inhomogeneity of the fractions. Very recently Benoit<sup>17</sup> developed a theory based on previous considerations of Zimm which allows one to draw conclusions on polydispersity and branching from the angular dependence of the reciprocal intensity of scattered light (for zero concentration). The important magnitude is the ratio of the initial slope  $(s_0)$  at low angles to the final asymptotic slope  $(s_{\infty})$  at large angles.

It was shown that equation 7 holds for monodisperse linear molecules

$$s_0/s_{\infty} = 2/3 \tag{7}$$

For polydisperse linear molecules

$$s_0/s_{\infty} = 2/3(\overline{M}_{s}/\overline{M}_{w}) \tag{8}$$

For monodisperse branched molecules

$$s_0/s_{\infty} = 2/3(\bar{R}^2/\bar{R}_0^2) \tag{9}$$

R is the radius of gyration of the branched molecule and  $R_0$  of a linear molecule with the same molecular weight.  $\overline{R}^2/\overline{R}_0^2 = g$  in the notation of Stockmayer and Zimm.<sup>18</sup>

For polydisperse branched molecules, we have

$$s_0/s_m = 2/3(\bar{M}_2/\bar{M}_w)(\bar{R}^2/\bar{R}_0^2) = 2/3C$$
 (10)

We have calculated  $s_0/s_{\infty}$  for all our samples wherever this was possible (0, 1-8). The results at the two wave lengths agreed fairly well and were averaged (see second column of Table V). From

TABLE V					
Sample	80/8	A	С	Ø	$\vec{R}_{0^{2}} \times 10^{-6}$
0	0.93	5.5	1.39		
1	. 20	8.5	0.30	0.17	50.5
2	.32	8.5	.47	. 26	24.5
3	.33	9	. 50	.28	21.5
4	.73	7	1.10	.61	5.6
5	.75	7	1.12	.62	5.1
6	1.00	3.5	1.50	.83	2.2
7	1.10	3	1.65	.92	1.7
8	1.15	2.5	1.69	.94	1.25

these figures C was calculated (column 4). Also given in Table V (column 3) is  $A = (kc/R_{\theta})/(kc/R_{\theta})$  at which  $s_{\infty}$  was taken. The numerical

(17) H. Benoit, J. Polymer Sci., 11, 507 (1953).
(18) B. H. Zimm and W. H. Stockmayer, J. Chem. Phys., 17, 1301 (1949).





value of A is also averaged for the two wave lengths. If C is plotted versus  $1/\overline{M}_{w}$  (Fig. 6) it can be seen that for decreasing molecular weights a limit of approximately 1.8 is approached. In this low molecular weight range the fractions of native dextran become increasingly linear (see Table II) so that for the limit  $1/M \rightarrow \infty$  with a certain approximation any deviations from  $s_0/s_{\infty} = \frac{2}{3}$  can be attributed to the polydispersity factor  $\overline{M}_z/\overline{M}_w$ 

$$\lim_{1/M \to \infty} C = 1.8 = \bar{M}_{z}/\bar{M}_{w}$$

As a rough approximation and being aware of its quantitative invalidity we shall now make the simplifying assumption that this figure represents the polydispersity of all our fractions. We thus get maximal numerical values for  $\overline{R^2}/\overline{R_0}^2 = g$  as given in column 5 of Table V. Knowing g, we can calculate  $\overline{R_0}^2$  for hypothetical linear dextran molecules (column 6). These values are also plotted in Fig. 5 and on this double logarithmic plot the relation between  $\overline{R_0}^2$  and  $\overline{M}_w$  seems to be fairly linear with a slope of 1.4.

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## CONCENTRATION OVERPOTENTIAL AT REVERSIBLE ELECTRODES<sup>1,2</sup>

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A study has been made of rate- and diffusion-controlled currents at a planar reversible electrode under applied potentials such that the reverse reaction makes an appreciable contribution to the over-all process. The ferrocyanide, ferricyanide and molybdocyanide systems were studied. The data obtained confirm an earlier prediction that the current under a potential substantially less than that corresponding to "limiting" current will converge at sufficiently long times to the value of the "limiting" current at the corresponding time. Values of the specific rate constants were calculated from the data and enable an approximate determination of the fraction of the ions which react upon impinging on the electrode. The relation between the specific rate constants and the applied potential agrees with the Eyring theory of absolute reaction rates and reasonable values of the activation free energies are obtained.

#### Introduction

Concentration overpotential effects at a planar electrode under potentials corresponding to limiting current flow have been investigated previously by Laitinen and Kolthoff.<sup>3</sup> Here it may be assumed that every ion diffusing up to the electrode surface reacts. The present investigation extends these studies to electrolysis under lower applied potentials where the rate limiting process at the electrode and the reverse reaction make appreciable contributions to the over-all reaction rate. The particular systems studied appeared to have but a single ratedetermining step at the electrode, probably electron transfer, and to be free from complicated side effects other than diffusion.

The primary purpose of the investigation was the experimental verification of the previously proposed boundary condition<sup>4.5</sup>

$$\lim_{x \to 0} c(x, t) = \frac{D}{K} \left( \frac{\partial c}{\partial x} \right)_{x \to 0}$$
(1)

for solving Fick's second law

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \tag{2}$$

for diffusion-controlled reactions. In these equations, c(x, t) denotes the concentration of the reactive species at the distance, x, from the electrode at the time, t, and D and k are the diffusion and specific rate constants, respectively. It is to be noted that the specific rate constant, k, as here used has the dimensions of length times reciprocal time. As previously pointed out,<sup>4</sup> the solutions obtained from eq. 2 using the boundary condition (1) lead to the interesting conclusion that, in the one-dimensional case, the reaction rate should eventually become independent of the fraction of the molecules arriving at the electrode which undergo an electron transfer. Thus the effect of a reaction probability less than unity is confined to an initial period and the observed rate converges to the rate corresponding to a reaction probability of unity after this ini-

(1) Dissertation of H. Rubin submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Polytechnic Institute of Brooklyn. Present address: Department of Chemistry, Syracuse University, Syracuse, N. Y.

(2) Presented at the Meeting-in-Miniature of the Metropolitan Long Island Subsection of the American Chemical Society's New York Section, February, 1953.

(3) H. A. Laitinen and I. M. Kolthoff, J. Am. Chem. Soc., 61, 3344 (1939).

(4) (a) F. C. Collins and G. E. Kimball, J. Colloid Sci., 4, 425 (1949);
 (b) F. C. Collins, *ibid.*, 5, 499 (1950).

(5) P. Delahay, J. Am. Chem. Soc., 73, 4944 (1951).

tial period has expired. This circumstance is of some interest as it tends to mask the effect of reaction probabilities less than unity.

In the present studies, the diffusion and reaction processes in both the forward and reverse reactions were taken into account by solving Fick's law for the interdependent diffusion processes as described in the next section of this paper. The specific rate constants for the forward and reverse reactions then were selected to provide the best fit between the experimental data and the theoretical equation for the current as a function of time. This led to values of the rate constants within a precision of about one per cent.

**Theoretical Discussion.**—Where both forward and reverse reactions must be taken into account, the diffusion processes involved in these reactions interact only at the electrode and the equations to be solved are<sup>6</sup>

$$\frac{\partial c_1}{\partial t} = D_1 \frac{\partial^2 c_1}{\partial x^2}$$
$$\frac{\partial c_2}{\partial t} = D_2 \frac{\partial^2 c_2}{\partial x^2}$$
(3)

with the initial conditions

$$c_1(x, 0) = c_1^{\circ} = \text{constant}$$
  

$$c_2(x, 0) = c_2^{\circ} = \text{constant}$$
(4)

and the boundary conditions

$$D_{1}\left(\frac{\partial c_{1}}{\partial x}\right)_{x=0} = k_{1}c_{1}(0, t) - k_{2}c_{2}(0, t)$$

$$D_{2}\left(\frac{\partial c_{2}}{\partial x}\right)_{x=0} = -D_{1}\left(\frac{\partial c_{1}}{\partial x}\right)_{x=0}$$

$$c_{1}(\infty, t) = c_{1}^{\circ}$$

$$c_{2}(\infty, t) = c_{2}^{\circ}$$
(5)

In eq. 3 to 5 the subscripts 1 and 2 refer to reactant and product, respectively.

The problem to be solved is equivalent to the conduction of heat in two semi-infinite slabs of different thermal conductivities with contact through a film at x = 0. The solution of this problem is well-known<sup>7</sup> and is

$$c_{1}(x, t) = c_{1}^{\circ} + \frac{k_{2}c_{2}^{\circ} - k_{1}c_{1}^{\circ}}{k_{1} + k_{2}(D_{1}/D_{2})^{1/2}} \left\{ \operatorname{erfc}\left[\frac{x}{2(D_{1}t)^{1/2}}\right] - \exp(h_{1}x + h_{1}D_{1}t)\operatorname{erfc}\left[\frac{x}{2(D_{1}t)^{1/2}}\right] + h_{1}(D_{1}t)^{1/2} \right] \right\}$$
(6)

(6) The assumption that D is independent of the concentration is probably a good approximation because the data upon which the rate constants below are calculated begin at two minutes, by which time the major changes in concentration at the electrodes have occurred.

(7) H. S. Carslaw and J. C. Jacger, "Conduction of Heat in Solids," p. 71, Oxford University Press, New York, N. Y., 1947, p. 71. where

and

$$h_1 = \frac{k_1}{D_1} + \frac{k_2}{(D_1 D_2)^{1/2}}$$

$$\operatorname{erfc} y = \frac{2}{\pi^{1/2}} \int_{y}^{\infty} \exp((-z^2) dz$$

The concentration of the product,  $c_2(x, t)$ , is given by a similar expression with the subscripts 1 and 2 permuted.

The current flow is given by the number flux converted to amperes

$$I = n \Im A D_1 \left( \frac{\partial c_1}{\partial x} \right)_{x=0}$$
  
=  $n \Im A (k_1 c_1^\circ - k_2 c_2^\circ) [\exp(h_1^2 D_1 t) \operatorname{erfc}(h_1 \sqrt{D_1} t)]$  (7)

Here n is the number of electrons transferred per ion,  $\mathfrak{F}$  is the Faraday, and A is the area of the electrode. The sign of the current will depend on whether oxidation or reduction is the forward reaction at the electrode.

For saturation potentials, the reverse reaction is negligible and eq. 7 becomes

$$I = n \mathfrak{F} A k_1 c_1^{\circ} \exp((k_1^2 t/D_1)) \operatorname{erfc}[k_1 (t/D_1)^{1/2}] \quad (8)$$

which, for large values of  $(\dot{\kappa}_1^2, t)$ , assumes the limiting form

$$I = n \mathfrak{F} A c_1^{\circ} (D_1 / \pi t)^{1/2}$$
(9)

This is the well-known limiting current equation obtained by considering only the reactant species and using the boundary condition<sup>8</sup>

$$\lim_{c \to 0} c(x, t) = 0 \tag{10}$$

"The process of liquid diffusion may be viewed as a random walk with molecular flights of average length  $\overline{s}$  occurring at a frequency  $\nu$ . The diffusion constant in terms of the random walk concept is then  $1/6 \nu \overline{s^2}$ , where  $\overline{s^2}$  is the mean square flight distance." The frequency of molecular encounters of the diffusing species per unit area at x = 0 is then  $1/6 \nu \overline{sc}(0)$  and the frequency of reaction is then  $\alpha$  $1/6 \nu \overline{sc}(0)$  where  $\alpha$  is the probability of reaction per encounter. The specific rate constant k as defined by eq. 1 is then related to the probability  $\alpha$ as<sup>44</sup>

$$k/D = \alpha/\rho \tag{11}$$

where  $\rho$  is the ratio of the mean square and the mean magnitude of the diffusional flight distance. The magnitude of  $\rho$  in liquids is uncertain, probably lying between  $3 \times 10^{-9}$  and  $5 \times 10^{-8}$  cm. Thus where the probability,  $\alpha$ , is unity, the specific rate constant, k, is of the order of  $10^3$  since  $D \simeq 10^{-5}$ . In this case, the current will obey the limiting law, eq. 10, for times larger than  $10^{-8}$  second. Thus the effect of the initial transient in the current will be observable only for extremely small values of the reaction probability,  $\alpha$ .

## Experimental

The electrolysis was performed in an H-cell of a type previously described.<sup>10</sup> A planar platinum electrode was placed in one arm of the cell and a 0.1 N calomel reference electrode in the other. To prevent a streaming of one solution into the other, electrolytic connection was made through a plug of 3% agar in 0.1 N KCl.

The linear diffusion electrodes<sup>3</sup> were constructed by sandwiching a thin piece of platinum sheet between the ends of two pieces of heavy-walled capillary tubing and bonding the outer edge of the junction with de Khotinsky cement. The electrodes were of two types, one straight for upward diffusion and the other with the electrode on one side of a U for downward diffusion. The straight electrode was used where the product was less dense than the reactant and the Uelectrode for the converse case to minimize convective effects.

The cell was supported in a water-bath thermostated at  $25.0 \pm 0.1^{\circ}$ . The bath was mounted on a suspension platform to minimize convective effects due to vibration. The resistance of the cell was measured with a conduc-

The resistance of the cell was measured with a conductivity bridge of the Klett Manufacturing Company. The electrical circuit used to apply a potential difference across the cell and to measure the current was a modification of that used by Lingane and Kolthoff.<sup>11</sup>

The potential drop across the cell was measured with a Leeds and Northrup Type K2 potentiometer while the cell current was measured with a previously calibrated Leeds and Northrup Type R galvanometer.

The electrode reactions investigated were (1) the oxidation of ferrocyanide, (2) the reduction of ferricyanide, and (3) the oxidation of molybdocyanide. These reactions were studied in the presence of a large excess of potassium chloride which served to eliminate the effect of the electrical potential gradient upon the diffusion of the reactants.

The potassium ferrocyanide, potassium ferricyanide, potassium chloride and mercurous chloride were all of analytical grade. The mercury was commercial triple-distilled. The potassium molybdocyanide was prepared by the standard synthesis<sup>12</sup> and was recrystallized several times from ethyl alcohol. All test solutions were 0.003000 M in the reactant species and 0.1000 M in potassium chloride and were prepared from carefully deoxygenated water. The solutions were freshly prepared before each run and were protected from oxygen by vigorous bubbling of nitrogen previous to the electrolysis. The nitrogen used was freed from oxygen by passing it over hot copper turnings. The electrolysis was carried out in closed vessels thus excluding atmospheric oxygen.

Four to six runs were made at each applied potential and observations of the current were made over a period of 22 minutes. The residual current due to the presence of the indifferent electrolyte was determined by making duplicate runs at each potential on 0.1000 M potassium chloride solutions. The observed values of the current in each of the runs were corrected for the residual currents thus obtained while the applied potentials were continuously corrected for the IR drop of the cell in order to maintain a constant effective applied potential. The ohmic potential drop was only of the order of 2% of the total applied potential in higher currents measured.

## Data and Discussion

A detailed tabulation of the data obtained has been presented elsewhere.<sup>13</sup> The experimental data are summarized in Figs. 1 to 4. In order to compare the data with the theoretical equation 8, it is necessary to resort to a method of trial and error. As the product species was not initially present in any of the runs,  $c_2^0 \simeq 0$ , throughout, and eq. 7 reduces to the form

$$I = n \Re k_1 c_1^{\circ} \exp(y^2 t) \operatorname{erfc} [y(t)^{1/2}]$$
(12)

where

$$y = k_1 / D_1^{1/2} + k_2 / D_2^{1/2}$$
(13)

For arbitrarily selected values of y, the rate constant  $k_1$  can be computed for each experimental

(11) J. J. Lingane and I. M. Kolthoff, J. Am. Chem. Soc., 61, 825 (1939).

(12) L. F. Audrieth, "Inorganic Syntheses," Vol. III, McGraw-Hill Book Co., Inc., New York, N. Y., 1950, p. 160

(13) H. Rubin, Doctoral Dissertation, Polytechnic Institute of Brooklyn, 1953.

<sup>(8)</sup> M. v. Smoluchowski, Ann. Physik, 48, 1103 (1915)

<sup>(9)</sup> S. Chandrasekhar, Rev. Modern Phys., 15, 1 (1943).

<sup>(10)</sup> J. J. Lingane and H. A. Laitinen, Ind. Eng. Chem., Anal. Ed., 11, 504 (1939).



Fig. 1.—Time dependence of the current at various values of the applied potential in the oxidation of ferrocyanide.





value of I and i using eq. 12. The value of y leading to the smallest standard deviation of  $k_1$  is then chosen. The best value of  $k_2$  may then be obtained

#### TABLE I

Diffusion Constants, Initial Concentrations of Reactant Species, Electrode Areas and Limiting Current Constants,  $I\sqrt{t}$ , for the Several Systems Studied

	Diffusion constants, $cm.^2/sec.$ $\times 10^6$		Initial concn., moles/ $cm.^{3} \times 10^{6}$	Elec- trode area,	Current const. X amp
System	$D_1$	$D_2$	c1°	A	$I\sqrt{i}$
Ferrocyanide oxidation	8.04	6.78	3.000	0.0633	28.2
Ferricyanide reduction	6.78	8.04	3.000	0.0611	28.30
Molybdocyanide oxidation	7.38	(7.38)	3.000	0.0620	27.51



Fig. 3.—Time dependence of the current at various values of the applied potential in the oxidation of molybdocyanide.





from eq. 13 as the diffusion constants  $D_1$  and  $D_2$  are found from limiting current data and eq. 9.

In the present studies, values of the diffusion constant for the bulk electrolyte were used in each case although physical considerations indicate that the diffusion constant for the individual reactant ion independent of the counter ion might be more appropriate. However, the error involved is probably no larger than the uncertainties in the bulk diffusion constants themselves and is constant throughout the calculations for any given system. The values of the diffusion constants and other essential data used in these calculations are given in Table I.

Applied potential,	$\left(\frac{k_1}{\sqrt{D_1}}+\frac{k_2}{\sqrt{D_2}}\right)$	$(k_1)$ BV., cm./sec. $\times 10^{+4}$	đ m	(k2) a v	$m \times 10^7$	$\alpha_2 \times 10^7$
		Ferro	cvanide oxidatior	1		
0.0500	0 121	0.608	0 002	2 78	0.90	3 5
. 1000	.110	1.73	.003	1.25	2.55	1.6
.1500	.121	2.86	.004	0.31	4.22	0.39
.2000	.200	5.03	.005	0.20	7.41	0.25
.2500	.328	8.41	.006	0.14	12.4	0.18
		Ferric	yanide reduction	1		
0.1250	0.175	0.90	0.004	3.72	1.12	5.49
. 1000	. 128	1.30	. 002	2.14	1.62	3.15
.0750	. 124	2.04	.005	1.36	2.53	2.00
.0500	. 130	2.90	.008	0.73	3.61	1.08
.0250	. 205	5.19	. 003	0.57	6.45	0.84
		Molybd	ocyanide oxidati	on		
0.4000	0.350	1.86	0.005	7.66°	2.52	10.39
. 4250	.350	3.52	.012	5.98ª	4.77	8 10
. 4500	. 320	5.44	. 011	3.26ª	7.38	4.42
. 4750	. 400	8.78	. 0 <b>0</b> 9	$2.09^{a}$	11.91	2.84
. 5000	. 435	10.82	. 014	1.00ª	14.67	1.36

TABLE II SUMMARY OF THE FINAL RESULTS GIVING SPECIFIC RATE CONSTANTS,  $k_1$  and  $k_2$ , the Mean Standard Deviation of  $k_1$ ,  $\sigma_m$ , and the Electrode Reaction Probabilities,  $\alpha_1$  and  $\alpha_2$ 

<sup>a</sup> These values were computed assuming  $D_1$  to be equal to  $D_2$ . A value of the diffusion constant,  $D_2$ , was not available in the literature.

The calculated values of the rate constants  $k_1$  and  $k_2$  for the oxidation of ferrocyanide ion at various applied potentials are given in Table II and illustrated in Fig. 5, as a logarithmic plot vs. the applied potential. The mean standard deviations of  $k_1$  corresponding to the finally selected values of y are also given in Table II. The deviations lie within the expected precision of the experimental measurements and indicate the validity of eq. 7 as an expression for the current and thus the applicability of the boundary condition (1) for the present electrode process.

Now  $k_1$  and  $k_2$  for the reduction of ferricyanide should be equal to  $k_2$  and  $k_1$ , respectively, for the oxidation of ferrocyanide at the same applied potential. These rate constants, together with the corresponding values of  $\alpha$ , the fraction of the ions reacting at the electrode, are given in Table II and Fig. 5. From Fig. 5, it appears that the agreement between these two sets of calculated rate constants is roughly of the same order as the internal agreement within each set. In spite of the careful preparation of the reagents, the absolute values of the rate constants may be systematically in error due to very small amounts of impurities in the reagents and by contamination by the deKhotinsky cement.

The calculated rate constants and reaction probabilities,  $\alpha$ , for the oxidation of molybdocyanide are given in Table II and Fig. 3 and have the same dependence upon the applied potential as in the ferrocyanide-ferricyanide case. It will be noted that the values of  $\alpha$  corresponding to the tabulated values of  $k_1$  are extraordinarily small in all cases.

The relation between the rate constant,  $k_1$  and  $k_2$ , for an oxidation electrode process and the overpotential is given by the absolute reaction rate theory and may be expressed as

$$k_{1}' = \frac{kT}{h} \exp\left(-\Delta F_{1} \neq /RT\right) \exp\left[\beta n \Im(E - E^{\circ})/RT\right] \quad (14)$$

$$k_2' = \frac{kT}{h} \exp\left(-\Delta F_2 \neq /RT\right) \exp\left[-(1-\beta)n\mathfrak{F}(E - E^\circ)/RT\right]$$
(15)

where  $\Delta F_1^{\pm}$  and  $\Delta F_2^{\pm}$  are the respective standard activation free energies, E is the applied single electrode potential,  $E^{\circ}$  is the standard electrode poten-



Fig. 5.—The logarithmic values of the rate constants,  $k_1$  and  $k_2$ , at various values of the applied potential for the oxidation-reduction of the ferrocyanide-ferricyanide couple. The points,  $o \bullet$ , were obtained with the microelectrode as an anode and the points,  $o \bullet$ , with the microelectrode as a cathode. The second half-cell was a 0.1 N calomel electrode.

tial for the given half reaction and  $\beta$  is the fraction of the potential promoting the forward reaction. Here  $E^{\circ}$  is the potential of the given half-cell with all substances in their standard states as customarily defined. The rate constants  $k_1$  ' and  $k_2$ ' are the conventional first-order chemical rate constants and have the dimensions of reciprocal time. They may be readily calculated from the virtual rate constants  $k_1$  and  $k_2$  which are defined by eq. 1. At any instant, the number of moles of ions available for electrolysis at the electrode is  $A \rho c(0, t)$  where  $\rho$ is the order of the mean diffusional flight length. From eq. 7, it is clear that  $k_1$  and  $k_2$  must be divided by  $\rho$  in order to become equal to the conventional first-order rate constants. For this purpose,  $\rho$  has been assumed to be equal to  $10^{-8}$  cm.

It should be noted that the potential difference,  $E - E^0$ , is the potential of the half-cell referred to the standard potential as zero, rather than the overpotential where the zero of potential is taken as the reversible potential at the given concentrations of reactant and product. The calculated activation free energies  $\Delta F_1^{\pm}$  and  $\Delta F_2^{\pm}$  will depend on the choice of the standard states of the substances involved as this will determine the reference zero of potential  $E^0$ . In addition, calculated activation free energies will depend on the magnitude chosen for  $\rho$ . The uncertainty in  $\rho$  is of the order of 3 which leads to an uncertainty of the order of 2 kcal./ mole in the calculated activation energies. Under the present convention, with both reactant and product present at unit activity and with the potential applied to the half-cell equal to the standard electrode potential, then  $E - \dot{E}^0 = 0$ , no current flows,  $k_1 = k_2$ , and hence the two calculated activation free energies should be equal.

As  $k_1$  and  $k_2$  are separately determined from the experimental data, Fig. 4 enables independent calculation of  $\Delta F_1^{\pm}$  and  $\Delta F_2^{\pm}$  as well as  $\beta_{obs}$  and  $(1 - \beta)_{obs}$ . The values so obtained are presented in Table III. The calculated activation free energies are of a reasonable order of magnitude and agree within 2 kcal. Similarly the values of  $\beta_{obs}$ and  $(1 - \beta)_{obs}$  are of the order of 0.5 as might be expected from a priori calculations. Thus the data

obtained appear to be consistent with eq. 14 and 15.

## TABLE III

ACTIVATION ENERGIES OF THE FORWARD AND REVERSE Reactions  $\Delta F_1^{\pm}$  and  $\Delta F_2^{\pm}$ , and the Fraction  $\beta_{obs}$  of the Electrical Potential Promoting the Forward Reaction. The Fraction  $(1 - \beta)_{obs}$  Promoting the REVERSE REACTION, AS CALCULATED, ALSO IS GIVEN

System	$\Delta F_1 \ddagger$ , kcal./ mole	$\Delta F_2 \ddagger$ , kcal./ mole	ßoba	(1 - β)odr
Ferrocyanide oxidn.	12.8	11.0	0.41	0.42
Molybdocyanide oxidn.			0.46	

Conclusion.—The agreement between theory and experiment shown by the small magnitude of the standard deviations of the specific rate constants at the various applied potentials shows that eq. 7 is a correct expression for the current as a function of time. Hence eq. 1 constitutes an appropriate boundary condition for electrode processes which are partially or completely diffusion-controlled. Where the applied potential is so small that only a fraction,  $\alpha$ , of the ions diffusing up to the electrode react, the observed current is smaller than the current corresponding to saturation potential only during an initial induction period and becomes equal to the saturation current for longer times. The fraction,  $\alpha$ , is required to be of the order of  $10^{-6}$  or less in order for this initial period to be sufficiently long for measurements to show a reduction of the current.

While the data for  $\alpha$  and the calculated specific rate constants show excellent internal precision, the absolute values of these quantities may be somewhat in doubt because of the possible presence of trace amounts of capillary-active substances at the electrode.

The calculated specific rate constants depend on the applied potential in the manner predicted by the Eyring absolute reaction rate theory. The activation free energies and the constants  $\beta$  and  $(1 - \beta)$  $\beta$ ) describing the fractions of the applied potential which promote the forward and reverse reactions respectively are found to be of the correct order of magnitude and to be internally consistent.

## FORMULA AND PRESSURE-TEMPERATURE RELATIONSHIPS OF THE HYDRATE OF DICHLOROFLUOROMETHANE<sup>1</sup>

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The pressure-temperature relationships of various Freon 21 hydrate systems were determined. The formula of Freon 21 hydrate was found to be CHCl<sub>2</sub>F.17  $\pm$  0.5H<sub>2</sub>O by the method of de Forcrand.

The formula and phase relationships of Freon 21 hydrate were determined as part of a series of studies intended to clarify further the nature of the hydrocarbon-type or lattice hydrates.

(1) From a thesis by William P. Banks, submitted in partial fulfillment of the requirements for the Ph.D. degree, 1953.

## Experimental

Materials.-Freon 21 of 99.0% purity obtained from The

Matheson Company was used. Apparatus.—The apparatus for obtaining the pressure-temperature relationships of Freen 21 hydrate consisted principally of a reaction vessel located in a constant temperature bath and connected to a mercury manometer.


Fig. 1.—Pressure-temperature relationships of Freon 21 hydrate: EFGA, Freon 21 hydrate-H<sub>2</sub>O-rich soln. (liq.)-vapor; AB, Freon 21 hydrate-ice-vapor; EC ( $_{O}$ ), Freon 21 hydrate-Freon 21-rich soln. (liq.)-vapor; EC ( $_{O}$ ), H<sub>2</sub>O-rich soln. (liq.)-Freon 21-rich soln. (liq.)-vapor; EC ( $_{O}$ ), H<sub>2</sub>O-rich soln. (liq.)-Freon 21-rich soln. (liq.)-vapor; EC ( $_{O}$ ), H<sub>2</sub>O-rich soln. (liq.)-vapor; FD ( $_{O}$ ), Freon 21 (liq.)-vapor.

The temperature of the bath was controlled to within 0.01°. The reaction vessel consisted of a 500-ml. Pyrex roundbottom flask to which had been fused a Pyrex reducing fitting. The buoyancy of a partly filled flask of this capacity overcame the weight of the flask and its contents, resulting in a more secure and leakproof attachment to the glass tubing than otherwise possible. The vessel was connected to the 8 mm. o.d., 6 mm.i.d. Pyrex tubing comprising the remainder of the system by Tygon tubing which had been treated to hold a vacuum by exposure to chloroform or carbon tetrachloride with several coats of spar varnish to further decrease their permeability to gases. The Tygon fubing was slipped over glass tubing coated with a high-vacuum grease (Silicone) and sealed by wrapping with wire. Easily flexible joints which did not leak after prolonged standing and flexing were thus formed. Mercury seal stopcocks were used exclusively. Shaking of the reaction flask was necessary to obtain equilibrium pressures and was effected by a shaker device made from an electric stirrer motor and a cam. Pressure was measured with a mercury filled manometer and a cathetometer to within 0.3 mm. of mercury.

**Procedure.**—The equilibrium pressure established for a definite temperature was determined by the following procedure.

A known weight of distilled water was added to the reaction flask and the total pressure of the system was reduced to less than 0.5 mm. of mercury by an oil vacuum pump. The formation of large bubbles from dissolved gases in the mercury and the consequent forcing of mercury through the tubing was prevented by forming a vacuum while an activated Tesla coil leak tester was moved along the manometer. Small bubbles were released continuously. Freon 21 was added and liquefied by cooling the reaction flask. Hydrate was readily formed by partial evacuation of a system consisting of Freon 21 (liquid) and water (liquid) at  $0^{\circ}$ . It is thought that cooling accompanying the rapid evaporation of the Freon 21 caused the formation of small ice crystals which seeded hydrate. Ice is a good seeding agent for many hydrocarbon-type hydrates, and small amounts of the hydrate are more satisfactory than ice.<sup>3</sup> Pressures reproducible to within 0.5 mm. of mercury were obtained for a given temperature but different total compositions. The desired temperatures were obtained both by increasing and decreasing the temperature of the reactants. Equilibrium pressures were obtained for the hydrate-icevapor system only when the hydrate was well dispersed in ice.

#### **Results and Discussion**

In discussions of hydrate equilibria the following phase designations will be used: H for hydrate,  $L_1$  for water-rich liquid,  $L_2$  for hydrate former-rich liquid, I for ice and V for vapor.

The data obtained for the Freon 21-water system are recorded in Tables I to V inclusive and are plotted in Fig. 1. The data may be represented over a limited temperature range by the equation, log P = A/T + B. The values of A and B required for the equation to fit the data are recorded in Table VI. A hydrocarbon-type hydrate existed at temperatures below 8.61  $\pm$  0.04°; the total pressure of the H-L<sub>1</sub>-V system at this temperature was  $758.6 \pm 1.8$  mm. of mercury absolute. The transition H–I–V to H–L<sub>1</sub>–V occurred at  $-0.13~\pm$  $0.03^{\circ}$ ; the total pressure of the system at this temperature was  $110.2 \pm 0.5$  mm. of mercury absolute. The curves for the equilibria,  $L_1-L_2-V$ and  $H-L_2-V$ , were indistinguishable. The curves for the equilibria, Freon 21 (liquid)-vapor and  $L_1-L_2-V$ , were found to almost coincide; at a temperature of 1.11° (1/T°K. = 0.0036460) the  $L_1-L_2-V$  curve is 3.8 mm. of mercury above the Freon 21 (liquid)-vapor curve, and at 7.11°  $(1/T^{\circ}K) = 0.0035680$  the L<sub>1</sub>-L<sub>2</sub>-V curve is 6.6 mm. of mercury above the Freon 21 (liquid)vapor curve. There was no tendency for H-L1-V to persist in regions of the phase diagram where

<sup>(2)</sup> J. E. Sampson, Ph.D. Thesis, University of Oklahoma, 1950.

<sup>(3)</sup> J. E. Sampson, M.S. Thesis, University of Oklahoma, 1948.

		IADL	51	
Freon	<b>21</b>	HYDRATE-WATER-	RICH SOLUTION	(Liquid)-
		VAPO	R	
Τ, °	°C.	Pressure, cm.	T, °C.	Pressure, cm.
0.0	)9	11.56	3.50	24.34
0.2	26	12.10	4.43	29.93
0.3	33	12.16	4.70	31.44
0.8	34	13.56	5.65	39.12
0.9	98	14.13	5.72	39.56
1.1	19	14.70	6.10	43.22
1.5	55	16.13	6.24	45.03
1.7	76	16.68	6.97	52.46
2.3	32	18.84	7.04	5 <b>2</b> .96
2.3	34	18.91	7.73	61.62
2.7	70	20.42	7.92	64.75

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TABLE II

FREON 21 HYDRATE-ICE-VAPOR

<i>T</i> , °C.	Pressure, cm.	<i>T</i> , °C.	Pressure, cm.
-3.82	8.91	-1.73	10.04
-3.43	9.21	-1.68	10.14
-2.89	9.30	-1.56	10.29
-2.74	9.58	-0.91	10.59
-2.58	9.62	-0.88	10.52
-2.50	9.62	-0.61	10.74
<b>-2</b> .09	9.81	-0.21	10.97
-2.03	9.92	-0.16	11.00

#### TABLE III

FREON 21 HYDRATE-FREON 21-RICH SOLUTION (LIQUID)-VAPOR

<i>T</i> , °C.	Pressure, cm.	<i>T</i> , °C.	Pressure, em.
-0.44	52.99	4.18	<b>63</b> .72
-0.08	53.60	4.45	64.41
+0.79	55.55	4.99	65.78
1.03	56.16	5.43	67.00
1.60	57.46	5.99	67.75
1.78	57.90	6.45	<b>69</b> .69
2.29	59.14	6.97	71.15
2.83	60.31	7.40	72.35
3.25	61.47	7.83	73.56
3.40	61.75		

# TABLE IV

#### FREON 21 (LIQUID)-VAPOR

	•		
<i>T</i> , °C.	Pressure, cm.	<i>T</i> , °C.	Pressure, cm.
-0.49	52.51	4.00	62.84
+0.31	54.19	4.70	64.67
0.72	55.09	5.01	65.34
1.20	56.24	6.06	68.14
2.16	58.36	6.56	69.56
2.32	58.76	7.08	70.93
2.88	60.12	7.95	73.34
3.29	61.11	8.82	75.82

# TABLE V

WATER-RICH SOLUTION (LIQUID)-FREON 21-RICH SOLUTION (LIQUID)-VAPOR

	(11.4012)	, , ,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	
<i>T</i> , ℃.	Pressure, cm.	<i>T</i> , °C.	Pressure, cm.
1.02	56.15	4.96	65.81
2.35	59.32	6.0 <b>2</b>	68.45
3.11	61.07	7.05	71.40
4.03	63.37	7.95	73.93

H–I–V were the stable phases; however, the equilibria,  $L_1-L_2-V$ , persisted in regions where  $H-L_1-V$  or  $H-L_2-V$  were the stable phases, and frequently the shift from metastable to stable equilibria would occur only upon seeding with ice or hydrate.

# TABLE VI

Evaluated Constants for Pressure-Temperature Relationships of Freon 21 Hydrate Expressed in Terms of the Equation  $\log P$  (mm.) =  $A/T^{\circ}K$ . + B

Equilibria	A	В	Curve in Fig. 1	Approxi- mate temp. range, °C.
Freon 21 hydrate-	$-7150 \pm 80$	28.230	GA	0.0-2.8
water-rich soln. (1	iq.)-vapor			
Freon 21 hydrate-	$-7658\pm75$	30.057	EFG	4.8-8.6
water-rich soln. (li	iq.)-vapor			
Freon 21 hydrate-	$-1860\pm85$	8.8553	AB	-4.0-0.0
ice-vapor				
Freon 21 hydrate-	$-1340~\pm~40$	7.6366	$\mathbf{EC}$	-0.5 - 7.8
Freon 21-rich soln	. (liq.)-vapor			
Freon 21 (liq.)-	$-1340~\pm~40$	7.6333	FD	-0.5-8.8
vapor				
Water-rich soln.	$-1340\pm40$	<b>7.63</b> 66	$\mathbf{EC}$	1.0-8.0
(liq.)-Freon 21-ric	h soln. (liq.)-va	por		

The formula of Freon 21 hydrate was determined by an approximate method of de Forcrand<sup>4</sup> as illustrated below.

The decomposition of 1 mole of Freon 21 hydrate to yield a vapor phase and an  $L_1$  phase is represented by the equation

# $(CHCl_2F \cdot xH_2O) \text{ (solid)} = (1 - a)(CHCl_2)$

$$- a)(\mathrm{CHCl}_{2}\mathrm{F})_{\mathrm{V}} + a(\mathrm{CHCl}_{2}\mathrm{F})_{\mathrm{L}_{1}} + b(\mathrm{H}_{2}\mathrm{O})_{\mathrm{V}} + (x - b)(\mathrm{H}_{2}\mathrm{O})_{\mathrm{L}_{1}} + \Delta H_{1} \quad (1)$$

The number of moles of water vapor, b, and the number of moles of Freon 21, a, dissolved in the water (liquid) are assumed to be negligible. Equation 1 reduces to the following

#### $(CHCl_2F \cdot xH_2O)(solid) =$

$$(CHCl_2F)_V + (x)(H_2O)_{L_1} + \Delta H_1$$
 (2)

If the equilibrium constant of the latter reaction is taken to be equal to the total dissociation pressure of the hydrate, the Clausius-Clapeyron equation is applicable to this equilibrium, and log  $P = -\Delta H_1/2.303RT + B$ . From the slope of curve GA (Fig. 1)  $\Delta H_1$  representing the heat of decomposition of a mole of hydrate to  $(CHCl_2F)_V$ and water (liquid) may be found.

$$\Delta H_1 = -(2.303)(1.987)(-7150) \pm 80) = +32720 \pm 370$$

The decomposition of Freon 21 hydrate into ice and vapor is represented by the equation

 $(CHCl_2F \cdot xH_2O)(solid) =$ 

 $(\mathrm{CHCl}_{2}\mathrm{F})_{\mathrm{V}} + b(\mathrm{H}_{2}\mathrm{O})_{\mathrm{V}} + (x - b)(\mathrm{H}_{2}\mathrm{O})_{\mathrm{I}} + \Delta H_{2} \quad (3)$ 

The quantity b is again taken to be negligibly small; thus eq. 3 reduces to

 $(CHCl_2F \cdot xH_2O)(solid) =$ 

$$(\mathrm{CHCl}_{2}\mathrm{F})_{\mathbf{V}} + x(\mathrm{H}_{2}\mathrm{O})_{\mathbf{I}} + \Delta H_{2}$$
 (4)

From the slope of curve AB (Fig. 1)  $\Delta H_2$ , the heat of decomposition of a mole of hydrate to ice and  $(CHCl_2F)_{\nu}$ , may be obtained.

$$\Delta H_2 = -(2.303)(1.987)(-1860 \pm 85) = +8512 \pm 390$$

By subtraction of  $\Delta H_2$  from  $\Delta H_1$  the heat of (4) R. de Forerand, Compt. rend., 134, 835 (1902). fusion of the number of moles of water per mole of hydrate is obtained. Division of this quantity by the heat of fusion of a mole of ice (1430 cal./g. mole) yields the number of moles of water per mole of hydrate or  $16.93 \pm 0.53$ . This result compares favorably with the formula, CHCl<sub>2</sub>F·17H<sub>2</sub>O, predicted by Claussen.<sup>5,6</sup>

(5) W. F. Claussen, J. Chem. Phys., 19, 259 (1951).

(6) W. F. Claussen, ibid., 19, 662 (1951).

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# ELECTRODE POTENTIALS IN FUSED SYSTEMS. I. SODIUM HYDROXIDE<sup>1,2</sup>

# By Kurt H. Stern and Jack K. Carlton

The Institute of Science and Technology, University of Arkansas, Fayetteville, Arkansas Received January 16, 1954

Potentials of silver, copper, nickel, cobalt and tungsten were measured in fused sodium hydroxide over the temperature range 340-600°, using gold as reference electrode. Potential-time curves were obtained. Potential changes are related to reactions occurring at the electrodes.

#### Introduction

This study was undertaken to determine if e.m.f. measurements offered a convenient method of detecting reactions between metals and molten compounds. Sodium hydroxide was selected because its reactions with various metals had been investigated previously<sup>3</sup> and because some work is currently being carried on in this Laboratory on the reaction between nickel and sodium hydroxide at high temperatures. In addition, we hoped to gain information of more general interest on the potentials of metals in foreign ion systems.

Virtually no work of this kind has been reported in the literature although several workers have studied foreign ion cells in aqueous solutions.4-8 The work of MacGillavry and co-workers on the potential of nickel in foreign ion solutions, including aqueous sodium hydroxide, is of interest and will be referred to later. Lux has studied reactions in various melts, particularly on the addition of oxides to a  $K_2SO_4$ -Li<sub>2</sub>SO<sub>4</sub> eutectic at 950°.<sup>9</sup> He found that gold electrodes could be used to follow the progress of a reaction by measuring the change in potential between a reference and an indicator electrode. Recently Hill and Porter<sup>10</sup> have studied the electrode potentials of various metals in a K<sub>2</sub>SO<sub>4</sub>-Li<sub>2</sub>SO<sub>4</sub> melt in the presence of oxygen, using an oxygen electrode as reference.<sup>10</sup> In that case, however, the system

(1) Presented in part at the Southeast-Southwest Regional Conclave of the American Chemical Society, New Orleans, December 1953.

(2) The authors wish to acknowledge the financial support of the U. S. Air Force under sub-contract AF 18(600)-960.

(3) M. Le Blanc and L. Bergman, Ber., 42, 4728 (1909).

(4) A. R. Tourcky and S. E. S. El Wakkad, J. Chem. Soc., 740, 749 (1948).

(5) L. Colombier, Compt. rend., 199, 273, 408 (1934).

(6) D. MacGillavry, J. H. Rosenbaum and R. W. Swenson, J. Electrochem. Soc., 99, 22 (1951).

(7) D. MacGillavry, J. Chem. Phys., 19, 1499 (1951).

(8) D. MacGillavry, J. J. Singer and J. H. Rosenbaum, *ibid.*, 19, 1195 (1951).

(9) H. Lux, Naturviss., 28, 92 (1940); Z. Elektrochem., 52, 220 (1948); ibid., 53, 43 (1949).

(10) D. G. Hill and B. Porter, THIS JOURNAL, in press.

is reversible with respect to oxide ion and no longeconstitutes a true foreign ion melt.

In the present work, oxygen was excluded from the system to preclude the possibility of reaction between the metal electrodes and atmospheric oxygen.

### **Experimental Part**

Materials.—Metal electrodes were obtained from various sources. All were spectroscopically pure. Copper, tungsten and silver electrodes were made from No. 10 B. and S. gage wire. Each nickel electrode consisted of a solid cylinder 1/4 inch in diameter and 1 inch long, welded to a rigid nickel wire. Cobalt electrodes were prepared from cobalt rondelles into which nickel wires were hammered to provide connection to the external leads. The sodium hydroxide used in most of the measurements was Mallinckrodt Analytical Reagent Grade containing about 2% sodium carbonate. In a few measurements a special grade of sodium hydroxide containing less than 0.1% sodium carbonate was used. This was kindly given to us by Dr. Overholzer of the Oak Ridge National Laboratory. Experimental Methods.—The construction of the furnace is shown in Fig. 1. All openings in the glass cover were

Experimental Methods.—The construction of the furnace is shown in Fig. 1. All openings in the glass cover were made as small as possible to prevent contamination of the system by air. The only openings in the furnace cover were those for the two electrodes, thermocouple wires and heater wires. These openings also served as exit for the gas passed through the system.

All measurements were made in a gold crucible since gold is the only metal known not to react with sodium hydroxide at high temperatures.

A heavy (No. 10) gold wire was fused to the crucible for use as electrode. The procedure in carrying out most of the measurements was as follows. The gold crucible was placed in the furnace and filled with 40-50 g. of sodium hydroxide. The furnace was then closed and the heating current turned on, while argon which had been bubbled through a potassium pyrogallate solution, concentrated sulfuric acid, and passed through a drying tube filled with calcium chloride, was passed through the cell. After the desired temperature had been reached, the metal electrode under study was lowered into the melt and the potential between it and the gold electrode measured by means of a Leeds and Northrup K-2 potentiometer. The temperature of the melt was measured by a chromel-alumel thermocouple whose hot junction was kept in the top of the furnace and could be lowered into the melt. Since the measured electrode potentials were relatively insensitive to temperature changes no attempt was made to control the temperature more accurately than  $\pm 3^\circ$ .



Fig. 1.—Apparatus for the measurement of electrode potentials.

When a gold wire was inserted in the melt small potentials (15-20 mv.) were measured, indicating a thermal gradient between the center and wall of the crucible. No corrections were made for this thermogalvanic potential or for any of the junction potentials in the system. Several runs were made to establish the reproducibility

Several runs were made to establish the reproducibility of the results. Using both copper and tungsten electrodes, the steady-state potentials of each of these metals could be duplicated to within  $\pm 0.5$  mv. Potential values were not affected by the pretreatment of the electrodes. Polishing with steel wool or emery paper, followed by washing in distilled water and drying with tissue paper, was sufficient.

At the end of each run the melt was dissolved in water and the crucible cleaned by soaking in concentrated nitric acid for several hours, washing with distilled water and drying at 110°. Analyses for metal content of the dissolved melts were carried out in many of the runs.

Figures 2 and 5 show the time-potential curves for cobalt, copper, nickel and silver. All the potentials shown are negative relative to gold. Our observations on the individual metals are given below. Nickel.—Up to 500° nickel does not react with molten sodium hydroxide if oxygen is excluded from the system. In the presence of average and average of average of

Nickel.—Up to 500° nickel does not react with molten sodium hydroxide if oxygen is excluded from the system. In the presence of even small concentrations of oxygen a black oxide coating forms on the electrode. During the formation of this oxide, probably NiO, which takes place very rapidly, the electrode potential drops from its initial value to zero. Analysis of the melt by the usual analytical methods shows less than 0.5 mg. of nickel ion, indicating that the potential drop is due only to reaction(s) occurring on the electrode surface.

It is interesting to note that the shape of the time-potential curves is quite similar to that of similar curves reported by MacGillavry and co-workers<sup>8</sup> for nickel in aqueous hydroxide solution. However, in aqueous solution the curve rises over a longer time interval.

Cobalt.—The behavior of cobalt is essentially like that of nickel. However, the metal reacts with sodium hydroxide at somewhat lower temperatures than does nickel. The slow decrease of potential at 535° is accompanied by a gradual accumulation of sludge in the melt. Cobalt is more resistant to air oxidation than nickel as shown by the relatively slight change in potential when oxygen is allowed to leak into the system.

Silver.—The potential of silver in sodium hydroxide is more sensitive to very low concentration of impurities in the melt than that of any other metals investigated. The heavy curves of Fig. 5 show the behavior of the metal in Mallinckrodt Analytical Reagent Grade sodium hydroxide. The potential decreases so rapidly from its initial value that no accurate measurements were possible. Thus the potential at zero time is quite uncertain. It was noted, however, that at the end of each run the electrode was coated with a dull white substance. Since the Mallinckrodt reagent con-



Fig. 2.—Electrode potentials of cobalt in molten sodium hydroxide:  $t_1$  °C.;  $\bigcirc$ , 350;  $\blacktriangle$ , 430;  $\blacktriangledown$ , 535.



Fig. 3.—Electrode potentials of nickel in molten sodium hydroxide: t, °C.;  $\bigcirc$ , 420;  $\bigtriangledown$ , 450;  $\triangle$ , 470;  $\bullet$ ,  $\blacktriangle$ , 580.

tains 2% sodium carbonate it was considered possible that the coating was silver carbonate. Measurements in a special grade of sodium hydroxide containing 0.01% sodium carbonate, kindly given to us by the Oak Ridge National Laboratory, gave the time potential-curve shown as the light curve in Fig. 5. Fisher Certified Reagent Grade, containing 0.1% sodium carbonate gave similar results. However, the addition of sodium carbonate to a melt of this reagent did not change the shape of the curve although it raised the potential. It was then noted that the Mallinckrodt Reagent contained 0.01% chloride whereas the Fisher reagent contained 0.00%. When a small amount of chloride is added to the Fisher reagent the results are the same as for Mallinckrodt sodium hydroxide. Hence, we conclude that the coating on the electrode responsible for the rapid decrease of potential is silver chloride.

Tungsten.—Tungsten reaches its final potential very quickly. Its value is 1.05 volts, almost independent of temperature. The metal behaves the same in both the presence and absence of oxygen. The addition of sodium tungstate to the melt produces no change in potential. Up to 500° tungsten dissolves slowly or not at all in sodium hydroxide since less than 0.5 mg. of tungsten is found in the melt. An appreciable amount of current can be drawn from the cell W/NaOH/Au without changing its potential. In one experiment six milliamperes were drawn from the cell for an hour. The cell regained its initial potential a few minutes after the circuit was opened. Copper.—This metal does not react with sodium hydroxide below  $400^{\circ}$  as shown by the steady potentials measured. At 535° the metal reacts slowly. Potentials are observed to fall slowly and a blue color appears in the melt. These observations are in agreement with those of Bergman and LeBlane<sup>3</sup> who report no reaction at 435° but find the melt becoming dark blue at 568°.

In the presence of trace amounts of oxygen (such as are present in unpurified tank argon) copper shows rapid blackening due to oxide formation. This is shown by the light curve in Fig. 4. Several measurements of this particular phenomenon show that the shape of the potential curve<sub>2</sub>accompanying oxidation is quite characteristic of copper. In addition to the initial relatively flat part of the curve which may last up to one hour and probably corresponds to the buildup of a critical thickness of oxide, the decreasing part of the curve shows an inflection at approximately 0.3 volt. So far we have no evidence as to the meaning<sup>T</sup> of this inflection.



Fig. 4.—Electrode potentials of copper in molten sodium hydroxide: t, °C.;  $\square$ , 340;  $\triangle$ , 400;  $\bullet$ , 535; —, in the presence of traces of  $O_2$  at 500°.

It is very difficult to determine the electrode reaction(s) responsible for the measured potentials, primarily because analysis of the melts, at the temperature under investigation, cannot be carried out. Hence we do not know what species are present in the system when the potential is being measured. It is only possible to dissolve the melt in water and analyze the solution.

For example, one attempt was made to study the potential dependence of the copper electrode on the copper ion concentration in the melt. Various concentrations of anhydrous CuBr<sub>2</sub> in NaOH in the range 0.005 to 0.05 molal were prepared and the potential of the copper electrode measured as above. Qualitatively, the potential decreased with increasing copper ion concentration. However, CuBr<sub>2</sub> reacts with molten NaOH according to the equation 2NaOH + CuBr  $\rightarrow$  2NaBr + H<sub>2</sub>O + CuO. Hence, the copper ion concentration decreases slowly from its initial value and the potential finally reaches the value it has in the absence of added CuBr<sub>2</sub>.

Analysis of solutions initially free from copper showed that they contained copper concentrations from 0.0001 to 0.003 molal with no change in measured potential.

When copper is made the anode of the cell Cu/NaOH/Au by imposing an external potential it is found that only about 10% of the total current passed results in the solution of copper from the electrode. For example, in one run 3  $\times$  10<sup>-4</sup> equivalent of copper was found in the melt or plated out on the gold cathode when 4  $\times$  10<sup>-3</sup> faraday of electricity had been passed. However, some gas evolution was observed at the anode. Similarly, when gold was made the anode, the resulting melt was less than 10<sup>-6</sup> molal in gold.

#### Discussion

From the above observations the following generalizations may be made:



Fig. 5.—Electrode potentials of silver in sodium hydroxide: t, °C.; □, 350; △, 400; ▽, 500.

1. Reproducible electrode potentials of copper, nickel, cobalt and tungsten can be measured in sodium hydroxide, using gold as reference electrode. No constant potential was obtained for silver but the highest value on a time-potential curve is reproducible.

2. Any change in potential may be due either to film formation on the electrode or to the solution of the metal in the melt. The potential change indicative of film formation is much more rapid than for solution.

3. Up to  $400^{\circ}$  none of the metals dissolves in sodium hydroxide to an appreciable extent in the absence of oxygen. At 500° none of the metals except copper does, and the latter only slowly. These results are in general agreement with the data of Bergman and LeBlanc<sup>3</sup> and a concurrent study of the high temperature reaction between nickel and sodium hydroxide carried on in our laboratory.<sup>11</sup>

4. The metals do not constitute polarizable electrodes in the sense that mercury in contact with an aqueous solution is polarizable. For example, when a steady potential has been reached the cell will recover from brief charges of several tenths of a volt in a few minutes. Hence, a mechanism for charge transfer across the metal-solution interface must exist.

5. Metals which are capable of forming films in sodium hydroxide, *i.e.*, whose films are insoluble in the medium, also show an "induction period," a time interval between the initial immersion of the metal in the melt and the time at which a steady potential is reached. This time interval is longer at lower temperatures and may extend to several hours near the melting point of sodium hydroxide. The phenomenon seems to be connected with the establishment of a reproducible surface on the metal. When a piece of metal has been immersed

(11) Unpublished results.

in the melt for some time the surface appears to have been "polished" more brightly and uniformly than would be possible by purely mechanical means. The more the metal has been polished before immersion the shorter is the induction period. Thus it appears likely that the induction period represents the removal of surface impurities. The final electrode potential is not affected by the previous treatment of the metal. On the other hand the potential of nickel in aqueous sodium hydroxide depends on the careful reduction and outgassing of the metal before immersion in the solution. Probably the solution of surface impurities occurs rapidly only at temperatures higher than the melting point of sodium hydroxide.

6. In Table I are listed the steady-state electrode potentials of the metals studied.

#### TABLE I

Electrode Potentials of Metals in Sodium Hydroxide at 400  $^\circ$ 

Meta	Potential (v.) relative to gold
Copper	0.61
Nickel	0.67
Silver	0.68
Cobalt	0.70
Tungsten	1.05

No theory has yet been formulated to account for the potentials observed in fused sodium hydroxide. One difficulty preventing such a formulation is our lack of knowledge as to what species exist in molten sodium hydroxide. For example, evidence exists<sup>11</sup> that above  $600^{\circ}$  Na<sub>2</sub>NiO<sub>2</sub>, H<sub>2</sub>O and H<sub>2</sub> are formed in the reaction between nickel and sodium hydroxide. Below 600° the reaction is so slight that products cannot be isolated. It is entirely possible, however, that very low concentrations of these compounds, while not detectable by ordinary chemical methods may be potential determining. Some evidence for this view rests on the fact that only a small part of the current passed through the system, as described above, results in solution of the metal. It is also possible that the potential is determined by more than one electrode reaction. For example, the observation of the plating out of copper at the cathode and simultaneous gas evolution at the anode indicate that the cells are not reversible with respect to the metal ions involved, or at least that other reactions besides  $M \rightleftharpoons M^{++} + 2e^{-}$  are responsible for the observed potentials. It is possible, for example, that at the anode  $O^= \rightarrow 1/2 O_2 + 2e^-$ , while at the cathode  $2OH^- + 2e^- \rightarrow H_2 + 2O^-$ . It is likely that our understanding of potentials

It is likely that our understanding of potentials in the sodium hydroxide system must await the study of potentials in simpler electrolytes.

# A STUDY OF GELATIN MOLECULES, AGGREGATES AND GELS<sup>1</sup>

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Samples of moderately high molecular weight gelatin were found to be molecular dispersed in 0.15 M NaCl at 40° and in 2 M KCNS. Light-scattering measurements of the molecular size showed the gelatin molecules to be random coils with mean configurations comparable to those of typical synthetic polymers. Gelatin solutions form gels when the temperature is lowered, provided that the gelatin concentration is sufficiently high and particular substances such as KCNS and uare are absent. Light scattering and viscometric studies at 18° show that aggregate formation occurs instead of gelation when the gelatin concentration. The size and weight of the aggregates increase with further lowering of the temperature and with the gelatin concentration. The distribution of mass within the aggregates are cross-linked. The nature of these cross-links is shown by the fact that these aggregates dissociate slowly and only to a limited extent upon dilution although, like gelatin gels and crystalline polymers in general, they dissociate completely in a narrow temperature range. This and other information indicates that the cross-links are very small crystallites. In gelatin gels at 18° the intensity of scattered light was found to be substantially greater than in the corresponding solutions. Evidence is presented that the scattering enters in the gels are density fluctuations similar in weight and volume to the aggregates studied in solutions and falling off in scattering does not necessarily indicate smaller scattering centers. The gelation of gelatin is attributed to the simultaneous growth and interlocking of aggregates arising from crystallite formation.

An examination of the extensive literature on gelatin shows that little is known concerning the relation of gelatin molecules, which can exist independently in solution, to the gel, which they can form at sufficiently high concentrations and low temperatures. Since gels fail to form upon cooling when the concentration is sufficiently low, we thought that in this situation gelatin molecules would, nevertheless, come together to form aggregates. Such aggregates were indeed readily detected and their study has served to bridge the gap between the independent molecule and the gel

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because they display the same forces that hold the gelatin molecules together in the gel state on a scale accessible to study in solution. Our work had two other motives as well. From the point of view of light scattering, it was difficult to believe the wide-spread assertion that gelatin gels do not scatter light except near the isoelectric point in the absence or near absence of added electrolyte. Moreover it was of interest to see how the light scattering of the gel, provided it scattered, differed from the corresponding solution, to see if an adequate explanation could be offered and to see what conclusions could be drawn about the structure of the gel. The second motive arose from the renewed interest in the molecular struc-

<sup>(1)</sup> Presented in part at the 123rd Meeting of the American Chemical Society, Los Angeles, March, 1953.

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ture and configuration of collagen from which gelatin is derived and the expectation of taking up the study of soluble collagen and its conversion to gelatin once the molecular behavior of gelatin had been established.

Following a summary of the essential experimental details, the presentation is divided into three nearly self-contained parts: the characterization of gelatin molecules, the aggregation of gelatin in dilute solutions, and the light scattering and structure of gelatin gels.

### I. Experimental Methods and Procedures

Gelatin.—The sample of gelatin used was an ossein gelatin, P111-20, obtained through the courtesy of Dr. D. Tourtellotte of the Charles B. Knox Gelatine Co.<sup>3</sup> The gelatin, supplied as 6% aqueous solution, was dialyzed against distilled water at 4° for three days and then electrodialyzed for two days and stored in sterilized bottles at 4°. Gelatin having this treatment is designated as P. Although no fractionation was attempted, alcohol precipitation was carried out in the following manner. Eighty per cent. ethanol was added slowly to about 500 cc. of 6% gelatin with constant stirring at 38° in accordance with the fractionation procedure used by Pouradier.<sup>4</sup> When the solution contained more than 50% alcohol by volume, a slight turbidity was observed which did not increase upon the addition of more alcohol. After two days, the clear supernatant was siphoned off and the dissolved gelatin recovered by vacuum distillation followed by lyophilization. The flaky white sheets of gelatin were stored in amber bottles in an evacuated desiccator. Since the sample at this point contained about 10% water, the dry weight of the sample was checked each time a solution was made up. The gelatin treated by this method is labeled A and B, corresponding to two separate precipitations.

two separate precipitations. Isoelectric Point.—The isoelectric point was determined by four different methods. The first two involved measuring the pH with a Beckman Model G pH meter, after all the salt had been removed either by electrodialysis, or by passing the solution through a mixed resin bed, consisting of 2.5 parts anion-exchange resin, IRA 400, and 1 part cationexchange resin, IR 120.<sup>6</sup> The third method consisted of determining the pH at which an 0.14% solution of gelatin in water had the maximum scattering (Fig. 1b). The fourth was obtained from titration data discussed below. These investigations showed the isoelectric point of gelatin (P, A and B) to be 5.10  $\pm$  0.05.

It is assumed here that the isoelectric and isoionic points are the same for solutions of gelatin in NaCl and are independent of ionic strength. This is supported by the absence of ion binding reported by Carr and Topol<sup>6</sup> and by our observation (Fig. 1a) that the pH of no acid or base binding is the same in 0 and 0.15 *M* NaCl.

Acid and Base Binding Capacity.—The gelatin solutions (about 0.5%) were titrated from pH 2.2 to 11.5 in water and 0.15 *M* NaCl with 0.1 *N* standard HCl and NaOH. The titration on the basic side of the isoelectric point was carried out in an atmosphere of nitrogen. Figure 1a shows the acid or base bound per gram of gelatin as a function of *pH*.

Concentration Determinations.—Because gelatin solutions do not have an absorption maximum in the ultraviolet, concentrations had to be determined by dry weight or by micro-Kjeldahl analysis for nitrogen (% N of P is 18.0). Solutions were made up by weight from a concentrated stock solution whose concentration had been determined precisely by both methods. In the light scattering experiments, possible errors due to transfer and centrifugation were shown to have been successfully avoided.

(4) J. Pouradier and A. M. Venet, J. chim. phys., 47, 11 (1950).



Fig. 1.—(a) Titration curves of gelatin B at  $25^{\circ}$ ; (b) scattering maximum of a 0.14 g./100 cc. solution of gelatin B in H<sub>2</sub>O at  $25^{\circ}$  at the isoelectric point.

Refractive Index Increment.—A Brice-Speiser Differential Refractometer which has a sensitivity of approximately  $3 \times 10^{-6}$  was used. One per cent. solutions of gelatin were made up in water, 0.15 *M* NaCl and 1.0 *M* NaCl. To make certain that the concentration of the salt was identical in the solution and solvent, the solutions were dialyzed against solvent for three days before  $\Delta n$  was measured. The results of duplicate determinations of  $\Delta n$  at 25° and 4360 Å. of gelatin solutions in water and 0.15 *M* NaCl agreed within 0.5%. Moreover, they agreed within 1% of the value one would calculate from the Gladstone–Dale mixing law

$$\mathrm{d}n/\mathrm{d}c = \left(\frac{n_2 - 1}{d_1}\right) - \left(\frac{n_1 - 1}{d_2}\right) \tag{1}$$

where  $n_1$  and  $n_2$  are the refractive indices of the solvent and solute, respectively, and  $d_1$  and  $d_2$  are the corresponding densities. The first term on the right side of equation 1, which includes the refractive index of the solute, can be calculated from a solution of known dn/dc. The value of dn/dc of gelatin-KCNS solutions was calculated from equation 1 because it was impossible to determine the concentration of gelatin in these solutions with sufficient accuracy due to the high nitrogen content of the salt. In all other cases, however,  $\Delta n$  was measured directly and c was determined by micro-Kjeldahl analysis. Both the calculated and experimental values of dn/dc and K are given in Table I.

#### TABLE I

# Refractive Index Increment and K ( $\lambda = 4360$ Å.) for Gelatin (P) in Various Salt Solutions

	$\mathrm{d}n/\mathrm{d}c$	$K \times 10^7$
$H_2O, pH 5.1$	0.194	6. <b>12</b>
0.15 M NaCl, pH 5.1	. 19 <b>25</b>	6.06
1.0 m NaCl, pH 5.1	. 186	5.64
1.0 M KCNS	. 185	5.61
2.0 M KCNS	. 173	4.88

<sup>(3)</sup> This preparation began with beef bones which were heated at 80° for six hours, crushed, extracted with 5% HCl for two weeks and washed. Following four weeks standing with saturated line water at  $15^{\circ}$  and four hours at  $65^{\circ}$  after the pH was adjusted to 4.5, the gelatin was autoclaved at 15 lb. pressure at  $120^{\circ}$  for 20 minutes.

<sup>(5)</sup> J. W. Janus, A. W. Kenchington and A. G. Ward, Research, 4, 247 (1951).

<sup>(6)</sup> C. W. Carr and L. Topol, J. Phys. Chem., 54, 176 (1950).



Fig. 2.-Housing for thermostating light scattering cell.

Light Scattering.—Except for the investigation of the scattering of gels, the light scattering measurements were interpreted in accordance with the well-known equation<sup>7,8</sup>

$$Kc/R_{\theta} = 1/[M_{w}P(\theta)] + 2Bc \qquad (2)$$

where  $R_{\theta}$  is the reduced intensity at the angle  $\theta$  and concentration c in g./cc.  $K = 2\pi^2 n^2_0 (dn/dc)^2/N \lambda^4$  where  $n_0$  is the solvent refractive index, dn/dc the refractive index increment, N Avogadro's number, and  $\lambda$  the wave length of light in vacuum.

For molecules which are smaller than 1000 Å.,  $P(\theta)^{-1}$  will be a linear function of angle no matter what the shape of the molecule is. Therefore one can obtain the molecular weight and size by the relatively simple "dissymmetry" method.<sup>7,8</sup>

Because of the small size of the gelatin molecule, the dissymmetry method was used almost exclusively for the investigation of gelatin solutions. In studying the gelatin aggregates and gels, however, the measurements were made over the angular range of 30-135° and when possible extrapolated according to equation 2.

From the angular dependence of the scattering, one can determine the racius of gyration,  $R_{\rm g}$ , which for a randomly kinked chain is equal to the root-mean-square end-to-end length ( $\tilde{r}^2$ )<sup>1/2</sup> divided by  $\sqrt{6}$  and for a rod is equal to its length divided by  $\sqrt{12}$ . All light scattering measurements were made on a slightly modified Brice–Speiser light scattering photometer, the description and calibration of which have been reported previously.<sup>9,10</sup> The blue line of mercury (4360 Å.), was used in all the measurements after it was established that the green line (5460 Å.) gave the same value of  $Kc/R_0$  showing thereby that fluorescence was negligible.

As the calibration of the photometer presupposes the use of the standard square cell, 30 mm. wide, and a 12 mm. slit system, it is necessary to calibrate any other cell-slit system against the standard one. It was found that the semi-octagonal "dissymmetry" cell could be used with the standard slit system without applying any correction.

- (8) P. Doty and J. T. Edsall, Advances in Protein Chem., 6, 35 (1951).
- (9) B. A. Brice, M. Halwer and R. Speiser, J. Optical Soc. Am., 40, 768 (1950).
- (10) P. Doty and R. F. Steiner, J. Chem. Phys., 18, 1211 (1950).

Three cylindrical cells, obtained from the Fischer and Porter Co., Hatboro, Pa., were used in angular measurements. One of these had specially ground flats at the 0 and 180° faces. The cells were 11.5 cm. tall, the inner diameter was 3.72 cm., the wall thickness was approximately 1.5 mm. They were calibrated by comparing the excess scattering over solvent of a Ludox solution observed in a square cell at 90° with that observed in the cylindrical cell. In addition, the angular envelope of each cell was checked by measuring the fluorescence of a very dilute fluorescein solution (approximately four times background). It was found that the observed intensity was independent of angle (from 30 to 135°) after the appropriate correction for the volume viewed has been made. An additional correction, the back reflec-tion correction, had to be made when either cylindrical or semi-octagonal cells were used. It had been shown earlier<sup>9</sup> that 4.5% of the incident intensity is reflected back through the solution. Since the reflected light will also be scattered but will have precisely the reverse angular dependence from that of the incident beam, the true angular distribution will be slightly altered.<sup>11</sup> To correct for this, one merely sub-tracts 4.5% of the 135° scattering from the 45° scattering, and 4.5% of the 45° scattering from that observed at 135°. In general, one can apply the equation

$$(R_{\theta})_{\text{real}} = (R_{\theta})_{\text{exp}} - 4.5\% (R_{180-\theta})_{\text{exp}}$$
(3)

Although the preliminary solution studies were made in a dissymmetry cell, the majority of the work was carried out in the cylindrical cells which fit into a specially constructed thermostated cell housing. The brass housing (see Fig. 2) consisted of two concentric cylinders with a 180° "window," slightly larger than the height of the light beam. A slit system, 5 mm. wide and 13 mm. high, was mounted on the front of the housing to minimize diffraction of the incident beam. The housing was mounted on the shaft inside the photometer in place of the table which ordinarily holds the light scattering cell. It was connected to a thermostat through tubing which was led out through the rear of the photometer. Cylindrical cells were mounted on circular brass bases. Two pins protruded from the bottom of the base and fit into two holes on the bottom of the housing. In mounting the cells, care was taken to center the cells with respect to the light beam.

The necessity of having solutions dust-free required as usual the use of glass distilled water to rinse light scattering cells, and pipets used in transfer. The solvent was cleaned by simply filtering it through an ultrafine sintered glass filter; the solutions were cleaned by centrifuging them in a Spinco preparative ultracentrifuge at 100,000 times gravity for 90 minutes. Nitrocellulose centrifuge tubes and specially constructed nylon-impregnated bakelite caps were used. Viscosity.—Measurements of the specific viscosity were

Viscosity.—Measurements of the specific viscosity were made in an Ostwald-Fenske viscometer having a water flow time near 240 sec. and in a modified Ubbelohde viscometer. Several solutions were measured in a specially constructed low gradient viscometer and since the gradient dependence down to about 60 sec.<sup>-1</sup> was identical (about 10%) with that found at higher gradients, the relatively high gradient Ubbelohde viscometer was used. The mean gradient of the three bulbs of this viscometer was not determined but was estimated to range from 1000 to 400 sec.<sup>-1</sup>. The extrapolation to zero gradient was made by plotting  $\eta_{ep}/c$ against h/at where h is the mean height of each bulb, a is a viscometer constant determined empirically for each bulb, and t is the flow time of the solution.

#### II. Gelatin Molecules in Solution

Molecular Weight.—The preliminary light scattering investigation of the solution properties of gelatin was carried out on sample A and the results are shown in Fig. 3. The weight average molecular weights obtained in various salt solutions at 25° were found to fall into two classes, those in KCNS solutions equal to 96,000  $\pm 3\%$  and those in NaCl solutions equal to 111,000  $\pm 3\%$ . Since it had previously been demonstrated<sup>12</sup> that 2 *M* KCNS solutions of gelatin are molecularly dispersed at this temperature, it was assumed that the lower of

(12) E. O. Kraemer, THIS JOURNAL, 45, 660 (1941).

<sup>(7)</sup> B. H. Zimm, J. Chem. Phys., 16, 1093, 1099 (1948).

<sup>(11)</sup> A. Oth, J. Oth and V. Desreux, J. Polymer Sci., 10, 551 (1953).



Fig. 3.—Light scattering of gelatin A in various salt solutions: -,  $25^\circ$ ; --,  $40^\circ$ .

the two values was the correct one. The 15%higher molecular weight observed in NaCl solutions is almost within experimental error of that found in KCNS and would not have been taken seriously had it not been found that heating the NaCl solutions to  $40^{\circ}$  for one hour caused the molecular weight to fall to the values obtained in

TABLE II

LIGHT SC	CATTERIN	G RESUL	TS ON GEL	ATIN A	
	$\left(\frac{Kc}{R_{00}}\right)_{c=1}$ × 10 <sup>4</sup>	[z]	M w	( <i>R</i> g)s, Å.	$B \times 10^{4}, mole cc./g.4$
		At 25°			
2 M  KCNS					
<b>pH 7</b> .1	1.14	1.10	95,000	175	4.8
pH 5.1	1.14	1,11	96,000	180	3.9
1 M  KCNS					
pH 6.3	1.17	1.19	97,000	<b>240</b>	5.0
1 M NaCl					
pH 6.3	1.035	1.16	108,000	210	
pH 5.1	1.03	1.21	112,000	240	• • •
0.15 <i>M</i> NaCl					
pH 6.3	1.05	1.22	111,000	<b>245</b>	
pH 5.1	1.02	1.24	114,000	<b>250</b>	
Immedi	ately afte	er remov	al from 40°	bath	
1 M NaCl					
pH 5.1	1.15	1,19	99,000	<b>2</b> 30	1.3
0 15 M NaCl					
p H 5.1	1.17	1.21	98,000	<b>240</b>	1.8



Fig. 4.—Reciprocal angular envelope of solutions of gelatin B in 0.15 M NaCl at the isoelectric point, 40°.

KCNS. Inasmuch as prolonged heating at the same temperature (for as along as six hours) did not further decrease the molecular weight, the possibility that a hydrolysis or degradation was occurring was eliminated. The results obtained are shown in Fig. 3 and summarized in Table II. The dissymmetry extrapolated to zero concentration, using a plot of  $(z - 1)^{-1}$  against c, is denoted as [z], the z-average of the root-mean-square of the radius of gyration as  $(R_g)_z$  and the second virial coefficient as B.

Additional light scattering measurements were carried out at  $40^{\circ}$  on samples B and P under several conditions. In these, great care was taken to obtain and use only solutions that were dust-free, and in two cases measurements were made over the entire angular range (Figs. 4 and 5) in order to obtain the most accurate estimate of the molecular



Fig. 5.—Reciprocal angular envelope of solutions of gelatin B in water at the isoelectric point, 40°.

weight, size and virial coefficient. The results are summarized in Table III. Our value for the molecular weight of Gelatin P (97,000) is in excellent agreement with the value of 95,000 obtained by Williams in an equilibrium ultracentrifuge study of the same sample in 2 M KCNS at 25°.<sup>13</sup>

TABLE III LIGHT SCATTERING RESULTS AT 40°.  $(R_g)_{t}$ Mw  $B \times 10^4$ Å. Gelatin B 1 M KCNS pH 5.1 90,000 175 2.60.15 M NaCl 2.9pH 5.1 89,000 165 pH 3.1 88,000 175 6.0 H<sub>2</sub>O, pH 5.1 92,000  $\sim -30$ . . . Gelatin P

Configuration of Gelatin Molecules in Solution. —The determinations of the radius of gyration as listed in Table II show a range from 175 to 250 Å. However, the more careful work on gelatin B (Table III) sets that value close to 170 Å. in the solvents employed.

97,000

165

2.9



Fig. 6.—Intrinsic viscosity of gelatin B solutions as a function of the charge per molecule.

Since the intrinsic viscosity is also related to size, this was determined under the same conditions employed in light scattering and the results are listed in Table IV. It is seen that the values are essentially constant averaging 0.39.

TABLE IV

INTRINSIC VISCOSITY OF GELATIN B SOLUTIONS °C. Salt πH [7] 2 M KCNS 25 5.10.388 9 M urea 40.2 8.0 .632 40.20.15 M NaCl 5.1.396 40.20.15 M NaCl 3.1. 403 40.2  $E_2O$ 5.1.381

The possibility that the size could be varied if the solvent was sufficiently altered was explored by means of viscosity measurements. With 9 Murea as solvent, the intrinsic viscosity increased to

(13) J. W. Williams, W. M. Saunders and J. S. Cicirelli, THIB JOUBNAL, 58, 774 (1954).



Fig. 7.—Light scattering of solutions of gelatin A molecules and aggregates in 0.15 M NaCl at the isoelectric point.

0.63, indicating a substantial expansion in this hydrogen bond-breaking solvent. Even greater expansion was found in salt-free solutions away from the isoelectric point in agreement with other investigators.<sup>4,14</sup> The measurements at different values of pH were linear when plotted as  $c/\eta_{sp}$ against  $\sqrt{c}$ . Interpreting the reciprocal of the intercept as the intrinsic viscosity, the results shown in Fig. 6 were obtained. The translation of pH to charge by use of the titration curve probably becomes inaccurate at high charge due to ion binding made possible by high potentials on the polypeptide chain. Since the ionic strength is about the same at the extremities of the graph in Fig. 7, the maximum at -50 may be due to differences in the distribution of negative and positive groups along the chain. In particular, this behavior could arise if the negative groups were more densely clustered at z = -50 than the positive groups at z = +50.

Accepting the molecular weight of gelatin B as 90,000, which corresponds to a degree of polymerization of 1000 and the  $(R_g)_z$  as 170 Å., we (14) G. Stainsby, *Nature*, 169, 662 (1952).

0.15 M NaCl pH 5.1

examine first what conclusions can be obtained by comparing the dimensions with molecular weight. Since light scattering yields a z-average dimension and a weight average weight, a correction is required based upon the polydispersity of the sample. Using the value of  $M_z/M_w$  of 2.6 found by Williams<sup>13</sup> in a sedimentation study of the same gelatin sample used here, and the assumption that  $r^2$ is proportional to M, a weight average dimension of  $(\overline{r^2})^{1/2} = 258$  Å. is obtained for a randomly coiled model. Let us compare this size and the intrinsic viscosity with that of a typical aliphatic polymer, such as polyisobutylene, having the same number of chain atoms. (The aliphatic chain would in this case be about 5% longer because of shorter bond lengths in the peptide group.) For such a chain (3000 carbon atoms) in a solvent of comparable thermodynamic properties, as judged from the second virial coefficient, polyisobutylene would have a value of  $(\overline{r^2})^{1/2}$  of 231 Å. and an intrinsic viscosity of 0.31. From these observations gelatin appears to behave as a linear polymer with mean configurations comparable to typical synthetic polymers. Since rotation about Ca-N bond is expected to be strongly restricted because of partial double bond character and since rotation is not possible in the 20–25% of the  $C_{\beta}$ -N bonds participating in proline residues, it appears that rotation in the remaining bonds is less restricted than in typical aliphatic polymers.

An examination of the same data with respect to the helical configuration associated with native collagen shows little support for this model. In this case the radius of gyration is translated into the length, L, of a rigid rod by multiplying by  $\sqrt{12}$ . Moreover, since M is proportional to L, the length obtained,  $L_z$ , must be multiplied by 1/2.5 in order to yield  $L_{\rm w}$  which can then be compared with  $M_{\rm w}$ . The resultant length is found to be 236 Å., which is less than one third the length of a collagen molecule of comparable molecular weight.<sup>15</sup> All other reasonable helical models fail to fit the dimension and molecular weight requirements by a comparable margin. Since this model also fails to account for the flexibility revealed by the variation of the intrinsic viscosity, it can be rejected. Accepting then the random coil model for gelatin molecules, we proceed to study their aggregates.

### III. The Aggregation of Gelatin Solutions

Aggregation in Very Dilute Solutions.—If the gelation of gelatin solutions is preceded by an aggregation of the gelatin molecules, the latter process should be discernible even in extremely dilute solutions which are incapable of gelling. The molecular weight determinations in salt solution described in the preceding section show that a small amount of aggregation does occur even at 25°. This was found even though the gelatin solution from which



Fig. 8.—Light scattering of solutions of gelatin A molecules and aggregates in 1.0 M NaCl at the isoelectric point.

dilutions were made had been heated to  $40^{\circ}$  for one hour to erase the thermal history of the sample.

The further study of this aggregation required the adoption of standard procedures and controlled conditions. As discussed in the next section studies on gels show that their equilibrium state can be approached more rapidly by first heating the material, then cooling it to several degrees below the temperature at which the measurements will be made. Consequently all the experiments carried out on gelatin aggregates and gels involved the following procedure: each concentration was made up separately; after centrifugation, the solution was heated to  $40^{\circ}$  for one hour and then stored at 4°; a day later it was placed in a thermostated bath and maintained at the desired temperature for 18 hours. By following this cycle, it was possible to obtain reproducible measurements.

The results obtained with four solutions of A ( $M_{\pi} = 97,000$ ) in 0.15 M and 1.0 M NaCl are given in Figs. 7 and 8. It is important to appreciate that the data in Figs. 7 and 8 represent the variation of scattering with temperature at constant concentration. The question immediately arises as to whether or not upon dilution  $Kc/R_{90}$  would increase along the lines connecting the points, since behavior of this type would show that

<sup>(15)</sup> Actually the length of rods corresponding to the weight average molecular weight would be somewhat shorter than 236 Å. because the length determined from light scattering measurements in the case of rods is not the length corresponding to the z-average molecular weight but a somewhat higher average. (See, for example, reference 8.)



Fig. 9.-Dilutions of solutions of gelatin P aggregates formed at various concentrations at 18°.

we are dealing with a very non-ideal solution of gelatin molecules or with aggregates which dissociate continuously upon dilution. Such a dilution experiment is shown in the lower part of Fig. 7 where a 0.16% solution of gelatin is diluted stepwise at 19°. The behavior found is that of a nearly ideal, non-dissociating unit. It was shown readily that if dilutions or concentrations were made within an hour or two, the aggregates formed at any temperature or concentration remained stable and could therefore be subjected to size and weight measurements. This kind of measurement is taken up in the next section. A few other observations are mentioned here.

If the scattering from a diluted solution of aggregates is measured as a function of time, it is found that a gradual decrease in scattering occurs. As an extreme case aggregates were formed in a 0.34 g./100 cc. solution at 18° and diluted 60-fold. The scattering fell rapidly at first (10% in the first ten hours) and then more slowly, reaching half the original scattering in about 200 hours. If, however, a solution of this very low concentration had been carried through the same temperature cycle, the scattering would have been indistinguishable from that of gelatin molecules. Consequently, it appears that in a practical sense aggregates do not dissociate reversibly at constant temperature.

The absence of reversibility in temperature cycles is also readily observed. One case is shown in Fig. 7 where it may be seen that there is a substantial difference in the scattering from solutions brought directly to  $25^{\circ}$  from  $4^{\circ}$  and those that are allowed to equilibrate at an intermediate temperature (18°) before being brought to  $25^{\circ}$ .

Finally, it is of interest to mention the observation that aggregates formed in 1 M NaCl were of the same average weight as those in 0.15 M. This suggests that electrostatic forces are not playing an important role in the aggregation. A 1 MKCNS solution, on the other hand, did not change its scattering even at 4°. The efficiency of KCNS in inhibiting aggregation must therefore be a specific effect unrelated to ionic strength.

The Weight and Size of Aggregates Formed in Moderately Concentrated Solutions.-Solutions of gelatin aggregates at  $18^{\circ}$  were studied under three conditions: 0.15 *M* NaCl, *p*H 5.1; 0.15 *M* NaCl, pH 3.1; and H<sub>2</sub>O, pH 5.1. The weight, size and shape of the aggregates at a given concentration were determined by measuring the angular dependence of the light scattered by the aggregated solutions and dilutions thereof. Some of the results, extrapolated to zero angle, are shown in The Zimm plots obtained in two typical Fig. 9. cases are shown in Figs. 10 and 11. Some of the results obtained from the Zimm plots, as well as from angular measurements on the aggregated solutions which were not diluted, are summarized in Table V.

#### TABLE V

 $Kc/R_0$  and Particle Weights for Gelatin Aggregates

c × 10 <sup>2</sup> , g./cc.	<i>Kc/R</i> ₀ × 10⁰	$M_{w} \times 10^{-6}$ (from Zimm plot)	$c \times \frac{10^2}{g./cc.}$	$rac{Kc/R_{ m f}}{ imes 10^6}$	$M_{w} \times 10^{-6}$ (from Zimm plot)
P in 0.15	M NaCl,	pH 5.1	B in 0.15	M NaCl,	pH 5.1
0.087	5.14	0.208	0.112	5.44	
. 203	2.71	0.476	.350	${f 2}$ , ${f 57}$	
. 386	1.68	1. <b>2</b>	. 500	1.55	
.539	1.21	5.9	. 640	1.14	
.755	0.96		.800	0.99	
B in 0.15	M NaCl,	pH 3.1	B in	H <sub>2</sub> O, <i>p</i> H	5.1
0.090	7.76		0.095	4.67	
. 30	4.91		. 25	1.5	
.75	3.55	1.65	. 40	0.089	
. 90	3.85		. 58	0.0062	40.0

Table V shows that the extent of aggregation in the two samples P and B in 0.15 M NaCl at pH5.1 is sufficiently similar to consider the two samples as interchangeable. The following conclusions are evident. (1) At the isoelectric point aggregation increases with concentration reaching



Fig. 10.—Reciprocal angular envelope of solutions of gelatin P aggregates formed at 0.203 g./100 cc. at  $18^{\circ}$  in 0.15 M NaCl at the isoelectric point.

weight average aggregate weights of several million. (2) Decreasing the pH to 3.1 decreases the aggregate weight substantially. (3) Aggregation is greatly enhanced at the isoelectric point in the absence of salt, relative to that in 0.15 M NaCl.

An attempt to determine the aggregate weight of 0.755% P in 0.15~M NaCl at the isoelectric point failed even though the angular dependence of seven dilutions was measured. The results could not be extrapolated to a finite intercept, probably because the solution contained a number of aggregates held together in an incomplete network rather than independent kinetic units.



Fig. 11.—Reciprocal angular envelope of solutions of gelatin P aggregates formed at 0.54 g./100 cc. at  $18^{\circ}$  in 0.15 M NaCl at the isoelectric point.

The viscosities of the aggregated solutions formed at a series of concentrations at 17.8° were measured. In Fig. 12, the reduced specific viscosities of gelatin B and P solutions are represented by points connected by full lines. In the case of the gelatin P, dilutions were made of the aggregates formed at various concentrations in order to obtain the intrinsic viscosities. These data are represented by points connected with dashed lines. It is apparent from these results that both the reduced specific viscosity and the intrinsic viscosity of the aggregated solutions depend on the concentration at which the aggregation took place.



Fig. 12.—Reduced specific viscosity of solutions of gelatin aggregates at 17.8°:  $\bullet$ , gelatin P;  $\odot$ ,  $\Box$  and  $\blacktriangle$ , gelatin B.

Next, it was important to determine if the gelatin aggregates in aqueous solution would expand when charged. To test this, the pH was lowered and the salt was removed from an aggregated 0.40 g./100 cc. solution by dialyzing it against  $10^{-3}$  N HCl at 17.8° for 12 hours. The intrinsic viscosity of the dialyzed solution was compared with that of an identical solution in 0.15 M NaCl at pH 5.1, after the concentration of the former had been checked by dry weight. It was found that the intrinsic viscosity had risen

from 1.7 in 0.15 M NaCl at pH 5.1 to 4.2 in water at pH 3.1. This means that the viscosity increased at least two and a half times when 7% of the amino acid residues carried a net positive charge.

An ultracentrifuge measurement of a 0.34 g./ $\overline{100}$ cc. of gelatin P aggregates ( $M_w = 900,000$ ) formed in 0.15 M NaCl at the isoelectric point at  $18^{\circ}$  was carried out in a Spinco analytical ultracentrifuge at the same temperature. The corrected sedi-mentation constant was 3.46 svedberg units, roughly twice that obtained for a 0.58 g./100 cc. solution of molecularly dispersed gelatin in 2 MKCNS  $(S_{20}^{\circ} = 1.74 \text{ S})$ . A comparison of the sedimentation diagrams obtained for the gelatin aggregates with that obtained for the molecules when both had sedimented a comparable amount (equal displacement of peaks from meniscus) shows that the aggregation of gelatin has brought about a considerable broadening of the particle weight distribution. In the case of the aggregates the half width is about doubled. The nature of the broadening indicates that most of the molecules have participated in forming aggregates rather than that a few combined to form very large aggregates.

In addition to the foregoing measurements the dependence of extinction angle on gradient was observed by a Rao Flow Birefringence Apparatus on several solutions of aggregates of gelatin B (0.15 *M* NaCl, *p*H 5.1, temp. 18°). Using the Stuart-Peterlin theory for interpreting the experimental data in terms of an ellipsoidal model, it was found that the rotary diffusion constant,  $\theta$ , varied from 4000 sec.<sup>-1</sup> when the concentration of formation was 0.28 g./100 cc. to 100 sec.<sup>-1</sup> when the concentration of sec.<sup>-1</sup> when the concentration of formation was 0.28 g./100 cc. to 100 sec.<sup>-1</sup> when the concentration of formation was above 0.7 g./100 cc. No attempt is made to interpret this because the theory for ellipsoids is considered inadequate. It is mentioned here so that comparison may be made with similar measurements in other investigations.

Discussion.—The evidence presented above on gelatin aggregates bears further examination from two points of view: first, the characteristics of the aggregates and, second, the nature of the forces holding the gelatin molecules together in aggregates.

In discussing the characteristics of the aggregates, it is important to note that the average values of particle weight and size which the measurements provide are fairly representative of the solute since the sedimentation diagrams showed no selective aggregation on the part of any one type of species. With this in mind it is of interest to examine some of the results assembled in Table VI. If the relation of intrinsic viscosity to particle weight is considered first, it is seen that  $[\eta]$  is approximately proportional to  $M^{1/2}$ . The unassociated gelatin, measured at a higher temperature, also fits this relation. Since this is not far from the behavior expected for a homologous series of polymers, it suggests that the association is either end-to-end or, in any event, it produces aggregates whose hydrodynamic character resembles higher molecular weight polymers of gelatin. However, it is clear from the limited expansion of aggregates when charged in the ab-

sence of electrolyte that the configurational mobility of an end-to-end aggregate does not exist and the possibility of this type of association must be ruled out. The simplest alternative model compatible with the particle weight-viscosity relation is one in which the gelatin molecules are held together at randomly occurring points on their surface producing a less flexible, cross-linked or branched structure. These occasional points of association within the aggregate would produce somewhat greater compactness, or segment density than in the end-to-end aggregate and would explain the fact that the dependence of  $[\eta]$  on particle weight is somewhat less than the values 0.64 to 0.88 found for gelatin molecules.<sup>13,16</sup>

Further support for this "brush heap" model of the gelatin aggregate can be found by examining the ratios of the particle weight to the first, second and third powers of the radius of gyration which are listed in Table VI. If the aggregates were rods of uniform density, the first ratio would be constant and if they were spheres of constant density, the third ratio would be constant. Neither of these extremes are satisfied but the intermediate case,  $M/R^2_{g}$ , is approximately valid. A number of possible forms can be imagined which would meet the approximate constancy of this ratio. But the simplest one, having discarded the end-to-end aggregate, is the brush heap model. Because the occasional branch points or cross-links in such an aggregate only moderately perturb its basic chain structure, this model would have a segment distribution with respect to the center of gravity that would be close to that of a linear randomly coiled chain and such a distribution does approximate a Gaussian one for which  $M/R^2_g$  is constant.

One more indication that this model is approximately correct is to be found in noting that the product of the second virial coefficient B and  $M^{1/2}$ is constant (Table VI). For a series of homologous polymers of different molecular weight, a somewhat lower exponent of M is found. The value of 1/2 lies in the direction of more compact, less easily penetrable particles and is very different from that expected for either of the extreme cases of rods or spheres.

Thus it is seen that three arguments, which may be summarized by saying that  $M/R^2_{g}$ ,  $[\eta]/M^{1/2}$ and  $BM^{1/2}$  are nearly constant, indicate that the aggregates are composed of individual molecular strands so arranged that the average density distribution resembles that of moderately branched or cross-linked polymers.

The discussion thus far has been restricted to the behavior of gelatin aggregates in 0.15 M NaCl at the isoelectric point. Without going into details, one can see from Table VI that the character of the aggregates is essentially unaltered when the pH is changed from 5.1 to 3.1 in salt solutions. There is, however, some increase in the virial coefficient and a decrease in the aggregate weight. We interpret this as the result of the net charge on the molecules, which creates a small repulsion between segments of different molecules making up the aggregate and between the aggregates as well.

(16) J. Pouradier and A. M. Venet, J. chim. phys., 47, 391 (1950).

		WEIGHT AND SHE OF GERAMM HOGHEGATES AT TO							
(1)	$c \propto 10^{2}$ , g./cc. Gelatin P:	$M_{\rm w} \times 10^{-6}$ 0.15 <i>M</i> NaCl.	[7] pH 5.1	Rg (Å.)	$rac{M}{R_{g}}$	$\frac{M}{R_g^2}$	$rac{M}{R_{ m g^3}} imes 10^8$	$B \times 10^4$ , mole cc./g. <sup>2</sup>	${}^{BM^{1/2}}_{10^2}  imes$
(-)	0.087 .203 .386	0.208 0.476 1.2	0.60 .80 1.32	230 376 650	895 1270 1860	3.97 3.38 2.86	1.73 0.91 .44	1.85 1.25 0.75	8.44 8.62 8.21
(2)	.539 Gelatin B: 0.75	5.9 0.15 M NaCl, 1.65	2.12 pH 3.1	1480 850	4200 1930	2.71 2.29	. 19 . 26	.35 1.25	8.52 16.1
(3)	Gelatin B: 0.58	H <sub>2</sub> O, pH 5.1 40		<b>42</b> 60	940	2.21	. 52	-0.33	

TABLE VI Weight and Size of Gelatin Aggregates at 18°

The aggregation in water at the isoelectric point is decidedly different, however. This can be clearly seen in the higher relative density,  $M/R_{g}^{3}$ , in the negative virial coefficient, and in the fact that an aggregate of 40 million particle weight has a reduced specific viscosity less than that observed for aggregates of 1 million particle weight in salt. The high density and the low viscosity must mean that the aggregates formed under these conditions are more compact and also more nearly spherical than those formed in salt since the viscosity of a sphere is independent of molecular weight. The negative virial coefficient, and the fact that we found that the angular dependence of the scattered light was no longer linear, implies that we are dealing with an essentially different type of aggregate. The decided upward curvature observed in the reciprocal angular envelope at infinite dilution indicates substantial ordering of the aggregates. In this case we have observed the persistence of ordering in a concentration as low as  $3 \times 10^{-5}$  g./cc. This, together with the observed negative virial coefficient, makes the deduction that electrostatic attractions are operative almost mandatory. We can thus conclude that the aggregation of gelatin molecules in water at the isoelectric point is greatly enhanced (and complicated) by electrostatic attractions which produce aggregates which are both more dense and more spherical than those formed in the presence of salt. This type of aggregation much more closely resembles the process one would expect to occur prior to precipitation than to gelation.

We turn now to a consideration of the forces responsible for the association of gelatin molecules into aggregates. If one examines the evidence dealing with this point presented above and the observations on the melting and forming of gels in the next section, it appears that each feature observed is consistent with the supposition that the association results from the formation of very small crystallites involving small sections of a small number of gelatin molecules. This proposition will first be defended and then examined with regard to its precise meaning.

Since the heat of melting of a crystalline polymer is positive (endothermic), it is necessary that the coexistence temperature (melting point of the polycrystalline polymer in equilibrium with solvent) decrease with dilution. Recognizing that a distribution of crystallite sizes are present in a swollen polycrystalline phase, dilution at constant temperature will be accompanied by a progressive melting of the crystallites. This type of behavior is well illustrated in the case of polyethylene and xylene.<sup>17</sup> The melting temperature of gelatin gels decreases with dilution in a similar way.<sup>18</sup> Since we assume that the association in the aggregates has the same origin as the gelation of more concentrated solutions of gelatin, this observation suggests that the association is due to crystallite formation.

The behavior of the aggregates upon dilution supports this suggestion. Not only is their dissociation very slow, as it would be if it involved the melting of crystallites, but the dissociation at 18° is only slight. Even in the case of the 60-fold dilution, the average particle weight was approaching a constant value after 200 hours corresponding to aggregates of four to five gelatin molecules. This would indicate that some but not all of the intraaggregate crystallites were unstable at this higher dilution.

The dependence of the aggregate size on thermal history (Fig. 7) is characteristic of polycrystalline materials and would be difficult to explain in any other way.

In spite of the coincidence of the behavior of these aggregates and that expected for aggregates of polycrystalline polymers, it may be argued that this system is still simply exhibiting the characteristic behavior of phase separation in an amorphous polymer-liquid system with some unusual time lags in the establishment of equilibrium. If this were a two-phase system of amorphous swollen polymer and very dilute polymer solution, the second virial coefficient of both the aggregates and the dissociated molecules at temperatures just above the phase separation point would be nega-The data in Figs. 3 and 9 show the second tive. virial coefficients to be positive. Hence there is no basis for this alternative point of view.

Little can be said with certainty of the nature of the forces involved in the crystallites believed to serve as cross-links and branch points in the aggregates. It is clear from the lack of influence of ionic strength that electrostatic forces play no dominant role. It is likely that the remaining possibilities of hydrogen bonds, dispersion forces and dipole interaction do contribute. There is

<sup>(17)</sup> R. B. Richards, Trans. Faraday Soc., 42, 10 (1946).

<sup>(18)</sup> J. D. Ferry, Advances in Protein Chem., 4, 1 (1948).



Fig. 13.—Light scattering of gelatin P gels in 0.15 M NaCl, pH 6.5, as a function of time.

high probability that the regions of association (crystallites) involve considerably more than single atomic groupings or amino acid residues because of the relative sharpness of the melting of the aggregates and gels. The basis of this conclusion lies in viewing the disappearance of the crystallites as a kinetic process. Since a very high energy of activation must be attributed to it, such a process could not occur at such low temperatures unless the entropy of activation were unusually high. Thus as in protein denaturation or the melting of simple crystals, a considerable disordering must be associated with the formation of the activated state. This requires that a degree of ordering must have been present in the initial state, and it is this ordered state that we have called "crystallites" throughout this discussion. These ordered regions in which gelatin chains are united may well be too small to be detected by X-ray diffraction. This point is discussed further at the end of the next part.

# IV. Gelatin Gels

The Effect of the Gel-Sol Transition on Transverse Scattering.—In order to survey the magnitude of the changes in light scattering brought about by melting and setting gelatin gels and to examine the time required for equilibrium to be established, four gelatin solutions in 0.15 M NaCl and at pH6.5 were placed in square cells and their scattering at 90° was followed through the gel-sol and sol-gel transition. The concentrations were 0.90, 1.50, 2.01 and 2.84 g./100 cc. After first heating the solutions to 40° and measuring their scattering there, the solutions were stored at  $4^{\circ}$  for a day and then thermostated at  $17.4^{\circ}$ . It is seen, first of all, that the scattering, both at 4 and at  $17.4^{\circ}$ decreases with increasing gelatin concentration. After being brought to  $17.4^{\circ}$  the scattering decreases with time reaching a constant value after about 12 hours. In the most dilute case, which had remained a solution, there was a slow drift to higher scattering that did not end even after a week's time although during this period it had set to a gel.

The gels were then warmed to  $25^{\circ}$  and the scattering measured as a function of time while they melted. The results show (Fig. 13) that the melting is very rapid, the scattering having become constant after 4 hours. An interesting feature of the melting process is the slight increase in scattering that precedes the rapid decrease. This is apparently the result of a temporary increase in disorder as the network breaks apart. When equilibrium is reached at this temperature, it is seen that the dependence of scattering on gelatin concentration has reversed and now stands in the normal order with the most dilute system scattering least.

Thus it is clear that substantial changes in light scattering do accompany the melting of gels, but that the magnitude of the change decreases with increasing concentration. The failure of early investigators to observe these changes may have been due to their working with more concentrated solutions, but more probably it was the result of their making measurements in the absence of salt. where external interference is so great that it would be impossible to observe such changes.

The reverse process, the formation of gels, was measured next. The four solutions were heated to  $40^{\circ}$ , and then placed in a  $17.4^{\circ}$  thermostat. The scattering was measured as a function of time for 70 hours. The results obtained during the first ten hours are also shown in Fig. 13. A comparison with the melting shown in the center of the figure shows that gel formation is a much slower process than melting. In either case, however, essentially the same final state is reached, provided one allows sufficient time. This was demonstrated by comparing the scattering of the four gels after 70 hours at 17.4°, the gels having been brought to this temperature from a lower temperature in one case and a higher temperature in the other. In all four systems the scattering values agreed to within 5%. Thus in both setting and melting it is found that the most concentrated solution undergoes the least change in scattering.

Finally, the scattering of the four solutions was measured as a function of temperature. In each case the solutions were heated at 40° for one hour, stored at 4° for one day, and then allowed to equilibrate at the desired temperature for 120 hours. The results were exactly what would be predicted from the previous observations. The scattering decreased steadily, leveling off at about  $25^{\circ}$ .

Angular Dependence of Scattering from Gelatin Gels.—Solutions in the concentration range of 1.0 to 2.3% in 0.15 M NaCl at pH 5.1 were heated at  $40^{\circ}$ , and the light scattering measured at this temperature. The solutions were then subjected to the same temperature conditioning as the more dilute ones. The angular envelopes of the scattered light were measured and the results are shown in Figs. 14 (B) and 15 (P). The striking difference between the scattering of gelatin gels and gelatin aggregates can best be seen in Fig. 14 where the results for the dilute solutions are included. Here we see that although the reciprocal angular envelopes of aggregated solutions are linear, and the scattering increases with concentration, quite the reverse is true for the gels. Starting with a 1%gel, the reduced scattering,  $R_0/c$ , decreases with concentration so that for a 2.3% gel the reduced scattering is less at zero angle than a 0.35% solution of gelatin aggregates. Furthermore, the angular dependence ceases to be linear. Thus the envelope of a 1% gel already has a slight upward curvature, while that of a 2.3% gel is almost J-shaped, the initial slope being zero, but  $Kc/R_{\theta}$  increasing rapidly from about  $70^{\circ}$  on.

Thus two observations on the difference between the scattering of the solutions and the gels are particularly significant because they bring into focus the essential distinction, at the molecular level, between solutions and gels. We shall examine at once the implications of the change in the shape of the reciprocal scattering envelope and take up in the next section a more detailed consideration of the concentration dependence of the reduced intensity  $R_0$ .

Examination of the reciprocal scattering en-



Fig. 14.—Reciprocal angular envelopes of gelatin B solutions and gels at 18°.

velopes in Figs. 14 and 15 shows that the progressive change in character of the envelopes with increasing concentration is due to a falling off of the low angle intensities, the angular dependence in the high angle region remaining essentially unchanged. This type of deviation from the reciprocal scattering envelope of independent (randomly located) scattering centers always arises when ordering occurs, that is, when the spatial arrangement of the scattering centers changes from a random one to one in which there is a tendency of the centers to be evenly spaced. Consequently we conclude that with increasing gelatin concentration the scattering centers, which as we shall see in the next section may be thought of as similar to the larger aggregates, become more uniformly distributed in space.

The argument leading to the foregoing conclusion will not be presented here because it derives essentially from the general theory of scattering and has been considered in some detail in two other publications dealing with formally similar problems.<sup>19</sup> One particular point, however, deserves special mention. Alteration of the reciprocal scattering envelope from that of independent particles can arise either in the manner just described where the effect is observed at low angles or in another manner in which the high angles are most affected. This latter possibility arises when rigid particles are in contact because in that case there is correlation between all pairs of volume elements in the two particles. This situation has

(19) (a) P. Doty and R. F. Steiner, J. Chem. Phys. 20, 85 (1952);
(b) G. Ehrlich and P. Doty, J. Am. Chem. Soc., 76, 3764 (1954).



Fig. 15.-Reciprocal angular envelopes of gelatin P gels at 18°.

no effect at zero angle but raises the reciprocal envelope progressively with increasing angle.<sup>20</sup> The absence of this effect in gelatin gels implies that the segments making up the scattering centers are not rigidly fixed and permits the assignment of the cause of the alteration of the envelope to the ordering of the scattering centers. The considerations of the next section also make it clear that the origin of this ordering is the spatial extent or volume filling capacity of the scattering centers themselves.

The Concentration Dependence of Scattering from Gelatin Gels.—Having dealt with the angular dependence of the intensity of light scattered from gelatin gels, we turn now to consider the dependence on the concentration. Since the scattering extrapolated to zero scattering angle,  $R_0$ , is the least complicated by interference effects and since it is this quantity which in solutions has a direct thermodynamic interpretation, our concern will be with  $R_0$ . We shall restrict our interest to the gels studied here, those at pH 5.1 in 0.15 M NaCl and at 17.4 or 18°

It is clear from Fig. 13 that the scattering of the gels is several times that of the corresponding solutions at 40° where the gelatin molecules are kinetically independent. Hence there is greater non-uniformity in the disposition of the gelatin molecules in the gel than in solution. In other words, the fluctuations of density of gelatin in the gel are greater than in solution. This situation might be expected to result from the existence in

the gel of aggregates such as were found to exist in more dilute solutions at the same temperature. If the scattering centers, that is the aggregates of gelatin molecules, were located quite at random, this suggestion could be readily explored because the scattering at any concentration could be directly interpreted in terms of the characteristics of the scattering centers. In particular the pro-cedure of Debye and Bueche<sup>21</sup> for treating the scattering from inhomogeneous solids could be applied to the interpretation of the angular data. However, there is strong evidence that the scattering centers are, in fact, arranged in a relatively ordered fashion. Part of the evidence was discussed in the foregoing section; the remaining direct evidence lies in the nature of the concentration dependence shown in Figs. 14 and 15. It is seen that with increasing concentration of gelatin, the value of  $Kc/R_0$  first falls, and then just inside the gel range it reverses and rises. Indeed the rise is so steep that  $R_0$  itself actually decreases with increasing concentration. If no other information were available, the decrease in scattering with increasing concentration would be interpreted as a gradual falling off in the average size of the scattering units, that is, the concentration fluctuations. However, the angular dependence of the scattering is such that it cannot be due to any possible mass distribution with the scattering units but is typical of the behavior caused by external interference, that is, an ordering of the scattering centers. Moreover, there is no reason to expect the regular increase of the size of the scattering units found in solution to reverse itself in the dilute gels. Conse-

(21) P. Debye and A. M. Bueche, J. App. Phys., 20, 518 (1949).

<sup>(20)</sup> In the ease of rigid particles equation 2 takes the form: Kc/R = $1/[MP(\theta)] + 2BP(\theta)^{1/2}c.$  See, e.g., G. Oster, Rec. trav. chim., 68, 1123 (1949).

quently, it is likely that the decrease in scattering with increasing concentration arises from an increasing ordering of the scattering units rather than a decrease in their size. The possibilities of testing this hypothesis further are, however, quite limited. The difficulty lies in the fact that there are three variables, the size of the fluctuation (scattering unit), its particle weight, and its distribution in space. Against these three variables, each of which is rather complicated, there are only two types of data, the angular dependence and the concentration dependence of the scattering. The extent of ordering in these gels, as judged from the deviations of  $Kc/R_{\theta}$  at low angles from that expected on the basis of high angle values in Fig. 14, is so great that the possibility of interpreting the angular dependence of the scattering must be given up. This is due to the fact that the present state of the theory allows the treatment of the angular data only if the second virial coefficient is sufficient to characterize the non-random arrangement of the scattering centers.

The only part of the problem remaining, therefore, is whether or not the concentration dependence of the zero-angle data could be interpreted without requiring that the weight of the scattering centers decreases with increasing concentration. At the outset, the assumption must be made (implied above) that the spacial distribution of the scattering centers is approximately like that which would occur if the gelatin strands that unite them were cut and they became kinetically independent. On this basis the only model for which  $R_0$  can be computed is that of a dense gas of hard spheres. The computation is given in the Appendix and the results are shown in Fig. 16. Here it is seen that a hard sphere gas composed of particles of diameter 795 Å. and having particle weights of 5,900,000 exhibit a maximum in scattering at about 1% concentration and beyond that behave approximately like the gels examined here. Since the selection of pairs of values for the particle size and weight were necessarily restricted to a limited range, it is seen that a collection of scattering centers not greatly different from the aggregates examined in dilute solution could, if distributed in space as are the particles in a dense sphere gas, give rise to scattering intensities at zero angle that would be similar to that observed for the gels.

Discussion.—Despite the limitations in the interpretation of the scattering from the gels, some qualitative views on the process of gelation can be deduced. First of all, it seems clear that the aggregates studied in solution must also form during the process of gelation at the same temperature but at higher concentrations. Indeed, most of the changes in scattering (Fig. 12) are over before the gel actually sets. Thus it appears that the aggregates form and grow and during the later states of growth become untied by smaller strands and occasional interlocking of the aggregates themselves. In this view the same forces are responsible for the stability of the aggregates as for the network which they form upon gelation.

With the provisional identification of the fully formed aggregate as the density fluctuation that



Fig. 16.—Comparison of the concentration dependence of the reduced intensity of gelatin gels with that predicted for a hard sphere fluid.

gives rise to the scattering as well as the major structural element of the gel, it would be expected that the views put forward here could find support or opposition from the many light scattering investigations of gelatin gels that have been carried out for almost half a century. However, this is not the case because almost all investigations, particularly those in which intensity was measured, were concerned with what we believe to be an essentially different problem. When gels are formed at the isoelectric point in the absence of salt, a strong opalescence develops. The scattering in this condition is many orders of magnitude greater than that studied here. The gel that is formed under these conditions is, however, very weak. Therefore, there appears to be little relation between this very strongly scattering state and the essential features of the gel state. Indeed, it is clear that due to the strong attraction of oppositely charged groups on different chains, the extra attraction produced by normal gelation will form extremely large dense aggregates that are held together by relatively few molecular strands. In other words, this is a precipitate imbedded in a very weak gel. The principal forces that cause the formation of these large, dense aggregates have nothing to do with the formation of gelatin gels and therefore a study of the consequences they produce did not seem profitable. Besides, the secondary scattering in this type of gel is so great as to greatly complicate the experimental aspects of the problem.

With the common variables of pH and ionic strength, gelatin gels can be divided into three other regions: (1) non-isoelectric, salt-free, (2) nonisoelectric with salt present, and (3) isoelectric with salt present. In the first region scattering falls to low levels when the pH is more than one unit removed from the isoelectric point and the gels are no longer weak. However, this is not an attractive region to study because the repulsion between the molecules in solution, the aggregates in solution and the aggregates in the gel is so strong that one is essentially examining this type of interaction instead of the structural aspects. For example, we found it impossible to determine the molecular weight of gelatin in salt-free solution at pH 3.1 because of the severe effects of external interference.

When sufficient salt is present (e.g., 0.15 M NaCl) the electrostatic interactions are so completely masked that it makes little difference whether a study is made at the isoelectric point or somewhat removed. In a few experiments away from the isoelectric point, it became clear that the aggregates that formed were smaller than in the comparable case at the isoelectric point. For example, at pH 3.1 the gelatin solution must be almost twice as concentrated to produce aggregates of the same weight as at pH 5.1.

Although the exact nature of the forces responsible for gelation cannot be deduced from this investigation alone, the involvement of crystallites, already considered in the discussion of aggregates, is clearly indicated by the melting and gelling behavior presented in the first section of this part. If we now look for other evidence to support this view, we find cn the one hand an abundance of experimental evidence of crystallinity in the gel state and its absence in the solution of melted gel but also a reluctance to assign crystallization as the cause of the aggregation or gelation. For example, it was shown sometime ago that the melting of a gel is accompanied by a liberation of heat<sup>22</sup> (12 cal./g.) and by an increase in specific volume. Yet this clear indication of a phase transition has been generally ignored.

Equally significant evidence for the existence of some crystalline structure is found in the appearance of sharp rings in the X-ray diagrams of gelatin films prepared from gels. When the films were prepared from warm solutions, however, only an amorphous diagram resulted. This evidence for crystallinity and its correspondence to the X-ray spacings observed for collagen lead to the suggestion that a gelatin gel is a network in which the network points are the result of a partial crystallization of the polypeptide chains.<sup>23</sup> This suggestion, which is identical with ours, was later rejected because the crystalline rings were known to persist for a short time after the gel melted and often did not appear until several hours after the gel formed.<sup>18</sup> This argument seems untenable in view of the gel structure proposed here. It would be expected that the larger crystallites would lie within the aggregates and that the first step in the melting of the gel would be the breaking up of the network and the freeing of the aggregates. Hence, in view of the rate of melting shown in Fig. 13, it is normal to expect the persistence of the crystallites for a few hours. Indeed, this sequence of events offers strong support to the concept that the network is built from aggregates that are to some extent preformed and which maintain some identity within the network. The retarded appearance of the diffraction lines when the gel is formed is due to the fact that the gelatin crystallites must reach a finite size (about 50 Å.) before sharp diffraction lines appear. Thus the discrepancy is resolved and the identification of crystallite forma-

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tion as the cause of gelatin gelation seems quite acceptable. Indeed, the close correspondence between the X-ray spacings in gelatin and collagen indicate that the same regions of the molecules are crystallizing in both cases. It has been suggested that these regions in collagen are the interband regions of the fibril and would therefore involve alternate regions about 50 to 100 Å. long in the polypeptide chain.<sup>24</sup> The gelation of gelatin can then be viewed as the disorderly and incomplete reassociation of damaged collagen molecules producing not an orderly collagen fibril but a highly randomized structure which retains only a remnant of its higher calling.

Acknowledgment.—The authors want to thank Professor David E. Waugh and Mr. David Yphantis for performing the sedimentation experiments on our samples. We are indebted to the Office of Naval Research (Contract No. N5ori-07654) for the support of part of this work.

#### Appendix

Application of the Hard Sphere Equation of State to the Scattering of Gels.—Einstein first showed that the relation between light scattering and osmotic pressure obtained from fluctuation theory was

$$Kc/R_0 = [RT(\partial \pi/\partial c)_{\mathrm{T,p}}]^{-1}$$
(1)

where  $\pi$  represents the osmotic pressure. Considering  $\pi$  equivalent to the gas pressure, p, we can characterize the scattering in terms of theories which describe deviations from ideality in dense gases or liquids. The oldest and most commonly employed of these is, of course, the virial expansion. Indeed, it already has been demonstrated<sup>18</sup> that the light scattering from concentrated solutions in which the molecular interactions were exceptionally large could be expressed by

$$KcM/R_0 = 1 + 2BMc + 1.875(BMc)^2 + 1.148(BMc)^3 + 0.964(BMc)^4$$
 (2)

This equation is obtained from equation 1 by using the Boltzmann virial coefficients for hard spheres. It is obvious that this equation can only be applied when the quantity BMc is less than one, since otherwise the right side will not converge. In the case of gelatin aggregates, we find that BMc in a 0.54 g./100 cc. solution is equal to 1.11, and equation 2 cannot be used.

It is necessary therefore to develop the light scattering properties of very non-ideal solutions in terms of the equation of state for hard sphere gases. For this purpose we use the results obtained by Kirkwood, Maun and Alder<sup>25</sup> which gives pv/NkTas a function of  $v/v_0$  where  $v_0$  is the volume per mole in a closed packed arrangement. By making use of the fact that  $N/v = cN_0/M$ ,  $v_0 = 2/Na^3$ , and  $B = 2\pi a^3 N_0/3M^2$ , pM/cRT is obtained as a function of BMc. Next, we let BM be a parameter, and calculate c from BMc for various values of BM. Then by multiplying pM/cRT by the c just calculated, one obtains pM/RT as a function of c for each value of BM. Finally, by plotting pM/RTvs. c, and determining the slope of the curves of

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Fig. 17.—Light scattering of a hard sphere fluid.

constant BM at a series of c, we obtain  $KcM/R_0$  as a function of c and BM. These results are plotted in Fig. 17.

As the first test of the applicability of the scattering of a hard sphere fluid to gelatin, we can see if the concentrated aggregated solution (0.54 g./100 cc.) for which equation 2 was inadequate can be accommodated. Since  $M = 5.9 \times 10^6$  and  $Kc/R_0$  is  $1.21 \times 10^{-6}$ , the value of  $KcM/R_0$  is 7.14. The location of this point on Fig. 17 shows that it should correspond to a system for which the product BM equals about 220. This is in quite good agreement with the experimental value of this product, 206. Thus we see that this theory appears to be applicable in one case where the deviations from ideality are so great that the virial expansion is not applicable.

We now wish to find out to what extent the theory of scattering of a hard sphere fluid can be applied to gelatin gels. We start out with two adjustable parameters, the particle weight, M, and the second virial coefficient for hard spheres, B. By recognizing the fact that no matter what model is employed for the scattering elements in the gel, B must bear some functional relation to M. It is clear that we are actually dealing with only one independent adjustable parameter. Consequently the curves of constant BM in Fig. 17 can be considered simply as curves of constant M. Since the ordinate involves M also, it follows that each of the family of curves in Fig. 17 corresponds to the scattering expected from a series of non-

ideal solutions (or gels) in which M remained constant as the concentration is varied. To compare the experimental results with theory, we must choose an arbitrary value for M, and multiply the observed values of  $Kc/R_0$  by this number and plot the results. Curve 1 in Fig. 17 shows the result for M = 5,900,000 (the highest particle weight observed for gelatin aggregates). It appears that the scattering is almost exactly that expected for a system in which BM = 100, and the particle weight, M, remained constant. Similar results are obtained for M = 1,400,000, except that in this case the experimental results correspond to the BM = 50 curve (see curve 2, Fig. 17).

Unfortunately there is no way we can decide which of several possible values of M is the correct one. However, some evidence that curve 1 is the better representation of the results can be obtained by comparing the experimentally observed values of  $R_0$  with those predicted by theory, assuming BM = 100 and M = 5,900,000. In Fig. 16, we saw that both the theoretical and experimental values of  $R_0$  go through a maximum as a function of concentration, and that this maximum actually occurs at roughly the same concentration. Since the location of the maximum depends on the value of BM, the correspondence of the maximum offers additional support that the choice of 100 for the parameter BM is approximately correct, and hence the mass of the scattering element in the gels is probably closer to 5,900,-000 than to 1,400,000.

# ION-EXCHANGE RESINS. X. MAGNESIUM-POTASSIUM EXCHANGE WITH A POLYSTYRENESULFONIC ACID CATION-EXCHANGE RESIN<sup>1</sup>

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The practical (molal) distribution coefficient for magnesium-potassium exchange with a polystyrenesulfonic acid cationexchange resin is  $0.14 \pm 0.02$  for a wide range of solution phase normalities (0.001-1.0) and resin phase compositions ( $X_{\rm k} = 0.01-0.78$ ). Also, truly monofunctional resins show exactly the exchange capacity toward magnesium as they do toward univalent cations.

This paper describes the selectivity coefficients obtained for magnesium-potassium exchange with a 10% cross-linked polystyrenesulfonic acid resin. The cationic composition of the resin phase was varied within wide limits, as was the ionic strength of the equilibrating solution. While polyvalent cation-exchange processes have been studied, notably by Bauman and Eichhorn,<sup>3</sup> Boyd, Schubert and Adamson,<sup>4</sup> Kressman and Kitchner,<sup>5</sup> Marinsky,<sup>6</sup> Duncan and Lister,7 and Hogfeldt, Ekedahl and Sillen,<sup>8</sup> these studies usually were carried out at a single ionic strength, or with no variation in the composition of the resin phase, or with a resin which was not monofunctional and could conceivably undergo specific reactions with some of the cations. Also, most of these studies employed the heavier alkaline earth metals or other cations where complications due to ion-pair formation with the sulfonic acid group might supervene, as pointed out by Gregor. 9, 10

#### Experimental

Resin.—The exchange studies were carried out with polystyrenesulfonic acid resins having about 10% cross-linking (Dowex-50, Dow Chemical Co.). The conditioning procedures were described in an earlier paper in this series.<sup>11</sup>

**Procedures.**—All experiments were performed using a small amount of resin (0.5-1 g.) in a small column. A large excess of solution was passed through this column until equilibrium was reached, as evidenced by an analysis of the effluent. In several instances, equilibrium was approached from both directions; the same state resulted. The ionic composition of the resin phase was determined by drawing off the excess solution by applying suction for a few moments, followed by passing through a few ml. of distilled water, and then eluting the resin with concentrated ammonium chloride solution. Where concentrated equili

(1) The authors thank the Office of Naval Research for the support given this work.

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ibrating solutions (1 molal) were used, the resin phase was separated by the centrifugation technique<sup>9</sup> since the nonexchange electrolyte content is appreciable at these concentrations, and was included in the resin phase composition. The centrifugation technique also was used when resin volumes were determined. All data were obtained for systems at room temperature (24-26°).

Potassium was determined by flame photometer (Perkin-Elmer, Model 52A), using calibration curves made up using appropriate concentrations of magnesium and ammonium chloride, which interfere in the determination. Magnesium was determined by the Schwarzenbach titration method. Duplicate determination agreed within  $\pm 1\%$ . Capacity Measurements.—The capacity of these resins is the same to all low molecular weight univalent cations or

Capacity Measurements.—The capacity of these resins is the same to all low molecular weight univalent cations or mixtures thereof at low concentrations, as was described in an earlier paper.<sup>11</sup> However, in this earlier study it was observed that in dilute solution the magnesium capacity was significantly larger (5.23 meq./g.) than for univalent cations (4.90 meq./g.), and that this excess capacity decreased gradually as the resin composition was varied in favor of the univalent ion (potassium). It was thought that complex ions as  $MgOH^+$  might be responsible. These results were obtained using a sample of the commercial resin (Dowex-50) which was quite black.

In the present study this point was re-examined using resin DVB 10, prepared in this Laboratory,<sup>11</sup> which had a light amber color; it was found that this resin capacity was the same toward both magnesium and potassium and all mixtures of these ions. As a check on the earlier work, a column of the same black resin used in the earlier study was placed in the hydrogen state, then treated with an excess of 0.1 N potassium chloride; 4.90 meq. of hydrogen ions was eluted. When the same column in the hydrogen state was treated with excess 0.1 N magnesium chloride, 5.12 meq. of hydrogen was eluted although the magnesium capacity was 5.23 meq. The difference between the equivalents of magnesium absorbed and of acid eluted by magnesium may be due to hydrolysis or the presence of acid absorbing groups in the resin.

The differences exhibited by these two resins are probably due to the presence of weak acid groups, presumably of the carboxyl type, which appear to be present in the black, commercial type resins. The Dowex-50 titration curves do show a small inflection at about pH 7, which is absent in the DVB 10 resin. The presence of these groups may be explained by the degradation of the polymer which is known to result from strong sulfonation procedures which leave the product charred. Samples of Dowex-50 obtained recently are lighter in color and more monofunctional, showing only 3% more capacity to magnesium than to the univalent ions. Both resin samples (Dowex-50) showed the same selectivity, within experimental error. Wet Weights.—The specific volume  $V_e^r$  (centrifuged

Wet Weights.—The specific volume  $V_{e^r}$  (centrifuged volume of 1 gram of hydrogen resin) of the resin samples in various exchange states is shown in Fig. 1 as a function of Xr<sup>r</sup>, the potassium equivalent fraction (equivalents of potassium per total equivalents present) in the resin phase. The corresponding weight of solvent  $W_{w^r}$ , calculated from the centrifuged weight and the resin composition, is also shown. The curves are regular. The larger volume of the magnesium form resin is presumably the result of the larger hydrated molar volume of the magnesium ion.

Distribution Coefficients.—Results of the determinations of distribution coefficients are shown in Table I for values obtained at four different normalities of the equilibrating solution, 1.0, 0.1, 0.01 and 0.001 N. The first column

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gives  $X_{\mathbf{K}}$ , the potassium equivalent fraction of the equilibrating solution, the second,  $X_{\mathbf{K}^{\mathsf{r}}}$  and the third the calculated practical (molal) distribution coefficient

$$K^{\mathrm{m}}_{\mathrm{d}} = K^{\mathrm{M}\mathbf{g}}_{\mathrm{K}} = \left(\frac{m_{\mathrm{M}\mathbf{g}}}{m_{\mathrm{K}}^2}\right)^{\mathrm{r}} \left(\frac{a_{\mathrm{K}^{+2}}}{a_{\mathrm{M}\mathbf{g}^{++}}}\right)$$

Here m is the molality and "a" the molal activity. Values of  $m^r$  for ion species present in the resin phase were calculated from the weight of the solvent in the centrifuged resin.

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DISTRIBUTION	Coefficients	FOR	MAGNESIUM-POTASSIUM		
EXCHANGE					

$X_{\rm K}$	Xĸ	$K_{\mathbf{K}}{}^{\mathbf{M}\mathbf{g}}$
	1.0 N	
0.74	0.72	0.17
. 68	.64	. 18
. 50	. 48	.16
. 29	.32	.12
	0.1 N	
0.98	0.78	0.12
.74	.39	. 15
.68	.36	.14
. 50	.25	.12
. 29	.13	.13
	<b>0.01</b> N	
0.99	0.52	0.14
. 87	. 28	. 12
. 32	.040	.12
	0.001 N	
0.98	0.20	0.16
.50	. <b>02</b> 9	. 12
.25	.010	. 16

A sample calculation of  $K_d^m$  from a typical experiment is as follows: Consider the line of data in Table I where the solution normality is 0.1,  $X_{\rm R} = 0.74$  and  $X_{\rm K}^r = 0.39$ . While the value of  $K_d^m$  does not depend upon the extensive properties of the resin phase, a given amount of resin is taken as a basis for calculation. Here we select the "specife" amount of resin, *i.e.*, one gram of dry, hydrogen resin. From Fig. 1 the total capacity is 5.20 meq./g., and at  $X_{\rm K}^r =$ 0.39 the specific weight of water in the resin phase is 0.73 g. Then the moles of potassium in the resin are 0.39 (0.00520) or 0.00203, the moles of magnesium 0.61 (0.00520)/2 or 0.00159. Since the water content is 0.73 g., the resin phase molality of potassium is 2.78, of magnesium is 2.18. The solution phase molalities are 0.074 for potassium, 0.013 for magnesium.

Then  $K_{d^m}$  (neglecting solution activity coefficients) is

$$K_{\rm d}{}^{\rm m} = \frac{2.18}{(2.78)^2} \times \frac{(0.074)^2}{0.013} = 0.12$$

The solution phase molal activity coefficients for the cationic species were calculated from the weight of the solvent in the centrifuged resin. The molal activities are for the cationic species. These were calculated on the assumption that in potassium chloride solutions  $\gamma_{+} = \gamma_{-} = \gamma_{\pm}$ , that in mixtures of potassium and magnesium chlorides  $\gamma_{\pm}^{\rm KCl}$  is the same as in solutions of potassium chloride of the same total ionic strength, and that under the same conditions  $\gamma_{\pm}^{\rm MgCl_2}$  is the same as for magnesium chloride solutions of the same total ionic strength. Accordingly,  $\gamma_{\rm Mg^{++}}$  and  $\gamma_{\rm K^+}$  can be calculated. This method is described by several authors, see, e.g., Sollner and Gregor.<sup>12</sup> It should be noted that this type of calculation is very approximate. The value of the term  $a^{2}_{\rm K^+}/a_{\rm Mg^{++}}$  calculated in this manner does not differ by more than 25% from the value calculated

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Fig. 1.—Specific centrifuged wet weight  $W_w^r$  ( $\bigcirc$ ) and wet volume  $V_s^r$  ( $\bigcirc$ ) for a polystyrenesulfonic acid resin (Dowex-50) as a function of the potassium equivalent fraction  $X_{\rm K}^r$ . Exchange capacity, 5.20 meq./g. as hydrogen form resin. Total normality of solution phase - 0.01.

#### Discussion

Exact expressions for equilibrium constants in ion-exchange processes are known.<sup>13,14</sup> Similar expressions for polyvalent ion-exchange processes are easily derived. Neglecting solvent transport and pressure-volume free energy terms, if one assumes that the standard chemical potential of each diffusible species is the same in both resin and solution phases, it follows that for divalent (A)-monovalent (B) cation exchange in an *ideal* system, using mole fractions

$$K_{\mathsf{d}}{}^{N} = \left(\frac{N_{\mathsf{A}}}{N_{\mathsf{B}}{}^{2}}\right)^{*} \frac{a_{\mathsf{B}}{}^{*2}}{a_{\mathsf{A}}{}^{**}} = 1$$

where  $K_d^N$  is the rational selectivity coefficient; the cationic activities in this and following expressions are expressed in a consistent frame of reference for expressing composition, namely, rational, molal, etc. For real systems, the experimentally determined value of  $K_d^N$  is then a function of deviations from ideal behavior. Subject to the simplifying assumptions made earlier, and if the activity coefficients in the resin phase are constant, and if other effects as ion-pair formation do not supervene,  $K_d^N$  should be sensibly constant. Assuming that the resin phase contains only the resinate salts and solvent (neglecting non-exchange electrolyte which is a micro-component in dilute solutions)

$$K_{\mathbf{d}}^{N} = \left[\frac{n_{\mathbf{A}}(n_{\mathbf{A}} + n_{\mathbf{B}} + n_{\mathbf{w}})}{n_{\mathbf{B}^{2}}}\right]^{r} \frac{a_{\mathbf{B}^{+2}}}{a_{\mathbf{A}^{++}}}$$

where the *n*'s refer to numbers of moles. Similarly, one can define the practical (molal) selectivity coefficient  $K_d^m$ 

$$\underline{K}_{d}^{m} = \left(\frac{m_{A}}{m_{B}^{2}}\right)^{r} \frac{a_{B}^{+2}}{a_{A}^{++}} = \left[\frac{n_{A}}{n_{B}^{2}} \times \frac{18n_{w}}{1000}\right]^{r} \frac{a_{B}^{+2}}{a_{A}^{++}}$$

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and the rational (molar) selectivity coefficient

$$K^{C}_{d} = \left(\frac{C_{A}}{C_{B}^{2}}\right)^{r} \frac{a_{B}^{+2}}{a_{A}^{++}} = \left(\frac{n_{A}}{n_{B}^{2}}V\right)^{r} \frac{a_{B}^{+2}}{a_{A}^{++}}$$

where the volume term V is the molar volume of the resin phase.

If both resin and solution phases are ideal and dilute, all three  $K_d$ 's are unity. For concentrated and ideal systems, only  $K_d^N$  would be unity. However, even at the total molalities which prevail in DVB 10 resins, ( $m_{K'} = 8$  at  $X_{K'} = 1$ ), terms for the solvent are so much larger than other terms that the numerical values of  $K_d$  are not very different. The same is, of course, true for real systems. For example, using the numerical values used previously

$$K_{d}^{m} = \left[\frac{1.59}{(2.03)^{2}} \times \frac{(18)40.5}{1000}\right]^{r} \frac{(0.074)^{2}}{0.013} \times \frac{1000}{(18)55.5}$$
$$K_{d}^{N} = \left[\frac{1.59}{(2.03)^{2}} (1.59 + 2.03 + 40.5)\right]^{r} \frac{(0.074)^{2}}{0.013} \times \frac{1}{55.6}$$

The two expressions differ only by the factor 40.5/55.5 in the  $K_d^m$  expression and (40.5 + 3.62)/55.6 in the  $K_d^N$  expression, or by about 8%. Relatively small differences would also be found when using the  $K_d^c$  expression.

Both  $K_d^N$  and  $K_d^m$  require the same data for their calculations; however, the practical (molal) expression is employed here because of its wider usage. The use of  $K_d^C$  is less attractive, because it requires volume data in addition. Some earlier authors have simply used numbers of moles, as

$$K_{\rm d} = \left(\frac{n_{\rm A}}{n_{\rm B}^2}\right)^r \frac{a_{\rm B}^{+2}}{a_{\rm A}^{++}}$$

but in this expression  $K_d$  becomes a function of the amount of resin taken. This factor has been corrected for by later authors who introduced the capacity Q of the resin, and used the expression

$$K_{\rm d}^{Q} = \left(\frac{n_{\rm A}}{n_{\rm B}^2}Q\right)^{r} \frac{a_{\rm B}^{+2}}{a_{\rm A}^{++}}$$

This latter expression is somewhat analogous to

 $K_{d}^{m}$  or  $K_{d}^{C}$  because Q is proportional to  $V^{r}$  or to  $W_{w}^{r}$ , except that it does not vary with resin phase composition.

For most exchange processes there is a change in  $W_{\rm w}^{\rm r}$ , the specific weight of sorbed water, with  $X_{\rm K}^{\rm r}$ . While this factor is part of the  $K_{\rm d}^{\rm m}$  and  $K_{\rm d}^{\rm N}$  expressions, this change is usually not significant. Values of  $W_{\rm w}^{\rm r}$  for a similar resin in different states taken from the data of Gregor, Gutoff and Bregman<sup>9</sup> is as follows: H, 0.88; Li, 0.88; Na, 0.77; K, 0.66; NH<sub>4</sub>, 0.67; Ag, 0.46; Mg, 0.86; Ca, 0.77; Sr, 0.72; Ba, 0.62. For magnesium-potassium exchange,  $W_{\rm w}^{\rm r}$  varies from 0.66 (K state) to 0.86 (Mg state), a variation of only  $\pm 15\%$ . For calcium-magnesium exchange the variation is zero. Therefore only relatively small errors will result from a neglect of changes in  $W_{\rm w}^{\rm r}$  alone.

Table I shows that the molal selectivity coefficient  $K_{\rm K}{}^{\rm Mg}$  is remarkably constant over the wide solution concentration range from 1.0 to 0.001 N, and over a wide range  $(X_{\rm K}{}^{\rm r} = 0.01-0.78)$  of resin compositions. First, it is important to point out that the numerical value of  $K_{\rm d}$  is determined to a minor extent by the choice of units, and that it contains a solvent term. The fact that  $K_{\rm d}{}^{\rm m}$  is less than unity does then not mean *per se* that the resin shows a preference for potassium, any more than it means the converse.

The fact that  $K_d^m$  is constant over a wide range of solution concentrations is consistent with ionexchange equilibria in general.<sup>14</sup> However,  $K_d^m$  is also constant at different values of  $X_{\mathbf{K}^{\mathbf{r}}}$ . In almost all cases of cation exchange, the selectivity coefficient  $K_{\rm B}{}^{\rm A}$  decreases as the equivalent fraction of the reference ion  $X_{A}^{r}$  increases. A typical example of this effect is to be found for potassium-tetramethylammonium exchange with sulfonic resins of different degrees of cross-linking.<sup>14</sup> The principal exception to this effect occurs when  $K_{\rm d}$  is unity for a particular exchange process, *i.e.*, neither ion is preferred. With potassium-magnesium exchange, one is then led to the conclusion that here neither ion is sorbed selectively, and as a result  $K_d$  does not vary with  $X_{\rm K}^{\rm r}$ .

# SLOW RELAXATION MECHANISMS IN CONCENTRATED POLYMER SOLUTIONS<sup>1</sup>

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The contributions of the slowest relaxation mechanisms to time-dependent mechanical behavior in concentrated polymer solutions can be derived from dynamic viscosity, stress relaxation, or (according to a recent theory of DeWitt) apparent viscosity in non-Newtonian flow. The results of such measurements are compared for four samples of polyisobutylene, one of polystyrene, and one of polyvinyl acetate. They are in close agreement with one exception. For samples not too heterogeneous with respect to molecular weight, the time-dependent behavior at the slow end of the time scale can be approximately predicted by a modification of the theory of Rouse, the only quantities needed being the molecular weight and steady flow viscosity. The elastic compliance of a linear polymer in steady-state flow is dominated by the slow relaxation mechanisms; according to the modified Rouse theory, it is  $J = (2/5)M_{1+1}M_x/M_x cRT$ , where c is concentration in g./cc. and the other symbols have their usual significance.

#### Introduction

Measurements of the time-dependent mechanical properties of concentrated polymer solutions<sup>3,4</sup> reveal the presence of elastic mechanisms with a wide distribution of relaxation times, similar in shape to the distributions obtained for undiluted linear polymers.<sup>5,6</sup> At short times, there is a large very broad peak associated with the transition from soft viscoelastic to glass-like consistency<sup>7</sup>; at longer times, a region of low or zero slope on a logarithmic scale; and at still longer times, a rather sharp drop where the elastic contributions vanish. The present paper is concerned only with this last region which describes the slowest relaxation mechanisms. The latter are of particular interest because they depend, more than any other, on molecular weight and molecular weight distribution. The steady flow viscosity<sup>9</sup> and the steady-state elastic compliance,<sup>9</sup> as well as the elastic energy stored in steady-state flow,9 and other practical aspects of behavior such as the apparent viscosity observed for flow through a short capillary,<sup>10</sup> depend primarily on the distribution of mechanisms with the longest relaxation times.

Examination of the slow relaxation mechanisms can now be facilitated by two recent developments. One is the elaboration of molecular theories<sup>11,12</sup> for the relaxation process, which are quite successful in predicting the time-dependent behavior of polymers homogeneous with respect to molecular weight, especially in dilute solution.<sup>11</sup> They show that the relaxation distribution function in this re-

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- (9) F. W. Schremp, J. D. Ferry and W. W. Evans, J. Appl. Phys., 22, 711 (1951).
  - (10) T. L. Smith, J. Polymer Sci., in press.
  - (11) P. E. Rouse, Jr., J. Chem. Phys., 21, 1272 (1953).
  - (12) F. Bueche, ibid., 22, 603 (1954).

gion is discrete rather than continuous, the discrete contributions corresponding to different modes of molecular motion. The magnitudes of the relaxation times depend on a segmental mobility,<sup>11</sup> B, or its reciprocal,  ${}^{12} f$ , which cannot be specified by theory. In dilute solution, B can be taken as the same for all segments and modes of segmental motion; and since the steady flow viscosity also depends on B, the latter quantity can be eliminated and the time-dependent properties are expressed in terms of the viscosity with no unknown parameters.<sup>11</sup> In concentrated solutions and undiluted polymers. B is not the same for all segments; the interlacing of molecules prolongs the long relaxation times more than the short ones,4 and the effective value of B derived from steady flow viscosity decreases markedly with increasing molecular weight.<sup>13</sup> Nevertheless, if the effective value of Bis the same for the four or five modes of motion with the longest relaxation times, this parameter can still be eliminated in terms of the viscosity, since the latter is strongly dominated by the slowest relaxation times. It should then be possible to predict time-dependent behavior at the slow end of the time scale from simply the steady flow viscosity and the molecular weight.

The other recent development is a macroscopic theory<sup>14</sup> which indicates that measurements of non-Newtonian flow in viscoelastic systems are equivalent to measurements of dynamic viscosity.

#### TABLE I

#### MOLECULAR WEIGHTS OF POLYMER SAMPLES

Polyme	r	Descrip- tion	$ ext{No.} \\  ext{av.} \\  imes 10^{-6}  ext{}$	Vis- cosity av $\times$ 10 <sup>-6</sup>	$\overset{\mathrm{Wt.}}{\overset{\mathrm{av.}}{\scriptstyle 10^{-6}}}$	Refer- ence
Polyisobutylene H		Blend	0.22	0.69	0.83	16
	FJ	Sharp fraction	11	1.00	1.00	17
	N	Unfrac- tionated		1.1		17
	W-2	Rough fraction	•••	2.51		17
Polystyrene	19F	Unfrac- tionated	0.20		0.37	3
Polyvinyl acetate	AYAX	Unfrac- tionated	0.14		а	15

<sup>a</sup> Probably quite high (a high-conversion commercial sample).

(13) F. Bueche, ibid., 20, 1959 (1952).

(14) T. W. DeWitt, J. Appl. Phys., in press.

This affords the opportunity of utilizing previously unpublished data for the dependence of viscosity on rate of shear, and comparing the results with those of dynamic viscosity and stress relaxation, as well as with the predictions of the Rouse theory modi-

fied for concentrated solutions. **Materials.**—The six polymer samples for which data are compared here have been described in more detail in previous publications.<sup>3,4,15-17</sup> Their average molecular weights are given in Table I.



Fig. 1.—Points, reduced apparent viscosity,  $\eta_a/\eta$ , plotted against reduced rate of shear for six polymer samples. Solid curves, reduced dynamic viscosity plotted against reduced circular frequency (19F and AYAX). Dashed curves, prediction of modified Rouse theory.

#### Non-Newtonian Flow

The dependence of rate of shear  $(\dot{\gamma})$  on shearing stress  $(\mathfrak{T})$ , obtained from measurements in coaxial cylinder apparatus, has been previously reported<sup>9</sup> for solutions of polymers N, W-2, and 19F in Decalin; at various temperatures and concentrations, it could be fitted by the equation  $\dot{\gamma} = k_1 \sinh k_2 \mathfrak{T}$ , and values of  $k_1$  and  $k_2$  were tabulated.<sup>9</sup> Similar data on polymers H and FJ in Decalin, not previously published, can be fitted by the same equation; values of  $k_1$  thus obtained have been used for analyzing stress relaxation data on their solutions.<sup>4</sup> Data on solutions of polymer AYAX in 1,2,3-trichloropropane do not follow the above equation, however; they require the parabolic relation  $\dot{\gamma} = k_3 \mathfrak{T} + k_4 \mathfrak{T}^2$ , originally proposed for liquid polyisobutylene<sup>18</sup> and later used for various polymer solutions.<sup>19,20</sup>

According to the theory of DeWitt,<sup>14</sup> the form of the dependence of  $\gamma$  on  $\mathfrak{T}$  should be related to

- (15) W. M. Sawyer and J. D. Ferry, J. Am. Chem. Soc., 72, 5030 (1950).
- (16) K. E. Van Holde and J. W. Williams, J. Polymer Sci., 11, 243 (1953).
- (17) M. F. Johnson, W. W. Evans, I. Jordan and J. D. Ferry, J. Colloid Sci., 7, 498 (1952).
  - (18) J. D. Ferry and G. S. Parks, Physics, 6, 356 (1935).
  - (19) J. D. Ferry, J. Am. Chem. Soc., 64, 1330 (1942).
  - (20) A. B. Bestul and H. V. Belcher, J. Colloid Sci., 5, 303 (1950).

the form of the relaxation distribution function, and it is therefore not surprising that different polymers should show different behavior. It would be expected that a sample homogeneous with respect to molecular weight would follow a dependence resembling the hyperbolic sine equation at quite low stresses, while samples with broad molecular weight distributions might deviate. Accordingly, rather than attempt an analytical description, we now simply examine the non-Newtonian behavior graphically, taking advantage of DeWitt's demonstration that reduced variables<sup>21</sup> are applicable and measurements at different concentrations and temperatures can be combined to form a single composite curve for a given sample.

If all relaxation times are identically dependent on concentration and temperature,<sup>21</sup> a single curve should be obtained by plotting the reduced variables  $\eta_{ar} = \eta_a/\eta$  against  $\dot{\gamma_r} = \dot{\gamma_\eta}T_0/Tc$ . Here  $\eta$  is the steady flow viscosity at vanishing rate of shear,  $\eta_a$ the apparent viscosity  $(\mathfrak{T}/\dot{\gamma})$ , c the polymer concentration in g./cc., T the absolute temperature, and  $T_0$  a standard temperature (298°K.).

The value of  $\eta$  obtained by extrapolation of the non-Newtonian flow measurements<sup>9</sup> was usually in fairly close agreement with that measured by the falling ball method at low shear rates,<sup>17</sup> and the former was used for the calculation of reduced variables. However, for sample H it was necessary to use the falling ball values of  $\eta$  to obtain reasonable results; the extrapolation from non-Newtonian flow (which gave considerably lower values) was unsatisfactory, probably because of the wide spread of molecular weights in this polymer. The extrapolated values of log  $\eta$  for sample 19F were also doubtful and had to be increased by 0.05 to 0.10 to obtain consistent results.

The value of  $\dot{\gamma}$  for these calculations was taken as the average integrated over the annular space between the coaxial cylinders, which for our instrument<sup>9</sup> differs by only 0.5% from the arbitrary average previously used (the geometric mean of the values at the surfaces of the two cylinders).

The composite graphs of  $\eta_{ar}$  against  $\dot{\gamma}_{r}$  are shown in Fig. 1. The individual temperatures (15, 25 and 35° in each case) and concentrations are not identified, but the concentration ranges may be summarized as follows: H, 33.3%; FJ, 15.8-24.8%; N, 15-25%; W-2, 12-20%; 19F, 30.4-46.4%; AYAX, 40.3%. In each case the points superpose very well to form a single curve, supporting DeWitt's prediction<sup>14</sup> that reduced variables apply to this sort of plot.

According to DeWitt's theory, this plot should be identical with that for  $\eta'/\eta$  against  $\omega_r = \omega \eta T_0/Tc$ , where  $\eta'$  is the real part of the complex dynamic viscosity and  $\omega$  the circular frequency.<sup>21a</sup> Dynamic viscosity measurements in the appropriate frequency range are available<sup>3,22</sup> for 19F and

(22) J. D. Ferry, W. M. Sawyer, G. V. Browning and A. H. Groth, Jr., J. Appl. Phys., 21, 513 (1950).

<sup>(21)</sup> J. D. Ferry, J. Am. Chem. Soc., 72, 3746 (1950).

<sup>(21</sup>a) According to a very recent molecular theory of Dr. F. Bueche (private communication), these two functions should be similar but not identical. The Bueche theory gives  $\eta'$  values somewhat lower than those of the Rouse theory (eq. 1 and 2), but  $\eta_{\rm R}$  values slightly higher than the corresponding Rouse values of  $\eta'$ .

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AYAX, derived largely from single transducer measurements; they are drawn as solid curves in Fig. 1. For 19F the agreement between the two functions is excellent. For AYAX the reduced dynamic viscosity lies to the right of the reduced non-Newtonian viscosity. The source of this discrepancy is not understood; it may be related to the wide spread of molecular weights and branching to be expected in this commercial sample.

# Comparison of $\eta_{\rm a}/\eta$ with Rouse Theory

The theory of Rouse predicts the frequency dependence of  $\eta'/\eta$  for a very dilute solution of a homogeneous polymer as follows<sup>11</sup>

$$\frac{\eta' - \eta_0}{\eta - \eta_0} = \frac{6}{\pi^2} \sum_{p=1}^N \frac{p^2}{p^4 + \omega^2 \tau_1^2}$$
(1)  
$$\tau_1 = 6(\eta - \eta_0)/\pi^2 nkT$$
(2)

where  $\eta_0$  is the solvent viscosity, *n* the number of molecules per cc., and k Boltzmann's constant. The index p refers to different modes of coordination of the polymer segments; the upper limit N is of no significance in the present application, since at low frequencies the series converges rapidly. These equations can be readily extended to concentrated solutions if it is assumed that all relevant relaxation times are prolonged by the same factor by the interlacing of foreign molecules through a given polymer coil. Since we are concerned here with the slow end of the relaxation spectrum, and the behavior is dominated by the first five modes or so, it is necessary only that the five longest relaxation times obey this condition. (The shorter ones, as a matter of fact, behave differently.<sup>4</sup>) For the concentrated solutions of Fig. 1,  $\eta_0$  is quite negligible. It is convenient then to recast equations 1 and 2 in terms of reduced variables, noting that nk =cR/M, where M is the molecular weight

$$\eta'_{\rm r} = \eta'/\eta = \frac{6}{\pi^2} \sum_{p=1}^N \frac{p^2}{p^4 + \omega^2 \tau_1^2} \tag{3}$$

$$\omega \tau_1 = \omega_r (6M/\pi^2 R T_0) \tag{4}$$

If  $\eta'_r$  as a function of  $\omega_r$  is equivalent<sup>14</sup> to  $\eta_{ar}$  as a function of  $\dot{\gamma}_r$ , equations 3 and 4 should predict also reduced curves of the type of Fig. 1.

For homogeneous polymers, in this formulation, plots of  $\log \eta'_r$  against  $\log \omega$  should all have the same shape, and their locations on the abscissa axis should depend only on their molecular weights. For a heterogeneous polymer, of course, the shape of the curve should depend on the molecular weight distribution, and for purposes of qualitative comparison the choice of an average molecular weight in (4) is arbitrary. The weight or viscosity average has been used for all except AYAX, where only the number-average is available. The theoretical curves are drawn as dashed lines in Fig. 1 for comparison with the experimental values of  $\eta_{ar}$ . For the sharp fraction FJ, the agreement is very close, although the experimental curve does not fall quite so steeply as the Rouse function, as would be expected for a moderate degree of molecular weight distribution. For samples W-2 and N the experimental curves are also closely similar in shape to the Rouse function and lie fairly near the predicted position on the  $\gamma_r$  scale. The other three experimental curves are less sharply curved than the Rouse function and lie to the left, as would be expected for a wide distribution of molecular weights. The deviation between theory and experiment is particularly marked for H (a blend of high and low molecular weight fractions) and AYAX (a high conversion polymer, probably branched).

The comparisons shown in Fig. 1 indicate that the Rouse theory can successfully predict the dynamic viscosity at low frequencies, and the non-Newtonian flow at low shear rates, for concentrated solutions of moderately homogeneous polymers. The only data required are the steady flow viscosity and the molecular weight. Since the Bueche theory<sup>12</sup> predicts a closely similar form for the dynamic viscosity, it should have approximately the same success. The effect of molecular weight heterogeneity (and branching) is qualitatively in the direction expected; in principle, the modified Rouse theory could also be applied to a distribution of molecular weights, but only with very tedious calculations.

#### Comparison with Stress Relaxation Data

Equivalent information concerning the slow relaxation mechanism should also be provided by stress relaxation data. Relaxation distribution functions derived from stress relaxation measurements following cessation of steady-state flow have been previously published<sup>4,9</sup> for all the above samples except AYAX. To extrapolate the new measurements on the latter to zero shear rate in the usual manner,<sup>9</sup> a revised calculation is necessary because the hyperbolic sine function previously used is inapplicable. The corresponding calculation for parabolic flow relaxation, outlined in Appendix I, gives

$$\Phi(\ln t) = -(d\mathfrak{T}/d\ln t)2r/t(R-1)$$
(5)

where  $r = k_4/k_3^2$  and  $R = (4r\dot{\gamma} + 1)^{1/2}$ . The latter quantities are obtained from analysis of the non-Newtonian flow and from the rate of shear,  $\dot{\gamma}$ , preceding relaxation. Values of  $\Phi$  calculated from measurements following different rates of shear agree quite well. Values of the reduced distribution function,  $\Phi_r = \Phi T_0/Tc$ , are plotted against reduced time,  $\tau_r = \tau c T/T_0 \eta$ , in Fig. 2 for different rates of shear at three temperatures at 40.3% and at 5° at 35.0%. The reduced variables bring all these data into close superposition.

For a homogeneous polymer whose time-dependent behavior follows Rouse's theory, such a function is fictitious,<sup>4</sup> since the relaxation spectrum at the slow end is discrete rather than continuous; and the fictitious  $\Phi$ 's calculated from stress relaxation and from  $\eta'$  (or  $\eta_a$ ) do not coincide. For a heterogeneous polymer, however, a continuous  $\Phi$  should have meaning, and the values previously calculated from stress relaxation may be compared with values derived from the curves shown in Fig. 1. For the latter calculation, a second approximation is used, analogous to that employed for dynamic viscosity<sup>23</sup>

$$\Phi_{\rm r} = -B\dot{\gamma}_{\rm r} \eta_{\rm ar} \,\mathrm{d} \,\log \eta_{\rm ar}/\mathrm{d} \,\log \dot{\gamma}_{\rm r} \tag{6}$$

where B is a numerical correction factor.<sup>23</sup> The (23) J. D. Ferry and M. L. Williams, J Colloid Sci. 7,  $3 \le 7$  (1952).

results are compared in Fig. 3 for polymers W-2, H, 19F and AYAX. The distribution functions derived from non-Newtonian flow and from stress relaxation lie close together in each case. It appears that the two types of measurement do indeed give equivalent information.



Fig. 2.—Reduced distribution function of relaxation times for polyvinyl acetate AYAX, calculated from measurements of stress relaxation following cessation of steady-state flow at various shear rates. Open circles, concentration 35.0%, 5°. Other circles, concentration 40.3%; pip down, 15°; right, 25°; up, 35°.

#### Calculation of Steady-State Compliance

The total elastic compliance of linear polymers in steady-state flow, J, has recently been found to depend markedly on molecular weight distribution.<sup>16,24,25</sup> For a concentrated solution, in terms of reduced variables, this quantity is related to the relaxation spectrum as follows

 $J_r = \int_{-\infty}^{\infty} \tau_r^2 \Phi_r \, \mathrm{d} \, \ln \, \tau_r$ 

or

$$J_r = \Sigma \tau^2 {}_{\rm pr} G_{\rm pr} \tag{8}$$

(7)

for a continuous<sup>9</sup> or a discrete spectrum, respectively (see Appendix II). Here  $J_r = JTc/T_0$ ,  $\tau_r = \tau cT/T_0\eta$ , and  $G_{\rm pr}$  is the elastic contribution associated with the *p*'th discrete relaxation time, also reduced by the factor  $T_0/Tc$ . Both expressions are weighted by long relaxation times, so the compliance depends primarily on the slow relaxation mechanisms whose distributions are portrayed in Fig. 3. It is of interest to calculate *J* from both theory and experimental data.

For a homogeneous polymer, the Rouse theory expressed in reduced variables specifies that  $G_{pr} =$ 

- (24) H. Leaderman, private communication.
- (25) R. L. Zapp and F. P. Baldwin, Ind. Eng. Chem., 38, 948 (1946).



Fig. 3.—Reduced distribution function of relaxation times for four polymer samples. Solid lines, from reduced apparent viscosity in non-Newtonian flow; dashed lines, from stress relaxation following cessation of steady-state flow.

 $RT_0/M$  and  $\tau_{\rm pr}=6M/p^2\pi^2 RT_0$ . It follows from the summation (8) that

$$J_{\rm r} = (2/5)M/RT_0 \tag{9}$$

so the steady-state compliance should be directly proportional to molecular weight.<sup>26</sup>

For a heterogeneous polymer, if it can still be assumed that the long relaxation times can be calculated by the Rouse theory,  $J_r$  can be expressed in terms of molecular weight distribution; as shown in Appendix II, the result is

$$J_{\rm r} = (2/5)M_{\rm z+1}M_{\rm z}/M_{\rm w}RT_{\rm 0}$$
 (10)

where the symbols for molecular weight averages have their usual significance. Thus the compliance should increase markedly with spread of molecular weight distribution, especially at the high end which weights  $M_z$  and  $M_{z+1}$ . This is in qualitative accord with experiment.<sup>16,24</sup> From the Bueche theory,<sup>12</sup> a corresponding equation can be derived<sup>27a</sup> which is identical with eq. 10 except that the factor 2/5 is replaced by 1/3.

The only sample to which eq. 10 can be applied is probably 19F, for which  $J_r$  has already been derived<sup>9</sup> by integration of stress relaxation data in concentrated solutions, in accordance with eq. 7, as  $1.69 \times 10^{-5}$  (cm.<sup>2</sup>/dyne) (g./cm.<sup>3</sup>). Since the weight and number average molecular weights are approximately in the ratio of 2:1, it may be assumed that the molecular weight distribution follows the "most probable" form and  $M_{z+1}:M_z:M_w$ 

(27a) F. Bueche, private communication.

<sup>(26)</sup> In this connection it is of interest that Spencer's parameter<sup>27</sup> describing non-Newtonian flow in molten polystyrenes is directly proportional to molecular weight. This parameter k may be identified<sup>27,18</sup> with (4/5) J; the lowest values of k/M in Spencer's table, corresponding presumably to the least polydispersity, are about 0.8  $\times$  10<sup>-11</sup> cm.<sup>2</sup> dyne<sup>-1</sup> g.<sup>-1</sup>, for temperatures in the neighborhood of 225°. According to this,  $Jr = 1.67 \times 10^{-11} M$ . Equation 9 gives  $1.62 \times 10^{-11} M$ , in very good agreement.

<sup>(27)</sup> R. S. Spencer, J. Polymer Sci., 5, 591 (1950).

= 4:3:2. Then equation 10, with  $M_{\rm w}$  = 370,000, gives  $J_r$  = 1.8 × 10<sup>-5</sup>, in quite good agreement with the value obtained from experimental data. A still more direct experimental measurement would be from elastic recoil following steady flow, but this is not available.

The value of J has been determined for sample H in the undiluted state.<sup>16</sup> It is impossible to calculate  $J_r$  from stress relaxation data (Fig. 3) and eq. 7 because the measurements do not extend to sufficiently long times to obtain the complete integral. The value of  $J_r$  predicted from eq. 10, using molecular weight averages derived from equilibrium ultracentrifuge measurements,<sup>16</sup> is too large by about a factor of 5. This may be due in part to uncertainty in  $M_z$  + 1, and in part to failure of the assumption that the first four or five modes of relaxation are equally affected by the polymeric medium for all molecules. For an extremely broad distribution, especially in the absence of any diluent, this assumption may not be satisfactory.

#### Conclusions

Dynamic viscosity at low frequencies, stress relaxation following steady-state flow, and non-Newtonian viscosity at moderately low shear rates appear to provide equivalent information concerning the contributions of slow relaxation mechanisms to time-dependent mechanical behavior in concentrated polymer solutions. Of these, the non-Newtonian viscosities are the easiest to measure. For homogeneous and perhaps moderately heterogeneous polymers, the time-dependent behavior at the slow end of the time scale can be approximately predicted by a slight modification of the Rouse theory, only the molecular weight and the steady flow viscosity being required for the calculation. For heterogeneous polymers, the relaxation mechanisms are naturally spread over a wider range of time scale. The modified Rouse theory can be used to predict the steady-state compliance of a heterogeneous polymer with some success.

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# Appendix I

Non-Newtonian Stress Relaxation for a Parabolic Dependence of Rate of Shear Upon Stress.— The calculation is analogous to that previously presented for relaxation of hyperbolic sine flow mechanisms.<sup>9</sup> It applies to relaxation after cessation of steady-state flow, not relaxation after sudden strain. We consider a series of rigidity mechanisms ( $G_i$ ) in parallel (the Maxwell model), each relaxed by a non-Newtonian parabolic flow mechanism such that  $\dot{\gamma}_i = k_{3i}\mathfrak{T}_i + k_{4i}\mathfrak{T}_i^2$ . In such a model, all  $\dot{\gamma}_i$  must be identical, and it can be shown that the relation between  $\dot{\gamma}$  and *total* stress can be parabolic only if  $k_{4i}/k_{3i}$  is the same for all elements; this ratio will be denoted by r. In this case, the stress on the *i*'th element in steady-state flow is  $\mathfrak{T}_{i0} = (R-1)/2rk_{3i}$ , and the total stress is

$$\mathfrak{T}_{0} = [(R-1)/2r]\Sigma(1/k_{3i})$$
(11)

where  $R = (4r\dot{\gamma} + 1)^{1/2}$ .

The relaxation at constant strain for a *single* parabolic Maxwell element can be derived from the differential equation

$$\mathbf{f} = (1/G_{i})(\mathrm{d}\mathfrak{T}_{i}/\mathrm{d}t) + k_{3i}\mathfrak{T}_{i} + k_{4i}\mathfrak{T}_{i}^{2} = 0$$

Since at t = 0 (cessation of steady-state flow and beginning of relaxation)  $\mathfrak{T}_i = \mathfrak{T}_{i0}$ , the solution is

$$\mathfrak{T}_{i}/(k_{\mathbf{3}i}+k_{\mathbf{4}i}\mathfrak{T}_{i})=[\mathfrak{T}_{i0}/(k_{\mathbf{3}i}+k_{\mathbf{4}i}\mathfrak{T}_{i0})]\exp\left(-G_{i}k_{\mathbf{3}i}t\right) \quad (12)$$

The relaxation time,  $\tau_i$ , may be defined as usual as the ratio of the dashpot viscosity at vanishing  $\mathfrak{T}_i$ to the spring rigidity, *viz.*,  $1/k_{3i}G_i$ . Solving (12) for  $\mathfrak{T}_i$  in terms of  $\tau_i$ , r and R yields

$$\mathfrak{T}_{i} = \frac{(R-1)G_{i}\tau_{i}e^{-t/\tau_{i}}}{r[R+1-(R-1)e^{-t/\tau_{i}}]}$$
(13)

The total stress as a function of time is  $\Sigma \mathfrak{T}_i$ , which may now be replaced by an integral, substituting  $\Phi$  d ln  $\tau$  for  $G_i$ . This is then approximated by a cut-off in which exp  $(-t/\tau_i)$  is replaced by zero for  $\tau_i < t$  and unity for  $\tau_i > t$ . The result is

$$\mathfrak{T}(t) = \frac{R-1}{2r} \int_{\ln t}^{\infty} \tau \Phi \, \mathrm{d} \, \ln \tau$$

The usual first approximation calculation of  $\Phi$  is then

$$\Phi(\ln t) = -(\mathrm{d}\mathfrak{T}/\mathrm{d}\ln t)2r/t(R-1) \tag{5}$$

Since the slope of the log-log plot in Fig. 2 is near -2, corresponding to a second approximation correction factor of unity,<sup>23</sup> the latter correction has not been applied.

#### Appendix II

Steady State Compliance of a Heterogeneous Polymer Derived from Modified Rouse Theory.— For a linear viscoelastic body, the energy per cc. stored in steady-state flow under stress  $\mathfrak{T}$  is  $J\mathfrak{T}^2/2$ , where J is the steady-state compliance. Expressed in terms of a series of Maxwell elements, this energy is  $(\mathfrak{T}^2/2)$  [ $\Sigma G_i \tau_i^2/(\Sigma G_i \tau_i)^2$ ]. Thus

$$J = \Sigma G_i \tau_i^2 / (\Sigma G_i \tau_i)^2$$
(14)

In the Rouse theory,<sup>11</sup>  $G_i$  is independent of molecular weight and equal to nkT for every mode of molecular motion. For long relaxation times  $\tau_i$ associated with the p'th mode for molecules of molecular weight M is

$$\tau_{\rm i} = \sigma^2 M^2 / 6\pi^2 p^2 B k T M_{\rm s}^2 \tag{15}$$

where  $M_{\rm s}$ ,  $\sigma$  and B are, respectively, the molecular weight, root mean square end-to-end separation, and mobility of a submolecule or segment. (The exact definition of the submolecule does not matter since these three quantities will cancel out.)

For a heterogeneous polymer, let  $\varphi(M) dM$  be the normalized number distribution of molecular weights, so that

$$\begin{cases} \int M\varphi dM = M_{\rm n} \\ \int M^2\varphi dM / \int M\varphi dM = M_{\rm w} \\ \int M^3\varphi dM / \int M^2\varphi dM = M_{\rm z} \\ \int M^4\varphi dM / \int M^3\varphi dM = M_{\rm z+1} \end{cases}$$
(16)

The sums in (14) are then given by

$$\Sigma G_{\mathbf{i}} \tau_{\mathbf{i}}^{2} = \sum_{p=1}^{\infty} \int (\varphi n k T \sigma^{4} M^{4} / 36 \pi^{4} p^{4} B^{2} k^{2} T^{2} M_{\mathfrak{s}}^{4}) \mathrm{d}M$$
  
$$\Sigma G_{\mathbf{i}} \tau_{\mathbf{i}} = \sum_{p} \int (\varphi n k T \sigma^{2} M^{2} / 6 \pi^{2} p^{2} B k T M_{\mathfrak{s}}^{2}) \mathrm{d}M$$

and

$$J = \sum_{p=1}^{\infty} (1/p^4) \int \varphi M^4 dM / nkT \left[ \sum_{p=1}^{\infty} (1/p^2) \int \varphi M^2 dM \right]^2$$
  
=  $(\pi^4/90) M_{z+1} M_z M_w M_n / nkT (\pi^2/6)^2 (M_w M_n)^2$   
=  $(2/5) M_{z+1} M_z / M_w cRT$   
In terms of reduced variables, since  $J_r = JTc/T_0$ ,  
 $J_r = (2/5) M_{z+1} M_z / M_w RT_0$  (10)

# STUDIES OF THE CROSS-LINKING PROCESS IN GELATIN GELS. III. DEPENDENCE OF MELTING POINT ON CONCENTRATION AND MOLECULAR WEIGHT

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The melting points of solutions of five degraded gelatin samples, with  $M_{\rm w}$  ranging from 33,000 to 72,000, were measured over a concentration range from 20 to 60 g./l. A nearly linear relation was found between the logarithm of the gelatin concentration and the reciprocal absolute temperature of melting. The relation between the logarithm of  $M_{\rm w}$  and the reciprocal absolute temperature of melting was also found to be nearly linear except for the sample of lowest  $M_{\rm w}$ . Annealed gels had generally higher melting points than gels formed by quick chilling. The experimental results are discussed in relation to the cross-linking process considered responsible for the gelation of gelatin solutions. Exothermic heats of reaction ranging from 50 to 220 kcal./mole are calculated for the formation of cross-links if these are assumed to result from a binary association of polymer chains.

#### Introduction

In a previous paper,<sup>1</sup> studies were reported of the rigidities and cptical activities of gelatin gels prepared from a series of degraded ossein gelatins of known average molecular weight. We wish now to report the melting points of gels prepared from the same gelatin stocks. These measurements were obtained at the same time as the rigidities and optical activities. We wish also to present a method of calculating the heat of reaction for the crosslinking process from the dependence of the melting point temperature on gelatin concentration or on weight-average molecular weight.

# Experimental

The following procedure<sup>2</sup> was used to determine the melting points of a number of gelatin gels, all containing 0.15 M NaCl and at pH 7. A 5-ml. sample of the gelatin solution, contained in a stoppered test-tube 11  $\times$  102 mm., was held



Fig. 1.—Relation between gelatin concentration and absolute temperature of melting.  $\bigcirc, \ominus, \odot, \bigcirc, \bigcirc, \bigcirc, \bigcirc$  denote  $M_w$  values of 72,100, 60,000, 52,700, 48,000 and 33,400, respectively. All gels chilled at 0°.

J. D. Ferry and J. E. Eldridge, THIS JOURNAL, 53, 184 (1949).
 R. S. Gordon and J. D. Ferry, Federation Proc., 5, 136 (1946).

at a temperature of  $37^{\circ}$  for one hour. Then the test-tube was plunged into ice-water and stored at 0° for 24 hours. Finally it was placed upside down in a well stirred water-bath at approximately 0° and the bath was warmed at the rate of about 12° per hour. The temperature at which the gel fell to the bottom of the test-tube was taken to be the melting point. When this procedure was followed, the melting point was rather sharp and reproducible to within 0.2°.

Dependence on Gelatin Concentration and Molecular Weight.—Table I gives the results of an investigation of the dependence of the melting point of a gelatin gel on the weight-average molecular weight and concentration of the gelatin. As might be expected, the melting point rises as the concentration and molecular weight increase. In Fig. 1 the logarithm of the gelatin concentration is plotted against the reciprocal absolute temperature of melting for samples of different average molecular weight. Using values interpolated from Fig. 1, the logarithm of the weight-average molecular weight can be plotted against reciprocal absolute temperature of melting, at constant concentrations, as shown by Fig. 2. The significance of these curves will be discussed subsequently.



Fig. 2.—Relation between weight-average molecular weight and absolute temperature of melting,  $\bigcirc$ ,  $\bigcirc$ ,  $\bigcirc$  denote gelatin concentration values of 55, 40 and 25 g./l., respectively. All gels chilled at 0°.

TABLE I

Dependen	CE OF	Melting	Роінт	ON	Gei	ATIN	Con	CEN-
TRATION,	WEIGH	IT-AVERAGE	e Mol	ECUI	LAR	Wei	GHT	AND
CHILLING TEMPERATURE								

Stock soln. diluted	$M_{\rm W} \times 10^{-3}$	Gelatir. concn.,	Melting 1 Chilled at	oint, °C. Chilled at
P6-00	72 1	20 3	27 0	29.2
10 00		28.6	28.0	29.78
		41.6	29.0	30.2
		59.6	29.9	30.5
P6-20	60.0	20.3	22.3	
		28.8	23.6	Not tested
		42.3	24.9	
		59.2	25.9	
L3-80	52.7	20.9	19.5	23.7
		29.5	20.8	24.7
		42.9	22.0	25.4
		61.4	23.0	25.9
L1-120	48.0	19.6	17.2	18.02
		27.7	18.7	22.5
		40.3	19.9	23.8
		57.7	21.0	<b>24.4</b>
P6-180	33.4	20.1	10.9	Did not
		28.4	13.4	$\mathbf{gel}$
		41.4	14.8	-
		59.2	16.0	

Effect of Thermal History.—The melting point of a gelatin gel, like many other of its physical properties, is not a function of state, but depends on the thermal history of the gel. To investigate this effect, the melting points of several samples were determined in the usual way except that the solutions were chilled at  $15^{\circ}$  instead of  $0^{\circ}$ . In every case where gelation occurred within the 24-hour gelling period, the gel melted at a higher temperature than formerly. Furthermore, the dependence of the melting point on concentration was generally diminished. The data are summarized in Table I. In Fig. 3 the logarithm of the gelatin concentration is plotted against the reciprocal absolute temperature of melting for gels chilled at  $15^{\circ}$ .

Other experiments have confirmed the general rule that the stability of a gelatin gel against thermal disruption is favored if the gel structure is formed slowly or if the gel is annealed before melting. For example, the melting point could be raised if the gelatin solution was cooled from 37 to 0° gradually (over the course of 50 minutes) rather than suddenly, or if the chilled gel was warmed more slowly than  $12^{\circ}$  per hour during the melting point determination. Similar conclusions have been reached by earlier investigators.<sup>3</sup>

#### Discussion

The gel point in a polymerizing system is considered to be the point at which a three-dimensional network, infinite in extent, first appears.<sup>4</sup> For the cross-linking of linear macromolecules having any arbitrary initial size distribution, Stockmayer<sup>5</sup> has shown that at the gel point

$$p_{\rm o} = 1/\rho(\lambda_{\rm w} - 1) \tag{1}$$

In this equation,  $\lambda_{w}$  is the weight-average degree of polymerization of the original macromolecules,  $\rho$ is the fraction of monomer units carrying groups capable of forming cross-links (either primary or secondary bonds), and  $p_{c}$  is the fraction of these cross-linkable units (distributed at random along the chains) which have actually formed cross-

(3) L. Arisz, Kolloid-Beih., 7, 12 (1915).

(4) P. J. Flory, J. Am. Chem. Soc., 63, 3083, 3091, 3096 (1941).
(5) W. H. Stockmayer, J. Chem. Phys., 11, 45 (1943); 12, 125 (1944).



Fig. 3.—Relation between gelatin concentration and absolute temperature of melting.  $\bigcirc, \odot, \odot, \bullet$  denote  $M_w$  values of 72,100. 52,700 and 48,000, respectively. All gels chilled at 15°.

links. Equation 1 is valid only if no cyclic structures are formed. If  $\lambda_w >> 1$ , eq. 1 may alternatively be written<sup>6</sup>

$$m_{\rm el} = c/2M_{\rm w} \tag{2}$$

where  $m_{\rm cl}$  is the concentration of cross-links in moles per liter at the gel point, c is the concentration of polymer in g./l., and  $M_{\rm w}$  is the weight-average molecular weight of the polymer before cross-linking. In applying this equation to gelatin, it is assumed that single cross-links are formed by binary associations between chains. Actually, crystallites may act as multiple cross-links, but for the purposes of the present discussion the cross-links are treated as single, all with the same free energy of association.

If the gelatin is in dilute solution, the formation of cyclic structures, *i.e.*, cross-links between two segments of the same molecule, or cross-links between molecules already joined, is very probable. In fact, recent light scattering studies by Boedtker and Doty<sup>6a</sup> indicate that the first stage of gelation is the formation of rather firmly linked aggregates which later join to give the gel. In this case,  $p_c > 1/\rho(\lambda_w - 1)$  and  $m_{\rm cl} > c/2M_w$  at the gel point. We assume, however, that if we designate the concentration of non-cyclic cross-links by  $fm_{\rm cl}$ , then the equation

$$fm_{\rm cl} = c/2M_{\rm w} \tag{3}$$

will hold at the gel (or melting) point even for dilute solutions. The coefficient f can be considered as a function of c,  $M_w$ , the absolute temperature T, and other variables affecting cross-linking.

Dependence on Concentration.—If we denote the molar concentration of free cross-linking loci on the gelatin molecule chains by  $m_i$ , then we may write the equilibrium constant for the binary association of these loci thus

$$m_{\rm cl}/m_{\rm l}^2 = K(T, M_{\rm w}) \tag{4}$$

Although independent of c, K would generally depend on other variables, some of which may not yet be identified.<sup>6b</sup> However, in our series of samples there was a one-to-one correspondence between these other variables and  $M_w$ . Thus, for our

<sup>(6)</sup> J. D. Ferry, Advances in Protein Chem., 4, 1 (1948).

<sup>(6</sup>a) H. Boedtker and P. M. Doty, THIS JOURNAL, **58**, 963 (1954). (6b) A. G. Ward, Brit. J. Appl. Phys., **5**, 85 (1954).

purposes, K is fixed by T and  $M_{\rm w}$ . Equations 3 and 4, on taking logarithms and differentiating with respect to temperature, holding  $M_{\rm w}$  constant, can be combined with van't Hoff's law to give

$$\left(\frac{\mathrm{d}\ln c}{\mathrm{d}T}\right)_{M_{\mathrm{w}}} \left[1 - 2\frac{\partial\ln m_{\mathrm{l}}}{\partial\ln c}\right] = \frac{\Delta H^{\circ}}{RT_{2}} + \left(\frac{\mathrm{d}\ln f}{\mathrm{d}T}\right)_{M_{\mathrm{w}}} + 2\frac{\partial\ln m_{\mathrm{l}}}{\partial T} \quad (5)$$

Here dT does not denote simply an infinitesimal change in temperature, but rather a change in the *gel point temperature*, accompanied by a change in *c* to keep  $fm_{cl}/c$  at the critical value of  $1/2M_w$  which is specified by eq. 3.  $\Delta H^0$  represents the heat of reaction for the process

2 moles cross-linking loci  $\longrightarrow$  1 mole cross-links

This reaction is understood to be carried out at the gel point temperature, and in aqueous solution sufficiently dilute that the solution may be considered ideal. If we assume now that the proportion of cross-linking loci combined is always small, as suggested by the proportionality between rigidity of the gel and the square of the gelatin concentration<sup>1</sup> at temperatures below the melting point, we may write, to a good approximation,  $\partial \ln m_1/\partial \ln c = 1$ , and  $\partial \ln m_1/\partial T = 0$ .

We have also assumed that  $(d \ln f/dT)_{M_w} = 0$ , *i.e.*, that the ratio of the number of non-cyclic crosslinks to the total number of cross-links is unchanged when a gelatin solution at the gel point is warmed and the concentration increased to keep the system at the gel point. For this assumption to be valid, it is sufficient that the heat of the cross-linking reaction be the same for cyclic and non-cyclic cross-links, and that the concentration of non-cyclic cross-links be proportional to the same power of c as is the total concentration of cross-links. It seems likely enough that the former condition will be fulfilled, but there might be some doubt regarding the latter if the chains were highly cross-linked. since the concentration of non-cyclic cross-links cannot exceed the concentration of original molecules,  $c/M_n$ . At the gel point, however, the con-centration of non-cyclic cross-links,  $c/2M_w$ , is only about one-fourth of this limiting concentration, and probably is not yet influenced by this limit. We should then expect the concentration of non-cyclic cross-links and the total concentration of cross-links both to be proportional to  $c^2$  in this region.

Equation 5 can now be written approximately as

$$-(c \ln c/dT)M_{\rm w} = \Delta H^0/RT^2 \tag{6}$$

which on integration gives

$$\log_{10} c = \Delta H^0 / 2.303 RT + \text{constant}$$
(7)

A plot of  $\log c vs.$  reciprocal absolute temperature of gelatin (or melting) should therefore give a straight line; the fact that the curves in Fig. 1 are so nearly linear suggests that the approximations made are permissible. Deviations from linearity, on the other hand, would not necessarily imply that the approximations were too rough. The tendency toward upward concavity in the lower concentration range of the curves (Figs. 1 and 3) may mean, for example, that in order to effect gelation at low concentrations, cross-links having lower heats of reaction must be formed instead of or in addition to the more stable ones. It has been remarked<sup>6</sup> that a continuous three-dimensional structure cannot be formed in a polymerizing system if the concentration of the polymer is so low that the dispersed chains cannot reach each other. The minimum concentration required for gelation of these gelatin solutions is about 1%, and if at this concentration a gel does form, it is probably connected by cross-links concentrated at the extremities of the chains.

Table II lists values of the heat of reaction  $\Delta H^{0}$ calculated from eq. 7 and the slopes of curves shown in Figs. 1 and 3. The slopes were measured in the higher concentration range where the curves are most nearly linear and where cross-links would not be restricted to chain extremities. The heat of reaction calculated from the melting point data of gels chilled at 15° is much higher than that calculated from data of the same solutions chilled at  $0^{\circ}$ . We interpret this fact to mean that some crosslinks are more stable than others, and when the gelation process is allowed to proceed slowly, these cross-links are formed in preference to others. When the solution is chilled quickly, however, cross-links are formed in a more haphazard manner. The value of  $\Delta H^0$  derived from the data of gels chilled at 0° are thus believed to represent a more or less average value for cross-links which can form at temperatures down to  $0^{\circ}$ , while the values de-rived from data of gels chilled at  $15^{\circ}$  approach the heats of formation for the most stable cross-links possible. This view is supported by the more rapid strengthening of bonds at higher temperatures which has been followed in detail by measurements of stress relaxation in this Laboratory.<sup>7</sup>

TINT	ТΤ
LABLE	

Heats	OF	Reaction	FOR	THE	Cro	SS-LI	NKING	Process
			$-\Delta$ .	H <sup>0</sup> , kc	al. per	mole	of cross	-links

$M_{w} \times 10^{-3}$	Gels chilled at 0°	Gels chilled at 15°
72.1	73	220
60.0	60	
52.7	62	130
48.0	56	120
33.4	49	

It is interesting to speculate somewhat concerning the physical nature of these cross-links. If we assume, for example, that they are due to hydrogen bonding between chains, and that the heat of hydrogen bond formation is about 5 kcal. per mole,<sup>8</sup> then, according to the values listed in Table II, a single cross-link may consist of fewer than 10 or as many as 45 hydrogen bonds, depending on its relative stability.

**Dependence on Average Molecular Weight.**— Equations 3 and 4, on taking logarithms and differentiating with respect to temperature, holding the gelatin concentration constant, can be combined with van't Hoff's law to give

$$\left(\frac{\mathrm{d}\ln\,M_{\mathrm{w}}}{\mathrm{d}T}\right)_{\mathrm{o}} \left[1 + \frac{\partial\,\ln f}{\partial\,\ln\,M_{\mathrm{w}}} + \frac{\partial\,\ln\,m_{\mathrm{el}}}{\partial\,\ln\,M_{\mathrm{w}}}\right] = -\frac{\Delta H^{\mathrm{o}}}{RT^{2}} - \frac{\partial\,\ln f}{\partial T} - 2\,\frac{\partial\,\ln\,m_{\mathrm{l}}}{\partial T}$$
(8)

(7) M. Miller, J. D. Ferry, F. W. Schremp and J. E. Eldridge, THIS JOURNAL, 55, 1387 (1951).

(8) L. Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, Ithaoa, N. Y., 1942. samples.6b

where again dT denotes an infinitesimal change in the gel point temperature. This equation is not as useful as eq. 5 for calculating  $\Delta H^0$ , because the terms  $\partial \ln f/\partial \ln M_w$  and  $\partial \ln m_{\rm cl}/\partial \ln M_w$  are difficult to evaluate. Nevertheless, we can assign approximate values to these terms and thereby obtain an independent, if rough, estimate of  $\Delta H^0$ . It should be remarked that the dependence of the equilibrium constant K on  $M_w$ , and hence a large part of the dependence of the melting point, may actually reflect an unknown variable which happens to parallel the weight-average molecular weight in this particular series but does not in fractionated

To evaluate  $\partial \ln m_{\rm ci}/\partial \ln M_{\rm w}$ , we make use of eq. 1 given in paper I for this series of gelatin samples, namely<sup>1</sup>

$$G^{1/2}/c = 1.22 \times 10^{-4} (M_{\rm w} - 3.1 \times 10^{10} e^{-7900/RT})$$
 (9)

where G denotes the rigidity of the gel. Ward<sup>9</sup> has pointed out that this relation may be fortuitous and that the rigidity, like the melting point, depends primarily on another unknown variable which happens to parallel the weight-average molecular weight in this particular series. However, the equation does hold for this series and so will suffice for the calculations which follow. Since we assume that G is proportional to the total concentration of cross-links, except in the neighborhood of the melting point and at higher temperatures,<sup>1</sup> we may change eq. 9 to read

$$m_{\rm cl}/c^2 = k(M_{\rm w} - 3.1 \times 10^{10} e^{-7900/RT})^2$$
 (10)

From this

$$\frac{\partial \ln m_{\rm cl}}{\partial \ln M_{\rm w}} = \frac{2M_{\rm w}}{(M_{\rm w} - 3.1 \times 10^{10} e^{-7900/RT})}$$
(11)

Because we want the value of  $\partial \ln m_{\rm cl}/\partial \ln M_{\rm w}$  at the melting point, we choose a value of T as close as possible to the melting point without jeopardizing the proportionality between G,  $c^2$  and hence  $m_{\rm cl}$ . Figure 5 in paper I suggests T = 295,  $M_{\rm w} = 60,000$ . Substitution of these values into eq. 11 gives

$$\partial \ln m_{\rm el} / \partial \ln M_{\rm w} = 7.0 \tag{12}$$

and we assume that the value of this derivative is not far different at the melting temperature.

The derivative  $\partial \ln f/\partial \ln M_w$  is probably a nega-(9) A. G. Ward, reported at the 2nd International Congress on Rheology, Oxford, 1953, and private communication. tive quantity; it is reasonable to suppose that the proportion of cross-links which are non-cyclic will decrease with increasing initial chain length. For want of better information, we suppose that f and  $M_w$  are inversely proportional, making

$$\partial \ln f / \partial \ln M_{\rm w} = -1$$
 (13)

The quantities  $\partial \ln f/\partial T$  and  $\partial \ln m_l/\partial T$  can be neglected if we assume that cyclic and non-cyclic cross-links have the same heats of reaction, and that the proportion of cross-linking loci combined is always small, respectively.

Equation 8 can now be written approximately as

$$(d \ln M_w/dT)_c = -\Delta H^0/7RT^2$$
 (14)

which on integration yields

$$\log_{10} M_{\rm w} = \Delta H^0 / 16RT + \text{constant}$$
(15)

Accordingly, the curves in Fig. 2 should be linear, as in fact they are except in the lower molecular weight range. The slopes of the linear sections, combined with eq. 15, give values for  $\Delta H^0$  of about -54 kcal. per mole for gels chilled at 0°. Because of the rough approximations made in deriving eq. 15, these values are not considered as reliable as those listed in Table II. It seems significant, nevertheless, that the values for  $\Delta H^0$  calculated from independent sets of data (concentration dependence and molecular weight dependence) agree fairly well; this fact would seem to support the Table II values and the applicability of eq. 3 to a gelatin solution at the gel point.<sup>10</sup>

Equation 3 may be applicable to solutions of other polymers which yield thermally reversible gels. If so, the methods just described could perhaps be used to calculate the heats of reaction for the corresponding cross-linking processes.

Acknowledgment.—This work was supported in part by the Research Committee of the Graduate School of the University of Wisconsin from funds supplied by the Wisconsin Alumni Research Foundation.

(10) Data of Pouradier and Venet<sup>11</sup> on 1.5% gels, prepared from fractionated samples (and chilled at 0°), indicate a value of [d log  $M_{\rm W}/d(1/T)$ ]<sub>c</sub> about 2.4 times as high as ours, which would indicate a  $-\Delta H^0$  of 127 kcal./mole if  $\partial \ln m_{\rm cl}/\partial \ln M_{\rm W}$  were in this case also 7.0. However, for fractions, it would appear from the work of Ward and his associates<sup>3</sup> that the latter derivative would be considerably smaller, perhaps decreasing  $-\Delta H^0$  to a value comparable with the 54 kcal./mole obtained above.

(11) J. Pouradier and A. M. Venet, J. chim. phys., 47, 391 (1950).

# THE VAPOR PRESSURE OF ZIRCONIUM FLUORIDE<sup>1</sup>

BY KARL A. SENSE, M. J. SNYDER AND R. B. FILBERT, JR.

Battelle Memorial Institute, Columbus, Ohio Received February 27, 1954

Using the transpiration method, the vapor pressures of  $ZrF_4$  were measured over the temperature range of 616-881° and the pressure range of 0.3-470 mm. The extrapolated sublimation point is 903°.

#### Introduction

This work was undertaken because no experimental data on vapor pressures of  $ZrF_4$  were available. The transpiration method was found to be a powerful tool in determining vapor pressures since a range greater than 10<sup>3</sup> mm. could be covered with

(1) Work performed under AEC Contract W-7405-eng-92.

good precision and accuracy using a relatively simple apparatus.

#### Experimental

The method and apparatus are essentially the same as described previously,<sup>2</sup> and will be briefly reviewed. An

(2) K. A. Sense, M. J. Snyder and J. W. Clegg, THIS JOURNAL, 58, 223 (1954).

inert gas (nitrogen in this case) is passed over the salt with which the gas becomes saturated. The saturated inert gas then passes through a condenser where the salt is deposited while the inert gas passes on through and is collected over water. From the moles of nitrogen collected over water, the moles of salt collected in the condenser, and the total pressure of salt and nitrogen in the apparatus, it is easy to calculate the vapor pressure of the salt. The amount of salt deposited in the condenser due to diffusion alone must be subtracted from the total quantity of salt deposited. The calculations were based on the ideal gas law and Daltons' law of partial pressures.

The following changes were made from previous procedure. For ease of operation, the inlet openings of the condensers were decreased to diameters of only 1/32 or 1/16''. This change decreased the diffusion of the salt into the condenser to such an extent that the correction due to diffusion amounted at most to only 0.3% of the obtained vapor pressure. Because of the low percentage correction, the condenser could be inserted into the apparatus at the beginning of a run while the latter was cold, as well as removed at the end of a run when the apparatus was cooled down again. Hence, when the desired temperature was reached it was necessary only to release a clamp (this action permitted the flow of nitrogen) at the exit end of the run, the same clamp was tightened and the apparatus was cooled rapidly by a jet of cold air. The condenser could then be removed with ease at a low temperature. The amount of salt diffusing into the condenser during the heating and cooling-off periods was negligible.

Temperatures were measured with a platinum vs. platinum-rhodium thermocouple which was periodically calibrated against the gold point. The temperature was controlled by an electronic controller-recorder in conjunction with a chromel-alumel thermocouple located in the hot zone.

Other changes consisted in the use of nickel radiation shields in the apparatus in place of the alundum plugs. The latter were eliminated because porosity of the alundum made purging difficult.

The  $ZrF_4$  was supplied by the Oak Ridge National Laboratories and reportedly had the following impurities present: 0.19% carbon; 0.01% chlorine; 250 p.p.m. iron; 150 p.p.m. aluminum; 125 p.p.m. nickel; 100 p.p.m. hafnium; the other impurities were less than 100 p.p.m.

#### Discussion

As an outgrowth of the previous study made on  $BeF_{2,2}$  efforts were made to establish the maximum rate at which nitrogen would be saturated when passing over the salt. This was particularly important at the low vapor pressures because of the length of time involved in making those runs. Comparison of two runs (see Table I) made at approximately 1 mm. pressure indicates that saturation of the carrier gas was achieved at a flow rate as fast as 51 cm.<sup>3</sup>/min. The permissible flow rate was therefore much greater than was previously supposed and permitted runs to be made much faster than before, the longest run requiring a little less than five hours. At high vapor pressures, it was found that

considerably lower flow rates must be used to assure saturation. For example, a run made at  $876.1^{\circ}$  with a flow rate of  $7.2 \text{ cm.}^3/\text{min.}$  gave a negative deviation of 5.6% which definitely indicates non-saturation. More runs were made in the high vapor pressure region to establish whether saturation occurred for certain flow rates. It appears that saturation was achieved in every run with the exception of the one made at a flow rate of  $7.2 \text{ cm.}^3/\text{min.}$  Convenience was the only guide in making runs at various flow rates in the medium vapor pressure range.

### TABLE I

#### VAPOR PRESSURES OF ZrF.

Temp., °C.	Pressur Obsd.	re, mm. Calcd.	Deviation, %	Flow rate, nitrogen, cm. <sup>3</sup> /min.
616.6	0.310	0.310	0.0	49.8
651.9	1.053	1.051	+0.2	50.9
6 <b>52</b> .3	1.064	1.065	-0.1	31.5
676.4	2.29	2.33	-1.7	32.5
713.3	7.24	7.15	+1.3	<b>25</b> .9
757.1	24.4	24.4	0.0	14.5
798.0	70.0	<b>70.2</b>	-0.3	21.1
838.3	186.6	184.1	+1.4	6.1
856.9	284	281	+1.1	6.5
872.0	389	<b>392</b>	-0.8	4.4
872.6	392	397	-1.3	2.8
873.6	413	405	+2.0	3.6
873.9	401	<b>40</b> 8	-1.7	2.9
876.1	404	428	-5.6	7.2
880.8	470	473	-0.6	4.7

### Results

The standard error of estimate<sup>3</sup> is 0.64% when the data listed in Table I (except for the run at 876.1° which is not valid) were fitted to a curve of the type log p = A + B/T. The derived results listed at the 66.7% confidence level were

$$log_{10} P_{mm} = A + B/T$$
  
 $A = 13.3995 \pm 0.0078$   
 $B = -12376.0 \pm 8.1^{\circ}$ 

 $\Delta H_{\text{sublimation}} = 56.63 \pm 0.04 \text{ kcal./mole}$ Extrapolated sublimation point = 903 °

There was no evidence of dissociation up to the highest temperature studied.

Acknowledgment.—The authors wish to acknowledge the very helpful assistance of Mr. C. A. Alexander in carrying out the experimental work.

(3) See, for example, M. Ezekiel, "Methods of Correlation Analysis," John Wiley and Sons, Inc., New York, N. Y., 1941, Chap. 7.

# VAPOR PRESSURE STUDIES INVOLVING SOLUTIONS IN LIGHT AND HEAVY WATERS. I. THE APPARATUS AND THE DETERMINATION OF VAPOR PRESSURES AT 30° OF SOLUTIONS OF SODIUM AND POTASSIUM CHLORIDES IN ORDINARY WATER<sup>1</sup>

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Contribution No. 124 from the Department of Chemistry, University of Tennessee, Knoxville, Tenn. Received March 15, 1954

An apparatus for the determination of the vapor pressures of solutions relative to the vapor pressure of water has been described. The vapor pressure lowerings of water caused by the presence of various concentrations of sodium chloride and potassium chloride have been determined.

Various methods for precise determination of the vapor pressure of salt solutions may be found in the literature. In general these are differential methods based on the determination of the differences between the vapor pressure of pure water and of a salt solution, both being maintained at the same temperature. Static methods have been employed by Frazer and Lovelace<sup>2</sup> who utilized the principle of the Rayleigh manometer, Chandler,<sup>3</sup> and Puddington.<sup>4</sup> Some difficulties and sources of error in the static method involve dissolved impurities, inadequate stirring of solutions, unsteadiness and unequal distribution of temperature, and change in concentration if small amounts of solution are used.

The transpiration or gas saturation method was used in a simple form by Walker<sup>5</sup> and was improved by Berkeley and Hartley,<sup>6</sup> Washburn and Heuse,<sup>7</sup> Gibson and Adams,<sup>8</sup> Pearce and Snow<sup>9</sup> and Bechtold and Newton.<sup>10</sup> In general the improvements involved the gas saturator or control of the gas flow. The transpiration method as it has usually been employed has the disadvantage that a really efficient saturator will generally cause some pressure drop in the gas stream and may also cause entrainment of mist or spray. It has been shown by Menzies<sup>11</sup> that the use of fine glass wool to remove the spray causes errors due to condensation on the glass surface.

While a few other methods have been used with some success, it seemed advantageous to use the gas-saturation method for the work to be described here, and hence attention was given to improvement of earlier designs.

#### Experimental

A schematic diagram of the apparatus finally adopted is shown in Fig. 1. The general design is similar to that of

(1) Work supported by The Atomic Energy Commission.

(2) J. C. W. Frazer, B. F. Lovelace, et al., J. Am. Chem. Soc., **36**, 2439 (1914); *ibid.*, **38**, 515 (1916); *ibid.*, **42**, 1793 (1920); *ibid.*, **43**, 102 (1921); *ibid.*, **45**, 2930 (1923); THIS JOURNAL, **30**, 1669 (1926).

(3) R. C. Chandler, *ibid.*, 44, 574 (1940).
(4) I. E. Puddington, Rev. Sci. Instruments, 19, 577 (1948); Can. J. Research, 27B, 1 (1949).

(5) J. Walker, Z. physik. Chem., 2, 602 (1888).

(6) Earl of Berkeley and E. G. J. Hartley, Proc. Roy. Soc. (London), **A77**, 156 (1906); Trans. Roy. Soc. (London), **A218**, 295 (1919).

(7) E. W. Washburn and E. O. Heuse, J. Am. Chem. Soc., 37, 309 (1915).

(8) R. E. Gibson and L. H. Adams, ibid., 55, 2679 (1933).

(9) J. N. Pearce and R. D. Snow, THIS JOURNAL, 31, 231 (1927).

(10) M. F. Bechtold and R. F. Newton, J. Am. Chem. Soc., 62, 1390 (1940).

(11) A. W. C. Menzies, ibid., 42, 978 (1920).

Bechtold and Newton,<sup>10</sup> the major differences being in the saturators and absorbers. The outstanding features of these saturators, represented by A and B in Fig. 1, were their negligible pressure drop combined with almost complete gas saturation in each stage. Each saturator contained four glass drums, 25 mm. in diameter, which dipped into the saturating liquid contained in four cells made of 38 mm. Pyrex tubing, each 7 inches long. The drums were rotated at a speed of 300-400 r.p.m. by a nickel-plated rotating alnico magnet outside the saturator. This was coupled through the saturator with a second magnet sealed within one end of the drum assembly; the latter was mounted on Teflon bearings. This glass rotor exposed a fresh film of solution to the gas stream without the formation of a mist or spray, gave turbulent flow to the gas, and stirred the solution. Preliminary experiments established the efficiency of each unit of the cell as approximately 95% thus giving an efficiency of the four-cell saturator of better than 99.999%. Furthermore, the vaporization of water, and hence the change in composition of the solution during a run, occurred primarily in the first cell. The saturator held 100 ml. of liquid.

It was found necessary to surround the exit tube with a vacuum jacket where the tubing emerged from the water bath; otherwise, there was slight condensation at this point. A drying cycle was employed to remove moisture from the connecting lines prior to the runs and after each run was completed. The cycles were controlled by means of mercury stopcocks (X and Y in Fig. 1). The saturators were immersed in a water-bath, the temperature of which was maintained constant to  $\pm 0.01^{\circ}$ .

The drying tubes used to absorb the water evaporated from the solutions (C and D in Fig. 1) were fashioned from thin-wall Pyrex tubing, and weighed 45-65 g. empty and 160-190 g. when filled with desiccant. The desiccant, which was placed in the U portion, was usually non-indicating Drierite covered on the exit side with a layer of Anhydrone, although for a few runs either Drierite or Anhydrone alone was used. The notch at the bottom of the U served to re-center the gas stream in the desiccant. In addition, the absorbers contained a water trap which was made to fit into a suitable hole in a 2-inch L-shaped copper rod. Part of the rod (inside the air bath) was insulated by means of a Dewar flask with a hole in the side to fit the water trap. The other end of the copper rod was immersed in a suitable coolant.

The drying tubes and connecting lines were covered with a hood which was maintained approximately 5° above the temperature of the thermostat. In Fig. 1, the portion of the apparatus in the hood is indicated by the heavy broken lines, and that in the thermostat by the light broken lines. The manometric fluid used to control both pressure and flow rate was a solution of o-nitrodiphenyl- and tetrabutylammonium iodide in dibutyl phthalate. It possessed low density, negligible volatility, and satisfactory electrical conductivity. These manometers as well as the thermostat were controlled by suitable electronic circuits.<sup>12,13</sup>

Oil-pumped nitrogen passed through Anhydrone was used as the carrier gas in all runs. It was passed through the apparatus at a rate of 25 to 30 liters per hour. Preliminary

(12) R. H. Linnell and H. M. Haendler, Rev. Sci. Instruments, 20, 364 (1949).

(13) W. P. Ratchford and M. L. Fein, ibid., 21, 188 (1950).



Fig. 1.—Vapor pressure apparatus: A and B are the saturators; C and D are the drying tubes; F is the pre-dryer for the drying cycle; E is the pressure control bulb for the contacts N to control the relay G; J is the flow control manometer for the contacts M to control the relay H; I is the escape valve; K and Llead to flasks which serve as ballasts to minimize pres-sure variations; O and P are manometers from which may be read the pressure difference in the two saturators; Q is the supcock used to set the pressure for a run; R and T are three-way stopcocks by which one may switch from run to drying cycle; S is a stopcock used to test for possible leaks in the system prior to a run; U leads to a drying tube and thence to a tank of oil-pumped nitrogen; V and W are ground glass stoppers which may be removed in order to obtain solution for analysis; and X and Y are the inlet tubes of the drying cycle. The circuit is shown open for a run; the drying section is closed. The part of the system which is in either the water-bath or the hood is surrounded by a dashed line, and that which is in the bath is surrounded by a dotted line.

runs showed that variation in the gas flow between 5 and 35 liters per hour gave no variance in the results. The usual length of each run was one hour. Evaporation of liquid from the saturators into the gas stream would cause cooling of the liquid, while the energy resulting from the notion of the glass drums in the satura-tors would cause a slight heating. Ordinarily these effects should be similar in the two saturators so that any variashould be similar in the two saturators, so that any variations from thermostat temperature would compensate each other. Thermocouples placed in the gas stream immediately following the saturators indicated variations in tempera-ture of less than 0.31°. The glass tubing near the thermo-couples was wrapped with tinfoil to eliminate effects of radiation. The agreement of the results obtained with this apparatus with the best data found in the literature also indicates no appreciable differences in the temperatures of the exit gas streams.

Since the saturator involves a series of four efficient Since the saturator involves a series of four efficient saturating cells, there should be a negligible amount of evaporation from the fourth cell. Any heat generated by the rotation of the glass drums would have to be dissipated by heat exchange through the glass walls of the saturator. It is conceivable that the heat generated might not be negligible, and might not be the same for water and con-centrated salt solutions. In order to test the magnitude of this effect, a thermocouple was set up with one junction of this effect, a thermocouple was set up with one junction in liquid water in the saturator and one end in the bath. With no gas flowing through the saturator, the rotors were turned at speeds of from 110 to 640 r.p.m. The thermocouple indicated no differences in temperature within experimental error  $(0.01-0.02^{\circ})$  between the bath and the liquid saturator, even at the highest speed of rotation.

These experiments were repeated using saturated sodium chloride solution (in contact with excess salt). Speeds of rotation greater than 530 r.p.m. were not used because of difficulty caused by solid sodium chloride in the bearings. Again no indication of a rise in temperature in the salt solution was found at any speed. It thus appears evident that errors caused by heat generated through rotation of the drums in the saturators were negligible for the solutions studied.

Sodium chloride was J. T. Baker C.P. grade, and the potas-sium chloride was J. T. Baker C.P. specially purified grade. The same quality distilled water was used in both the water and solution saturators.

Weights obtained for the drying tubes were reproducible to  $\pm 0.0004$  g. The capped tubes were weighed before each run; the caps were then removed and the drying tubes placed in the lines. Synthetic rubber gaskets were used to seal the ball and socket joints which were held together with spring clamps. After each run the tubes were allowed to cool, wiped with a damp cloth, and allowed to equilibrate with room conditions for at least an hour before they were weighed. The usual weighing precautions were observed.

Gravimetric analyses of the salt solutions were made before and after each run. The samples for analysis were taken from the last cell of the saturator through the ground glass plug provided for this purpose.

# Calculations and Results

The vapor pressures of the salt solutions were calculated from the relation

$$\frac{p_0 - p_1}{p_0} = \frac{m_0(B + \Delta p_0) + p_0(m_1 - m_0) - m_1(B + \Delta p_1)}{m_0(B + \Delta p_0) + p_0(m_1 - m_0)}$$

where  $p_0$  is the saturated vapor pressure of pure water at the temperature of the thermostat, and  $p_1$ is the vapor pressure of the liquid in the saturator;


Fig. 2.—Vapor pressure lowering of sodium chloride solutions: O, Bousfield and Bousfield (18°) (*Proc. Roy. Soc.* (*London*), A103, 429 (1923)); O, Gibson and Adams (25°); •. this investigation (30); •, this investigation (25°).

	TABLE I				
VAPOR PRESS	URES OF SALT S	olutions	ат 30.01°		
	Vapor pressure lowering po - p1		Vapor pressure lowering $p_8 - p_1$		
Molality	Pa	Molality	$p_0$		
Na	Cl	KCl			
3.755	0.139	0.754	0.0225		
4.563	.174	1.081	.0341		
4.910	. 190	1.665	. 0559		
5.070	. 196	1.869	.0593		
5.162	. 200	2.629	.0845		
$4.910(25.00^{\circ})$	. 188	2.824	.0925		
		3.957	. 130		

ries of runs was  $0.0001 \pm 0.0018$ . The vapor pressure lowerings of the solutions of sodium and potassium chlorides are given in Table I. The deviations (95% confidence level) for the sodium chloride solutions are 0.003-0.004 and for the potassium chloride solutions are 0.001-0.002.

According to Raoult's law, a plot of  $(p_0 - p_1)p_0$ against mole fraction (or for these solutions against



Fig. 3.—Vapor pressure lowering of potassium chloride solutions: O, Lovelace, Frazer and Sease (20°); O, Pearce and Snow (25°);  $\phi$ , this investigation (25°), CaSO<sub>4</sub> as drying agent;  $\bullet$ , this investigation (30°); Mg(ClO<sub>4</sub>)<sub>2</sub> as drying agent;  $\bullet$ , this investigation (30°), CaSO<sub>4</sub> with Mg(ClO<sub>4</sub>)<sub>2</sub> as drying agent.

 $m_0$  is the weight gain of the drying tube after the water saturator,  $m_1$  is the weight gain of the drying tube after the solution saturator,  $\Delta p_0$  and  $\Delta p_1$  are the pressure drops across the saturator-absorber combination for the pure water and the solution due almost entirely to the absorber, and B is the barometric pressure. When water was run in both saturators, the value of  $(p_0 - p_1)/p_0$  for a se-

molality) should give a line which is essentially straight, and which is independent of temperature. Figure 2 shows such a plot for the sodium chloride solutions and Fig. 3 for those of potassium chloride. The results show that this apparatus gives excellent agreement with the best data in the literature, even though such data were obtained at other temperatures.

# VAPOR PRESSURE STUDIES INVOLVING SOLUTIONS IN LIGHT AND HEAVY WATERS. II. THE VAPOR PRESSURE OF HEAVY WATER AND THE SEPARATION FACTOR OF THE MIXED WATERS<sup>1</sup>

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The vapor pressure of deuterium oxide has been precisely determined over the temperature 10 to 55°. The results are slightly different from those previously reported. The separation factor  $\alpha = (H/D)_{gas}/(H/D)_{liquid}$  has also been determined for a mixture of the two waters.

In a previous paper<sup>2</sup> an apparatus for the precise determination of vapor pressure differences has been described. This apparatus has now been used in the determination of the vapor pressure of heavy water and mixtures containing approximately 50% D<sub>2</sub>O.

#### Experimental

For vapor pressure measurements, the two saturators which have already been described<sup>2</sup> were filled, one with distilled water and one with deuterium oxide. The latter was stated by the suppliers<sup>3</sup> to be 99.8% D<sub>2</sub>O and this analysis was checked by density measurements. Calculations showed that the errors caused by the 0.2% of ordinary water present were negligible. The heavy water gave no visible or weighable residue upon evaporation of a two-ml. portion. The drying tubes were filled with Drierite covered with a layer of Anhydrone.

For measurement of separation factors, one of the saturators was filled with distilled water and the other with a mixture of the two waters. At the end of each run a sample of the waters was withdrawn from the last stage of the saturator and analyzed. For these runs the absorbers were filled with Drierite only (anhydrous calcium sulfate), and the total water absorbed from the mixed water saturator was recovered by heating the absorbers at 290° in an evacuated system until all of the water was condensed in a cold trap kept at acetone-Dry Ice temperature. The water in this trap was then analyzed for isotopic hydrogen ratio.

total water absorbed from the mixed water saturator was recovered by heating the absorbers at 290° in an evacuated system until all of the water was condensed in a cold trap kept at acetone-Dry Ice temperature. The water in this trap was then analyzed for isotopic hydrogen ratio. All analyses of the water mixtures were made by the falling drop method. By this method drops of identical volume are allowed to fall through a liquid of constant density and the time of fall between certain reference marks established. The combination of liquids used for the reference fluids was 1-bromonaphthalene ( $d_{35}$  1.474, b.p 281°) and 1-methylnaphthalene ( $d_{35}$  1.018, b.p. 241°). The latter liquid has been used by others.<sup>4</sup> Mixtures of these allowed the determination of the heavy water content in a concentration rang? from about 10% to 100%. It was found that these liquids of high and similar boiling points suffer negligible changes in composition under most conditions of exposure to the air. A saturated solution of the  $\alpha$ -bromonaphthalene in water at 35° was found to have a density only 17 p.p.m. greater than that of pure water. This solubility was low enough, even if the drops falling through the reference mixture became only partially saturated before the measurements were made, to preclude serious errors from this source.

The materials used for the references had to be specially purified. The 1-methylnaphthalene was prepared from the diesel reference fuel grade supplied by the Reilly Tar and Chemical Co. This material had to be washed with 50% sulfuric acid, 20% sodium hydroxide and 85% phosphoric acid solutions before the redistilled product was pure enough to eliminate discoloration on standing. The 1bromonaphthalene was prepared by fractional distillationof Eastman Kodak Co. white label grade. The distillations were done *in vacuo* in a four-foot Vigreux column.

The pipet for the introduction of the drops into the refer-

(2) H. A. Smith, R. L. Combs and J. M. Googin, THIS JOURNAL, 58, 997 (1954).

(4) V. J. Frillette and J. Hanle, Anal. Chem., 19, 984 (1947).

ences fluid has appeared in several forms.<sup>5-7</sup> The one used here differed from all of these. It was based on a com-mercially available micro-buret control.<sup>8</sup> With this it was found necessary to have a horizontal reservoir for the mercury used to displace water. When this was not done, there was a drift in the drop sizes as the head of mercury on the screw of the control changed. It was also found advisable to have the amount of mercury in the pipet at a minimum to avoid significant changes in the volumes of the drops as the temperature of the room, and hence of the pipet, changed. Since the drop size used was that delivered by one turn of the control screw, either the pipet had to be insensitive to temperature changes between drops, or two drops had to be expelled in quick succession to get an accurate volume. A stop was added to the buret control to The make precise duplication of one revolution possible. drop delivered was 10 cubic millimeters in size, but a drop of half this size could have been used equally well. Another essential difference between this pipet and the ones used essential difference between this pipet and the ones used previously was the tip which delivered the drop into the refer-ence solution. This tip has customarily been made of glass. The glass, wetted by the water, made it necessary to raise the tip through the surface of the reference liquid to force off the drop. It was found that this technique of the drop size, and that the exposure of the tip to errors in the drop size, and that the exposure of the tip to room temperature made it necessary to wait about ten minutes between drops for the currents generated by the motion of the tip and the difference in temperature of the tip and the solution to subside. Other investigators have used room temperatures controlled at one or two de-grees above the temperature of the bath. This prevented interference because the tip after exposure to the air warmed the upper layers of the solution and the less dense warm layer floated without causing convection currents. The varia-tions in room temperature experienced in the laboratory used in this investigation made such a procedure impractical.

To avoid these difficulties a tip was fashioned out of the plastic Teflon. This tip was about three inches long and had a fifteen thousandths of an inch capillary. The nature of the Teflon surface allowed the reference solution to wet the tip in preference to the water, but the effect was not strong enough to cut the water column in the capillary immediately. It was found that the drop would, in most cases, break free from the tip within a few seconds after it has been expressed. When it did not, a gentle tap on the pipet was sufficient to break the small thread of water holding the drop. Thus, with this tip there was no need to remove the pipet from the constant temperature bath after the formation of each drop, and the drops could be formed in quick succession without the introduction of errors due to convection currents in the reference solution tubes.

The liquid mixtures were contained in tubes of one cm. diameter and two reference marks 10 cm. apart were made on them. These were placed in a constant temperature bath held at 35° with a variation of less than 0.001°. Standard mixtures of deuterium oxide and water were prepared gravimetrically. Table I shows the reproducibility of the droptime, and the analytical precision. Table II illustrates the stability of the reference solutions. A plot of the mole per cent. of  $D_2O$  wersus the reciprocal of the drop time is linear over a composition range of several per cent.

- (7) E. S. Fetcher, ibid., 16, 412 (1944).
- (8) Arthur H. Thomas Co., 1950 Catalogue, Item 2461 F.

<sup>(1)</sup> Work supported by the Atomic Energy Commission.

<sup>(3)</sup> Stuart Oxygen Company, San Francisco, California.

<sup>(5)</sup> S. Hochberg and V. K. La Mer, Ind. Eng. Chem., Anal. Ed., 9, 291 (1937).

<sup>(6)</sup> F. Rosebury and W. E. Van Heyningen, ibid., 14, 363 (1942).

	1 AB	LE I	
STAND	ARDIZATION OF A	Reference So	OLUTION
Mole % D2O	Av. time, sec.	Deviation (95 Seconds	% confidence) D₂O, %
48.23	51.9	0.2	0.01
47.18	86.2	. 5	.008
46.65	130.3	.3	.002
46.26	207.6	.3	.001
	Таві	ь II	

Stabili	ty of a Referen	CE SOLUTION
Days between determinations	Original	Drop-time at indicated time
4	54.1	54.1
5	49.3	<b>49</b> . <b>2</b>
7	213.3	213.6

### **Experimental Calculations and Results**

The vapor pressure of deuterium oxide was calculated using the equation

$$\frac{p_0 - p_1}{p_0} = \frac{p_0(m/M)_1 - (m/M)_0 + (m/M)_0(B + \Delta p_0) - (m/M)_1(B + \Delta p_1)}{p_0(m/M)_1 - (m/M)_0 + (m/M)_0(B + \Delta p_0)}$$
The values of the separation factor are calculated from the defining equation

where p is the vapor pressure, m/M the number of moles, B the barometric pressure, and  $\Delta p$  the difference between barometric pressure and that within the saturators. The subscript "o" refers to light water and "l" to heavy water. The values of  $(p_0 - p_1)/p_0$ , the ratio of vapor pressures of the two waters, and the calculated vapor pressure of heavy water are shown in Table III. A com-

## TABLE III VAPOR PRESSURE OF D<sub>2</sub>O

Temp., °C.	$\frac{p_0 - p_1}{p_0}$	$p_{ m H2O}/p_{ m D2O}$	рн20 <sup>а</sup> , mm.	pD <sub>2</sub> O, mm.	Deviation (95% confidence)
10.00	0.164	1.196	9.21	7.70	0.02
14.98	. 155	1.183	12.79	10.81	.02
20.01	. 146	1.171	17.54	14.98	.03
25.08	. 137	1.158	23.76	20.51	.04
30.01	. 129	1.148	31.82	27.72	.05
35.00	. 120	1.137	42.18	37.11	.07
40.03	. 115	1.130	55.32	49.0	.1
44.99	. 107	1.119	71.88	<b>64</b> . $2$	. 1
50.01	. 101	1.112	92.5	83.2	.1
55.00	.0970	1.107	118.0	106.6	.2

<sup>a</sup> E. W. Washburn, Ed., "International Critical Tables of Numerical Data, Physics, Chemistry and Technology," Vol. III, McGraw-Hill Book Co., New York, N. Y., 1926-1933, p. 211-212.

(9) Isidor Kirschenbaum, "Physical Properties and Analysis of Heavy Water," McGraw-Hill Book Co., Inc., New York, N. Y., 1951, p. 25. parison of these vapor pressure values with those previously reported<sup>9</sup> is given in Fig. 1.



Fig. 1.—Vapor pressure ratio of light and heavy water: O, data from this investigation;  $\bullet$ , data from Kirschenbaum.

lculated from the defining equation

$$\alpha = \frac{(H/D)_{gaa}}{(H/D)_{liquid}}$$

the values of (H/D) having been determined in the manner already described. The results are shown in Table IV. These values cannot be obtained directly from the vapor pressures of light and heavy

		TAI	ble IV		
VAPOR	Pressure	AND SEP	ARATION	Factor	FOR WATER
		MD	TURES		
Temp., °C.	% D₂O in liquid	$\frac{p_0 - p_1}{p_0}$	<b>p</b> , mm.	α	$\sqrt{\frac{p^{\circ}H_{2}C}{p^{\circ}D_{2}C}}$
9.84	48.23	0.0824	8.45	1.1003	1.094
20.00	45.97	.0705	16.30	1.0873	1.082
25.00	45.97	.0659	22.19	1.0815	1.076
30.00	45.97	.0602	29.91	1.0747	1.071
30.01	48.24	.0615	29.87	1.0749	1.071
40.01	48.22	.0544	52.31	1.0629	1.063
50.00	48.21	.0503	87.86	1.0510	1.055

water because of the presence of the equilibrium  $H_2O + D_2O \rightleftharpoons 2HDO$ . They may, however, be approximately calculated from the relationship<sup>10</sup>

$$\alpha = \sqrt{\frac{p^{\circ}_{\rm H_2O}}{p^{\circ}_{\rm D_2O}}}$$

The value of this latter quantity is included in Table IV for comparison purposes.

(10) G. N. Lewis and R. E. Cornish, J. Am. Chem. Soc., 55, 2616 (1933).

## SOLVENT EFFECTS IN ORGANIC SPECTRA: DIPOLE FORCES AND THE FRANCK-CONDON PRINCIPLE

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All organic electronic spectra in solution are subject to a generalized *polarization red shift* which is due to solvent polarization by the transition dipole and which depends on the solvent refractive index. This can be obscured by the effect of dipole-dipole and dipole-polarization forces if the solute is polar, when the application of the Franck-Condon principle shows that the solvent cage around the excited solute molecule is point, when the application of the *Plance-Condult* principle shows that the solvent cage around the excited solute molecule is momentarily strained. Orientation strain and packing strain are defined, of which the former is more important. The absorption frequencies of polar solutes are shifted to the red in solution if the dipole moment increases during the transition; they may be shifted to the blue (relative to the gas) if the dipole moment decreases. Four cases are discussed according to whether solute and solvent are polar or non-polar. The place of  $\pi^* \leftarrow n$  transitions is discussed.

There have been several papers recently in which solvent effects on organic spectra have been correlated with various properties of the solute and the solvent. For example Kasha<sup>1</sup> and McConnell<sup>2</sup> have proposed the use of solvent effects as an aid to the distinction between  $\pi^* \leftarrow \pi$  and  $\pi^* \leftarrow n$ transitions, Nagakura and Baba<sup>3</sup> have explained solvent shifts in aromatic compounds by assuming that hydrogen bonding causes an electron migration in the solute molecule, and Brooker<sup>4</sup> and also Ungnade<sup>5</sup> have suggested that some solvent effects are due to the stabilization of preferred resonance structures in the solute by certain solvents as the result of their dielectric constants or of their electron donor-acceptor properties. Coggeshall and Lang<sup>6</sup> in dealing with solvent effects in the spectra of phenols have drawn attention to the importance of dipole-dipole interaction, of hydrogen bonding, and of the change in dipole moment during the solute transition.

Now the interpretation of solvent effects is made difficult because they are often small and not easy to measure precisely, and also because they are often the resultants of several individual effects which sometimes reinforce one another and sometimes cancel out. There is also some difficulty in the fact that the most easily measured and most often recorded solvent effect is the displacement or shift of the absorption maximum, whereas theoretical considerations of electronic energy states should be related to the position of the (0, 0) band, which is not necessarily affected in the same way as the maximum. Since it is practically impossible to locate the (0, 0) band in diffuse or structureless solution spectra, the spectral shifts discussed here and in the following paper are referred to absorption maxima, which provide the only possible experimental reference points. It is the purpose of this paper to present a scheme by which many solvent effects in organic spectra can be interpreted at least qualitatively in terms of dipole, polarization and hydrogen bonding forces between solute and solvent, bearing in mind three factors that have not always been given due recognition, namely, the (a) momentary transition dipole during the optical

- (1) M. Kasha, Discs. Faraday Soc., No. 9, 14 (1950).
- (2) H. McConnell, J. Chem. Phys., 20, 700 (1952).
- (3) S. Nagakura and H. Baba, J. Am. Chem. Soc., 74, 5693 (1952).
- (4) L. G. S. Brooker, et al., ibid., 73, 5332, 5350 (1951).
   (5) H. E. Ungnade, ibid., 75, 432 (1953).
- (6) N. D. Coggeshall and E. M. Lang, ibid., 70, 3283 (1948).

absorption process, (b) the difference in permanent dipole moment between the ground and excited states of the solute and (c) the effect of the Franck-Condon principle. It will be seen that the effect of hydrogen bonding fits naturally into the proposed scheme, which can provide a consistent explanation of the experimental results referred to in the preceding paragraph. A following paper<sup>7</sup> will give additional experimental examples.

Two recent papers<sup>8,9</sup> from this Laboratory have dealt with the solvent effect that results from the momentary polarization that is induced in the solvent by the transition dipole of the solute, the predicted result being a red shift that is a function of the solvent refractive index, the transition intensity and the size of the solute molecule. The theory of this *polarization shift*, as we may call it, is quite general even though it is approximate, and therefore should be applicable to all solution spectra. However although the polarization shift seems experimentally to be dominant when the solute is nonpolar, we shall see below that it can be obscured by other effects when the solute is polar,<sup>10</sup> including those cases when there is hydrogen bonding between solute and solvent.

It is convenient to relate the frequency shift of an absorption spectrum in solution to what we shall for the present call the solvation energies of the solute in its ground and excited states. If these are s'' and s', respectively, it is obvious from Fig. 1 that the frequency displacement  $\Delta \nu = \nu(\text{soln}) - \nu(\text{gas})$  is given by  $\Delta \nu = s'' - s'$ , s being taken as positive if the energy of the solute is decreased in solution. The important point is that while s" is the normal solvation energy of the solute in its ground state and in equilibrium with the solvent, the application of the Franck-Condon principle will show that the appropriate s' for the excited solute molecule is not necessarily the equilibrium value.

Solvation energies depend on various types of intermolecular interaction such as dipole-dipole, dipole-polarization, dispersion and hydrogen bonding forces. Dispersion forces are usually smaller than the others mentioned, but in any case they are

- (7) N. S. Bayliss and E. G. McRae, THIS JOURNAL, 58, 1006 (1954).
- (8) N. S. Bayliss, J. Chem. Phys., 18, 292 (1950).
- (9) N. S. Bayliss and L. Hulme, Australian J. Chem., 6, 257 (1953).
- (10) We use the term polar to describe a molecule with a permanent dipole moment, or with strongly localized groups that are permanent dipoles.



always operative whether solute and solvent are polar or non-polar. In this paper we shall regard them as contributing equally to s'' and s', and we shall therefore confine our attention to the dipoledipole, dipole-polarization and hydrogen bonding forces. We first consider the nature of the optical transition and the effect of the Franck-Condon principle.

The Optical Transition.—In classical theory the absorption of light is associated with the forced oscillation of an electric dipole. In quantum theory the absorbing molecule undergoes a change in charge distribution which may or may not cause a change in the permanent dipole moment. In the simplest possible example of the H atom it is obvious from the wave functions that the  $2p \leftarrow 1s$ transition causes a change in charge distribution, yet neither state has a dipole moment. In the more complex example of a non-polar molecule such as benzene, it is clear from symmetry considerations that the excited states as well as the ground state have zero dipole moment, and it is the instantaneous change in charge distribution without the creation of a permanent dipole that leads to the polarization shift that is mentioned above. On the other hand it is to be expected that a molecule that is polar in its ground state will have in each of its excited states an altered dipole moment which may be greater or less than the ground state moment.

The Franck-Condon Principle.—Consider solute molecule in its ground state which is in equilibrium (modified by thermal motion) with the surrounding solvent molecules that form its The solvation energy of this equilibrium cage. state involves (a) a packing factor depending on the geometry of the solute and solvent molecules, and (b) a factor which depends on the degree of mutual orientation interaction if solute and solvent are polar or if there is hydrogen bonding between them. Bohon and Claussen<sup>11</sup> for example have discussed the contributions of packing and orientation entropy to the entropy of solution of aromatic compounds in water. To the extent that the size, charge distribution and dipole moment of the solute molecule are different in the excited state, the configuration of the solvent cage in equilibrium with the excited state is different from that of the ground stage cage. Now it is the essence of the Franck-Condon principle that an optical transition occurs within a time that is short compared with the period of nuclear motions. At the instant of its formation, *i.e.*, when it is in what might be called the Franck-Condon state, the excited solute molecule is momentarily surrounded by a solvent cage whose size and orientation are those that are appropriate to the ground state. The equilibrium excited configuration is only reached subsequently by a process of relaxation, which requires at least several mo-lecular vibration periods ( $\sim 10^{-13}$  sec.) as far as readjustment for size is concerned, and a time of the order of  $10^{-11}$  sec.<sup>12</sup> if a readjustment of the solvent orientation is required. The lifetime of the excited state is known to be of the order of  $10^{-8}$  sec., which is ample for equilibrium with the solvent to be es-

s V(gas) V(soln) ٢'

Fig. 1.-Formal diagram of the effect of the solvation energies s' and s" on the relation between the absorption frequencies in the gas state and in solution.

tablished before deactivation eventually occurs. (This time factor may be of importance in comparing solvent effects in absorption and in fluorescence.) The Franck-Condon excited molecule and its solvent cage are thus in a state of strain whose energy is necessarily greater than that of the equilibrium state, and the excited state solvation energy s' to be used in finding  $\Delta v$  is less than the equilibrium value (and in certain cases as in case IVa below it may even be negative). In discussing this strain it is convenient to use the general term Franck-Condon strain, while its two components can be called packing strain and orientation strain.

Orientation strain may be expected when solute and solvent are polar, and when the solute dipole moment changes during the transition. It is similarly to be expected if there is hydrogen bonding between solute and solvent that is changed in degree as a result of the transition. Pauling<sup>13</sup> showed that what we have here called orientation strain is a major factor in causing the large positive displacement (to the blue) of the absorption spectra of halide ions in solution. Packing strain is to be expected when the solute molecule is substantially bigger in the excited than in the ground state. This concept has been used by one of the authors<sup>14</sup> and by Rees<sup>14a,15</sup> to explain the positive shift in the "brown" solutions of iodine and bromine, and although an alternative explanation of this phenomenon in terms of complex formation is currently accepted,<sup>16</sup> packing strain seems to be the only way of accounting for Prikhotko's observation<sup>17</sup> of a positive shift of 1300 cm. $^{-1}$  in the spectrum of bromine in pentane at low temperatures.<sup>14b</sup> However, packing strain is probably unimportant in many organic spectra where the relative changes in size on excitation are not marked.

Blurring of Vibrational Structure.-There is an important consequence of the concept of Franck-Condon strain and of the relaxation time of the solvent cage. The Franck-Condon excited state as such is of very short life owing to the relaxation of the solvent during a time of the order of molecular vibrations. In terms of the principle of indeterminacy this will prevent the establishment of

- (14) (a) N. S. Bayliss and A. L. G. Rees, J. Chem. Phys., 8, 377 (1940); (b) N. S. Bayliss, A. R. H. Cole and B. G. Green, Australian J. Sci. Res., A1, 472 (1948).
  (15) A. L. G. Rees, J. Chem. Phys., 8, 429 (1940).
- (16) R. S. Mulliken, J. Am. Chem. Soc., 72, 600 (1950); 74, 811 (1952)
- (1951). (12) D. H. Whiffen, Quart. Revs., 4, 131 (1950).

(11) R. L. Bohon and W. F. Claussen, J. Am. Chem. Soc., 73, 1571

(17) A. Prikhotko, Acta Physicochim. U.R.S.S., 16, 125 (1942).

<sup>(13)</sup> L. Pauling, Phys. Rev., 34, 954 (1929).



Fig. 2.—The effect of solvation energies on the solution absorption frequency when dipole-polarization forces are dominant and when there is no orientation strain, *i.e.*, when the Franck-Condon and the equilibrium excited state have the same solvation energy: (a) solute dipole moment decreases, and (b) it increases, during the transition.

vibrational quantization in the excited state, with the result that the vibrational structure of the spectrum is blurred. This we believe is a frequent cause of the blurring or obliteration of structure in the spectra of polar molecules in polar solvents. In cases such as non-polar benzene, where strain is absent, vibrational structure is preserved in polar solvents.<sup>9</sup>

We now discuss typical cases as follows

Case I, non-polar solute in non-polar solvent

Case II, non-polar solute in polar solvent

- Case IIIa, polar solute in non-polar solvent; solute dipole moment decreases during the transition
- Case IIIb, polar solute in non-polar solvent; solute dipole moment increases during the transition

Case IVa, polar solute in polar solvent; solute dipole moment decreases during the transition

Case IVb, polar solute in polar solvent; solute dipole moment increases during the transition

Cases IVa and IVb include hydrogen bonding that is, respectively, decreased or increased by the transition.

**Case I.**—The solvation energy in both ground and excited states is due to dispersion forces and is assumed to be about the same in the two states. Since there is no dipole moment in either state, there are no solute-solvent orientation forces, and hence there is no orientation strain in the Franck-Condon state. In the absence of packing strain, which as mentioned above seems usually to be small in the case of relatively large organic molecules, the solution spectrum is shifted to the red owing to the polarization effect; the shift depends on the solvent refractive index.<sup>8</sup> The solution spectrum will tend to retain vibrational structure if it is present in the gas.

**Case II.**—Although the solvent is polar, the absence of a solute dipole moment means that there are no solute-solvent orientation forces and orientation strain is therefore absent. The case is thus identical with case I, and the dominant solvent effect is the red polarization shift depending on the

solvent refractive index. The effect of slight packing strain will probably be more important than in case I, since dipolar and more particularly hydrogen bonding forces between the solvent molecules themselves will tend to increase the solvent cage relaxation time after the transition.<sup>14a</sup> Thus there may be increased blurring though not necessarily obliteration of vibrational structure.

Case IIIa.—Since the solvent is non-polar, there will be no orientation strain. The forces contributing to the solvation energy are dispersion forces and dipole-polarization forces (polarization of solvent molecules by the solute dipole), and the latter are probably the greater. When the solute dipole moment decreases as a result of the transition, the contribution of the dipole-polarization forces to the solvation energy is decreased, and s' is less than s" (see Fig. 2a). This will cause the solution spectrum to shift to the blue by an amount that depends on the solvent refractive index and on the change in the solute dipole moment. On this shift will be superimposed the polarization red shift, and the resultant shift may be either to the red or to the blue, depending on the relative magnitudes of two effects. Vibrational structure will tend to be preserved.

**Case IIIb.**—The argument is the same as in case IIIa, except that the increased solute dipole moment in the excited state makes s' greater than s'' (see Fig. 2b). Thus the solution spectrum is shifted to the red by an amount depending on the solvent refractive index. The polarization red shift is also operative, so that the resultant is always to the red. Vibrational structure will tend to be preserved.

Case IVa.—To make the argument clear we take the extreme case where the dipole moment in the excited state is zero. The ground state solvation energy is largely due to dipole-dipole forces, and the solvent cage is oriented. In the equilibrium excited state the solvation energy is much smaller since there is no dipole-dipole contribution (see Fig. 3a). In the Franck-Condon state, the nonpolar excited solute is in a cage of oriented dipoles (orientation strain), and, as Pauling<sup>13</sup> showed, this contributes a negative term to the Franck-Condon solvation energy which is equal to the energy input required to orient solvent dipoles around a non-polar molecule. As shown in Fig. 3a the effect on the solution spectrum will be to give it a positive displacement to the blue as compared with the gas. The effect will be less, but in the same direction, if the dipole moment in the excited state is not zero. provided it is less than the ground state moment.

The magnitude of the blue shift will depend on several factors, including the magnitude of the change in dipole moment during the transition, the value of the solvent dipole moment, the extent to which the solute and solvent dipoles are "exposed," and the sizes of solute and solvent molecules. If the solvent molecules are small, for example, more of them can get close to the solute dipole with the result of greater interaction. The superimposed polarization red shift will usually be dominated by this dipole blue shift.

The same arguments apply if the solute-solvent

forces (including orientation) are largely due to hydrogen bonding provided it is less in the excited state. Owing to the existence of orientation strain, vibrational structure will be obliterated.

**Case IVb.**—The dipole–dipole forces between solute and solvent are greater in the excited state than in the ground state. The Franck-Condon excited state is formed in an already partly oriented solvent cage, so that even though there is orientation strain,<sup>18</sup> s' will be greater than s", and the solution spectrum is shifted to the red. The energy relations are shown in Fig. 3b. The superimposed polarization shift is also to the red. The magnitude of the shift depends on the same factors as in case IVa. Vibrational structure is probably blurred or obliterated; but it might be preserved if there is orientation saturation in the ground state.<sup>18</sup> The same red shift will occur in the case of hydrogen bonding that is increased in the excited state.

Discussion.—The 2600 and 2000 Å. transitions of benzene are examples of the non-polar solute of cases I and II. The frequency displacements are to the red by amounts depending on the solvent refractive index with slight anomalies in water (2600 Å.) and ethanol (2000 Å.).<sup>9</sup> Condensed aromatic hydrocarbons also show the polarization shift of cases I and II<sup>19,20</sup> although exceptions have been reported.<sup>21</sup> The solvent effects in the spectra of toluene (2600 Å.) and chlorobenzene (2600 and 2000 Å.) are also dominated by the red polarization shift of cases I and II,<sup>9</sup> even though the solutes are polar. The reason is doubtless that these transitions are  $\pi^* \leftarrow \pi$  and closely resemble the corresponding benzene transitions, and that the electron displacement in the  $\pi$  shell has little effect on the dipole moment of the  $-CH_3$  and -Cl substituent groups.

However when the spectrum of a polar solute is definitely associated with the polar group, either one of cases III and IV should apply. Thus Hammond and Modic<sup>22</sup> have recently shown that the characteristic 2600 Å. band of aromatic nitro compounds has an increasing red shift in the solvents ethanol, water and sulfuric acid in that order. This is a case IVb effect, consistent with the increase in dipole moment if the transition involves obvious resonance forms such as



The observed red shift is also consistent with increased H-bonding in the excited state as suggested by Hammond and Modic.<sup>22</sup> The red shift in nitroolefin spectra in ethanol as compared with *n*-hexane as a solvent, described by Braude, Jones and Rose,<sup>23</sup>

(18) If solute-solvent orientation has reached "saturation" in the ground state, there will be no orientation strain in the Franck-Condon state since no further orientation is possible.

(19) N. D. Coggeshall and A. Pozefsky, J. Chem. Phys., 19, 980 (1951).

(20) G. M. Badger and R. S. Pearce, Spectrochim. Acta, 4, 280 (1951).

(21) R. Schnurmann and W. F. Maddams, J. Chem. Phys., 19, 1430 (1951).

(22) G. S. Hammond and F. J. Modic, J. Am. Chem. Soc., 75, 1385 (1953).

(23) E. A. Braude, E. R. H. Jones and G. G. Rose, J. Chem. Soc., 1104 (1947).



Fig. 3.—Solution spectrum when dipole-dipole forces are dominant between solute and solvent, and when there is orientation strain in the Franck-Condon excited state: (a) dipole moment of solute decreases, and (b) it increases, during the transition.

is also case IVb, suggesting a transition such as

It is to be noted that the normal refractive index dependent red shift has been "swamped" in these two cases. (Nitromethane and nitrobenzene spectra are discussed in the following paper.<sup>7</sup>)

Ungnade<sup>5</sup> has quoted data on the "primary" bands (analogous to benzene 2000 Å.) of benzoic acid, acetophenone and benzaldehyde, which all have a small red shift of 2 to 9 Å. in water as compared with ethanol. The transitions are  $\pi^* \leftarrow \pi$ , and each compound has a double bond conjugated with the ring system. An increase in the dipole moment (or of H-bonding) is to be expected from



in conformity with case IVb. The analogcus case of crotonaldehyde will be seen in the next paper to behave similarly.<sup>7</sup> The same author<sup>5</sup> has shown that the "primary" and "secondary" bands (analogous, respectively, to benzene 2000 and 2600 Å.) of anisole, diphenyl ether, acetanilide, dimethylaniline and iodobenzene show blue shifts in the order of solvents cyclohexane, alcohol and water, the gas data not being quoted. In terms of the concepts of this paper these shifts are in the direction consistent with the shift being predominantly the polarization shift of cases I and II, since the solvent refractive indices decrease in the same order. The transitions are  $\pi^* \leftarrow \pi$ , and none of the compounds has a double bond conjugated with the ring; the cases are therefore analogous to toluene and chlorobenzene quoted previously.

Solvent Effect on  $\pi^* \leftarrow \pi$  and  $\pi^* \leftarrow n$  Transitions.—Kasha<sup>1</sup> and McConnell<sup>2</sup> have proposed solvent effects as one criterion for distinguishing between  $\pi^* \leftarrow \pi$  and  $\pi^* \leftarrow n$  transitions, and the latter author describes bands as "red shift" or "blue shift" according to their displacement in the solvent order paraffin, alcohol, water, without reference to the gas frequency. McConnell states that all known  $\pi^* \leftarrow n$  transitions are blue shift, but that the converse is not necessarily true, quoting the case of the  $\pi^* \leftarrow \pi$  2600 Å. transition of benzene, which is blue shift in his terminology. Now the case of benzene has been shown definitely by Bayliss and Hulme<sup>9</sup> to be a polarization red shift (cases I and II), and in fact *all* polarization red shifts are "blue" shifts in McConnell's sense, since the refractive indices decrease in the order paraffin, alcohol, water. McConnell's definition fails to make the important distinction between (a) "blue shifts" that are red shifts compared with the gas as in cases I and II, and (b) "blue shifts" that are blue shifts compared with the gas as in cases IIIa and IVa.

However it is readily seen that a  $\pi^* \leftarrow n$  transi-

tion is likely always to conform to cases IIIa and IVa, since it involves a non-bonding (n) electron localized on a hetero-atom which is usually exposed or terminal to a conjugated system. During the transition it is excited into a  $\pi^*$  orbital associated with a neighboring double bond or with a non-localized conjugated system. There is thus an electron displacement away from the hetero-atom, and this will usually decrease the dipole moment or the H-bonding capacity. The cases of acetone, croton-aldehyde, nitromethane and nitrobenzene are instructive in this regard, and are described in the following paper.<sup>7</sup>

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# SOLVENT EFFECTS IN THE SPECTRA OF ACETONE, CROTONALDEHYDE, NITROMETHANE AND NITROBENZENE

### BY NOEL S. BAYLISS AND EION G. MCRAE

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The ultraviolet absorption spectra of acetone (I), crotonaldehyde (II), nitromethane (III) and nitrobenzene (IV) have been measured in polar and non-polar solvents. The  $\pi^* \leftarrow n$  transitions of I, II and III are accompanied by a decreased dipole moment in the excited state and relative to the gas are displaced to the blue in polar solvents, and either to the red (I, III) or to the blue (II) in non-polar solvents. The  $\pi^* \leftarrow \pi$  transitions of II and IV have an increased dipole moment in the excited state and are displaced to the red in both polar and non-polar solvents. These effects are interpreted in terms of dipole-dipole, hydrogen bonding, dipole-polarization and transition dipole interactions in accordance with the general theory proposed by the authors in a previous paper. Quantitative data are given for the 2800 Å. transition of nitromethane gas.

In the previous paper<sup>1</sup> the authors outlined the solvent effects in electronic absorption spectra to be expected from (a) the presence of a dipole moment in the solute or solvent molecule, (b) the change in dipole moment during the optical transition, and (c) the operation of the Franck-Condon principle. The present paper describes solution spectrum data for acetone, crotonaldehyde, nitromethane and nitrobenzene, which illustrate these principles. The known ultraviolet absorption spectra of these compounds and their probable assignments are now summarized.

Acetone.—There are two diffuse ultraviolet bands; the first at 2800 Å. is very weak with its oscillator strength  $f \sim 0.0004$ , and the second at about 1900 Å. is moderately intense with a maximum extinction coefficient<sup>2</sup>  $\epsilon_m \sim 1000$ . McMurry<sup>3</sup> has identified the 2800 Å. band as a forbidden  $\pi^* \leftarrow$ n transition involving excitation of a non-bonding O electron to an anti-bonding  $\pi$  orbital between the C and O of the carbonyl group. The 1900 Å. band, which is not dealt with in this paper, is ascribed by McMurry to the excitation of a  $\pi$  electron into an orbital with  $\sigma$  symmetry between the C and the O, *i.e.*, it is a  $\sigma^* \leftarrow \pi$  transition, although Hartmann regards it as  $\pi^* \leftarrow \pi$ .<sup>2</sup>

Crotonaldehyde.—Again there are two ultraviolet bands; the first at 3300 Å. is weak ( $f \sim$ 

(1) N. S. Bayliss and E. G. McRae, THIS JOURNAL, 58, 1002 (1954).

- (2) H. Hartmann, Z. physik. Chem., 195, 58 (1950).
- (3) H. L. McMurry, J. Chem. Phys., 9, 231 (1941).

0.0004) and the second at 2200 Å. is intense ( $f \sim 0.4$ ). The weak 3300 Å. band is a  $\pi^* \leftarrow n$  transition resembling the 2800 Å. band of acetone,<sup>3</sup> and its appearance at lower frequency in crotonaldehyde is because of the lower energies of the excited  $\pi^*$  orbitals in the more extended conjugated system C= C-C=0. The intense 2200 Å. band is a  $\pi^* \leftarrow \pi$  transition involving this conjugated system.<sup>3</sup>

Nitromethane.—There is a weak diffuse band at 2800 Å.<sup>4</sup> with about the same intensity as acetone (2800 Å.). This similarity in position and intensity suggests that the nitromethane case is likewise a forbidden  $\pi^* \leftarrow n$  transition involving a non-bonding O electron. More intense absorption, with which we are not concerned here, sets in at about 2300 Å.<sup>45</sup>

**Nitrobenzene.**—The spectrum is complex and possibly consists of the following transitions: (a) an intense band whose maximum lies below 2000 Å., (b) a shoulder at about 2150 Å. that appears in polar solvents, (c) an intense band ( $f \sim 0.1$ ) at 2600 Å., and (d) two weak bands or shoulders at about 2900 and 3600 Å.<sup>6-8</sup> We are concerned with

 <sup>(4)</sup> A.P.I. Research Project 44; Carnegie Institute of Technology, Catalog of Ultraviolet Spectral Data: Serial No. 104, Nitromethane.
 (5) Contributed by California Research Corporation, Richmond, Calif.

 <sup>(6)</sup> Landolt-Börnstein, "Physikalisch-chemische Tabellen," Springer, Berlin, 1951, 6th ed., Part 3 (II), p. 267.

<sup>(7)</sup> G. S. Hammond and F. Modic, J. Am. Chem. Soc., 75, 1385 (1953).

<sup>(8)</sup> H. Ungnade, ibid., 75, 432 (1953).

the 2600 Å, band which has been shown by Doub and Vandenbelt<sup>9</sup> to be related to the  $\pi^* \leftarrow \pi 2000$ Å. band of benzene which has about the same intensity.

#### Experimental

Purification of Materials.—Acetone for use as solute was purified through the sodium iodide compound; b.p. 56.1°  $(56.2^{\circ}), n^{15}$ D 1.3609 (1.3616).<sup>10</sup> For use as solvent, acetone of British Drug Houses Analar grade was dried over anhydrous calcum sulfate and fractionated; b.p. 56.1° (56.2°),  $n^{20}$ p 1.3591 (1.3591).

Crotonaldehyde (British Drug Houses laboratory reagent) was dried over calcium chloride and fractionated; b.p.  $102^{\circ}$  (104°),  $n^{20}$ p 1.4381 (1.4375).<sup>11</sup>

Nitromethane (L. Light and Co.) was fractionated twice; b.p. 101.5° (101.2°), n<sup>20</sup>D 1.3820 (1.3820). Nitrobenzene of commercial grade was dried over an-

hydrous calcium sulfate, six times fractionally crystallized

and fractionated twice under reduced pressure; b.p. 101° (20 mm.) (100° (20 mm.)),  $n^{16}$  D 1.5546 (1.5545). *n*-Heptane (technical) was repeatedly shaken with concentrated sulfuric acid and washed with water, sodium carbonate and water. It was dried over anhydrous calcium sulface acid and constrained for the soliton of the soliton acid for the soliton of the s sulfate, refluxed over sodium and fractionated; b.p. 97.9° (98.4°),  $n^{25}$ D 1.3849 (1.3852).

Cyclohexane (British Drug Houses "special for spectrocopy") was crystallized six times, refluxed over sodium and fractionated; b.p.  $80.6^{\circ}$  ( $80.8^{\circ}$ ),  $n^{20}$ p 1.4261 (1.4263). Benzene (British Drug Houses "Analar") was shaken four times with concentrated sulfuric acid, washed and

dried over calcium chloride. It was then crystallized three times, refluxed over sodium and fractionated; b.p. 80.1° (80.1°),  $n^{25}$ D 1.4980 (1.4981)

Carbon tetrachloride (technical grade) was shaken with sodium hydroxide in water-ethanol, washed, dried over potassium hydroxide and fractionated; b.p. 76.6° (76.7°),  $n^{20}$ D 1.4600 (1.4604).

Chloroform (Judex analytical reagent) was dried with calcium chloride and fractionated less than six hours before

use; b.p.  $61.0^{\circ}$  ( $61.2^{\circ}$ ),  $n^{20}$ D 1.4452 (1.4455). Ethanol, a commercial "absolute" grade containing a trace of benzene was fractionated with  $\frac{1}{10}$  of its volume of water, refluxed over calcium oxide in a nitrogen atmosphere, distilled, refluxed with silver nitrate and potassium hydrox-ide, and fractionated; b.p.  $78.2^{\circ}$  (78.3°),  $n^{16}$ D 1.3632 (1.3633).

Sulfuric acid was a "pure" grade of local manufacture containing 90% by weight of H<sub>2</sub>SO<sub>4</sub>.

Water was twice distilled.

Spectra.-The solution spectra were measured with a Beckman quartz spectrophotometer, model DU. Path lengths were 1 cm. or 0.1 cm. (1-cm. cell with 0.9-cm. spacer). Slit widths were kept as small as possible by sub-stituting when necessary a 10,000 megohm phototube load resistor for the usual 2000 megohm resistor. To ensure that comparisons were valid, the slit width was kept constant in spectra to be compared, i.e., for one solute in a series of solvents.

The gas spectra of acetone and nitromethane, which were investigated primarily to fix the position of their maxima, were measured<sup>12</sup> by introducing into the 10-cm. Beckman gas absorption cell slightly more of the liquid than was required to saturate the space with the vapor. Ample time was allowed for equilibrium, and the temperature of the cell enclosure was continuously observed during the measurements. The vapor concentration was obtained from recorded vapor pressures.<sup>13</sup> Although positive thermostating was not employed, the temperature of the enclosure was quite steady on each occasion, and repeated measurements on days with different ambient temperatures were in good agreement.

### Results

Quantitative data on the 1800 Å. spectrum of nitromethane vapor do not seem to be available in the literature, and are therefore presented briefly in Table I and in Fig. 1. Our measurements on

TABLE I

Specopput	OF N		NE	TADOD
SPECTRUM	$OF \Gamma$	NITROMSTHA	INE	VAPOR

	DOTION OF THIS	OM STIMMA THIOR	
$\nu \times 10^{-4}$ (cm. <sup>-1</sup> )	¢	$\nu \times 10^{-4}$ (cm1)	£
3.2	2.0	3.8	7.3ª
3.4	5.0	4.0	4.5
3.6	$7.7^{a}$	4.1 (min.)	3.0
3.63 (ma	ax.) $8.0^{a}$	4.3	10

There is a weak diffuse structure near the maximum.



Fig. 1.—The nitromethane (2800 Å.) band in: V, vapor; B, benzene; CF, chloroform; CT, carbon tetrachloride; E, ethanol; S, sulfuric acid; W, water. Maxima are indi-cated, and in ethanol only the portion of the curve near the maximum is shown. Note red shift in non-polar, and blue shift in polar, solvents (see text).

the 2800 Å. spectrum of acetone vapor, using the same technique, were in good agreement with those of Porter and Iddings.<sup>14</sup> The nitromethane spectrum had weak, diffuse and reproducible structure that was most noticeable near the maximum, and that was associated with a frequency interval of the order of 500 cm. $^{-1}$ . The acetone gas spectrum showed considerably weaker, but we believe definite, indications of similar structure.<sup>15</sup>

The solution spectra are recorded in Tables II and III, which give the wave number  $\nu_m$  and the molar extinction coefficient  $\epsilon_m$  at the maximum, as well as the oscillator strength f of each band.  $\epsilon$ is defined by the relation

#### $\log_{10} I_0 / I = \epsilon c l$

<sup>(9)</sup> L. Doub and J. M. Vandenbelt, J. Am. Chem. Soc., 69, 2714 (1947).

<sup>(10)</sup> Except where indicated otherwise, physical constants in parentheses are from Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier, Amsterdam, 1950.

<sup>(11) &</sup>quot;The Merck Index," 5th ed., Merck & Co. Inc., 1940, p. 173. (12) These measurements carried out by Mr. C. J. Brackenridge.

<sup>(13)</sup> Reference 10, pp. 354, 577

<sup>(14)</sup> C. W. Porter and C. Iddings, J. Am. Chem. Soc., 48, 40 (1926) (15) G. W. Luckey, A. B. F. Duncan and W. A. Noyes, J. Chem-Phys., 16, 407 (1948)

TABLE II

			π •	$- n \operatorname{Tr}$	ANSITIO	NS					
	Solve 2800	nt n <sup>a</sup> 3300	Acet _m × 10 <sup>-4</sup>	tone, 2800	Å. f×	Nitron Pm X 10 <sup>-</sup>	methane, 28 4	00 Å. f ×	Crotonald <sup>µ</sup> m × 10 <sup>-4</sup>	lehyde,	3300 Å. ∫ ×
Solvent	Á.	Å.	cm1	em	104	cm1	¢m	104	cm1	€m	104
Gas			3.62	11.2	3.4	3.63	8	$2.4^{c}$	3.049 <sup>d</sup>	18	4.7
Non-polar											
n-Heptane	1.42	1.40°	3.584	13.0	4.3	3.602	18.2	5.1	3.058	<b>24</b>	7.0
Cyclohexane	1.47	1.45	3.574	14.7	4.9	3.595	18.2	5.1	3.055	21	6.0
Carbon tetra-											
chloride	1.52	1.49	3.571	20.1	6.5	3.612	20.5	5.7			
Benzene	1.62	1.56	3.577	17.5		>3.6	>31		3.086	32	8.6
Polar											
Chloroform	1.50	1.47	3.625	17.3	5.4	3.627	19.6	5.4			
Acetone	1.40	1.39							3.060	24	
Ethanol	1.37	1.38	3.677	16.0	5.1	3.65	16.9	4.8	3.300	40	9.7
Water	1.36	1.35	3.776	17.9	5.2	3.72	15.4	4.3			
Sulfuric acid $(90\%)$						3.96	15.6				

<sup>a</sup> Refractive indices from Landolt-Börnstein, "Physikalisch-chemische Tabellen," 5th Ed., Springer, Berlin. <sup>b</sup> These values are actually for hexane. <sup>c</sup> Gas values for acetone and nitromethane by Mr. C. J. Brackenridge.<sup>12</sup> <sup>d</sup> Gas values for crotonaldehyde from Blacet, Young and Roof, J. Am. Chem. Soc., 59, 608 (1937).

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			TABLE I	11				
$\pi^* \leftarrow \pi \text{ TRANSITIONS}$ Solvent $n^a$ Nitrobenzene, 2500 Å.					Crotonaldebyde, 2200 Å.			
Solvent	2500 Å.	2200 Å.	$\nu_{\rm m} \times 10^{-4}$ (cm. <sup>-1</sup> )	€m	ſ	νm × 10-4	€m	
Non-polar								
<i>n</i> -Heptane	1.43	1.46	3.974	8350	0.23	4.704	16,000	0.3
Cyclohexane	1.48	1.52	3.954	9900	0.26	4.675	13,000	0.3
Carbon tetrachloride	1.54		3.917	9790				
Polar								
Chloroform	1.52		3.815	8330	0.25			
Ethanol	1.40	1.44	3.858	8240	0.26			
Water	1.38	1.40	3.737	8190	0.26	4.476	15,000	0.4
Sulfuric acid (90%)			3.456	8500	0.30			
<sup><i>a,b</i></sup> See <i>a</i> and <i>b</i> of Table II.								

where  $I_0$  and I are incident and transmitted intensities, c is concentration in mole  $l.^{-1}$ , and l is path length in cm. The absorption maxima are rather flat, and there is a consequent uncertainty of the order of 50 cm.<sup>-1</sup> in our estimates of  $\nu_{\rm m}$ . The spectra are also shown in Figs. 1–5.

#### Discussion

The  $\pi^* \leftarrow n$  Transitions.—The weak bands in acetone (2800 Å.), nitromethane (2800 Å.) and crotonaldehyde (3300 Å.) all involve the transfer of a non-bonding O electron to a  $\pi^*$  orbital whose "center of gravity" is nearer the center of the molecule. Since each of these molecules has a dipole with the negative end directed toward the oxygen, the transfer of electronic charge away from the oxygen will in each case cause the permanent dipole moment to be *decreased* in the excited state. Thus the spectra should conform to cases IIIa and IVa of the preceding paper.<sup>1</sup>

In non-polar solvents there is competition between the polarization shift (refractive index dependent and to the red) and the dipole-polarization shift to the blue (case IIIa) depending on the change in the permanent dipole moment and on the solvent refractive index. There is no orientation strain. Now in Table II (also Fig. 2) it is seen that there is a progressive shift to the red of acetone

(2800 Å.), varying with refractive index, in the solvents heptane, cyclohexane and carbon tetrachloride. This conforms to predominance of the polarization shift. In benzene, the non-polar solvent of highest refractive index, there is a lessened red shift which we interpret as due to the increasing importance, but not dominance, of the case IIIa blue In nitromethane (2800 Å.) (Fig. 1) the reshift. sults are similar, except that the case IIIa blue shift begins to be apparent, but still not dominant, in carbon tetrachloride. The very high intensity of nitromethane in benzene suggests some specific interaction of which we offer no explanation. In crotonaldehyde (3300  $\overline{A}$ .), the shifts in non-polar solvents are all to the blue and roughly parallel to solvent refractive index, suggesting that the case IIIa blue shift has attained dominance over the polarization red shift (Fig. 3). It is obvious that this result can be understood only if the change in the permanent dipole moment is considerably greater in the crotonaldehyde (3300 Å.) transition than in acetone (2800 Å.) and nitromethane (2800 Å.), since the magnitude of the case IIIa blue shift depends on this change. Now the transition in acetone transfers electronic charge from the oxygen to a  $\pi^*$  orbital distributed over C=O, while in crotonaldehyde the  $\pi^*$  orbital is distributed over the longer conjugated system C=C-C=O. Thus the elec-



Fig. 2.—The acetone (2800 Å.) band in: V, vapor; B, benzere; CF, chloroform; CT, carbon tetrachloride; E, ethanol; H, *n*-heptane; W, water. Only portions near the maxima are shown for B, CF and E. The blue shift V, E, W and the red shift V, H, B, CT are clearly shown, with CF little shifted (see text).



Fig. 3.—The crotonaldehyde (3300 Å.) band in: V, vapor; A, acetone; B, benzene; H, *n*-heptane; W, water. The shifts are all to the blue, and the diffuse structure is absent in A and W (see text).

tronic displacement, and hence the decrease in permanent dipole moment, should be greater in crotonaldehyde than in acetone, in agreement with the



Fig. 4.—The crotonaldehyde (2200 Å.) band in: CH, cyclohexane; H, *n*-heptane; W, water. The polar solvent here causes a red shift (see text).



Fig. 5.—The nitrobenzene (2500 Å.) band in: CF, chloroform; CH, cyclohexane; CT, carbon tetrachloride; E, ethanol; H, *n*-heptane; S, sulfuric acid; W, water. Maxima only are shown for CF, CH and E. Polar solvents cause a red shift (see text).

above interpretation of the solution spectra. Nitromethane appears to present an intermediate case.

In polar solvents (case IVa) there is the additional effect of dipole-dipole interaction (and possibly also of hydrogen bonding) together with ori-

entation strain. We have previously stated<sup>1</sup> that dipole-dipole forces should be dominant over the effect of dipole-polarization and over the polarization red shift. In chloroform, both acetone (2800 Å.) and nitromethane (2800 Å.) show almost no shift (Table II and Figs. 1, 2), showing that the case IVa blue shift has just cancelled the polarization red shift, since if the latter alone were operative the red shift would be similar to that in carbon tetrachloride. In acetone, ethanol and water there are in all spectra increasingly large blue shifts whose magnitude doubtless depends on several factors: (a) orientation strain, (b) decreased dipole-dipole interaction in the excited state, (c) decreased hydrogen bonding in the excited states and (d) decreasing size of the solvent molecules so that more of them come within the range of nearest neighbor interaction. Conforming with our case IVa interpretation, it is to be noted that Hartmann and Schläfer<sup>16</sup> have observed progressive blue shifts when polar solvents (including acetone itself) are added to solutions of acetone in cyclohexane.

It is also important to note that diffuse vibrational structure, which is present in the nitromethane and crotonaldehyde spectra in the gas and in non-polar solvents, is obliterated in the polar solvents (Figs. 1, 3). This is the predicted result of orientation strain. There may well be specific interaction in the case of nitromethane in sulfuric acid (Fig. 1).

The  $\pi^* \leftarrow \pi$  Transitions.—The transitions concerned here are those of crotonaldehyde (2200 Å.) and nitrobenzene (2500 Ä.). The experimental data are shown in Table III and in Figs. 4 and 5. In the absence of gas data it is seen that the crotonaldehyde band is displaced to the red in the solvent order heptane, cyclohexane, water. The first two are non-polar, the spectrum being rather further to the red in the solvent of greater refractive index. There is a substantial further red shift in the polar solvent water. In nitrobenzene, there are red shifts varying qualitatively with refractive index in the non-polar solvents heptane, cyclohexane and carbon tetrachloride. There are still greater red shifts in polar solvents in the order ethanol, chloroform, water, sulfuric acid. (The possibility of specific interaction in sulfuric acid cannot be overlooked; but it seems to be significant that in both nitromethane and nitrobenzene the displacement caused by sulfuric acid is in the same direction as, but greater than, that caused by water.)

These effects are all consistent with cases IIIb and IVb of the previous paper,<sup>1</sup> *i.e.*, with what would be expected if the dipole moment *increases* during the transition. In non-polar solvents (IIIb) the polarization red shift and the effect of dipole polarization forces are in the same direction (red shift) in contradistinction to case IIIa. In polar solvents (IVb) the dominant dipole-dipole forces or hydrogen bonding forces cause the greater shift to the red.

Consideration of the type of transition makes it appear highly probable that the dipole moment increases; in fact one might suggest the solvent ef-

(16) H. Hartmann and H. L. Schläfer, Z. Elektrochem., 54, 337 (1950).

fect as evidence for the increase. Using obvious important resonance forms, the transitions are probably represented by

$$c = c - c = 0 \longrightarrow c = c - \bar{0}$$

and by

$$= N \left( \begin{array}{c} & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & &$$

where in both cases there is a greater dipole moment in the excited state. In this connection it should be noted that Braude, Jones and Rose<sup>17</sup> have found that the  $\pi^* \leftarrow \pi$  transition in nitroölefins is shifted to the red in ethanol as compared with hexane, consistent with the case IVb effect of an increased dipole moment as a result of

From the above it is seen that the measured spectra conform qualitatively to the scheme described in the previous paper.<sup>1</sup> Work is now in progress to place the theory on a more quantitative basis, one of the outstanding questions being whether dipoledipole interaction or hydrogen bonding is the more important type of solute-solvent interaction between a polar solute and a polar solvent. Each case considered here has oxygen at the negative end of the solute dipole, and either type of interaction is qualitatively consistent with the experimental facts. The blue shifts in the cases where the solute dipole moment decreases, and the red shifts where it increases, occur in either of the solvent orders chloroform, ethanol, water (acetone 2800 Å., nitromethane 2800 Å.) or ethanol, chloroform, water (nitrobenzene 2500 Å.). Now the order of both dipole moments and hydrogen bonding capacity is chloroform, ethanol, water, and it appears as if the anomalous position of chloroform in the nitrobenzene case is due to the superposition of the polarization red shift resulting from its large refractive index. The order chloroform, ethanol, water is also that of decreasing molecular size, and while this factor will not affect hydrogen bonding interactions, it will affect the dipole-dipole interaction since more solvent dipoles are closer to the solute dipole if the solvent is small.

The solvent displacements also conform to McConnell's<sup>18</sup> "blue shift" and "red shift" criteria to distinguish between  $\pi^* \leftarrow n$  and  $\pi^* \leftarrow \pi$  transitions. However we have already shown<sup>1</sup> that the McConnell criteria are a special case of our more general scheme, and moreover that they have the theoretical disadvantage of omitting consideration of the gas frequency.

Solvent Effect on Spectral Intensity.—In Tables II and III we have presented for record purposes the oscillator strengths f of the gas spectra (where available) and of the solution spectra. There is currently no satisfactory theoretical approach to the problem of spectral intensities in solution. The remarkably high intensity of nitromethane

(17) E. A. Braude, E. R. H. Jones and G. G. Rose, J. Chem. Soc., 1104 (1947).

(18) H. McConnell, J. Chem. Phys., 20, 700 (1952).

(2800 Å.) in benzene is similar to other cases where Bayliss and Hulme<sup>19</sup> have noted a specific enhancement when the solute has an absorption band close to one of the solvent; however it is difficult to see why acetone does not behave similarly. The high

(19) N. S. Bayliss and L. Hulme, Australian J. Chem., 6, 257 (1953).

intensity of crotonaldehyde (3300 A.) in water must be due to some other cause. We feel that further comment at present would be premature.

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## THE SOLUTION OF ARGON IN LAYERS OF KRYPTON<sup>1,2,3</sup>

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The adsorption isotherms for argon on pre-adsorbed krypton films on graphitized carbon black have been measured. After an initial decrease the volume of argon adsorbed increased steadily with the quantity of krypton, indicating a solution process. The data do not obey Raoult's law or ideal solution theory and are interpreted on the basis of a modified regular solution theory. It is shown that there is a limiting value of the thickness of a krypton layer deposited on the adsorption sample. The solution of argon in bulk krypton has been investigated at  $77^{\circ}$ K.

### Introduction

In a previous paper<sup>4</sup> the adsorption of argon on pre-adsorbed layers of xenon has been reported. At the temperature of liquid nitrogen the vapor pressure of krypton is low enough (1.5 mm.) so that it was expected that similar isotherms for argon on krypton layers would be observed. However, it was found that the argon dissolved in the krypton. Instead of approaching a limiting shape with increased pre-adsorbed krypton, the volume of argon, adsorbed at a given partial pressure, increased indefinitely with the amount of krypton.

#### Experimental

The apparatus and adsorbent have been described in a previous paper.<sup>4</sup> The sample of graphitized carbon black was maintained at a temperature of  $77.1^{\circ}$ K. by use of a cryostat containing liquid nitrogen at a constant vapor pressure.<sup>5</sup> For the deposition of one or less layers of krypton the sample was slowly cooled to  $77^{\circ}$ K. in the presence of helium, as described for the deposition of xenon layers.<sup>4</sup> With two or more krypton layers it was shown that identical results were obtained either by this method or by allowing the krypton to reach equilibrium with the sample by standing at  $77^{\circ}$ K. for four hours. As the vapor pressure of krypton was greater than 1 mm., it was not necessary to add helium to maintain temperature equilibrium in the sample during cooling. It was shown that the argon isotherms were reversible by making desorption measurements.

Krypton Isotherm.—To obtain the krypton isotherm at 77°K. a small McLeod gage of about 50-ml. capacity was added to the adsorption system. The gage could also be connected to a krypton vapor pressure thermometer placed in the center of the sample bulb, to measure the krypton saturation pressure. The large increase in dead space did not appreciably reduce the accuracy of measurement because of the low gas pressure. The diffusion of gas between the McLeod gage and the sample bulb was slow. To assist rapid equilibrium the gage was not connected to the adsorption bulb until 10 minutes after the addition of a dose of

(3) A more detailed form of this paper has been deposited as Document number 4250 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document no. and 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.

(4) J. H. Singleton and G. D. Halsey, THIS JOURNAL, 58, 330 (1954).

(5) W. J. C. Orr, Proc. Roy. Soc. (London), A173, 349 (1939).

krypton, when adsorption was complete. To determine the effect of thermal transpiration on the measurements, two different diameters (4 and 8 mm.) of tubing were used to connect the sample in the cryostat to the McLeod gage. These gave identical krypton isotherms. Solution of Argon in Bulk Krypton.—To investigate the

Solution of Argon in Bulk Krypton.—To investigate the solution of argon in bulk krypton, a glass bulb replaced the sample of carbon black. Krypton was condensed in the bulb and maintained at 77°K. in the cryostat. Total pressure data were obtained for samples of 3 and 11 ml. S.T.P. of krypton.

## A Crude Theory

The treatment of Fowler and Guggenheim<sup>6</sup> for strictly regular solutions will be modified to take account of the adsorption potential. It would appear at first sight that the assumption of this theory would be nearly true for solid solutions of the rare gases. Fowler and Guggenheim's zeroth approximation, which assumes completely random mixing of the two components, will be used here. Their equation 817.3 (omitting communal entropy) for the Helmholtz free energy is

$$F = N_{\rm A} \left\{ -\chi_{\rm A} - kT \ln (\phi_{\rm A}v_{\rm A}) + kT \ln [N_{\rm A}/(N_{\rm A} + N_{\rm B})] \right\} + N_{\rm B} \left\{ \chi_{\rm B} - kT \ln (\phi_{\rm B}v_{\rm B}) + kT \ln [N_{\rm B}/(N_{\rm A} + N_{\rm B})] \right\} + \frac{1}{\overline{X}} w_{\rm AB} \quad (1)$$

It will be convenient to express the number of molecules of the species A and B,  $N_A$  and  $N_B$ , in terms of the number of monolayers of gas adsorbed,  $\theta_A$ and  $\theta_B$ . Note that one of the assumptions of strictly regular solution theory requires that the species A and B have equal molar volume, and that the number of molecules in a monolayer,  $N_M$ , must therefore be the same for the two species. Thus,  $\theta_A = N_A/N_M$  and  $\theta_B = N_B/N_M$ . Also the energy and free volume terms,  $-\chi_A - kT \ln(\phi_A v_A)$  and  $-\chi_B - kT \ln(\phi_B v_B)$ , for the pure compounds are conveniently replaced by  $F_A^0$  and  $F_B^0$ . With these changes equation 1 becomes

$$F = N_{\rm M}\theta_{\rm A} \{F_{\rm A}^{0} + kT \ln [\theta_{\rm A}/(\theta_{\rm A} + \theta_{\rm B})]\} + N_{\rm M}\theta_{\rm B} \{F_{\rm B}^{0} + kT[\theta_{\rm B}/(\theta_{\rm A} + \theta_{\rm B})]\} + \overline{\overline{X}}w_{\rm AB} \quad (2)$$

Without the last term,  $\overline{X}w_{AB}$ , this equation leads to Raoult's law and the ideal solution. For the

(6) R. H. Fowler and E. A. Guggenheim, "Statistical Thermodynamics," Cambridge University Press, 1949.

<sup>(1)</sup> This research was supported by Contract AF 19 (604)-247 with the Air Force Cambridge Research Center.

<sup>(2)</sup> Presented at the 125th National Meeting of the American Chemical Society, Kansas City, March 23-April 1, 1954.

strictly regular solution, the zeroth approximation yields the result (cf. Fowler and Guggenheim,<sup>6</sup> equation 818.4)

$$\overline{\overline{X}}w_{AB} = \frac{N_{M}\theta_{A}\theta_{B}}{\theta_{A} + \theta_{B}}w_{AB}$$
(3)

where  $w_{AB}$  is the "energy of mixing." Terms will now be added to equation 2 to take account of the free energy of adsorption. The expression for the total free energy of the system includes a term,  $F_{\rm s}$ , the contribution from the adsorbent, but, since this is constant throughout and makes no contribution to the final result, it has been omitted. For the pure components

$$F_{\rm A} = kT \int_0^{N_{\rm A}} \ln P^{\rm A}_{\theta} \, \mathrm{d} \, N_{\rm A} \tag{4}$$

$$= N_{\rm M} kT \int_0^{\theta_{\rm A}} \ln P^{\rm A}_{\theta} \, \mathrm{d}N_{\rm A} \tag{5}$$

with a similar expression for component B. The expression  $P^{A}_{\theta}$  indicates the partial pressure for the pure component A at coverage  $\theta$ .

The simplest assumption in keeping with the requirements of strict regularity is that the two components do not interfere with each other's adsorption potential and that they are mixed randomly. The free energy of adsorption,  $F_{ads}$ , is then the average, weighted by the mole fractions. The integrations are carried out to the total coverage because, by hypothesis, both species are randomly mixed in every layer. Thus

$$F_{ads} = N_{M} kT \left\{ \frac{\theta_{A}}{\theta_{A} + \theta_{B}} \int_{0}^{\theta_{A} + \theta_{B}} \ln P^{A}_{\theta} d\theta + \frac{\theta_{B}}{\theta_{A} + \theta_{B}} \int_{0}^{\theta_{A} + \theta_{B}} \ln P^{B}_{\theta} d\theta \right\}$$
(6)

The substitution of equation 3 and the addition of equation 6 to equation 2 yields the expression

$$\frac{F}{N_{\rm M}} = \theta_{\rm A} \left\{ F_0^{\rm A} + kT \ln \frac{\theta_{\rm A}}{\theta_{\rm A} + \theta_{\rm B}} + \frac{kT}{\theta_{\rm A} + \theta_{\rm B}} \int_0^{\theta_{\rm A} + \theta_{\rm B}} \right. \\ \left. \ln P^{\rm A}_{\theta} \, \mathrm{d}\theta + \theta_{\rm B} \left\{ F_0^{\rm B} + kT \ln \frac{\theta_{\rm B}}{\theta_{\rm A} + \theta_{\rm B}} + \frac{kT}{\theta_{\rm A} + \theta_{\rm B}} \int_0^{\theta_{\rm A} + \theta_{\rm B}} \ln P^{\rm B}_{\theta} \, \mathrm{d}\theta \right\} + \frac{\theta_{\rm A}\theta_{\rm B}}{\theta_{\rm A} + \theta_{\rm B}} w_{\rm AB} \quad (7)$$

This must be differentiated with respect to  $N_{\rm A}$  to obtain the chemical potential,  $\mu_{\rm A}$ . For this purpose it is arranged

$$\frac{F}{N_{\rm M}} = \theta_{\rm A} F_0^{\rm A} + \theta_{\rm B} F_0^{\rm B} + kT \int_0^{\theta_{\rm A} + \theta_{\rm B}} \ln P^{\rm A}_{\theta} d\theta + kT \frac{\theta_{\rm B}}{\theta_{\rm A} + \theta_{\rm B}} \int_0^{\theta_{\rm A} + \theta_{\rm B}} \ln \left(\frac{P^{\rm B}_{\theta}}{P^{\rm A}_{\theta}}\right) d\theta + \frac{\theta_{\rm A}\theta_{\rm B}}{\theta_{\rm A} + \theta_{\rm B}} w_{\rm AB} + kT \theta_{\rm A} \ln \frac{\theta_{\rm A}}{\theta_{\rm A} + \theta_{\rm B}} + kT \theta_{\rm B} \ln \frac{\theta_{\rm B}}{\theta_{\rm A} + \theta_{\rm B}}$$
(8)

Fowler and Guggenheim show that F = G, the Gibbs free energy, so

$$\mu_{A} = \frac{\partial G}{\partial N_{A}} = \frac{1}{N_{M}} \frac{\partial G}{\partial \theta_{A}} = \mu^{A_{0}} + kT \ln P^{A}_{\theta_{A} + \theta_{B}} + \left(\frac{\theta_{B}}{\theta_{A} + \theta_{B}}\right)^{2} w_{AB} + \ln \frac{\theta_{A}}{\theta_{A} + \theta_{B}} + kT\theta_{B} \,\delta_{\theta_{A} + \theta_{B}} \quad (9)$$

where the function

$$\delta = \frac{\partial}{\partial \theta_{A}} \left\{ \frac{1}{\theta_{A} + \theta_{B}} \int_{0}^{\theta_{A} + \theta_{B}} \ln \left( \frac{P^{B}_{\theta}}{P^{A}_{\theta}} \right) d\theta \right\} \quad (10)$$

If the isotherms  $P^{A}_{\theta}$  and  $P^{B}_{\theta}$  are identical, or bear a constant ratio to each other,  $\delta$  vanishes. It is possible that the lower range of the integration will be uncertain, owing to uncertainties in the isotherms at low coverages. To investigate this possibility the integration is split at a value  $\theta_0$  below which the isotherms are not investigated or are uncertain

$$\delta = \frac{\partial}{\partial \theta_{A}} \left\{ \frac{1}{\theta_{A} + \theta_{B}} \int_{0}^{\theta_{0}} \ln\left(\frac{P^{B}_{\theta}}{P^{A}_{\theta}}\right) d\theta + \frac{1}{\theta_{A} + \theta_{B}} \int_{\theta_{0}}^{\theta_{A} + \theta_{B}} \ln\left(\frac{P^{B}_{\theta}}{P^{A}_{\theta}}\right) d\theta \right\} = \frac{\text{const.}}{(\theta_{A} + \theta_{B})^{2}} + \frac{1}{\theta_{A} + \theta_{B}} \ln\left(\frac{P^{B}_{\theta}}{P^{A}_{\theta}}\right) - \frac{1}{(\theta_{A} + \theta_{B})^{2}} \int_{\theta_{0}}^{\theta_{A} + \theta_{B}} \ln\left(\frac{P^{B}_{\theta}}{P^{A}_{\theta}}\right) d\theta$$
(11)

Note that the uncertain value of the constant gives a term inversely proportional to  $(\theta_{\rm A} + \theta_{\rm B})^2$ .

Following a procedure similar to that used by Fowler and Guggenheim to obtain their equation 818.8, one finds

$$\ln \left(\frac{p}{p_{0}}\right)^{A} = \ln \left[\frac{\theta_{A}}{\theta_{A} + \theta_{B}}\right] + \ln P_{\theta_{A} + \theta_{B}}^{A} + \frac{w_{AB}}{kT} \left(\frac{\theta_{B}}{\theta_{A} + \theta_{B}}\right)^{2} + \theta_{B}\delta \quad (12)$$

A similar expression gives  $\ln(p/p_0)^{B}$ . The sign of the function  $\delta$  is minus and  $\theta_A$  and  $\theta_B$  are interchanged.

It emerges that the term in  $w_{AB}$  depends on  $\theta_A$ in the same manner as the uncertain part of  $\delta$ . Therefore one can test the theory at constant  $\theta_{\rm B}$ without knowing the isotherms to  $\theta = 0$ . Any error in the lower part of the computation of  $\delta$  will give a false but constant value of  $w_{AB}/kT$  if the theory applies.

### **Discussion of Results**

The Simple Isotherms.—The isotherms for the two pure gases are shown in Fig. 1. Because of the requirements of the regular solution theory they were plotted to the same scale, by volumes of gas at S.T.P. It remained to select the monolayer value,  $v_{\rm m}$ , which must be assumed the same for the two adsorbates. It is noteworthy that the krypton isotherm shows sharp steps, even compared with the argon isotherm, which has previously been given as an example of an isotherm with pronounced steps. The scale of  $\theta$  was accordingly adjusted to make the tread of the first (krypton) step occur at  $\theta = 1$ . Within experimental error, the second tread is situated at  $\theta = 2$ . The argon data do not fit the B.E.T. isotherm but the visually estimated "point B" is close to  $\theta = 1$  and this agrees with the adjusted krypton scale. The "point B" for krypton is considerably lower at  $\theta = 0.94$ . It will appear below that the choice for krypton was substantially correct.

The factor  $\delta$  was then computed from the data for argon and krypton. Below  $\theta = 0.8$  the data were not accurately known. The insert (Fig. 1) shows that the two isotherms roughly coincide below  $\theta = 0.8$ . This was assumed to be exactly true in computing  $\delta$ . It was pointed out above that such an arbitrary choice does not affect the test of the theory above  $\theta_A + \theta_B = 0.8$ . The integral in  $\delta$  was evaluated numerically by summing inter-



Fig. 1.—The adsorption isotherms of argon and krypton on graphitized carbon black at 77°K. Insert shows the isotherms up to  $p/p_0 = 0.014$  on a large scale.

vals of 0.1 monolayer. The resulting function, which is shown in Fig. 2, could not be carried beyond  $\theta = 6$  because the krypton isotherm appears to intersect the axis  $p/p_0 = 1$  near this value.

to intersect the axis  $p/p_0 = 1$  near this value. The Mixed Isotherms.—The isotherms for various values of  $\theta_B$  are shown in Fig. 3. The pressure plotted is not exactly equal to  $(p/p_0)^A$ . To obtain this quantity analyses of the gas mixture would have been required at each point. Nevertheless, the vapor pressure of krypton is so low (1.5 mm.) that except at very low values of  $\theta_A$  the total pressure is almost equal to the argon pressure alone. The  $p/p_0$  values plotted are the total pressures, minus the initial vapor pressure of krypton, over the vapor pressure of argon. This pressure is identical with  $(p/p_0)^A$  as  $\theta_A$  approaches zero, or when



Fig. 2.—The function  $\delta$  derived from equation 11.

 $\theta_{\rm B}$  is less than 1, and it is never further away than the error involved in the crude theoretical treatment.

The isotherms for 0.94 monolayer and 1 monolayer, plotted in Fig. 4, show that the choice of scale for  $\theta$  is nearly correct. The isotherm for 0.94 layers would be for 1 layer on the basis of the "point B" of the krypton isotherm. It has a small "point B" of about 0.06 monolayer which shows that the first layer is not complete. An increase in the krypton volume of 0.06 monolayer caused the "point B" to disappear, in keeping with the assignment of the value one to this total quantity of krypton. A similar adjustment was required in the case of xenon on the same sample.<sup>4</sup>



Fig. 3.—The adsorption isotherms of argon on layers of krypton, pre-adsorbed on graphitized carbon black at 77 °K.



Fig. 4.—The adsorption isotherms of argon on 1 and 0.94 layer of krypton, pre-adsorbed on graphitized carbon black at  $77^{\circ}$ K.

In Table I the krypton surface area was calculated from the density of liquid krypton at  $-146^{\circ 7}$  and is less than that which would be obtained from the density of the solid.

#### TABLE I

COMPARISON OF SURFACE AREA OF CARBON BLACK CALCU-LATED FROM DATA

Adsorption	vm, ml./g.	Area, m.²/g.
Nitrogen at $-195^{\circ}$ , from "point B"		$12.5^{3}$
Argon at -195°, from "point B"	3.08	$11.9^{3}$
Xenon at $-124^\circ$ , from "point B"	2.30	11.6 <sup>3</sup>
Krypton at $-195^{\circ}$ , from "point B"	2.86	13.5
Krypton at $-195^{\circ}$ , from position and height		
of steps	3.15	14.9

It is seen that the area obtained from the final assignment of the krypton monolayer is considerably larger than any other value. It should be noted that in Table I of cur previous paper<sup>4</sup> an error was made in recording the values of  $v_{\rm m}$  for argon on carbon black and anatase. In both cases the correct figure is 3.08 ml./g.

It is of interest to compare the isotherms obtained on krypton layers (Fig. 2) with those for xenon on the same sample shown in Fig. 2 of the previous paper.<sup>4</sup> The argon isotherm on 0.47 layer of krypton shows an initial step of about  $\theta =$ 0.5 and subsequent steps occur at  $p/p_0 = 0.25$  and 0.75, each being one monolayer high. In this case, since solution is involved, the krypton is spread uniformly over the surface, making up the total monolayer with argon, rather than providing a new set of adsorption sites as occurred with xenon adsorption. Thus on 0.43 layer of xenon<sup>4</sup> the initial step of  $0.5 \theta$  in the argon isotherm was followed by subsequent poorly defined steps at irregular intervals. On 0.94 layer of krypton a step occurs at  $p/p_0 = 0.08$  but further inflections are absent and the isotherm crosses that on 0.47 layer, when  $p/p_0$ = 0.8, as the increasing effect of solution is noted. At about 1.88 layers of krypton the lower limit of

(7) "International Critical Tables," McGraw-Hill Book Co., New York, N. Y., 1926.

the argon isotherms is reached, for values of  $p/p_0$ below 0.4. Above this value the argon isotherm rises more rapidly, crossing those on 0.47 and 0.94 layer of krypton; the solution effect is obviously of primary importance. This contrasts with the xenon-argon isotherms<sup>4</sup> where the limiting argon isotherm does not occur until three layers of xenon and no solution is observed even at high argon partial pressures to many layers of xenon. On all krypton coverages greater than two layers the solution of argon is so large that the isotherms rise continuously with increasing values of  $p/p_0$ .

Experiments with Bulk Krypton and Argon.-In the measurement of argon adsorption on krypton layers equilibrium was established very rapidly. When bulk argon-krypton mixtures were investigated the rate of solution was found to be very slow and was incomplete in 12 hours. Attempts to obtain equilibrium by condensing mixtures of argon and krypton, either very rapidly or slowly, gave serious fluctuations in the argon pressure and did not remove the slow drift. When 3 ml. of krypton was used, in place of the 11-ml. sample, the rate of solution increased but true equilibrium could not be obtained and the reproducibility was not satisfactory. In Fig. 5 the partial pressure of argon is plotted against the mole fraction. Regular solution theory was applied to the data obtained and using equation 818.8 of Fowler and Guggenheim<sup>6</sup> with the notation slightly changed to agree with that used above

$$\left(\frac{p}{p_0}\right)^{\mathbf{A}} = \frac{N_{\mathbf{A}}}{N_{\mathbf{A}} + N_{\mathbf{B}}} \exp \left\{\frac{w_{\mathbf{A}\mathbf{B}}}{kT} \left(\frac{N_{\mathbf{B}}}{N_{\mathbf{A}} + N_{\mathbf{B}}}\right)^2\right\}$$

the values of  $w_{AB}/kT$  were obtained: these varied widely. From each series of experiments with a given ratio of argon to krypton, the value of  $w_{AB}/kT$  for the lowest pressure obtained was selected and the average for eight figures was found to be 1.32; the extreme values ranged from 1.20 to 1.60. The curve shown in Fig. 5 was calculated using this value of  $w_{AB}/kT$ .



The Limiting Thickness of the Krypton Layer.— In the work on the argon-xenon systems, there was strong indication that the xenon thickness reached a limiting value and that further xenon condensed as bulk crystals of low surface area. The present



Fig. 6.—Adsorption of argon on 5.6 and more layers of krypton, pre-adsorbed on graphitized carbon black at  $77^{\circ}$ K.: —, 5.64;  $\bullet$ , 6.0;  $\bigcirc$ , 7.52.

work confirms that indication. In laying down one layer or less of krypton, slow cooling was necessary

to obtain reproducible results, because the adsorption reduced the krypton vapor pressure very greatly. For 1.88 up to 5.6 layers, the data could be reproduced without any precautions. Krypton and argon could be introduced over the adsorbent at  $77^{\circ}$ K. and equilibrium was readily established.

When it was attempted to lay down more than 5.6 layers no amount of care produced reproducible results. The typical scattering of points, along with the last reproducible isotherm, is shown in Fig. 6. Recalling the experience with bulk krypton, it is clear that the easy explanation is the bulk crystals form if one attempts to push the krypton coverage above about 5 layers.

It is interesting to note that the scattered points lie below the last reproducible isotherm. If the 6 layers of krypton were stable, even when mixed with added layers of argon, the scattered points would necessarily lie above the last isotherm. It appears that the mixed layers are metastable somewhere above 5 layers total coverage.

Comparison of Theory with Experiment.—Because the krypton isotherm intercepts  $p/p_0 = 1$ near  $\theta = 6$  and because of the apparent instability of more than 5 layers, calculations were taken only to a total coverage of 5 layers. The krypton and argon isotherms and the averaged bulk value of  $w_{AB}/kT$  (1.32) were used to calculate the theoretical



Fig. 7.—Theoretical adsorption isotherms of argon or krypton layers, calculated from equation 12.

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mixed isotherms shown in Fig. 7. There are thus no adjustable constants. These isotherms reproduce only the qualitative features of the experiments. The two sets of experimental points illustrate the degree of agreement. For a krypton coverage of 0.47 the agreement is satisfactory; disagreement increases with the krypton coverage until, at 3.76 layers the pressures are off by as much as 20%. Leaving  $w_{AB}/kT$  as an adjustable parameter merely improves the fit in one region at the expense of another. The values of  $w_{AB}/kT$ necessary for perfect fit, calculated from the experimental points and equation 12, fluctuate, but in addition show a definite increasing trend with the ratio of argon to krypton, both within a given isotherm and with the isotherms considered together. This is shown in Fig. 8 where the experimental values of  $w_{AB}/kT$  are plotted for the isotherms on 0.47 and 3.76 layers of krypton. No adjustment in the low coverage uncertainties of the function  $\delta$  will remedy the lack of a constant  $w_{AB}/kT$  within the isotherm when applied to these data. In other words, the argon is too soluble in krypton-rich layers, and krypton is not soluble enough in argon-rich layers. A suitable refinement of the theory would abandon the assumption that the two components were randomly mixed. Arnold,<sup>8</sup> in treating the adsorption of oxygen-nitrogen mixtures on anatase concluded that there was an enrichment of nitrogen on the stronger sites. The complications caused by such an improvement would be very great, because a local population function would have to be calculated by minimizing the free energy. Merely going on to the quasi-chemical approximation of Fowler and Guggenheim would neglect the effect

(8) J. R. Arnold, J. Am. Chem. Soc., 71, 104 (1949).



Fig. 8.—The variation of  $w_{AB}/kT$ , calculated from the isotherms in Fig. 3:  $\bigcirc$ , 0.47 layer;  $\bigcirc$ , 3.76 layers.

of the adsorption potential on local concentrations, and would therefore be of doubtful significance.

# THERMODYNAMICS OF VAPOR-PHASE MIXTURES OF IODINE AND BENZENE, WITH APPLICATION TO THE RATE OF RECOMBINATION OF IODINE ATOMS\*

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A study has been made of the pressure-temperature-volume relationships of vapor-phase mixtures of iodine and benzene, and the equilibrium constant for the association of iodine and benzene to form a complex  $C_6H_6$ ·I<sub>2</sub> has been calculated for a range of temperatures. The magnitude of the equilibrium constant and the energy of association can be accounted for by van der Waals forces. The amount of the association is, however, sufficient to account for the high rate of dissociation of iodine molecules in the presence of benzene (as computed from the rate of association of iodine atoms and the equilibrium constant of the reaction  $2I \rightleftharpoons I_2$ ). The entropy of association of benzene and iodine to form the complex has been explained in terms of a physical picture. Finally, the present results have been compared with those of Benesi and Hildebrand in liquid solution, and it is shown that the type of association found by them may be expected to be negligible in the vapor phase.

Studies of the recombination of iodine atoms in the presence of benzene vapor<sup>1</sup> indicate that the rate of this process is very rapid. This can be seen by considering the reverse process, namely, the dissociation of  $I_2$  due to collisions with benzene, which

\* Work supported by the Office of Naval Research.

 E. Rabinowitch and W. C. Wood, Trans. Faraday Soc., 32, 907
 (1936); J. Chem. Phys., 4, 497 (1936); K. E. Russell and J. Simons, Proc. Roy. Soc. (London), A217, 271 (1953). can be calculated from the rate of association of iodine atoms in the presence of benzene and the equilibrium constant for the reaction  $I_2 \rightleftharpoons 2I$ . From calculations of this sort, based on the results of Rabinowitch and Wood, one of  $us^{2a}$  estimated that the effective collision diameter  $\sigma_0$  for an  $I_2$ -

(2) (a) O. K. Rice, J. Chem. Phys., 9, 258 (1941); (b) for effect of rotation of Is, see O. K. Rice, *ibid.*, 21, 750 (1953).

benzene collision was about 28 A. If the results of Russell and Simons were used the effective diameter would be about 20 Å. In making the calculation the effect of the rotation of the  $I_2$  molecule on the probability of dissociation was neglected.<sup>2b</sup> Correction for this would give values of  $\sigma_0$  about half as great. The resulting values of 10 to 14 Å. are still high, though not far outside the range of reasonable possibilities with such large molecules. However, effective values of  $\sigma_0$  for other inert gases suggest that the collision process is not too efficient, and comparison with these gases (even for  $CO_2$  the value of  $\sigma_0$  is only about half as great as for benzene) leaves little doubt that the recombination of iodine atoms in the presence of benzene is anomalously fast.

In order to explain these large rates it has been postulated that a  $C_6H_6$ .I complex forms in the case of the association reaction and a  $C_6H_6$ .I<sub>2</sub> complex in the case of a dissociation reaction. As a matter of fact, if an explanation is to be obtained on this basis, it is necessary to suppose that both complexes are formed.<sup>2a</sup> The dissociation reaction will proceed according to the mechanism

$$C_6H_6 + I_2 \xrightarrow{\sim} C_6H_6 \cdot I_2 \qquad (a)$$

$$C_6H_6 \cdot I_2 \longrightarrow C_6H_6 \cdot I + I$$
 (b)

We let  $K_c$  be the equilibrium constant of (a), expressed in terms of concentration, and  $k_b$  be the rate constant for (b). The over-all rate of reaction will then be given by

$$-d[I_2]/dt = k_b[C_6H_6I_2] = k_bK_c[C_6H_6][I_2]$$
(1)

and a large apparent collision diameter can be explained through a sufficiently large value for  $K_c$ .





Fig. 1.-Schematic sketches of apparatus.

There are other reasons which might lead one to believe that there are some special forces which result in complexing of iodine and benzene, for example the work of Benesi and Hildebrand<sup>3</sup> on solutions of iodine in liquid benzene, and theoretical considerations of Mulliken.<sup>4</sup> It therefore appeared

(3) H. A. Benesi and J. H. Hildebrand, J. Am. Chem. Soc., 70, 2832 (1948); 71, 2703 (1949).

(4) R. S. Mulliken, *ibid.*, **72**, 600 (1950); **74**, 811 (1952); Tris JOURNAL, **56**, 801 (1952). desirable to investigate the pressure-volume-temperature relations of mixtures of iodine and benzene in the vapor phase. It may be said that these studies have resulted in the conclusion that there is no special type of complex, which is of importance in the vapor phase, all the complexing being adequately explained by van der Waals forces. It does turn out, however, that the effects are sufficient to account for the recombination experiments.

## Experimental

Materials.—A known weight of A. R. grade iodine, which had previously been sublimed from potassium iodide, was introduced together with a small amount of potassium iodide into bulb A of the purification train shown in Fig. 1a. was cooled in a Dry Ice-carbon tetrachloride mush and quickly sealed to the train. This train had been previously sealed to a vacuum system, and liquid air placed around trap F to prevent back diffusion of mercury to the train. The iodine was sublimed slowly from A to B, with a liquid air trap around E and a Dry Ice-acetone bath around B, pump-ing all the time. The iodine in B was then allowed to sublime at room temperature with continuous pumping for six hours, by which time it was thought that all bromine, occluded air and water would have been removed. sample was sublimed into C which was pulled off to form a capsule with a breakseal. Any iodine remaining was condensed into D and the iodine content of D and E was deter-mined by titration with sodium arsenite. Thus, the amount in the capsule could be fairly accurately estimated by difference. The total iodine content of the capsule was again determined at the end of the experiment by titration with sodium arsenite.

A. R. grade benzene, thiophene free, was fractionated at atmospheric pressure through an efficient column, rejecting the first and last fractions. About 20 ml of the middle cut was introduced into trap A [Fig. 1b] and several trap to trap distillations were carried out, stopcock D being open when distilling into B, and stopcock E open when distilling in the reverse direction. The benzene vapor in all distillations was led through a phosphorus pentoxide trap, C, to remove moisture. The fraction of benzene used was distilled from B to F, a small appendix in the gas reservoir G, with the pump cut off by a stopcock. B was weighed before and after this final transfer. A vacuum technique was employed throughout.

Procedure.-The gas reservoir G [Fig. 1b] of approximately one liter capacity, was fitted with a side arm H. At the base of H a stout glass cross served to hold the iodine capsule and plunger. A soft glass spoon gage, I, was at-tached to the system through a graded seal, and the pressure inside the spoon balanced by the pressure of dry air admitted to the outer jacket, the pressure of the latter being measured in a manometer by means of a cathetometer. The spoon gage, which had been annealed together with the gas reservoir, was calibrated with pressure differences of 0-3 cm. over a total pressure range of 0-760 mm. and at temperatures up to 200°. It was always arranged that the total pressure in the spoon was greater than that in the jacket in the following determinations. Under this condition of operation the sensitivity of the gage remained sensibly unchanged, at 13.7 mm. per mm. movement of the pointer, throughout the whole pressure and temperature range to be investigated. A Pyrex reference pointer J was inserted in the jacket; both pointers could be focussed simultaneously by a traveling microscope, which was mounted so as to be free from vibration.

The thermostat, which consisted of a well insulated glass bath containing about five gallons of polyethylene glycol "600," was supported on a platform, and could be raised so that the gas reservoir and spoon gage were immersed to a level about two inches above K. Temperature control was maintained by sealed mercury regulators in conjunction with a thyratron circuit to better than  $\pm 0.005^{\circ}$ , and the temperature was measured using a platinum resistance thermometer (calibrated by the Bureau of Standards).

Before inserting the benzene, the iodine capsule and plunger were put into the side arm which was then sealed. The volume of G was measured roughly by a sharing method, using dry air from a calibrated volume of approximately oneliter capacity, the pressures being read on a constant volume manometer. The required amount of benzene was then frozen into F and the reservoir sealed at K. After a series of measurements the contents of the reservoir G could be removed through the break-seal L and collected in the trap M.

The pressure of the known weight of benzene was measured as a function of temperature before the capsule containing the iodine was broken, and using values for the second virial coefficient, B, of benzene calculated from an expression quoted by Guggenheim<sup>5</sup>

$$B = 68 - 13.2 \times 10^{7} T^{-2} \text{ ml./mole}$$
(2)

values for the volume of the system were obtained. This equation was stated by Allen, Everett and Penney to be correct within about 40 ml./mole up to  $360^{\circ}$ K. We tested the equation by noting the consistency of the calculated volume from measurements at  $10^{\circ}$  intervals from about 350 to nearly  $470^{\circ}$ K. The values showed no trends over this range, and the probable error of the mean volume was of the order 0.01 to 0.02%. In the sharing method of measuring the volume the probable error was considerably larger, so the method based on eq. 2 was used. In every case the internal volume of the capsules was added to obtain the total volume in which the mixture of iodine and benzene was measured.

Vapor pressure values obtained for benzene were in good agreement with those of Baxendale, Enüstün and Stern<sup>6</sup> and this was a good criterion of the purity of the sample.

After breaking the iodine capsule, the iodine was completely sublimed into F by heating gently with a blowtorch flame. In this manner the subsequent volatilization of the iodine and the attainment of equilibrium was enormously hastened.

At the end of each run the breakseal, L, was broken and the iodine condensed into M, which was removed, and the iodine titrated. In the first experiment quoted here two capsules were broken consecutively to give two samples (samples 1 and 2) with different amounts of iodine; the total amount of iodine was estimated by titration and compared with the sum of the original weighings; agreement was within 0.8 mg. In the last and most exhaustive run only one capsule was employed, and the estimates agreed within 0.4 mg.

#### Results

The pressure-temperature data for the three mixtures are given in Table I. All the pressures p of the mixture of benzene and  $I_2$  have been corrected to mm. at 0°. At all temperatures, the benzene pressures  $p_1$  which would obtain were no iodine present were calculated from the weight, and the volume found as indicated above, using eq. 2 for B. This effectively smooths the measurements of the benzene pressure made before the iodine capsule was broken.

An equation of state given by Gerry and Gillespie<sup>7</sup> was used to calculate the iodine pressures which would exist if no benzene were present

$$p_{2} = \frac{nRT}{V} + \left(B_{0} - \frac{A_{0}}{RT} - \frac{C_{0}}{T^{3}}\right) \frac{n^{2}RT}{V^{2}} \qquad (3)$$

The following values were used (units amospheres, liters, degrees Kelvin)

$$A_0$$
 $B_0$ 
 $C_0$ 
 $R$ 
 Mol. wt.
 Ice-point

 17.0
  $0.325$ 
 $4.0 \times 10^7$ 
 $0.08206$ 
 $253.864$ 
 $273.13$  °K.

The data on which this equation was based extended to about 370°K. We made some measurements over the range 390 to 450°K. with only iodine present, and with the volume measured by the sharing method. The spread of the measurements

(5) E. A. Guggenheim, "Mixtures," Oxford Univ. Press, N. Y., 1952, p. 235. See P. W. Allen, D. H. Everett and M. F. Penney, *Proc. Roy.* Soc. (London), **A212**, 149 (1952).

(6) J. H. Baxendale, B. V. Enüstün and J. Stern, Phil. Trans. Roy. Soc., A243, 169 (1951).

(7) H. T. Gerry and L. J. Gillespie, Phys. Rev., 40, 269 (1932).

of the volume made in this way was about 3.5 ml. or a little over 0.3% in a volume of about 1100 ml. In addition, since the volume had to be sealed off with a capsule of iodine in it, some further corrections had to be made. However, using the iodine pressure measurements to find the volume from eq. 3, we obtained results as consistent as we did with benzene and agreeing with the volume measured by sharing to within the accuracy of the latter. It is to be further noted that the virial correction in eq. 3 is only about 0.6% of the total pressure. On the basis of all this evidence we believe that eq. 3 cannot be more than 0.1% in error.

#### TABLE I

#### Calculation of $K_p$

Sample 1: 0.015085 mole benzene, 0.010956 mole iodine in 1161.11 ml.; sample 2: 0.015085 mole benzene, 0.016433 mole iodine in 1162.23 ml.; sample 3: 0.019918 mole benzene, 0.011653 mole iodine in 1164.19 ml.

Sam	ple °K.	No. of obser- va- tions	р1- (С6Н6), mm.	$p_{2}$ -(I <sub>2</sub> ), mm.	<i>p</i> , mm.	$-\Delta p,$ mm.	$K_{p} \times 10^{2}$ , atm. <sup>-1</sup>
1	427.27	2	343.31	<b>249</b> .84	589.36	3.79	4.00
1	427.74	2	343.70	250.12	589.99	3.83	4.02
1	435.96	2	350.43	255.01	601.71	3.73	3.80
1	445.18	<b>2</b>	357.97	260.51	614.90	3.58	3.54
1	466.59	1	375.47	<b>273.24</b>	645.45	3.26	3.02
2	437.43	2	351.26	382.27	728.01	5.52	3.74
<b>2</b>	445.50	2	357.86	389.52	741.86	5.52	3.62
<b>2</b>	466.55	<b>2</b>	375.04	408.38	778.56	4.86	3.01
3	429.62	6	452.94	266.15	713.82	5.27	3.94
3	439.05	4	463.12	<b>272</b> .11	730.15	5.08	3.68
3	439.13	4	463.20	<b>272</b> .16	730.17	5.19	3.74
3	439.27	4	463.35	272.25	730.48	5.12	3.70
3	445.50	4	470.08	276.18	741.09	5.17	3.63
3	446.73	4	471.41	276.96	743.19	5.18	3.62
3	447.36	4	472.09	277.35	744.30	5.14	3.58
3	465.06	8	491.21	288.52	774.83	4.90	3.21

## **Discussion of Errors**

As may be seen from Table I, the temperature coefficient of the difference,  $\Delta p = p - p_1 - p_2$  between the total measured pressure and the sum of the separate pressures of benzene and iodine, is quite small. It therefore becomes very necessary carefully to assess the errors which may arise in the individual measurements.

(1) Errors in total pressure measurement.

(a) Manometry Errors.—The manometer used to measure the pressure of the air surrounding the spoon gage was constructed of 26 mm. bore tubing and was viewed through a rigidly supported Gaertner cathetometer. Independent observations of a fixed line were made, and after each setting the telescope was raised through about 700 mm., lowered and reset. The maximum irreproducibility for ten such settings was  $\pm 0.02$  mm. Thus any individual pressure reading, involving two such settings, exhibits a maximum irreproducibility of  $\pm 0.04$  mm.

During the duration of a measurement the temperature of the manometer does not vary more than  $\pm 0.1^{\circ}$  corresponding to an error of 0.02 mm. The traveling microscope used to follow the pointer of the spoon gage could be read reproducibly to 0.01 mm. and this incurred an error of  $\pm 0.14$  mm. in any single pressure measurement.

From these sources we obtain a total maximum manometry error of  $\pm 0.20$  mm. (b) Thermostat Fluctuations.—The tempera-

(b) Thermostat Fluctuations.—The temperature control was to better than  $\pm 0.005^{\circ}$  and the error in the pressure (sum of pressures of benzene and iodine) due to this fluctuation is 0.001% or less than 0.01 mm.

The maximum error in the total pressure will thus be 0.21 mm. However, in the last mixture several readings of the pressure were taken at each temperature, and the mean of these readings taken. It is felt that much more weight should be given to these values.

(2) Errors in the Benzene and Iodine Pressures. —These pressures were calculated for the stated temperature from the equations of state. Any errors in thermcmetry are to be referred to the total pressure. The errors in the benzene and iodine pressures arise from the other quantities which appear in the equations of state, and will be systematic for any given mixture. The errors may arise from the measured volume or the weight of the samples.

(a) Weighing Errors.—In the case of the iodine this error is estimated as  $\pm 0.001$  g. for the first two runs and  $\pm 0.0004$  g. for the last run, resulting in errors in the iodine pressure of about 0.11 and 0.05 mm., respectively. In the case of the benzene it is estimated as  $\pm 0.0002$  g., causing an error of 0.06 mm. in the pressure.

(b) Volume Errors.—Since the volume of the vessel was calculated from the equation of state of benzene using eq. 2, and since the pressure of benzene was then obtained by reversing the calculation, no inconsistencies can be introduced by the use of eq. 2 and the error in the pressure of benzene can be considered to be equal, percentagewise, to the probable error of the volume. The latter was about 0.025% for the first two mixtures and 0.010% for the last one; the resulting errors in the benzene pressure are about 0.10 mm. for the first mixture, about 0.05 mm. for the last one.

Any error in the volume which is caused by inaccuracy in eq. 2 will be reflected in the pressure of iodine. According to Allen, Everett and Penney the error in *B* will be about 6%, which will cause about 0.06% error in the volume, and hence in the calculated iodine pressure, in the first two runs, and about 0.07% in the last one. Accepting 0.1% as the error in eq. 3, we believe then that the overall error in the iodine pressure will surely be less than 0.2%; which would amount to about 0.5 mm. in the first mixture, about 0.8 mm. in the second, and about 0.55 mm. in the last.

If all the errors were added (including 0.2% error in the iodine pressure) we could have a total error in  $\Delta p$  of about 0.98 mm. or 28% in the first mixture, of about 1.28 mm. or 25% in the second mixture and of about 0.92 mm. or 18% in the third mixture. The actual errors may, on the whole, be expected to be considerably smaller than these. Temperature coefficients may be expected to be reasonably accurate also, since the non-systematic part of these errors is small enough so that it should not too

greatly affect the results if a careful average is made.

We have made no correction for the local value of the acceleration due to gravity. This will affect all the pressures in the same way, and so the effect on  $\Delta p$  will be negligible.

## Treatment of the Data

It was pointed out some time ago by Goodeve<sup>8</sup> that, since the attractive forces between two molecules tend to make them move faster when in the neighborhood of each other, on this basis alone the attractive forces would only make the effective excluded volume larger, and so could not result in the lowering of the total pressure. Though it is not certain that Goodeve allowed sufficiently for collisions which would have been near misses were it not for the attractive forces, still the lowering of pressure by the attractive forces will occur largely because some of the pairs of molecules have less than enough mutual translational energy to escape from each other, and so form "complexes." This is true even if only the van der Waals type of force is operative. In the present case  $\Delta p$  is sufficiently small so that we may conjecture that only van der Waals forces are involved, but we may interpret  $\Delta p$ in terms of complex formation.9

The equation of state for n moles of gas may at sufficiently low pressures be approximated by

$$p = nRT/V + n^2 RTB/V^2 \tag{4}$$

where B is the second virial coefficient. B contains contributions from pair formation and from the excluded volume. At pressures as low as one atmosphere we may take the excluded volume into account by subtracting it directly from V. We do this only in the large (first) term on the right-hand side of eq. 4, obtaining thus

$$p = nRT/(V - nb) + n^2 RTB^0/V^2$$

where  $B^0$  is that part of the virial coefficient arising from pair formation. Expanding the first term we obtain, to the second power of  $V^{-1}$ 

$$p = nRT/V + n^2 RT(B^0 + b)/V^2$$
 (5)

whence we see that

$$B^0 = B - b \tag{6}$$

In the case of a pure gas b will be given by

$$b = N(2\pi/3)\sigma^3 \tag{7}$$

where  $\sigma$  is the effective collision diameter (not, of course, the same as  $\sigma_0$ ), and N is Avogadro's number. Hirschfelder, McClure and Weeks<sup>10</sup> chose quite a large value for  $\sigma$ , which might be done to allow for the effect of the attractive forces noted by Goodeve, though their point of view was somewhat different. However, we do not believe that this effect will actually be very great, since the depth of the potential well with which we have to deal will, at its deepest point, be at most about double the radial mutual velocity component, and, of course, there is one point, the turning point of the collision, where this component of velocity is zero. We

(8) C. F. Goodeve, Nature, 140, 424 (1937).

(9) See also A. Eucken and L. Meyer, Z. physik. Chem., 5B, 452 (especially 465 f) (1929).

(10) J. O. Hirschfelder, F. T. McClure and I. F. Weeks, J. Chem. Phys., 10, 201 (1942).

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shall therefore obtain b from viscosity data using the equation of Chapman<sup>11</sup>

$$\sigma = 2.14 \times 10^{-10} M^{1/4} \eta_{273.1}^{-1/2} (1 + C/273.1)^{-1/2}$$
(8)

Here M is the molecular weight, C is Sutherland's constant,  $\eta_{273.1}$  is the viscosity at 273.1°K. We then obtain from eq. 7 and 8, using data tabulated by Partington<sup>12</sup>

$$\sigma_{11} = 4.76 \times 10^{-3} \text{ cm. (benzene)}$$
 (9a)

$$\sigma_{22} = 4.37 \times 10^{-8} \text{ cm. (iodine)}$$
 (9b)

Equation 8 is based on the fairly crude model of attracting rigid spheres, but should be sufficient for our purposes.

We may apply eq. 4, 5 and 6 to mixtures of gases if we set

$$b = x_1^2 b_{11} + 2x_1 x_2 b_{12} + x_2^2 b_{22} \tag{10}$$

$$B = x_1^2 B_{11} + 2x_1 x_2 B_{12} + x_2^2 B_{22} \tag{11}$$

$$B^{0} = x_{1}^{2}B_{11}^{0} + 2x_{1}x_{2}B_{12}^{0} + x_{2}^{2}B_{22}^{0}$$
(12)

whence it follows that

$$B_{11}^{0} = B_{11} - b_{11}; \ B_{12}^{0} = B_{12} - b_{12}; B_{22}^{0} = B_{22} - b_{22} \quad (13)$$

 $x_1$  and  $x_2$  are mole fractions of molecules of species 1 and species 2, respectively, while the subscripts on the b's, B's and  $B^{0}$ 's have a fairly obvious significance. We will have

$$b_{11} = N(2\pi/3)\sigma_{11}{}^3; \ b_{12} = N(2\pi/3)\sigma_{12}{}^3; b_{22} = N(2\pi/3)\sigma_{22}{}^3$$
(14)

where, at least to a good approximation

$$\sigma_{12} = (\sigma_{11} + \sigma_{22})/2 \tag{15}$$

The significance of eq. 10 can be seen from the following considerations. The total volume excluded by all other molecules for a molecule of species 1 is  $2nx_1b_{11} + 2nx_2b_{12}$  and that for a molecule of species 2 is  $2nx_2b_{22} + 2nx_1b_{12}$ . In each case 2b, with appropriate subscript, is the volume (per mole) of the exclusion sphere. The average excluded volume will therefore be

$$\frac{1}{2}[x_1(2nx_1b_{11} + 2nx_2b_{12}) + x_2(2nx_2b_{22} + 2nx_1b_{12})] = nx_1^2b_{11} + 2nx_1x_2b_{12} + nx_2^2b_{22}$$

the factor 1/2 appearing as usual, because otherwise each exclusion sphere is counted twice, once for each molecule of a pair. It will be seen that this amounts to an average according to pairs, since the ratios of the numbers of pairs of different kinds are  $x_1^2:2x_1x_2:x_2^2$ . The B<sup>0</sup>'s should clearly be averaged in the same way. The usual equation,<sup>13</sup> eq. 11, will then follow.

If species 2 were absent, the observed pressure of species 1 would be, from eq. 5

$$p_1 = nx_1 RT/V + n^2 x_2^2 RT(B_{11}^0 + b_{11})/V^2 \quad (16)$$

while if species 1 were absent the pressure of species 2 would be

$$p_2 = nx_2RT/V + n^2x_2^2RT(B_{22}^0 + b_{22})/V^2 \quad (17)$$

Applying eq. 5 to the total pressure of the gas, using

(11) See T. S. Wheeler, Rec. trav. chim., 51, 1204 (1932).
(12) J. R. Partington, "An Advanced Treatise on Physical Chemistry," Longmans, Green and Co., New York, N. Y., 1949, Vol. I, pp. 858 f.

(13) J. E. Lennard-Jones and W. R. Cook, Proc. Roy. Soc. (London), 115A, 334 (1927).

eq. 10 and 12, subtracting eq. 16 and 17 from the result, and recalling that  $x_1 + x_2 = 1$ , we obtain

$$\Delta p = p - p_1 - p_2 = 2x_1 x_2 n^2 R^{\gamma} (B_{12}^0 + b_{12}) / V^2 \quad (18)$$

 $\Delta p$  is essentially the quantity we have measured in the case of the iodine-benzene mixtures. The change of pressure arising from pair formation, which we will call  $\Delta p^0$ , is given by

$$\Delta p^{0} = \Delta p - 2x_{1}x_{2}n^{2}RTb_{12}/V^{2} = 2x_{1}x_{2}n^{2}RTB_{12}^{0}/V^{2} \quad (19)$$

Since the gas imperfections are relatively small we may use the ideal gas law for the pressures of the unpaired molecules. Thus they are approximately  $n_1 RT/V$  and  $n_2 RT/V$ , respectively, where  $n_1 = x_1 n$  and  $n_2 = x_2 n$ . The equilibrium constant for the formation of pairs will be approximately

$$K_{\rm p} = -V^2 \Delta p^0 / n_1 n_2 (RT)^2 \tag{20}$$

Values of  $K_p$  are included in Table I. These were calculated directly from the values of  $\Delta p$ given in the table, by means of eq. 20 and the first relation of eq. 19, using eq. 9a, 9b, 15 and 14 to ob-tain  $b_{12}$ . In Fig. 2 we have plotted log  $K_p$  against  $T^{1-1}$ , and have put the best straight line through these points by least squares, weighting according to the number of observations given in Table I. The slope of the line may be used to calculate  $\Delta H$ , the heat of formation of a pair. The thermodynamic functions for formation of a pair at 450°K., taking 1 atm. pressure as the standard state, are as follows

$$\Delta H = -2.44 \text{ kcal. mole}^{-1}$$
 (21)

$$\Delta G^0 = 3.00 \text{ kcal. mole}^{-1}$$
 (22)

$$\Delta S^{0} = -12.1 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$$
 (23)

For comparison we have included in Fig. 2 curves representing  $-2B_{11}^{0}/RT$  (benzene) and  $-2B_{22}^{0}/RT$ (iodine), calculated from eq. 2 and 3, respectively.  $(K_{\rm p}$  for association in a pure gas actually has the form  $B_{\rm ii}/RT$ , but the comparison should be with  $2 B_{\rm ii}/RT$  to reflect the actual difference in molecular forces.) It will be seen that they are of the same order of magnitude and have the same general behavior as  $K_{\rm p}$  or  $-2B_{12}^0/RT$ , which indicates that the forces between iodine and benzene are of the van der Waals type.



Fig. 2.-Van der Waals association constants.

## Effective Cross Section for Dissociation of $I_2$ by Benzene

In order to see whether we can account for the apparent large collision diameter for dissociation of  $I_2$  by benzene, it will first be necessary to correct  $K_p$  to around 300°K. Taking  $\Delta H$  as roughly constant we find  $K_p$  at 300°K. to be 0.14 atm.<sup>-1</sup>, and  $K_c = 3400$  ml. mole<sup>-1</sup>.

The effective collision diameter  $\sigma_0$  for the dissociation was calculated by Rice<sup>2a</sup> by assuming that the over-all rate constant,  $k_d$ , expressed in molal concentration units, was given by

$$k_{\rm d} = A e^{-\Delta E_{\rm I_2}/kT}$$
(24)

where  $\Delta E_{I_2}$  is the dissociation energy of  $I_2$  and

$$= 200 \sigma_0^2 N (2\pi RT/\mu)^{1/2}$$
 (25)

where N is Avogadro's number and  $\mu$  is the reduced mass in molecular weight units. If we now assume that the activation energy for reaction (b) is equal to<sup>14</sup>  $\Delta E_{I_2}$  (which is the dissociation energy of an *unattached* iodine) we may write for the over-all rate constant for reactions (a) and (b)

$$\dot{k}_{\rm b}K_{\rm c} = 5\nu_{\rm I_2}K_{\rm c} \,e^{-\Delta E_{\rm I_2}/kT} \tag{26}$$

where  $\nu_{I_3}$ , the frequency of vibration of  $I_2$  in its ground state, which is approximately  $6.4 \times 10^{12}$ sec.<sup>-1</sup>, is taken as the frequency factor for the rate of decomposition, and the factor 5 allows for the number of energy levels from which  $I_2$  can dissociate, as explained in reference 2a. In order to find the expected value of  $\sigma_0$  we therefore set

$$200\sigma_0^2 N (2\pi RT/\mu)^{1/2} = 5\nu_{12} K_e \qquad (27)$$

Using the value of  $K_c$  found above we obtain  $\sigma_0 =$ 13 Å. It is to be noted that the correction arising from rotation of the iodine molecules<sup>2b</sup> has not been included in either eq. 25 or eq. 26. This is effectively a correction in the number of states from which decomposition of  $I_2$  can occur, and should affect the value of A and of  $k_{\rm b}$  roughly in the same ratio, so that the calculation of  $\sigma_0$  from eq. 27 will be affected only slightly. The value  $\sigma_0 = 13$  Å. may therefore be compared directly with the corrected experimental values of  $\sigma_0$  (10 to 14 Å.) given at the beginning of the paper and is seen to be of the same order of magnitude. The van der Waals association can therefore account adequately for the ob-served rate of reaction. This fact lends some weight to the suggestion of Russell and Simons<sup>1</sup> that there is a relation between the rate of recombination of iodine atoms and the boiling point of the inert substance used to furnish the third body.

If the third body is a monatomic molecule, like argon, a complex between iodine and the inert molecule, having enough energy to dissociate the  $I_2$ , could not be stabilized, since there are no internal degrees of freedom to take care of the excess energy. It has been noted,<sup>2a</sup> however, that a one step reaction

$$A + I_2 \longrightarrow A \cdot I + I$$
 (c)

could result in a lowering of the activation energy. Indeed, since the transition state of reaction (c) would be entirely similar to that of reaction (b) it would appear that (c) would have the same effect as (a) and (b), and that the rate could be calculated as though the reaction took place in two steps. Thus the relation between boiling point and rate of association can reasonably be extended to these cases.

(14) This means that we assume that the energy to split the complex is the same for  $C_eH_e$ . Is as for  $C_eH_e$ . I.

Russell and Simons<sup>1</sup> have measured temperature coefficients for the association of iodine atoms using several different inert gases. They found an activation energy of -2360 cal. per mole-reaction with benzene as the inert gas. If the activation energy for the reverse of reaction (b) is zero, and if our assumption regarding the activation energy of the direct reaction (b) is correct, then this activation energy represents the negative of the heat of dissociation of the complex. It is seen that it is of just the right order of magnitude. The most puzzling feature of Russell and Simons' results is the rather small range of activation energies for the different inert gases. Thus the activation energy with helium is about -1510 cal. per mole-reaction; since the attractive forces in the case of helium would be expected to be very small, the absolute value of the activation energy seems somewhat high. Furthermore, the difference between -2360 and -1510cal. per mole-reaction would account, through the exponential factor for a difference in the rate of reaction of only about 4-fold at room temperature. Since the rate of association in the presence of benzene is at least 100 times as great as in the presence of helium, this would appear to put too great a burden on the entropy factor, particularly in the light of the analysis of the entropy of the complex given in the following section.

## The Structure of the Benzene-Iodine Complex

From the entropy of association  $\Delta S^0$  we may obtain a rough pictorial idea of the tightness with which the complex is held together. The value of -12.1 cal. mole<sup>-1</sup> deg.<sup>-1</sup> is very much lower in absolute value than would be expected if the two molecules were held together by valence-bond forces. We may use the expression

$$-\Delta S^{c} = R \ln \left( v_{2}' e / v_{2} \right)$$
 (28)

to calculate the volume  $v_2$  in which an iodine molecule is localized in the presence of a benzene molecule. Here  $v_2'$  is the molecular volume of free iodine molecules in their standard state, one atmosphere pressure. The factor e takes care of the sharing of the volume by the iodine molecule, *i.e.*, it gives the communal entropy, and it does not appear in the denominator of the fraction because we deal only with the case in which only one iodine is attached to a given benzene molecule.

At 450°K. the value of  $v_2'$  is 6.13 × 10<sup>4</sup>Å.<sup>3</sup>. Then we find from eq. 28,  $v_2 = 370$ Å.<sup>3</sup>.

We can roughly assume that the center of the  $I_2$ molecule is located somewhere between two spheres, the inner one of which has a volume of  $4\pi\sigma_{12}^3/3$  or  $2b_{12}$ , which is equal to 400 Å.<sup>3</sup>, and an outer one of 400 + 370 = 770 Å.<sup>3</sup>. The diameter of the inner sphere is  $\sigma_{12} = 4.57$  Å. and that of the outer sphere is 5.69 Å. The average range of the vibration of the iodine against the benzene is thus, according to this rough calculation about 1.12 Å., as compared to effective distances of the order of a few tenths of an angström for the relative vibration of the two atoms in a diatomic molecule in which valence-type forces are operative. This, of course, assumes that the I<sub>2</sub> molecule rotates freely when attached to benzene.

A similar calculation could, of course, be made

for the benzene-benzene complex and the iodineiodine complex, and results of the same order of magnitude would be obtained.

## Comparison with Results of Benesi and Hildebrand

Benesi and Hildebrand<sup> $\epsilon$ </sup> (1949) found that in carbon tetrachloride solution the equilibrium constant K corresponding to a reaction like reaction (a) was 1.72 (mole fraction)<sup>-1</sup> at room temperature. There seems to be no question that this is a different type of complex from that which we have studied in the present paper. In solution in carbon tetrachloride, the I<sub>2</sub>, the C<sub>6</sub>H<sub>6</sub> and the complex are all continually under the influence of the van der Waals forces of the surrounding molecules. Only something of a different nature would result in the shift of the absorption band by which the complex was detected. Carbon tetrachloride has a molar volume of 96.5 ml. In a dilute solution, a given mole fraction x corresponds to a concentration of x moles per 96.5 ml., or, calculating gas pressures as though the other molecules were not there, a pressure of about 254x atm. at  $25^{\circ}$ . Thus on this basis  $K_{\rm p} = 0.68 \times 10^{-2}$  atm.<sup>-1</sup>. However in the gas phase  $K_{\rm p}$  would be smaller, since this calculated value takes no account of the fact that the free volume for molecules in solution is less than the total volume. Our value of  $K_{\rm p}$ , even above 400°K., is around  $4 \times 10^{-2}$  atm.<sup>-1</sup>. Complexes of the type observed by Benesi and Hildebrand should, therefore, have a completely negligible influence on our experiments.

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# FLAME QUENCHING BY A VARIABLE-WIDTH RECTANGULAR-CHANNEL BURNER AS A FUNCTION OF PRESSURE FOR VARIOUS PROPANE-OXYGEN-NITROGEN MIXTURES

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Flame quenching distances for a variable-width water-cooled rectangular-channel burner as a function of pressure for various propane-oxygen-nitrogen mixtures are presented. The relation between pressure p and quenching distance d, is given by  $d\alpha p^{-\tau}$ , with  $r \approx 1$  for equivalence ratios approximately equal to one (for pressures of 0.1 to 1.0 atm. and for volumetric oxygen fractions of the oxidant mixture of 0.17, 0.21, 0.30, 0.50 and 0.70). For lean and stoichiometric mixtures, it is shown that an equation based on a diffusion mechanism may be used successfully to correlate the observed quenching data.

Various investigators have attempted to relate quenching distance to the fundamental properties characterizing the combustion wave. Reference 1 relates quenching distance to minimum ignition energy and burning velocity by assuming that a consideration of heat-transfer processes alone is sufficient to explain the behavior of the combustion wave. No thorough test of this theory has been made, chiefly because of the lack of low pressure burning velocity data. A quenching theory is proposed in reference 2 in which the diffusion of H, O and OH radicals in the flame front plays the vital role in determining whether or not the flame will be quenched by a given wall geometry. This latter theory can be readily applied (once flame equilibrium radical concentrations are calculated) and has been successful in correlating quenching distance data for propane-air, ethylene-air and isooctane-air flames over a range of pressures. One objection to this diffusional mechanism for flame quenching is based on the observation that surfaces which may display widely different chain breaking efficiencies all display the same flame quenching effects.<sup>3</sup> However, such varying chain breaking wall efficiencies have not been demon-

(2) D. M. Simon, F. E. Belles and A. E. Spakowski, "Fourth Symposium (International) on Combustion," The Williams and Wilkins Co., Baltimore, 1953.

(3) R. Friedman and W. C. Johnston, J. App. Phys., 21, 79 (1950).

strated for the case of high temperature flames near cold walls.

The present work, in addition to supplying the data necessary to describe the wall quenching of propane-oxygen-nitrogen flames as a function of fuel-oxidant ratio, oxygen content of the oxidant mixtures, and pressure, is intended as an additional test of this current concept of flame quenching.

Apparatus.—The rectangular channel quenching distance burner used in making these measurements was made of stainless steel. The burner length was 5 inches and the slit width, established by adjusting the movable burnerlip assembly, was never more than 1/2 inch. Two insidethickness gages were used at the ends of the rectangular slot to determine the burner wall separation. The burner itself was mounted in a 3.5 cubic foot capacity, pressure-controlled chamber.

The desired fuel-oxidant mixture was introduced through three inlets located at the bottom of the burner channel. Fine glass beads were sandwiched between two leyers of 200-mesh stainless steel screen which served both as a flow straightener and as a flame arrestor. The jacketed walls of the burner were kept at  $40^{\circ}$  by circulating water. This wall temperature was sufficiently high to prevent condensation of water on the burner lip. A spark igniter was used to establish a flame atop the rectangular burner port. A thermocouple was employed to measure local temperatures and to indicate flash back of the flame through the rectangular channel of the burner. Fuel and oxidant were supplied from separate cylinders and were separately metered through critical flow orifices.

Oxygen-nitrogen mixtures for which the volumetric oxygen fraction  $\alpha$  was 0.17, 0.21, 0.30, 0.50 and 0.70 were used as oxidants. The supplier's stated accuracy was  $\pm 0.1\%$ 

<sup>(1)</sup> B. Lewis and G. von Elbe, "Combustion, Flames and Explosion of Gases," Academic Press, Inc., New York, N. Y., 1951, p. 413.

O<sub>2</sub>. The propane used in these experiments had a stated purity of 99.9%.

Quenching data were obtained by first fixing the burner wall separation and then finding the highest pressure at which a flame of known air-fuel ratio would not flash back. This pressure (hereafter called the limiting pressure) could be estimated to within 0.02 inch of mercury.

Effect of Burner Channel Geometry.—Reference 4 shows that the quenching behavior of plane parallel plates of infinite extent and a rectangular channel of finite length to width ratio may be successfully related by the equation

> $d_{\rm p} = d_{\rm r} \left[ 1 - 0.300 \left( \frac{d_{\rm r}}{b_{\rm r}} \right) - 0.047 \left( \frac{d_{\rm r}}{b_{\rm r}} \right)^2 \right]$ (1)

where

 $d_{\mathbf{r}} = \operatorname{rectangular} \operatorname{channel} \operatorname{width}$ 

 $b_r$  = rectangular channel length

 $d_{\rm p}$  = plane parallel plate separation

In view of the fact that the  $(d_r/b_r)$  values employed in this experiment were always equal to or less than 0.1, it follows from equation 1 that the error incurred in assuming that the observed data are equivalent to plane parallel plate data is always less than 3%.

## **Experimental Results**

Curves of limiting quenching pressure as a function of oxidant-fuel ratio for four different burner widths and for each of the  $\alpha$  values 0.17, 0.21, 0.30, 0.50 and 0.70 were obtained.



Fig. 1.—Relation of limiting quenching pressure to O/F and  $\varphi$  for various burner wall separations. Oxygen fraction,  $\alpha$ , 0.50.

(4) A. L. Berlad and A. E. Potter, Jr., "Fifth Symposium (International) on Combustion," to be published.

Typical of such sets of curves, is the set obtained for  $\alpha = 0.50$  (Fig. 1). An equivalence ratio scale  $\varphi$ , as well as an oxidant-fuel mass ratio scale O/F, is indicated. The extent of the data to limiting values of  $\varphi$  on either side of  $\varphi = 1$  was essentially determined by either the ability to seat a stable flame on the burner or the pressure range for the investigation. Data taken from these curves were used to construct least squares logarithmic plots of quenching distance against pressure for each of the five  $\alpha$  values investigated and for as wide a range of equivalence ratio  $(\varphi)$  values as the data covered. The slopes of these lines define r, the negative of the power describing the pressure dependence of the quenching distance,  $d\alpha p^{-r}$ . These values of r are given in Table I.

#### TABLE I

COMPARISON OF PREDICTED AND OBSERVED PRESSURE DEPENDENCE OF QUENCHING DISTANCE

Oxygen fraction, a	Equivalence ratio, $\varphi$	Pressure de guenching Obsd.	pendence of distance, r Predicted
0.17	0.943	0.90	0.88
	1.000	.89	.85
	1.340	.84	.75
	1.530	.71	.75
0.21	0.738	0.85	0.86
	. 864	84	.89
	1.000	.89	.93
	1.240	.95	.78
	1.490	.98	.76
0.30	0.566	0.76	0.87
	. 662	.93	89
	.773	1.06	.92
	1.000	0.98	.94
	1.380	. 93	.86
	1.903	.74	.76
0.50	0.476	1.01	0.91
	.544	1.01	. 93
	. 680	0.96	. 96
	1.000	.93	. 97
	1.358	.91	.95
	1.940	. 88	.82
0.70	0.345	1.12	0.91
	. 395	1.12	. 93
	.494	1.02	. 96
	1.000	1.01	. 98
	1.234	1.07	. 98
	1.829	0.60	. 89

Quenching Distance Equation.—The diffusional quenching distance equation for plane parallel plates (2) may be written

$$d^{2} = \frac{A}{k_{i}}\psi = \frac{A}{k_{i}}\left[\left(\frac{T_{r}}{T_{0}}\right)^{n}\frac{12}{N_{f}\sum_{i}\frac{p_{i}}{D_{i}}}\right]$$
(2)

where

- d = quenching distance, cm.
- A = fraction of molecules present in gas phase which must react for flame to continue to propagate  $k_i$  = specific rate constant for reaction of active particles
- of one kind with fuel molecules,  $(cm.^3)$ (molecules<sup>-1</sup>)(sec.<sup>-1</sup>)  $T_r$  = reaction temp. = (0.7) flame temperature, °K.  $T_0$  = cold gas temperature, °K.

n = power describing the temp. dependence of the diffusion coefficient,  $D\alpha T^n$ 

 $N_{\rm f}$  =  $^{1}\!/_{2}$  of fuel molecules per cc. in unburned gas at  $T_{\rm r}$ 

$$\sum_{i} \frac{p_{i}}{D_{i}} = \frac{p_{\mathrm{H}}}{D_{\mathrm{H}}} + \frac{p_{\mathrm{OH}}}{D_{\mathrm{OH}}} + \frac{p_{\mathrm{O}}}{D_{\mathrm{OH}}}$$

- $p_{\rm H}$ ,  $p_{\rm OH}$ ,  $p_{\rm O}$  = partial pressures of hydrogen atoms, hydroxyl radicals and oxygen atoms, respectively, atm.
- $D_{\rm H}, D_{\rm OH} D_{\rm O} =$  diffusion coefficients for hydrogen atoms, hydroxyl radicals and oxygen atoms, respectively, which diffuse into unburned gas at 27° and atmospheric pressure, sq. cm./sec.

**Calculations.**—Values of 1.02, 0.29 and 0.26 square cm. per second were calculated for the diffusion coefficients of hydrogen atoms, oxygen atoms and hydroxyl radicals, respectively, into a stoichiometric propane-air mixture at a pressure of 1 atmosphere and a temperature of  $27^{\circ}$ . Binary diffusion coefficients were obtained through the use of the equation given by Chapman and Cowling.<sup>5</sup> The necessary molecular and atomic diffusion radii were found to be

$r_0$	=	1.28	Х	10 <sup>-8</sup> cm.	$r_{\rm H}$	=	1.17	$\times$	10 <sup>-8</sup> cm.
$r_{02}$	=	1.66	×	$10^{-8}$ cm.	TH2	=	1.25	Х	10 <sup>-8</sup> cm.
TNS	=	1.72	Х	10 <sup>-8</sup> cm.	rCaH8	=	2.85	Х	10 <sup>-8</sup> cm.

these values are about 8% below those calculated from viscosity measurements. The relation suggested in reference 6 was employed to calculate the slight variation of the diffusion coefficients with composition of the unbraned gas. The proper temperature dependences for  $D_i$  are uncertain, although the value of n = 2 used in reference 2 appears quite high. The expected range for n is  $(^3/_2 \leq n \leq 2)$ , with n decreasing as absolute temperature increases. It is here assumed that n =1.67.

The quantities  $T_{\rm f}$ ,  $T_{\rm r}$ ,  $N_{\rm f}$ ,  $p_{\rm H}$ ,  $p_{\rm O}$  and  $p_{\rm OH}$  were computed by the same methods employed in reference 2. The tables of thermodynamic constants of reference 7 and the value of the heat of formation of propane given in reference 8 were used, together with the matrix method of reference 7 to calculate equilibrium product concentrations and adiabatic flame temperatures. The calculated values of  $p_{\rm i}$ and  $T_{\rm f}$ , associated with various flames and quenching conditions, are given in Table II.

**Pressure Dependence of Quenching Distance.**— Equation (2) may be used to predict that

$$\log \sum_{i} p_{i}/D_{i} = m \log p + \text{constant}$$
(3)

where m is defined by the equation

$$n = 2r - 1 \tag{4}$$

Both theory and experiment show that r tends to increase as  $\alpha$  increases and that the value of rdoes not vary greatly and is close to unity over the range of  $\alpha$  values investigated. It should be noted that equation 4 is derived from a quenching equation which is intended for use with lean or stoichiometric mixtures only. Despite this, equation 4 does predict reasonably reliable values

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(6) C. F. Curtiss and J. O. Hirschfelder, J. Chem. Phys., 17, 550 (1949).

(7) V. N. Huff, S. Gordon and V. E. Morrell, Natl. Advisory Comm. Aeronaut., Rep. 1037 (1951).

(8) F. D. Rossini, et al., Circular C461, Nat. Bur. Standards, 1947.

## Table II

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QUENCHING CONDITIONS AND THE ASSOCIATED EQUILIBRIUM FLAME TEMPERATURES AND ACTIVE PARTICLE CONCENTRA-

		TION	S FOR $\varphi$	≥ I		
Quench-	Equiva-	Pres-	Flame	Pa	rtial pressi	ires,
ing dis-	lence	sure,	temp.,	1	atm. $\times$ 10	8
in.	$\varphi$	atm.	°K.	$p_{\text{OH}}$	$p_{\mathrm{H}}$	$p_{ m o}$
			$\alpha = 0.17$			
0.215	1 000	0.6584	2045	0 511	0.0717	0.0317
.300	1.000	.4595	2039	.398	.0600	.0275
.375		.3720	2037	.340	.0543	.0251
. 500		.2530	2032	. 257	.0453	.0215
			a = 0.21			
			u = 0.21		A	0.007
0.150	1.000	0.4719	2219	1.52	0.311	199
.200		.3352	2214	1.13	. 200	125
.300		.2075	2208	. (40	, 190	. 135
. 500	•		2200	1 07	0700	
. 150	0.804	. 0007	2120	1.37	.0700	.215
.200		.4027	2120	0.710	0527	142
. 300		1283	2112	414	0389	0883
		. 1200	2100		.0000	116
.150	.738	.8388	1940	.844	.0947	.110
.200		. 0353	1939	.080	.0803	.0974
.300		. 3970	1937	209	0600	.0733
. 500		.2180	1934	. 308	.0003	.0010
			$\alpha = 0.30$			
0.100	1.000	0.3419	2495	4.334	1.606	1.321
. 175		.1872	2459	2.479	1.051	0.845
.215		.1521	2446	2.070	0.900	.718
.300		.1133	2429	1.549	. 733	. 577
.100	0.7726	.3786	2353	3.484	. 419	1.121
.175		.2079	2331	2.040	. 298	0.729
.215		.1848	2325	1.840	.279	.669
.300		.1343	2313	1.378	.232	. 537
.100	.6623	.5297	2215	2.739	.127	.707
.175		.2871	2202	1.640	.0966	.481
.215		.2346	2198	1.390	.0885	. 424
.300		. 1611	2190	1.012	.0756	.336
.100	.5662	.9451	2035	1.922	.0237	.322
.175		.4615	2031	1.100	.0189	.218
.215		. 3589	2029	.901	.0173	.189
.300		.2189	2026	.612	.0149	.145
			$\alpha = 0.50$			
0.040	1.000	0.4659	2776	17.21	9.11	8.08
.075		.2420	2716	8.97	5.39	4.64
.100		.1758	<b>2687</b>	6.53	4.19	3.53
.115		.1477	2671	5.47	3.61	3.03
.040	0.6798	.5648	2651	16.70	3.33	8.63
.075		.3028	<b>2</b> 606	9.10	2.12	5.13
.100		.2115	2580	6.42	1.64	3.83
. 115		. 1932	2573	5.90	1.54	3.58
.040	.5438	.7175	2519	13.84	1.31	6.35
.075		.3897	2488	7.87	0.901	4.00
.100		.2824	2472	5.82	.739	3.13
.115		.2583	2467	5.39	.701	2.95
.040	.4759	.9090	2412	11.60	.601	4.52
.075		.4853	2390	6.67	.434	2.93
. 100		.3606	2380	5.13	.372	2.40
.115		.3235	2376	4.08	.352	2.22
			$\alpha = 0.70$			
0.040	1.000	0.3118	2852	17.98	11.99	10.68
.050		.2480	2827	14.22	9.89	8.70
.075		. 1765	2792	9.95	7.39	6.38
.100		.1240	2755	6.99	5.49	4.68
.040	0.4938	.4876	2665	18.76	2.96	12.13
.050		.3890	2648	14.90	2.48	9.95
.075		. 2680	2620	10.40	1.90	7.32
. 100		. 1965	2597	7.72	1.53	5.69
.040	.3951	.6584	2528	15.65	1.169	8.61
.050		.5163	2515	12.50	1.001	7.19
.075		.3535	2495	8.83	.787	5.34
.100		.2948	2485	7.43	.713	4.68
.040	.3452	.8689	2424	13.57	. 569	6.24
.050		.6557	2414	10.50	. 487	5.09
.075		,4555	2401	7.61	. 403	3.93
. 100		.3914	2395	0.71	. 375	3.28

of r even for  $\varphi$  greater than unity. This relatively good behavior on the rich side is plausible if it is noted that (1) even where  $\sum_{i} p_i/D_i$  becomes quite

small, *m* is not greatly reduced; (2) an equation similar to equation 2 might be possible for rich mixtures if  $N_{\rm f}$  and  $\sum_i p_i/D_i$  are replaced by other terms having approximately the same pressure

dependence.

Comparison of Experimental and Predicted Quenching Distances.—To test the usefulness of equation 2 over the range of  $\varphi(\varphi \leq 1)$ ,  $\alpha$  and pencountered,  $d^2$  was plotted against  $\psi$  for each value of  $\alpha$ . Separate plots for  $\alpha = 0.17$ , 0.21, 0.30, 0.50 and 0.70 each define a good straight line. The slope of any one line is given by  $(A/k_i)$  and is found to vary from a value of  $0.1694 \times 10^{12}$ molecule-seconds per cubic centimeter for  $\alpha =$ 0.17, to a value of  $0.2360 \times 10^{12}$  for  $\alpha = 0.70$ . Table III lists the  $(A/k_i)$  value for each of the five  $\alpha$ -values examined as well as the percentage deviations of the predicted from the experimentally determined quenching distances for  $\varphi \leq 1$ .



Fig. 2.—Correlation of quenching distance data with  $\psi$  for all values of oxygen fraction  $\alpha$  examined; equivalence ratio,  $\varphi \leq 1.0$ .

A summary correlation is shown in Fig. 2. It appears that the term  $(A/k_i)$  is a proportionality factor that is mildly dependent upon  $\alpha$ . When so considered, equation 2 was found to predict propane-oxygen-nitrogen system quenching distances within 4.2% of the experimental values for a range of  $\alpha$  and p values where  $\varphi \leq 1$ . The investigators.

TABLE III

SUMMARY	OF	RESULTS	OF	$d^2$	versus	ψ	Plots
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Oxygen fraction, a	Least squares slope, $(A/k_i)$ , molecule sec. cc. <sup>-1</sup>	Equiv. ratios examined, $\varphi$	$\operatorname{Dev.}_{\substack{\text{of } d,\\ \%}}$
0.17	$0.1694 \times 10^{12}$	1.000	2.4
0.21	$0.1737 \times 10^{12}$	0.738 0.864 1.000	3.7
0.30	0.1751 × 10 <sup>12</sup>	0.566 .662 .773 1.000	5.2
0.50	$0.2205 \times 10^{12}$ •	0.476 .544 .680 1.000	2.6
0.70	$0.2360 \times 10^{12}$	0.345 .395 .494 1.000	5.7

of reference 2 obtained good agreement using a temperature dependence for the diffusion coefficients of n = 2, and values for  $D_{\rm H}$ ,  $D_{\rm O}$  and  $D_{\rm OH}$  of 1.8, 0.40 and 0.28 cm.<sup>2</sup>/sec., respectively. For this research, good agreement was obtained using what were felt to be better values of n and  $D_{\rm i}$  (n = 1.67 and  $D_{\rm H}$ ,  $D_{\rm OH}$  and  $D_{\rm OH}$  equal to 1.02, 0.29 and 0.26 cm.<sup>2</sup>/sec., respectively).

As noted earlier, equation 2 cannot be expected to hold for values of  $\varphi > 1$ . However, if equation 2 is applied to data of rich mixtures, it is found that the equation represents the data very badly for low values of  $\alpha$  but that it improves markedly as  $\alpha$ increases to 0.70.

## Conclusions

1. The pressure dependence of the quenching distance does not vary greatly with oxygen concentration of the oxidants investigated, 0.17, 0.21, 0.30, 0.50 and 0.70.

2. An equation based on diffusion processes may be successfully used to predict propaneoxygen-nitrogen quenching distances for a range of pressures, fuel-oxidant ratios, and oxygen concentrations of the oxidant mixture for values of  $\varphi > 1$ . This does not, however, rule out the possibility that a thermal theory of flame quenching could be made to work as well.

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## MICELLAR MOLECULAR WEIGHTS OF SELECTED SURFACE ACTIVE AGENTS

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Using light scattering methods, the micellar molecular weights of six anionic and non-ionic surface-active agents were determined in unbuilt aqueous solution in the concentration range of 0.2 to 1.0%. The effects of one alkaline and two neutral builders on the micellar size of an alkyl aryl sulfonate surfactant were found to be considerable. While practically no dissymmetry was found for unbuilt solutions, the reverse was generally true of built surfactants. The possibility of a continuous change in micellar size with increase of concentration for some unbuilt surfactants is indicated.

#### Introduction

During the course of a project whose over-all objective is the development of a scientific method of selection of surfactants (surface-active agents) for specific soil-surface detergent applications, it has seemed that an undetermined variable was influencing results. These results, reported in earlier papers,<sup>1,2</sup> include comparative data for the physico-chemical factors of detergency for the important types of surfactants. Analysis of these data together with an unpublished study of the additive effects of combinations of anionic and nonionic surfactants point to micellar size as such a variable. The present investigation was undertaken because it was believed that micellar molecular weight data would be correlatable with the prime physico-chemical factors<sup>1</sup> of the detergency process, thus permitting the implementation of a scientific method of selection of surfactants.<sup>1</sup>

## Experimental

Apparatus.—Absolute turbidity and dissymmetry (ratio of corrected galvanometer deflections at 45 and  $135^{\circ}$  to the incident radiation) were measured with a Brice–Phoenix light scattering photometer,<sup>3</sup> using green 5460 Å. radiation for all tests. Refractive index differences between solutions and solvents were determined with a Rayleigh interferometer (Baird Associates, Inc.). Measurements were made with 5460 Å. monochromatic light, the zero-order bands being labeled with white light.

With 9400 A. information light, the zero-order bands being labeled with white light. Materials.—The surfactants were commercial, 100%active products, with the exception of Product 4 which was 95% active. The active content of Product 4 was allowed for in preparing test solutions. All surfactants were used directly except Product 1 which was first vacuum dried at  $75^{\circ}$  for 1 hour. These materials are listed in Table I. Technical grade sodium tripolyphosphate (Na<sub>3</sub>P<sub>3</sub>O<sub>10</sub>) and trisodium phosphate monohydrate (Na<sub>3</sub>PO<sub>4</sub>·H<sub>2</sub>O), and analytical reagent sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) were used as builders.

**Theory.**—Micellar molecular weights were determined by Debye's method.<sup>4,6</sup> Since it was found that solute turbidities did not vanish below the critical micellar concentration, confirming the findings of other investigators,<sup>6</sup> the modified method<sup>7,8</sup> for micellar aggregates was not used.

blottes did hot valish below the critical internal contentration, confirming the findings of other investigators,<sup>6</sup> the modified method<sup>7,8</sup> for micellar aggregates was not used. **Procedure.**—The only practical way of supplying the large amounts of "clean" water required for preparing test solutions was found to be Debye's method<sup>8</sup> of distilling water from a dilute alkaline potassium permanganate solution. Several pellets of C.P. NaOH were added to about 850 ml.

(1) A. M. Mankowich, Ind. Eng. Chem., 44, 1251 (1952).

- (4) P. Debye, J. Appl. Phys., 15, 338 (1944).
- (5) P. Debye, This JOURNAL, 51, 18 (1947).

(6) R. F. Stamm, T. Mariner and J. K. Dixon, J. Chem. Phys., 16, 423 (1948).

(7) P. Debye, This JOURNAL, 53, 1 (1949).

of ordinary distilled water and 50 ml. of approximately 0.1 N KMnO<sub>4</sub> solution contained in a 1-liter flask. The solution was distilled in an all-glass still, previously flushed by several distillations, discarding the first and last 250-ml. portions, and retaining the middle 400-ml. portion. This latter portion of the distillate had an absolute turbidity at  $25-26^{\circ}$  of  $0.198 \times 10^{-4}$  cm.<sup>-1</sup>, with an average deviation of  $\pm 0.009 \times 10^{-4}$ .

In agreement with other investigators,<sup>9,10</sup> the preparation of "clean" aqueous test solutions free from large particle size foreign matter was found to be extremely difficult. Of the available methods,<sup>8,9,11</sup> filtration through Pyrex sintered glass filter crucibles of  $0.9-1.4\mu$  maximum pore size, high speed centrifugation, and filtration through bacteriological filters of  $0.6-\mu$  maximum pore size were unsatisfactory. Pressure filtration (with a maximum of 6 cm. of mercury) through a porcelain bacteriological filter (manufactured by Selas Corporation of America, Philadelphia, Pa.) of  $1.2-\mu$  maximum pore size, using a technique that takes advantage of protective action, gave filtrates with reproducible 90° light scattering values. "Clean" test solution was prepared as follows:

Pa.) of  $1.2\mu$  maximum pore size, using a technique that takes advantage of protective action, gave filtrates with reproducible 90° light scattering values. "Clean" test solution was prepared as follows: A 1% (weight to volume) aqueous solution of the test surfactant was poured into the Selas filter mantle and forced through the  $1.2\mu$  pore size filter for 2 hours at a rate of approximately 1 drop per 15 seconds. The mantle was emptied and refilled with purified water, which was then forced through the filter for 15 minutes at about 1 drop per 10 seconds. The mantle was again emptied, and the preceding step repeated. The mantle was again emptied, and refilled with test solution (surfactant or straight builder), which was forced through the filter for 15 minutes at a rate of 1 drop per 6–10 seconds depending on the solution. After again emptying the mantle, the preceding step was repeated. The mantle was then emptied, refilled with test solution, and filtrate for light scattering measurements collected in a clean semi-octagonal cell (40 × 40 × 120 mm. high) placed in a Fisher Scientific Company filtrator. Total time to prepare 45 ml. of builder solution was 4.5-5 hours, and 5.5-6 hours for surfactant solution. When test surfactants were changed, purified water was forced through the filter for 2 hours before beginning the solution preparation procedure.

Refractive index differences were determined in a constant temperature (77°F.) room in which solution temperatures were allowed to come to equilibrium before testing.

tures were allowed to come to equilibrium before testing. Micellar molecular weights of built sodium dodecylbenzenesulfonate were obtained by determining Hc/T at 0.8 and 1.0% concentrations, and mathematically extrapolating the Hc/T versus c line between these concentrations to infinite dilution.

#### Results

**Experimental Data.**—Table II covering the 90° scattering data for isoöctylphenol nonaethylene glycol ether illustrates the reproducibility of the 90° scattering measurements. Micellar molecular weights in Table III are based on calculated values of the intercepts on the ordinate axis (zero concen-

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(10) D. A. Goring and P. Johnson, Trans. Faraday Soc., 48, 367 (1952).

(11) R. S. Stein and P. Doty, J. Am. Chem. Soc., 68, 159 (1946)

<sup>(2)</sup> A. M. Mankowich, ibid., 45, 2759 (1953).

<sup>(3)</sup> B. A. Brice, H. Halwer and R. Speiser, J. Opt. Soc. Am., 40, 768 (1950).

<sup>(8)</sup> P. Debye and E. W. Anacker, ibid., 55, 644 (1951).

## TABLE I

### SURFACTANTS USED<sup>a</sup>

Prod- uct	Description	Туре	Mol. wt.	Formula
1	Sodium docecylbenzenesulfonate	Anionic: alkyl aryl sulfonate	348	$C_{12}H_{25} \cdot C_6H_4 \cdot SO_3Na$
<b>2</b>	Sodium dioctylsulfosuccinate	Anionic: aliphatic sulfonate	444	$(C_8H_{17})_2 \cdot (OCO)_2 \cdot CH_2 \cdot CH \cdot SO_3Na$
3	Isoöctylphenol nonaethylene glycol ether	Non-ionic: alkyl aryl polyethylene glycol ether	602	$\mathrm{C}_8\mathrm{H}_{17}\text{\cdot}\mathrm{C}_6\mathrm{H}_4\text{\cdot}\mathrm{O}\text{\cdot}(\mathrm{C}_2\mathrm{H}_4\mathrm{O})_9\text{\cdot}\mathrm{H}$
4	t-Dodecylnonaethylene glycol thio- ether	Non-ionic: alkyl polyethylene gly- col thioether	598	$C_{12}H_{25}\cdot S\cdot (C_2H_4O)_{\theta}\cdot H$
5	Polyethylene glycol tall oil ester	Non-ionic: polyethylene glycol tall oil ester	•••	
6	Polyoxyethylene-polyoxypropylene glycol	Non-ionic: polyoxyethylene-poly- oxypropylene glycol	7200- 7700	

<sup>a</sup> It is understood that none of the above products is a pure chemical compound. In each case, at least one of the groups is composed of a mixture of several polymers following closely a theoretical distribution of molecular sizes.



Fig. 1.—Sodium dodecylbenzene sulfonate: O, experimental data;  $\triangle$ ,  $Y = 2.38X^{-0.766}$ .

tration), with best straight lines determined by the method of least squares. In Fig. 1, the Hc/T versus c data for sodium dodecylbenzenesulfonate is represented by a smooth curve for which an empirical equation has been determined. Table IV gives micellar molecular weight results of the built surfactants, as well as the surfactant dissymmetry values of the various combinations (corrected for solvent).

**Discussion.**—Since the osmotic coefficient is substantially the ratio of the observed to the theoretical vapor pressure lowering, it is also a measure of the degree of aggregation of a solute. The reciprocal of the osmotic coefficient is thus the aggregation number of a surfactant. Huff and co-workers<sup>12</sup> reported osmotic coefficient vs. square root of molality data for aqueous sodium dodecylbenzenesulfonate solutions. Recalculation of their data gives aggregation numbers of 1.3 at 0.35% and 2.7 at 1.4% concentrations. · Results reported herein were an aggregation number of 3.0 at concentra-

(12) H. Huff, J. W. McBain and A. P. Brady, THIS JOURNAL, 55, 311 (1951).

TABLE II

90° Scattering of Isoöctylphenol Nonaethylene									
			GLYC	OL ETHER					
Concn., c, g./ml.	I 90 ° a	Turb cm. <sup>-1</sup> Solu- tion	idity, × 10⁴ Solute, T	n — no	$\frac{n-n_0}{c}$	$\overset{H}{\times}$ 10 <sup>5</sup>	Hc T $\times 10^{6}$		
0.010	72.7 70.1 71.6 72.5	15.410	15.203	0.0015055	0.1506	0.2501	16.45		
0.008	60.0 56.1 58.9 58.0 59.0	12.546	12.339	0.0012090	0.1511	0.2501	16.22		
0.005	40.5 38.5 38.5 39.0	8.407	8.200			0.2501	15.25		
0.004				0.0006045	0.1511				
0.003	23.5 22.2 23.3 24.0	4.996	4.789			0.2501	15.67		
0.002	16.2	3.480	3.273	0.0003010	0.1505	0.2501	15.28		
<sup>a</sup> $I_{90^{\circ}}$ = galvanometer deflection for 90° scattered light.									

tions of 0.2-0.5%, and 5.0 at concentrations of 0.5-1.0%. The agreement is considered good. However, the cryoscopic data of Gonick<sup>13</sup> for isooctylphenol nonaethylene glycol ether, when recalculated to aggregation numbers, are at wide variance with results obtained herein. Results of this investigation were an aggregation number of 111 in the concentration range of 0.2-1.0%, while the former's results are aggregation numbers of 3.7 to 5.8 as the concentration varied from 0.36 to 1.6%. It is questionable if the cryoscopic method is applicable to micellar particles with high aggregation numbers because of the small effects involved.

The corrected micellar molecular weights and characteristic dimensions of Table IV were obtained by Debye's method,<sup>8</sup> modified to be applicable to our data. The maximum dissymmetry obtained at each builder concentration was used in the determination of the characteristic dimension of the particular builder-surfactant solution. Analysis of the data indicated that the micelles of the built sodium dodecylbenzenesulfonate are most likely to be rigid rods, circular in cross-section with

(13) E. Gonick and J. W. McBain, J. Am. Chem. Soc., 69, 334 (1947).

TABLE	III
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MICELLAR MOLECULAR WEIGHTS OF UNBUILT SURFACTANTS

Product	Surfactant	Concn., %	Intercept, ordinate axis	Micellar mol. wt., uncor.	Aggregation no.	Solute dissymmetry, concn. note1, %
1	Sodium dodecylbenzene sulfonate	0.2-0.5 .5-1.0	$10.04 imes 10^{-4}\ 5.87 imes 10^{-4}$	1,000 1,700	3.0	0.5-0.86
<b>2</b>	Sodium dioctylsulfosuccinate	.2-1.2	$13.93 imes10^{-5}$	7,200	16.0	1.0-1.15
3	Isoöctylphenol nonaethylene glycol ether	.2-1.0	15.00 × 10 <del>~</del> 6	66,700	111.0	1.0-1.01
4	t-Dodecyl nonaethylene glycol thioether	.25–0.5 .5–1.0	$24.82 imes10^{-6}$ $19.37 imes10^{-6}$	40,300 51,600	67.0 86.0	0.8-1 00
5	Polyethylene glycol tall oil ester	.2-1.0	$1.08 imes10^{-5}$	92,600		0.8-1.00
6	Polyoxyethylene-polyoxypropylene glycol	.2-1.0	11.9 × 10 <sup>-5</sup>	8,400	<i>ca.</i> 1.1	0.8–1.11 1.0–1.43

	~ •	BUILT SODIUM	DODECYLE	ENZENESULI	FONATE SOLUTI	ONS		
Builder eoncn., %	Surfactant concn., c, g./ml.	Surfactant turbidity, T, cm. <sup>-1</sup> $\times$ 10 <sup>4</sup>	$rac{Hc}{T}  imes 10^{5}$	Surfactant dis- symmetry	Micellar Uncor.	mol. wt. Cor.	Aggrega- tion no.	Red length, Å.
0.3% Na3PO4·H2O	0.008 .010	$\begin{array}{c} 5.954 \\ 6.203 \end{array}$	$\begin{array}{c} 5.19 \\ 6.11 \end{array}$	1.55 1.25	66,200	93,300	268	1700
0.6% Na <sub>3</sub> PO <sub>4</sub> ·H <sub>2</sub> O	.008 .010	$\begin{array}{c} 6.055 \\ 7.140 \end{array}$	$5.11 \\ 5.41$	$\begin{array}{c} 1.15 \\ 1.09 \end{array}$	25,600	28,200	81	870
0.9% Na <sub>3</sub> PO <sub>4</sub> ·H <sub>2</sub> O	. 008 . 010	$\begin{array}{c} 6.791 \\ 8.851 \end{array}$	$\begin{array}{c} 4.55\\ 4.37\end{array}$	$\begin{array}{c}1.14\\1.23\end{array}$	19,000	22,000	63	1080
1.5% Na <sub>3</sub> PO <sub>4</sub> ·H <sub>2</sub> O	.008 .010	$15.694 \\ 15.500$	$\begin{array}{c} 1.97 \\ 2.49 \end{array}$	$\begin{array}{c} 2.38 \\ 1.20 \end{array}$	50,300	126,000	362	3270
2.0% Na <sub>3</sub> PO <sub>4</sub> ·H <sub>2</sub> O	. 008 . 010	$\frac{27.987}{31.953}$	$\begin{array}{c}1.11\\1.21\end{array}$	1.01 0.98	141,000	141,000	405	<409
0.3% Na <sub>2</sub> SO <sub>4</sub>	.008 .010	$\begin{array}{c} 5.088 \\ 6.434 \end{array}$	$\begin{array}{c} 5.99 \\ 5.92 \end{array}$	$\begin{array}{c} 1.07 \\ 1.15 \end{array}$	15,900	17,500	50	870
0.6% Na <sub>2</sub> SO4	.008 .010	$\begin{array}{c} 6.076 \\ 7.692 \end{array}$	$\begin{array}{c} 5.02\\ 4.95\end{array}$	$\begin{array}{c} 1.10\\ 1.15 \end{array}$	18,900	20,800	60	870
0.9% Na <sub>2</sub> SO4	.008 .010	$\begin{array}{c} 6.346 \\ 7.692 \end{array}$	4.80 4.95	0.93 0.93	23,800	23,800	68	<409
1.5% Na <sub>2</sub> SO4	.008 .010	$11.643 \\ 13.977$	2.62 2.73	$\begin{array}{c} 2.06 \\ 1.99 \end{array}$	45,900	91,800	<b>2</b> 64	2660
2.0% Na <sub>2</sub> SO <sub>4</sub>	.008 .010	$\frac{28.962}{33.602}$	1.05 1.13	$\begin{array}{c} 1.29 \\ 1.56 \end{array}$	137,000	193,000	555	1700
0.3% Na <sub>5</sub> P <sub>3</sub> O <sub>10</sub>	.008 .010	$\begin{array}{c} 5.017\\ 5.916\end{array}$	$\begin{array}{c} 5.94 \\ 6.29 \end{array}$	1.29 1.13	22 , $200$	26,900	77	1220
0.6% Na <sub>3</sub> P <sub>3</sub> O <sub>10</sub>	.008 .010	$5.763 \\ 6.733$	5.09 5.45	1.23 1.30	24,000	29,300	84	1240
0.9% Na <sub>5</sub> P <sub>3</sub> O <sub>10</sub>	.008 .010	6.19 <b>2</b> 7.493	$\begin{array}{c} 4.65 \\ 4.80 \end{array}$	1.18 1.17	24,800	27,800	80	950
1.5% Na <sub>b</sub> P <sub>3</sub> O <sub>10</sub>	.008 .010	$6.786 \\ 8.079$	4.19 4.40	$\begin{array}{c} 1.21 \\ 1.11 \end{array}$	29,900	34,400	99	1030
2.0% Na5P3O10	.008 .010	$\begin{array}{c} 7.930 \\ 8.784 \end{array}$	$\begin{array}{c} 3.57\\ 4.03 \end{array}$	1.23 1.10	57,700	66,900	192	1080

TABLE IV

a diameter equal to 48 Å. It is significant that while increase in neutral builder content ( $Na_2SO_4$ and  $Na_8P_3O_{10}$ ) progressively increased micellar molecular weight, similar additions of an alkaline builder ( $Na_3PO_4$ ·H<sub>2</sub>O) to sodium dodecylbenzenesulfonate solutions produced a relatively high molecular weight at low builder concentration, followed by a decrease to a minimum and then a steady increase. With all three builders, there was no instance of steady increase in dissymmetry with increase in builder concentration, the opposite of what would be expected where micellar molecular weight increased with increase in builder concentration. The increases in micellar weight with si-

multaneous decreases in dissymmetry can be explained as due to closer packing brought about by (a) differences in bonding between gegenions, polar heads of surfactant molecules and micelles, (b) concentration effects of gegenions, and (c) concentration effects of other surface-active species in the solution (*i.e.*, mixed micelles).

Figure 1 showed that an exponential type of curve could be applied to the experimental data of sodium dodecylbenzenesulfonate, and that with the adoption of such a mathematical expedient, a constantly varying micellar molecular weight is indicated theoretically for some surfactants in certain concentration ranges. Available osmotic coefficient data<sup>12</sup> would seem to confirm such postulation for some surfactants.

Acknowledgment.—Acknowledgment is made for the coöperation and advisory assistance of fellow workers of the Paint and Chemical Laboratory, Aberdeen Proving Ground, Md., Drs. C. F. Pickett, Chief, and Myer Rosenfeld; also to Rebecca Flickinger for help in obtaining many of these data.

# THE EFFECT OF ALKALI AND ALKALINE EARTH METAL IONS ON THE ACTIVITY OF CRACKING CATALYSTS

### By Joseph D. Danforth

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The poisoning effect of the alkali metal ions and barium ion on three cracking catalysts has been determined. When a small fraction of the catalyst surfaces is covered by lithium ion, a residual activity is attained which does not show an appreciable decrease on the addition of more lithium hydroxide. The amount of lithium hydroxide required to reach this base conversion, appears to be a measure of the acid sites which are active for the cracking of cetane. The poisoning effect of barium ion is identical with the poisoning effect of potassum ion on a molar basis. The dependence of the poisoning effect of the alkali ions on the radius indicates that the catalyst may be formed by the deposition of polymeric chains of hydrated alumina on the sil.ca micelle.

In a previous paper<sup>1</sup> the effect of lithium hydroxide on the activity of several cracking catalysts was reported. It was assumed that the amount of lithium hydroxide required to eliminate the activity of the catalyst for cetane cracking represented a measure of the active acid sites. It was also indicated that potassium hydroxide was a more effective poison than lithium hydroxide, and the greater poisoning effect was attributed to the larger ionic radius of potassium. Since the effect of ion size would appear to give some indication of the arrangements of active sites on the catalyst surface, an extensive investigation of the effect of ion size and ion charge on the activity of cracking catalysts was initiated. Bitepazh<sup>2</sup> has studied the effect of the alkali metal ions on cracking catalysts.

In his work freshly formed silica-alumina gels containing alkali metal ions were exchanged with increasing quantities of hydrogen ion, and the activity of the calcined catalyst determined for cracking kerosene and reforming a naphtha fraction. A large increase in catalyst activity was observed for the first amount of acid added. The large alkali metal ions were observed to have a greater poisoning effect than the smaller ions.

Mills<sup>3</sup> has reported the effect of potassium ion and quinoline as poisons for calcined and uncalcined silica-alumina cracking catalysts.

The present paper reports the data obtained when three calcined cracking catalysts were impregnated with dilute solution of the hydroxides of lithium, sodium, potassium, cesium and barium, and their activities for the cracking of cetane determined. Several interesting deductions can be drawn from the data relative to some of the structural characteristics of the catalyst.

Materials.—The U.O.P. Type B catalyst contained 86.2% silica, 9.4% zirconia and 4.3% alumina'. It was received as 1/s'' pills which had been calcined at their source. It had picked up 3.5 wt. % of material which was volatile on calcination for two hours at 500°; 25-ml. samples of

this catalyst represented a dry weight of 14.73 g. The reported surface area (B.E.T. method) was 346 m.<sup>2</sup>/g. The Socony-Vacuum synthetic bead catalyst contained

The Socony-Vacuum synthetic bead catalyst contained 10% by weight  $Al_2O_3$  on silica. Although calcined at its source, this catalyst contained 1.88% volatile at  $500-550^\circ$ ; 16.0 g. of catalyst represented 25 ml. and calculations of milliequivalents per gram were based on a dry weight of 15.70 g. The surface area was  $420 \text{ m.}^2/\text{g.}$ 

A second large batch of Socony-Vacuum synthetic bead catalyst was presumably identical in composition with the earlier batch and was so represented. A large portion of this batch was calcined at 500° for 3 hours before impregnation. The weight of the 25-ml. sample thus dried was 17.3 g. indicating a higher density than the earlier batch. Subsequent testing showed this batch of catalyst to be markedly inferior to the early batch giving 17.0% conversion of cetane versus 25% conversion obtained in the earlier sample. This catalyst has been designated as low activity synthetic bead catalyst.

The various alkalies used were designated as reagent grade. Cesium hydroxide was prepared by the solution of double distilled cesium metal in distilled water under an atmosphere of nitrogen.

atmosphere of nitrogen. Du Pont cetane was the charging stock in all tests.

#### **Apparatus and Procedure**

Impregnation of Catalysts.—The indicated weight of 25 ml. of each catalyst was weighed on an analytical balance to the nearest pill or bead. The catalysts contained several per cent. volatile matter due to the adsorption of water on standing. All calculations were made on the basis of the dry catalyst which was arbitrarily taken after heating a sample in a muffle furnace for 3 hours at  $500^{\circ}$ . The catalyst was covered with distilled water, the amount of alkali required to give the desired milliequivalents per g. was added, and the solution made up to 200 ml. by the addition of distilled water. When the supernatant liquid was acid to phenolphthalein, it was considered that equilibrium had been attained and the liquid was decanted. The catalyst was dried overnight at 110° and calcined for 2 hours at  $500^{\circ}$ . At high concentrations of caustic the solutions did not become acid to phenolphthalein. In these cases the catalysts were allowed to stand for a minimum time of 6 days with occasional shaking, the liquid decanted and the unadsorbed caustic determined by titration with standard acid.

Catalyst activities were determined in an apparatus similar to that previously described<sup>1</sup> using 25-ml. samples of catalyst and charging 100 ml. of cetane for a period of 1 hour at atmospheric pressure and 500°.

Weight percentages of gas, gasoline (to  $200^{\circ}$ ) and bottoms (over  $200^{\circ}$ ) were determined by conventional procedures. Conversions were recorded as the weight percentage of gas plus gasoline on a loss free basis. Coke on the catalyst was found to represent less than 0.2% conversion at the highest

P. Stright and J. D. Danforth, THIS JOURNAL, 57, 448 (1953).
 Yw. A. Bitepazh, J. Gen. Chem. (U.S.S.R.), 17, 199 (1947).

<sup>(3)</sup> G. A. Mills, E. R. Boedeker and A. G. Oblad, J. Am. Chem. Soc., 72, 1554 (1950).

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conversion reported, and was not determined or accounted for in the remaining runs. The tables summarizing the data have been omitted because of their voluminous size and because they do not add appreciably to the information which is presented in the figures. was obtained with glass chips. On each of the three catalysts the poisoning effect per milliequivalent of alkali ion becomes greater as the size of the ion increases. In a rather arbitrary manner, it was









## Results

The conversion of cetane has been plotted as a function of the milliequivalents of the adsorbed metal ion in Figs. 1, 2 and 3 for the Socony-Vacuum synthetic bead, the U.O.P. Type B, and the low activity synthetic bead catalysts, respectively. The plot of the activity against alkali content may show an initially high drop in conversion for very small amounts of alkali ion, followed by a straight line portion in which the decrease in conversion is proportional to the amount of the ion. At higher concentrations of the alkali ion, the dependence of conversion on alkali concentration becomes less and the approximately horizontal portions of the curves have been considered as the base activity of the catalyst after covering the active acid sites. This base activity appears to lie in the range of 4 to 8% conversion, while a thermal conversion of 1.7%

direct function of the ionic radius.





decided that the points of intersection of the horizontal portions of the curves and the portions in which the decrease in conversion depended directly on the amount of alkali, represented the milliequivalents of the particular ion necessary to cover the active acid sites. The curves have been drawn to emphasize this value, and these points of intersection have been termed the milliequivalents of alkali per g. of catalyst required to reach the base conversion.

An additional useful value has been obtained from the slopes of the curves in the range in which the catalyst activity decreases directly with added alkali. By dividing the slope of the curves by the weight of 25 cc. of catalyst, a value representing the loss in conversion per milli-equivalent of alkali can be obtained. The milliequivalents of alkali per g. of catalyst required to reach the base conversion, the loss in conversion per milliequivalent of alkali and the ionic radius of the impregnating ions have been summarized in Table I.

In Fig. 4 the milliequivalents of alkali required to reach the base conversion have been plotted as a function of the radii of the impregnating ions. On each of three catalysts the values for sodium, potassium and cesium lie on a straight line and show that the milliequivalents of alkali per g. of catalyst required to reach the base conversion is a

TABLE	Ι
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Summary of the Loss in Conversions per Meq. Alkali and Meq. Alkali/G. Required to Eliminate Cetane

	C C		
	Meq. a_kali/g. to reach base conv	Loss in conv. . per meq. alkali	Radius of alkali ion, A
	High Activi	ity Synthetic Bead	
LiOH	0.46	1.59	0.6
NaOH	.81	3.90	0.95
KOH	.21	5.15	1.33
CsOH	.13	7.60	1.69
	U.O	P. Type B	
LiOH	0.31	3.8	
NaOH	.21	6.2	
KOH	. 15	8.15	
CaOH	.11	11.2	
	Low Activi	ty Synthetic Bead	
LiOH	0.25	2.9	
NaOH	. 165	4.7	
KOH	. 125	<b>6</b> . <b>5</b>	
CsOH	. 10	8.4	

The smaller lithium ion does not fall on this straight line, but extrapolated values to zero ionic radius for two of the three catalysts give values which correspond quite closely to the milliequivalents of lithium ion per g. of catalyst required to reach the base conversion. These observations



Fig. 4.—Meq. Me per g. catalyst to reach break point vs. ionic radius, Å.:  $\bullet$ , UOP type B;  $\bigcirc$ , high activity synthetic bead;  $\times$ , low activity synthetic bead.

have been interpreted to mean that the very small lithium ion is capable of poisoning only a single active center, and that the milliequivalents of lithium hydroxide required to reach the base conversion represents a close approximation to the milliequivalents of acid sites active in cetane cracking. Since soluble hydroxides of ions smaller than lithium do not exist, it appears to be difficult to prove conclusively that a lithium ion covers one, and only one, active site. It is not exactly clear why different base conversions should be obtained with the different alkali metal ions, but there is a general tendency for the base conversion to increase with a decrease in size of the metal ion. Since the base conversions for sodium, potassium and cesium ions are essentially the same, and the only marked increase in base conversion occurs with the lithium ion, this could be interpreted to mean that the lithium ion may coördinate in the structure and may contribute acidity and some activity in its own right.

The loss in conversion per milliequivalent of alkali is plotted as a function of the ionic radii in Fig. 5. Straight lines are obtained on three catalysts and this implies certain interesting conclusions concerning the geometry of the cracking catalyst.



Fig. 5.—Loss in conversion per meq. Me<sup>+</sup> vs. ionic radius, A.:  $\bullet$ , UOP type B; O, high activity synthetic bead;  $\times$ , low activity synthetic bead.

The fact that the ion size has such a significant effect on the poisoning of a catalyst implies that adjacent active sites must be so close together that a single large alkali ion can cover or make inaccesible more than one active site. If the poisoning is a function of the radius, rather than the square of the radius, as shown in Fig. 5, it would seem to imply that the active sites are in a linear chain rather than in clusters. The chain could be cyclic provided the radius of the circle were large relative to the distance between the active sites.

That this proposed structure is not inconsistent with the inorganic chemistry involved in catalyst preparation is supported by a considerable amount of literature on isopolybases. Jander<sup>4</sup> and Souchay<sup>5</sup> have shown beyond any doubt that the neutralization of a soluble aluminum salt gives polymeric ions before the precipitation of aluminum hydroxide occurs. The degree of polymerization and the exact structure of the polymer may be questionable but there is no doubt that polymeric hydrated alumina exists in solution before precipitation. On this basis it is believed that the laving down of a chain of alumina on the surface of a silica micelle results in a chain of active acid sites. The data do not indicate whether the alumina is four or six coordinated, or whether the acid sites are Brønsted or Lewis acids.

The zirconia in the Type B catalyst would be expected to be deposited in a manner similar to that described for alumina.

Although three different catalysts have been used in determining the indicated correlations, it is significant that the activities, the percentage compositions and the degree of calcination are very similar on the three catalysts. It is planned to extend this study to high alumina catalysts at varying degrees of calcination as well as to other catalytic composites.

(5) P. Souchay, Bull. Soc. Chim. France, 914 (1947).

<sup>(4)</sup> G. Jander and K. E. Jahr, Kolloid Beih., 43, 295 (1936).

Since considerable emphasis has been placed on the fact that poisoning of the cracking catalyst is a function of the size of the poisoning ion, it seemed worthwhile to investigate the poisoning effect of the barium ion. The barium ion was chosen because it was available as a soluble hydroxide, had the same ionic radius as a potassium ion and had a dipositive charge. The data of Figs. 6 and 7 compare the relative poisoning effects of potassium hydroxide and barium hydroxide on the Type B catalyst and the high activity synthetic bead catalyst. On the Type B catalyst it is clearly and quantitatively demonstrated that the poisoning effect of a mole of barium ion is exactly the same as that of a mole of potassium ion. This relationship does not hold for the synthetic bead catalyst as shown in Fig. 7. The discrepancy could not be due to sulfates on the catalyst, since the catalyst had been calcined above

the decomposition point for sulfates before impregnation, and no sulfates could be found after exhaustive extraction of the original catalyst with boiling water.

The discrepancy observed in Fig. 7, and, indeed, the occasional large variation for certain points of Figs. 1, 2 and 3 have been rationalized on the basis of the following considerations.

When metal hydroxides are added to a catalyst, the hydroxide may be adsorbed randomly on the surface of the catalyst, or it may exchange the metal ion for hydrogen ion at the active acid sites. Dilute solutions of metal hydroxides favor exchange rather than adsorption. Alkali metal ions are much less strongly

adsorbed than divalent metal ions such as barium.<sup>6</sup> For reasons which are not clear the adsorption of barium ion represented a significant amount on the synthetic bead catalyst and only exchange was significant on the Type B catalyst. The amounts of adsorbed alkali metal ion are considered to be negligible when compared to exchanged metal ion when impregnations were made from very dilute solutions of the metal ion, and when equilibrium conditions corresponded to substantially complete removal of the metal ion from the solution.

If the mechanical adsorption of barium ion can be accepted as an explanation for the discrepancy of Fig. 7, the exact agreement observed between the poisoning effect of equal molar amounts of barium ion and potassium ion shown in Fig. 6 can be taken to prove that the poisoning of cracking catalysts by metal ions of this type is almost entirely a function of the size of the ion. It would appear that this observed dependence upon ion size would be in-

(6) G. E. Boyd, J. Schubert and A. W. Adamson, J. Am. Chem. Soc., 69, 2818 (1947).



Fig. 6.—Conversion vs. moles metal ion on UOP type B catalyst: ●, KOH; ○, Ba(OH)<sub>2</sub>.



Fig. 7.—Conversion vs. moles metal ion on high activity synthetic bead catalyst:  $\bullet_{v}$  KOH;  $\bigcirc$ , Ba(OH)<sub>2</sub>.

consistent with the recent suggestion that the catalyst can be treated as a liquid.<sup>7</sup>

Summary.—Evidence is presented that the milliequivalents of lithium hydroxide required to poison a catalyst for cetane cracking represent a measure of the active acid sites of the catalyst. A barium ion is equal in its poisoning effect to a potassium ion of the same size. Large alkali metal ions are more effective poisons per ion than the small alkali metal ions, and the poisoning effect is a function of the radius of the ion.

The data indicate that a cracking catalyst can be represented as containing chains of active sites, which represent only a small portion of the total catalyst surface. Such chains could be formed by the condensation of polymeric alumina chains on the surface of a silica micelle.

Acknowledgment.—The assistance of Beverly Carlson and Dean F. Martin and the financial assistance of the Office of Naval Research are greatly appreciated.

(7) A.G. Oblad, S.G. Hindin and G.A. Mills, ibid., 75, 4096 (1953).

## DISTRIBUTION OF CHARGED POLYMERS AT EQUILIBRIUM IN A CENTRIFUGAL FIELD<sup>1</sup>

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Equilibrium ultracentrifugation of monodisperse polymer systems in the presence of supporting electrolytes is discussed with particular emphasis on low molecular weight polymers of relatively high charge. Errors introduced in the estimation of molecular weights by neglect of this charge are evaluated. An equation is developed for the determination of molecular weights or degrees of aggregation of charged polymers in the presence of supporting electrolyte. Application of this equation to the usual centrifuge data involving refractive index gradients is described.

The procedure for the calculation of molecular weights of charged solutes from the results of equilibrium centrifugations is not at present clear. Svedberg,<sup>2,3a</sup> Tiselius<sup>4</sup> and Pedersen<sup>3a</sup> concluded that for ionized solutes of low charge to weight ratio the effect of the charge could be effectively suppressed by the addition of an excess of slightly sedimenting "supporting" electrolyte. They then interpreted the data as if the solute were neutral.

While this procedure is very convenient, it can be considered only a first approximation which becomes increasingly poor as the charge to weight ratio of the solute increases, as was earlier discussed by Lamm.<sup>5</sup> It is the purpose of this paper to derive equations and indicate procedures by which molecular weights in charged systems can be estimated with considerably less drastic assumptions. In addition, through computations of distributions in certain idealized cases, the magnitudes of the errors resulting from the use of different methods of interpretation will be compared.

1. Equilibrium Centrifugation in Charged and Uncharged Systems.—The equilibrium distribution of any component in a centrifugal field, whether the component is dissociated into ions or not, is described by the equation<sup>3b</sup>

$$d \ln a_{k} = \frac{M_{k}(1 - \bar{v}_{k}\rho)\omega^{2}}{2R^{T}} d(x^{2}) = \frac{L_{k}\omega^{2}}{2RT} d(x^{2}) = A_{k} d(x^{2})$$
(1)

where  $a_k$  is the activity of component k,  $m_k$  the formula (molecular) weight,  $\overline{v}_k$  the partial specific volume,  $\rho$  the density of the solution,  $\omega$  the angular velocity, R the gas constant, T the absolute temperature, x the radius measured from the axis of rotation,

and d ln  $a_k$  is an abbreviation for  $\sum_i \left(\frac{\partial \ln a_k}{\partial \ln m_i}\right)_{p.T.x.m}$ d ln  $m_i$ , in which  $m_i$  is the molality of component i and i is summed over all the components. The components may be the ions with the condition that the solution is everywhere electrically neutral. For convenience the definitions

$$L_{\mathbf{k}} = M_{\mathbf{k}}(1 - \bar{v}_{\mathbf{k}}\rho) \tag{1a}$$

$$A_{\mathbf{k}} = \frac{M_{\mathbf{k}}(1 - \bar{v}_{\mathbf{k}}\rho)\omega^2}{2RT} = \frac{L_{\mathbf{k}}\omega^2}{2R\bar{T}}$$
(1b)

are made. Equation (1) holds only if  $\bar{v}$  is constant<sup>6</sup> (see equation 10, ref. 6); otherwise, the differential equation for centrifugal equilibrium is somewhat more complicated. For convenient integration the density  $\rho$  of the solution will be considered constant in this paper.

If a material dissolves as a neutral monodisperse species (U), the activity coefficient of the species<sup>7</sup> (g) is often constant to a good approximation and equation 1 becomes

$$d \ln m_{\rm U} = A_{\rm U} d(x^2) \tag{2}$$

Thus a plot of  $\ln m_{\rm U}$  (or  $\ln m_{\rm U}$ , where  $m_{\rm U}$  is proportional to  $m_{\rm U}$ ) vs.  $x^2$  should yield a straight line with slope  $A_{\rm U}$  from which the molecular weight of the species  $(M_{\rm U})$  may be evaluated if  $\bar{v}$  and  $\rho$  are determined through separate measurements.

The determination of the molecular weight of a solute which dissociates into ions is considerably more complicated, not only because the assumption d ln  $g_{\pm} = 0$  may be less satisfactory for an electrolyte than the assumption d ln g = 0 for neutral species, but also because knowledge of the charge of the ion is usually lacking, although needed for a unique answer. Thus, for a solute PX<sub>z</sub> which dissociates into the ions P<sup>+z</sup> and zX<sup>-</sup>, equation 1 becomes

$$d \ln a_{PX_z} = d \ln m_P m_X^z g_P g_X^z = (z+1) d \ln m_{\pm PX_z} g_{\pm PX_z} = A_{PX_z} d(x^2)$$
(3)

Since d ln  $m_{\pm PX_2} = d \ln m_{PX_2}$ , it is apparent that for d ln  $g_{\pm} = 0$  a plot of ln  $m_{PX_2} vs. x^2$  has the slope  $A_{PX_2}/(z + 1)$ . Centrifugation of such a twocomponent system thus does not yield the molecular weight  $M_{PX_2}$ , but only  $M_{PX_2}/(z + 1)$ .

This difficulty can be reduced by centrifugation in the presence of a supporting electrolyte  $BX^{2-4}$ . This device reduces the magnitude of the term z d ln  $m_X$  of equation 3. If this term should become zero, equation 3 would assume the form

$$d \ln m_{\rm P} = A_{\rm PX_z} d(x^2) \tag{4}$$

(6) T. F. Young, K. A. Kraus and J. S. Johnson, J. Chem. Phys., 22, 878 (1954).

<sup>(1)</sup> This document is based on work performed for the Atomic Energy Commission at the Oak Ridge National Laboratory.

<sup>(2)</sup> T. Svedberg, *Kolloid-Z. Zsigmondy Festschrift Erg. Bd.*, 36, 53 (1925).

<sup>(3)</sup> T. Svedberg and K. O. Pedersen, "The Ultracentrifuge," The Clarendon Press, Oxford, 1940, (a) p. 15, 23ft, 53ff; (b) p. 51; (c) p. 267.

<sup>(4)</sup> A. Tiselius, Z. physik. Chem., 124, 449 (1926).

<sup>(5)</sup> O. Lamm, Arkiv Kemi, Mineral. Geol., 17A, No. 25 (1944).

<sup>(7)</sup> A distinction is made between the activity coefficients g of species and the stoichiometric activity coefficients  $\gamma$ . Equation 1 permits calculation of the ratios of stoichiometric activity coefficients of a component for any assigned formula weight M. If estimates regarding variations of the activity coefficients of species (d ln g) are available some information regarding these species may be obtained (See Ref. 9) and M becomes the molecular weight of the species. When estimation of the molecular weights of species is the objective, usually the activity in the solute is expressed and experimental conditions are selected in such a way that d ln g = 0 is as good an approximation as possible.
*i.e.*, it would become formally identical with the equation for uncharged solutes, and  $M_{PX_z}$  would be obtained rather than  $M_{PX_z}/(z + 1)$ . In addition, the presence of the supporting electrolyte increases the ionic strength of the solution, decreases the relative change in ionic strength, and makes the assumption d ln  $g_{\pm} = 0$  more plausible. However, if z is large or if the supporting electrolyte sediments considerably, z d ln  $m_X$  will not be negligible and the theory for un-ionized solutes will not be applicable. Instead, as pointed out by Lamm,<sup>5</sup> sedimentation of the polymer and the supporting electrolyte must be considered simultaneously.

2a. Simultaneous Equations for Three-component Systems.—Three-component systems will be discussed subject to the following restrictions:

(1) The polymeric electrolyte  $PX_z$  dissociates into the ions  $P^{+z} + zX^{-,8}$  Although the polymeric ion  $P^{+z}$  will be considered to have a constant charge z under the conditions of any experiment, it could be a complex of a more highly charged polymeric ion, e.g.,  $M^{+(y+z)}$ , with the anion  $X^-$ , or  $P^{+z} = MX_y^{+z}$ . The limitation that z does not change then is equivalent to stating that the degree of complexing is invariant in the range of concentrations and pressures covered by an experiment.

(2) The polymer is monodisperse.

(3) The partial specific volumes  $\overline{v}$  of  $PX_z$  and BX are constant.

(4) The density  $\rho$  of the solution is constant. This limitation is imposed for convenience of integration, although this restriction and that in paragraph 3 cannot generally apply simultaneously for physical systems.

(5) The appropriate activity coefficient products of all species are constant.

By restriction 5, d ln  $g_P g_X^z = (z + 1)$  d ln  $g_{\pm P X_z} = 0$  and d ln  $g_B g_X = 0$  and the equilibrium distribution of the two solutes is given by the simultaneous solution of the equations

d ln 
$$a_{\mathrm{FX}_s}$$
 = d ln  $m_{\mathrm{P}}m_{\mathrm{X}}^s$  =  $\frac{L_{\mathrm{PX}_s}\omega^2}{2RT}$  d( $x^2$ ) =  $A_{\mathrm{PX}_s}$  d( $x^2$ )  
(5)

$$d \ln a_{BX} = d \ln m_B m_X = \frac{L_{BX} \omega^2}{2RT} d(x^2) = A_{BX} d(x^2)$$
(6)

$$zm_{\rm P} + m_{\rm B} = m_{\rm X} \tag{7}$$

with the condition that the total amount of each component in the cell at equilibrium is determined by the initial composition.

The simultaneous solution of equations 5 to 7 for the case where the polymer concentration is vanishishingly small, so that effectively  $m_{\rm X} = m_{\rm B}$  (or d ln  $m_{\rm X} = {\rm d} \ln m_{\rm B}$ ), yields

d ln 
$$m_{\rm P} = (A_{\rm PX_z} - (z/2)A_{\rm BX}) d(x^2)$$
 (8)

Thus, as already pointed out by Lamm,<sup>5</sup> in this limiting case the slope of a plot of  $\ln m_{\rm P} vs. x^2$  does not yield  $M_{\rm PXz}(1 - \bar{v}_{\rm PXz}\rho)$  but only  $M_{\rm PXz}(1 - \bar{v}_{\rm PXz}\rho) - (z/2)M_{\rm BX}(1 - \bar{v}_{\rm BX}\rho)$ , which will be called  $(L_{\rm PXz})_{\rm max}$ .

At finite concentrations of  $m_{\rm P}$  the contribution of the term z d ln  $m_{\rm X}$  to the "apparent molecular weight" is even larger. Lamm<sup>5</sup> obtained an approximate solution of equations 5 to 7 which took this variation of  $m_X$  into consideration. The error incurred in neglecting the term z d ln  $m_X$  and the degree to which Lamm's equation avoids this error will be illustrated in Section 5c.

2b. Refractive Index Gradients.—In most ultracentrifuges in current use concentration distributions are indirectly obtained from observations of refractive index gradients as a function of radius. The total refractive index gradient can be considered the sum of the gradients due to the solutes,  $(\partial n/\partial m_i) dm_i/dx$ , due to pressure effects on the solution,  $(\partial n/\partial p) dp/dx$ , and extraneous gradients,  $\epsilon$ , such as may result from distortion of cell window,<sup>3c,9</sup> *i.e.* 

$$(\mathrm{d}n/\mathrm{d}x)_{\mathrm{a}} = \Sigma_{\mathrm{i}} \left( \partial n/\partial m_{\mathrm{i}} \right) \mathrm{d}m_{\mathrm{i}}/\mathrm{d}x + \left( \partial n/\partial p \right) \mathrm{d}p/\mathrm{d}x + \epsilon$$
(9)

where subscript i denotes a solute and where  $(dn/dx)_a$  is the observed total refractive index gradient. In practice a "background" experiment is performed under the same conditions except for the absence of the polymeric solute. The resulting values of the refractive index gradient,  $(dn/dx)_b$ , are then subtracted from  $(dn/dx)_a$ . This difference, which will be defined as  $dn^*/dx$ , is generally assumed to be equal to the polymer term  $(\partial n/\partial m_{PXz})dm_{PXz}/dx$ . This is usually a good approximation for a two-component system provided the density of the solution does not differ greatly from that of the solvent. Otherwise, the pressure term  $(\partial n/\partial p) dp/dx$  and  $\epsilon$  might be different for the two cases.<sup>9</sup>

Refractive index gradients can be readily used for the estimation of molecular weights in twocomponent systems. Equation 2 can be written in the forms

$$\mathrm{d}m_{\mathrm{U}}/x \,\mathrm{d}x = 2A_{\mathrm{U}}m_{\mathrm{U}} \tag{10}$$

and

$$d \ln (dm_U/x dx) = d \ln m_U$$
(10a)

When  $dn^*/dx = (\partial n/\partial m_U) dm_U/dx$  and when  $(\partial n/\partial m_U)$  is constant, as is usually the case in dilute solutions, equation 10a becomes

 $d \ln (dn^*/x dx) = d \ln (\partial n/\partial m_U) dm_U/x dx =$ 

d ln 
$$(dm_U/x dx) = A_U d(x^2)$$
 (11)

Thus the slope d ln  $(dn^*/x dx)/d(x^2)$  is equal to  $A_U$ and the molecular weight can be obtained without computation of concentration as a function of radius. Analogous considerations apply when the solute dissociates into ions.<sup>10</sup> In the three-component case, particularly if the solutes are ionic, this procedure may be quite unsatisfactory. In this case  $dn^*/dx$  is given by the equation

$$dn^*/dx = (dn/dx)_{a} - (dn/dx)_{b} = (\partial n/\partial m_{PX_z}) dm_{PX_z}/dx + (\partial n/\partial m_{BX})(dm_{BX}/dx)_{a} + E_a - (\partial n/\partial m_{BX})(dm_{BX}/dx)_{b} - E_b$$
(12)

where subscripts a and b refer to the "polymer" and "background" experiments, respectively, and where  $E = (\partial n/\partial p)dp/dx + \epsilon$ . Even if  $E_a = E_b$ , the approximation  $dn^*/dx = (\partial n/\partial m_P) dm_P/dx$  implies the assumption that  $(\partial n/\partial m_{BX}) (dm_{BX}/dx)_a =$   $(\partial n/\partial m_{BX}) (dm_{BX}/dx)_b$ . However, this is a poor (9) J. S. Johnson, K. A. Kraus and T. F. Young, J. Am. Chem. Soc.,

76, 1436 (1954).
(10) K. O. Pedersen, Z. physik. Chem., A170, 41 (1934).

<sup>(8)</sup> The treatment is symmetrical with respect to charge type and would apply equally well for a negatively charged polymeric ion with positively charged counter-ions.

assumption even when  $(\partial n/\partial m_{\rm BX})$  does not change, since at finite polymer concentration  $(dm_{\rm BX}/dx)_{\rm a} \neq (dm_{\rm BX}/dx)_{\rm b}$ .

In addition to this difficulty, the relationship between d ln m and d ln (dm/x dx) is not as simple as in equation 10a for an uncharged two-component system, since for the three-component system the simultaneous equations 5 and 6 replace the single equation 2.

3. Redefinition of Polymeric Components. (a). Three-component System.—An alternate definition of the polymeric components used to circumvent similar difficulties in osmotic pressure studies<sup>11</sup> decreases the errors discussed in Sections 2a and 2b, leads to an equation similar to Lamm's,<sup>5</sup> and indicates a path for the interpretation of data which are based on refractive index gradients. Instead of defining the polymer component as  $PX_z$ , one defines a new component 2,  $PX_{z/2}B_{-z/2}$ , which is identical with  $PX_z - z/2$  BX. With this definition the polymeric component has one mole of particles per mole of solute, a molecular weight  $M_2 = M_{PX_z}$  $- z/2 M_{BX}$ , and  $L_2 = M_2(1 - \bar{v}_{2}\rho) = M_{PX_z}(1 - \bar{v}_{PX_z}\rho) - z/2 M_{BX}(1 - \bar{v}_{BX}\rho)$ , which is identical with the maximum observable quantity  $(L_{PX_z})_{max}$ (see equation 8). Component 2 has the same molal concentration  $(m_2)$  as  $PX_z$ , *i.e.* 

$$m_2 = m_P = m_{PX_e} \tag{13}$$

but has a different chemical potential. Its activity  $(a_2)$  is given by the equation

$$a_2 = m_{\rm P} m_{\rm X}^{z/2} m_{\rm B}^{-z/2} g_{\rm P} g_{\rm X}^{z/2} g_{\rm B}^{-z/2}$$
(14)

The supporting electrolyte remains component BX. Its chemical potential is unchanged by the redefinition of components although its concentration depends on whether the polymer component is  $PX_z$ or component 2. To emphasize this difference in concentration, we shall designate the component BX in the presence of component 2 as component 3. Its activity  $c_3$  and its concentration  $m_3$  can then be expressed by the equations

$$m_3 = m_B + (z/2)m_2 = m_X - (z/2)m_2$$
 (15)

$$a_{2} = a_{BX} = m_{B}m_{X}g_{B}g_{X} = m_{3}^{2} \left[ 1 - \left(\frac{zm_{2}}{2m_{4}}\right)^{x} \right] g_{B}g_{X}$$
 (16)

With the restriction of constancy of the activity coefficients, the distribution equation becomes  $d \ln a_2 = d \ln m_P m x^{z/2} m_B^{-z/2} =$ 

$$d \ln m_2 \left(\frac{m_3 + zm_2/2}{m_3 - zm_2/2}\right)^{z/2} = d \ln m_2 \left(\frac{1+\eta}{1-\eta}\right)^{z/2} = d \ln m_2 \left(\frac{1+\eta}{1-\eta}\right)^{z/2} = d \ln m_2 + \frac{z}{2} d \ln \frac{1+\eta}{1-\eta} = d \ln m_2 + \frac{z}{1-\eta^2} = d \ln m_2 + \frac{z}{1-\eta^2} = d \ln m_2 + \frac{z\eta}{1-\eta^2} = d \ln m_2 + \frac{z\eta}{1-\eta^2$$

where  $\eta = zm_2/2m_3$  and  $A_2 = M_2(1 - \bar{v}_2\rho)\omega^2/2RT$ . This equation is analogous to equation 5 for component PX<sub>s</sub>, but has the advantage that d ln  $m_2$  (which is equal to d ln  $m_{PX_z}$ ) is closer to  $A_2 d(x^2)$  than to  $A_{PX_z} d(x^2)$  since  $(z/2) d \ln (1 + \eta)/(1 - \eta)$  is considerably smaller than z d ln  $m_X$ .

For the distribution of component 3

where  $A_3 = A_{BX}$ . Since  $(1 - \eta^2)$  is usually near unity, presence of the polymer will not change d ln  $m_3$  greatly; hence the background experiment will approximate the distribution of supporting electrolyte much more closely if the polymeric component is defined in this way. The approximation that d ln dn\*/x dx = d ln dm\_2/x dx = d ln dm\_{PXz}/x dx is therefore good.

However, the computation of concentration distribution from refractive index data is still not completely straightforward. The gradient  $dn^*/dx$ approximates  $(\partial n/\partial m_2) dm_2/dx$ , but  $(\partial n/\partial m_2)$ cannot be calculated from separately available refractive index data on PX<sub>z</sub> without knowledge of z and, in some cases, where reaction with the solvent (e.g., hydrolysis) occurs, without knowledge of the extent of such reaction. In addition, it is often convenient to avoid refractive index measurements. Thus a procedure is desirable which utilizes directly the value of d ln  $(dn^*/x dx)/d(x^2)$  and does not require prior knowledge of  $(\partial n/\partial m_2)$ .

If  $\eta^2$  is neglected compared with 1 and d ln  $m_3$  compared with d ln  $m_2$ , equation (17) becomes

d ln 
$$a_2 = d \ln m_2 + z\eta d \ln m_2 = A_2 d(x^2)$$
 (19)

Hence

$$dm_2/x dx = 2A_2m_2 - (z^2m_2/2m_3)(dm_2/x dx) \qquad (20)$$

and

d ln 
$$(dm_2/xdx) = d \ln [m_2(2A_2 - (z^2/2m_3)(dm_2/x dx))]$$
  
(20a)

The approximation d ln  $(dm_2/xdx) = d \ln m_2$  thus involves neglect of the term d ln[2  $A_2 - (z^2/2 m_3)$  $(dm_2/xdx)$ ], which may cause a serious error.

Rearrangement of equation 19 also yields

$$L_{2} = L_{PX_{2}} - \frac{z}{2} L_{BX} = (2RT/\omega^{2})(d \ln m_{2}/d(x^{2}) + (z^{2}/2m_{3}) dm_{2}/d(x^{2}))$$
(21)

After integration equation 21 becomes virtually the same as Lamm's equation 9, which with molalities rather than molarities may be written as

$$L_{\text{PX}_{s}} - \frac{z}{2} L_{\text{BX}} = \frac{2RT}{\omega^{2}(x^{2} - x_{0}^{2})} \left[ \ln \frac{m_{\text{PX}_{s}}}{(m_{\text{PX}_{s}})_{0}} + \frac{z^{2}}{2m_{\text{BX}}} (m_{\text{PX}_{s}} - (m_{\text{PX}_{s}})_{0}) \right]$$
(22)

**3b.** Four-component Systems.—A four-component system consisting of solvent, polymeric component and two supporting electrolytes with a common anion will be considered. For development analogous to that in Section 3a, the polymer component 2 is assigned the formula  $PX_{z/2}$ · $H_{-zms/2(m_3 + m_5)}B_{-zm_5/2(m_4 + m_5)}$ . The supporting electrolytes HX and BX are components 3 and 5. The concentrations of the various ions in terms of these components are given by the equations

$$m_{\rm P} = m_2$$

$$m_{\rm H} = m_3 - zm_2 m_3/2(m_3 + m_5) = m_3(1 - \eta^*)$$

$$m_{\rm B} = m_5 - zm_2 m_5/2(m_3 + m_5) = m_5(1 - \eta^*)$$

$$m_{\rm X} = m_3 + m_5 + zm_2/2$$
(23)

where  $\eta^* = zm_2/2(m_3 + m_5)$ . With the same restrictions regarding monodispersity, constancy of

<sup>(11)</sup> G. Scatchard, J. Am. Chem. Soc., 68, 2315 (1946).

activity coefficients, etc., as for the three-component system, the equilibrium equation becomes  $d \ln a_2 =$ 

d ln 
$$m_{\rm P}m_{\rm X}^{s/2}m_{\rm H}^{-[zm_{\delta}/2(m_{\delta}+m_{\delta})]}m_{\rm B}^{-[zm_{\delta}/2(m_{\delta}+m_{\delta})]}$$

$$= d \ln m_{2} + \frac{z}{2} \times d \ln \frac{m_{3} + m_{6} + zm_{2}/2}{(m_{3} - m_{3}\eta^{*})^{m_{4}/(m_{4} + m_{6})} (m_{5} - m_{6}\eta^{*})^{m_{6}/(m_{4} + m_{6})}}$$
$$= A_{2} d(x^{2})$$
(24)

Equation 24 reduces to

$$A_2 d(x^2) = d \ln m_2 + \frac{z}{2} \left[ \frac{2 d \eta^*}{1 - \eta^{*2}} - \ln \frac{m_3}{m_5} d \frac{m_3}{(m_3 + m_5)} \right]$$
(25)

4. Treatment of Experimental Results. (a). Three-component System.—For the interpretation of the experimental results, it is convenient to rewrite equation 17 with the approximation  $1 - \eta^2 = 1$  in the form

d ln 
$$a_2 = d \ln m_2' + z' \eta N(d \ln m_2' - d \ln m_3)$$
  
=  $N A_2' d(x^2)$  (26)

where N is the degree of polymerization and where the primed symbols refer to the "monomer unit." The following equations relate the primed and unprimed quantities

$$m_{\rm P}' = N m_{\rm P}; \ M_{\rm PX_z}' = M_{\rm PX_z}/N; A_{\rm PX_z} = A_{\rm PX_z}/N; \ z' = z/N \ (27)$$

Solving equation 26 for N yields

$$N = \frac{\mathrm{d} \ln m_2'/\mathrm{d}(x^2)}{A_2' - z'\eta(\mathrm{d} \ln m_2'/\mathrm{d}(x^2) - \mathrm{d} \ln m_3/\mathrm{d}(x^2))}$$
(28)

With neglect of the term  $c \ln m_3/d(x^2)$  and the additional approximation  $d \ln (dn^*/xdx) = d \ln m_2'$ , equation 28 simplifies to

$$N = \frac{S/A_{2}'}{1 - z'\eta S/A_{2}'} = \frac{S/A_{2}'}{1 - \frac{(z')^2 m_{2}'}{2m_{3}} \frac{S}{A_{2}'}}$$
(29)

where

$$S = \frac{\mathrm{d}\,\ln\,(\mathrm{d}n^*/x\mathrm{d}x)}{\mathrm{d}(x^2)} \tag{30}$$

Except for the value of z', equation 29 is in terms of experimental data or of quantities for which good estimates can be made from experimental conditions. Equation 29 should, therefore, be useful as a starting point for iterations.

4b. Four-component System.—The equation analogous to equation 28 for the four-component system is obtained from equation 25 by neglecting  $(\eta^*)^2$  compared with 1

$$N = \frac{\frac{d \ln m_2'/d(x^2)}{dx^2}}{A_2' - z'\eta^* \left\lfloor \frac{d \ln m_2'}{d(x^2)} - \frac{d \ln (m_3 + m_5)}{d(x^2)} \right\rfloor - \frac{z'}{2} \ln \frac{m_3}{m_5} \frac{d (m_3/(m_3 + m_5))}{d(x^2)}}$$

with neglect of the terms

d ln 
$$(m_3 + m_5)/d(x^2)$$
 and  $\frac{z'}{2} \ln \frac{m_3}{m_5} \frac{d(m_3/(m_3 + m_5))}{d(x^2)}$ 

and with the additional approximation d ln  $(dn^*/xdx) = d \ln m_2'$ , equation 31 simplifies to

$$N = \frac{S/A_{2'}}{1 - z'\eta^* S/A_{2'}} = \frac{S/A_{2'}}{1 - \frac{(z')^2 m_{2'}}{2(m_3 + m_5)} \frac{S}{A_{2'}}}$$
(32)

This equation differs from equation 29 for the threecomponent case only by replacing  $m_3$  by  $(m_3 + m_6)$ . 5. Comparison of Methods of Interpreting Results. (a). Distribution in Idealized Threecomponent Systems.—To compare the different methods of interpretation for three-component systems of ionized solutes, concentration distributions were calculated<sup>12</sup> for idealized systems, limited by the five restrictions given in Section 2a. After integration simultaneous solution of equations 5 to 7 yields

$$m_{\mathbf{X}^{z+1}} - (m_{\mathbf{B}}m_{\mathbf{X}})_{0} m_{\mathbf{X}^{z-1}} \exp A_{\mathbf{B}\mathbf{X}}(x^{2} - x_{0}^{2}) - z(m_{\mathbf{P}}m_{\mathbf{X}^{z}})_{0} \exp A_{\mathbf{P}\mathbf{X}_{z}}(x^{2} - x_{0}^{2}) = 0 \quad (33)$$

where subscript 0 indicates values at an arbitrary point,  $x_0$ , at which arbitrary molalities were assigned. Values of  $m_X$  as a function of x were computed and from these  $m_P$  and  $m_B$ . The refractive index gradients which should be observed were then calculated.<sup>13</sup>

The parameters of some of the computations were selected to simulate distribution of low molecular weight inorganic polymers<sup>14</sup> which are of particular interest to us. For these  $(1 - \bar{v}_{PX_z}\rho)$  is generally large (0.7 to 1). Systems of high charge to weight ratio were stressed. Some calculations with parameters representing low molecular weight proteins under conditions away from the isoionic point were included. For these  $L_{PXz}$  was selected to be 4,000 and 15,000, which corresponds to  $M_{PXz} =$ 16,000 and 60,000 since for proteins in general (1 - $\overline{v}_{PX_2\rho}$ ) is ca. 0.25. Parameters were varied (see Table I) to simulate changes in conditions which might be of interest experimentally, e.g., concentration of polymer, concentration of supporting electrolyte and molecular weight of supporting electrolyte. In addition, the effect of the magnitude of z was investigated.

**5b.** Procedure for Neutral Species.—If an actual experiment is interpreted by the procedure applicable to neutral species,  $\ln (dn^*/xdx)$  is plotted  $vs. x^2$  and  $L_{PX_z}$  computed from the slope  $A_{PX_z}$  (see equation 11). This procedure was followed for the computed idealized cases. A curvature downward was found rather than the linearity expected for an ideal neutral case. Since the curvature was relatively small (see Fig. 1 for the extreme case No. 1,

(12) We are indebted to Dr. N. Edmondson, formerly of ORNL Mathematics Panel, for suggesting the method of calculation, and to Mrs. Elizabeth Drabkin of the Mathematics Panel and to Miss Zella Bonner and Mrs. Leonard W. Magnusson, Jr., of ORNL Chemistry Division for assistance with the computations.

(13) The details of the computations are as follows: Values of  $m_X$ as a function of z were calculated with equation 33 by Newton's method (see e.g., W. E. Milne, "Numerical Calculus," Princeton 1949, p. 36). Speeds of rotation more selected to give ratios of mu

tion were selected to give ratios of mp of 2 to 4 at the extremes of the cell (6.0 to 7.2 cm.). Values of mp and m<sub>B</sub> were computed from the (integrated) equations 5 and 6. By the use of orthogonal polynomials (*ibid.*, pp. 265 fl.) these were fitted to cubic equations in z which on differentiation gave  $dm_{PX_z}/dz$ and  $dm_{DX}/dz$ . With assigned values of  $(\partial n/\partial m)$  and neglect of pressure and distortion effects,  $(dn/dz)_n$  was calculated by equation 9. To simulate "background experiments" ratios of  $m_{DX}$  were calculated directly from the integrated equation 6, and  $(m_{DX})_0$  chosen to give the same total quantity of BX as in the three-component system. Values of  $(dm_{DX}/dz)_b$  were then computed by an equation analogous to (10), and from these  $(dn/dz)_b$ . Subtraction of  $(dn/dz)_b$  from  $(dn/dz)_a$  gives  $dn^*/dz$ , which would be observed experimentally in such systems (except, of course, for pressure and distortion effects).

(14) K. A. Kraus and J. S. Johnson, J. Am. Chem. Soc., 75, 5769 (1953).

TABLE	Ι
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SUMMARY OF RESULTS OF COMPUTATIONS OF EQUILIBRIUM DISTRIBUTION IN 3-COMPONENT SYSTEMS	5
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 $(T = 300 \text{ °K.}, x = 6.0-7.2 \text{ cm.}, (\partial n/\partial m_{BX}) = 0.01, x_0 = 6.6 \text{ cm.}, \text{ calculations: } 1-6, 27,700 \text{ r.p.m.}; 7-10, 10,000 \text{ r.p.m.}; 11-15, 5,000 \text{ r.p.m.})$ 

No.	$(m_{PX_2})_0$	$(m_{\mathrm{BX}})_0$	$L_{BX}$	2	$\left(\frac{\partial n}{\partial m_{\rm PX_g}}\right)$	LPXs	$(L_{PX_s})_{app.}$	(LPX <sub>s</sub> ) <sub>max</sub> .
1	0.015	1.0	100	8	0.1	1,000	315	600
2	.0075	1.0	100	8	. 1	1,000	395	600
3	.015	2.0	100	8	.1	1,000	385	600
4	.0075	1.0	100	16	.2	2,000	425	1,200
5	.015	1.0	50	8	. 1	1,000	375	800
6	.015	1.0	100	4	. 1	1,000	615	800
7	.0005	0.1	40	10	<b>3</b> . $2$	4,000	2,450	3,800
8	.0005	0.1	40	5	3.2	4,000	3,340	3,900
9	. 0005	1.0	40	10	3.2	4,000	3,600	3,800
10	.0001	0.1	40	10	3.2	4,000	3,500	3,800
11	.0001	0.2	40	20	12	15,000	12,100	14,600
12	.0001	1.0	40	<b>20</b>	12	15,000	14,250	14,600
13	.0001	0.2	40	10	12	15,000	14,400	14,800
14	. 00002	0.2	40	<b>20</b>	12	15,000	14,000	14,600
15	.0001	0.2	40	30	12	15,000	9,700	14,400

Table I), apparent values of  $M_{PX_z}$   $(1 - \bar{v}_{PX_z}\rho)$  or  $(L_{PX_z})_{app.}$  were computed from the average values of the slopes. These values of  $(L_{PX_z})_{app.}$  (Table I, column 8) are considerably smaller than the parameters  $L_{PX_z}$  used in the calculations (Table I, column 7).



Fig. 1.—Linearity test of function  $\log dn^*/xdx$  for case 1, Table I: solid line, computed curve; dotted line, "average" slope.

The sources of the large discrepancy between  $(L_{PXz})_{app.}$  and the parameter  $L_{PXz}$  may be summarized as follows.

(1) The maximum observable value of  $L_{PX_{2}}$ ,  $(L_{PX_{2}})_{max.}$ , (Table I, column 9) is considerably less than the parameter  $L_{PX_{2}}$ . This discrepancy (equation 8) will increase with the charge of the polymer ion and with the value of  $L_{BX}$ . The effect is relatively small for high molecular weight polymers of low charge, such as proteins under conditions not far removed from the isoionic point. However, it may be of considerable importance for low molec-

ular weight polymers of high charge or for proteins under conditions far removed from the isoionic point. Unfortunately, in the interpretation of an actual experiment the difference between  $L_{PXz}$ and  $(L_{PXz})_{max}$  cannot be ascertained until an estimate of the charge z is available.

(2) The use of the theory for uncharged solutes makes the implicit assumption mentioned earlier, that z d ln  $m_X$  is negligible. However, if z is high, zd ln  $m_X$  may become an appreciable fraction of d ln  $m_P$ , particularly at high  $L_{BX}$ . For example, if in case 1, Table I, refractive index difficulties described below were avoided by direct observation of  $m_P$ (e.g., by optical absorption) and  $(L_{PXz})_{app}$  calculated from d ln  $m_P/d(x^2)$ , a value of 425 would be found rather than 600, the corresponding  $(L_{PXz})_{max}$ . For case 7,  $(L_{PXz})_{app}$  would be 3,000 compared with  $(L_{PXz})_{max} = 3,800$ . Even for case 11, with a considerably more favorable charge to weight ratio,  $(L_{PXz})_{app}$ . would be only 13,200 compared with  $(L_{PXz})_{max} = 14,600$ .

(3) The distribution of BX is not the same in the presence and absence of  $PX_z$  and therefore  $dn^*/dx$  does not represent solely the contribution of  $PX_z$  to the refractive index gradient. This disturbance of the background is not of great importance for proteins of relatively low charge but for a polymer with parameters of case 1, Table I, it amounts to ca. 33% of the value of  $(\partial n/\partial m_{PXz})/(dm_{PXz}/dx)$  (see Table II, row 5). For a light supporting electrolyte  $dm_{BX}/dx$  may actually become negative when centrifugations in the presence of polymer are carried out.

(4) For the ionized solute  $PX_z$  in a supporting electrolyte, d ln  $m_P = d \ln m_{PX_z}$  is not equal to d ln  $(dm_P/xdx)$ , as for a neutral solute. For case 1, Table I, d ln  $m_{PX_z}/d(x^2)$  is 0.0723 while (d ln  $dm_{PX_z}/xdx)/d(x^2)$  is 0.0546. For case 7 the corresponding values are 0.0658 compared to 0.0548 and for case 11, 0.0725 compared to 0.0649.

5c. Lamm's Equation.—Lamm's equation (equation 22) would lead to a good approximation of  $M_{PX_2}$  if the necessary information were available. Thus, apparent values of  $L_{PX_2}$  of 1,000 to

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TABLE	Π
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Approximations in Molecular Weight Determinations

untertions for some 1 T-1	1. f		
DUTATIONS FOR Case 1, 1 ap.	іс і: ан геігасыу	e index gradients a	are multiplied by

	(Computations to	r case 1, 1 au	ne r; an ren	active mucx	gradients ar	e muniphea	by 10°.)	
1	x	6.0	6. <b>2</b>	6.4	6.6	6.8	7.0	7.2
2	$(\partial n / \partial m_{\mathrm{PX}_z}) \mathrm{d} m_{\mathrm{PX}_z} / \mathrm{d} x$	0.819	0.993	1.197	1.432	1.698	1.997	2.331
3	$(\partial n/\partial m_{\mathbf{B}\mathbf{X}})(\mathrm{d}m_{\mathbf{B}\mathbf{X}}/\mathrm{d}x)_{\mathtt{B}}$	. 688	. 678	. 660	. 636	. 605	. 568	. 526
4	$(dn/dx)_{b}$	.946	. 998	1.052	1.109	1.169	1.232	1.298
5	RBXª	315	3 <b>22</b>	327	<b>—</b> .330	332	332	331
6	$(\partial n/\partial m_2)\mathrm{d}m_2/\mathrm{d}x$	. 492	. 596	.718	.859	1.019	1.199	1.399
7	$(\partial n/\partial m_3)(\mathrm{d}m_3/\mathrm{d}x)_{\mathtt{B}}$	1.016	1.075	1.139	1.209	1.284	1.367	1.458
8	$R_{3}^{b}$	. 142	. 129	. 121	. 116	. 113	. 113	.114
9	$1 - \eta^2$	.999	. 998	. 998	. 997	. 996	.994	. 992
$ {}^{a} R_{\rm PX} = \left( (\partial n / \partial m_{\rm BX}) (dm_{\rm BX} / dx)_{\rm B} - (dn / dx)_{\rm b} \right) \left/ \left( \frac{\partial n}{\partial m_{\rm PX}} \right) \frac{dm_{\rm PX}}{dx} $								

$$R_3 = \left( (\partial n/\partial m_3) (\mathrm{d} m_3/\mathrm{d} x)_{\mathrm{a}} - (\mathrm{d} n/\mathrm{d} x)_{\mathrm{b}} \right) \left/ \left( \frac{\partial n}{\partial m_2} \right) \frac{\mathrm{d} m_2}{\mathrm{d} x}.$$

1,070 were determined from the computed values of  $m_P vs. x$  for the rather extreme conditions of case 1, Table I, in good agreement with the original parameter 1,000. However, to apply equation 22, one needs, in addition to z, the weight concentration as a function of x and  $M_{PX_2}$ , to obtain  $(m_{PX_2} - (m_{PX_2})_0)$  from the difference in weight concentrations. Since these quantities are the objectives of the investigation, an iterative procedure is implied. Of the difficulties discussed in Section 5b, only the first two are considered in Lamm's equation. In addition, those difficulties which are peculiar to measurement of refractive index gradients were not resolved by Lamm, although strongly pointed out.

5d. Alternate Definition of Components.—Definition of the polymer component as component 2, though originally mainly introduced to provide a polymer component with one mole of particles per mole of component, was shown in Section 3 to be a convenient device for simplifying interpretation of ultracentrifugations. Thus, component 2 has the molecular weight observable at infinite dilution. Further, this device has led to the equation of Lamm with only two approximations, which usually introduce only a small error:

(1) The neglect of  $\eta^2$  in comparison with unity (see row 9, Table II).

(2) The neglect of d ln  $m_3/d(x_2)$  in comparison with d ln  $m'_2/d(x^2)$ . Values of these quantities are, for case 1, 0.0092 and 0.0723, respectively, at x =6.6. The error in  $M_{PX_2}$  is smaller than indicated by the difference between these numbers since d ln  $m_3/d(x^2)$  only modifies a correction term.

These approximations are also made in equation 29, where however the concentration parameters are in terms of "observed" refractive index gradients,  $dn^*/dx$ . The resulting errors were shown qualitatively to be smaller or more amenable to reduction by iteration than for the component PX<sub>z</sub>. A quantitative discussion of the implied additional approximations follows for case 1.

(1) The distribution of supporting electrolyte

was assumed not to be disturbed by the polymer. Comparison of rows 3, 4 and 7, Table II, shows that  $(dn/dx)_{b}$  is much closer to  $(\partial n/\partial m_{3})$   $(dm_{3}/dx)_{a}$  than to  $(\partial n/\partial m_{\rm BX})$   $(dm_{\rm BX}/dx)_{\rm a}$  and similarly comparison of rows 5 and 8 shows that the error relative to the refractive index gradient of the polymer component is much smaller for  $PX_{z/2}B_{-z/2}$  than for  $PX_{z}$ . Thus the quantity  $dn^*/dx$  is much closer to (2m/2m)/(dx)/(dx) $(\partial n/\partial m_2)$   $(dm_2/dx)$  than to  $(\partial n/\partial m_{PX_2})$   $(dm_{PX_2}/dx)$ dx). If separate data of refractive index as a function of concentration were available, the alternate definition of components is particularly advantageous. Without such data, the constancy of this relative error with x (rows 5 and 8) is of interest. It indicates that even in this extreme case d ln  $(dn^*/$ xdx/d( $x^2$ ) = d ln ( $dm_2/xdx$ )/d( $x^2$ ) is a good approximation.

(2) The error in the substitution of d ln  $(dm'_2/xdx)/d(x^2)$  for d ln  $m_2'$  is the same as in the analogous substitution for component PX<sub>z</sub>, since  $m_2 = m_{PX_z}$ . For case 1 the values are 0.0546 and 0.0723, respectively, but with this definition of components an iteration loop including equation 20a will eliminate the error.

To summarize, the determination of the degree of polymerization N cannot be accomplished independently of the charge z'. However, for any assumed value of z', N can be determined by an iterative procedure starting perhaps with equation 29, and the various approximations can be eliminated to any extent desirable. For a unique solution, experiments performed under different conditions of polymer concentration, supporting electrolyte concentration, molecular weight of the supporting electrolyte, or speed of rotation are necessary. In principle, one centrifugation is sufficient, since a range of polymer concentrations is obtained. In practice, two or more experiments will probably be required and with an iterative procedure one can then select best values of N and z'. Thus a complete solution limited only by the adherence of the physical system under study to the limitations of this discussion can be obtained.

#### THE VAPOR PRESSURE OF ACETIC ACID AND ACETIC-d<sub>3</sub> ACID-d. THE LIQUID DENSITY OF ACETIC-d<sub>3</sub> ACID-d

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The vapor pressures of CH<sub>3</sub>COOH and CD<sub>3</sub>COOD have been measured by a static method from 25 to 125° and the data fitted to an Antoine equation. The liquid density of CD<sub>2</sub>COOD has been measured in the same temperature range and the data fitted to a cubic function of the temperature.

In the course of a study in this Laboratory on the vapor density of CD<sub>3</sub>COOD, it became necessary to know the vapor pressure and liquid density of this substance over a considerable range of temperature. Data available<sup>2,3</sup> on the vapor pressure of CD<sub>3</sub>COOD are discordant, and having been determined by comparison with CH<sub>3</sub>COOH, depend on a knowledge of the vapor pressure of the ordinary acid. The vapor pressure of ordinary acetic acid itself does not seem to be accurately known, however, as normal boiling points reported in the literature, 4-6 range from 117.75 to 118.6°. It was therefore decided to remeasure the vapor pressure of CH<sub>3</sub>COOH as well. This article reports the results of these measurements together with measurements of the density of liquid  $CD_3COOD$ .

Acetic-d<sub>3</sub> Acid-d.<sup>2,3</sup>—Thirty-five grams of Materials. carbon suboxide,<sup>7</sup> prepared from diacetyl tartaric anhydride and purified by several bulb-to-bulb distillations in vacuo, were introduced into a vacuum system and condensed by liquid air into a 500-cc. reaction tube equipped with a breakliquid air into a buo-cc. reaction tube equipped when a break able joint. The tube was then charged with 300 cc. of CCl<sub>4</sub> and 20 g. of 9.5% D<sub>2</sub>O, and sealed off under vacuum with the contents frozen.<sup>8</sup> The reaction tube was allowed to warm to room temperature and shaken for 48 hours. The reaction proceeded smoothly with no parasitic decom-position of the carbon suboxide. The tube was then sealed to the vacuum line through the breakable joint, the solvent distilled out, and the remaining malonic  $d_2$  acid  $d_2$  baked under vacuum for one hour at 100°. The temperature was then raised to 160° for decarboxylation, the resulting CD<sub>3</sub>-COOD being collected in a Dry Ice trap. The crude acid COOD being collected in a Dry Ice trap. The crude acid was distilled twice through a Piros-Glover microstill operat-ing at about 25 theoretical plates and then fractionally crystallized three times. The melting point remained at  $15.92 \pm 0.07^{\circ}$  after the last two fractional freezings. The final yield was 18 g. of acetic- $d_3$  acid-d (53% based on the carbon suboxide). Mass spectrographic analysis of a sample of hydrogen prepared by reaction of the acid with magnesium showed a deuterium content of 95%  $\pm 3\%$ . Acetic Acid — Beagent grade acetic acid was fractionally

Acetic Acid.—Reagent grade acetic acid was fractionally crystallized twenty times. The melting point of the final residue was  $16.54 \pm 0.07^{\circ}$ , and it was used without further purification.

Both materials were stored under vacuum in tubes equipped with several breakable joints for removal of partial samples.

Vapor Pressure.-Vapor pressures were measured by the simple static method. The pressure exerted by acetic acid vapor in equilibrium with liquid acetic acid was observed on a manometer connected to the vapor chamber.

(2) C. L. Wilson, J. Chem. Soc., 492 (1935).

(3) J. O. Halford and L. C. Anderson, J. Am. Chem. Soc., 58, 736 (1936).

(4) N. Alpert and P. H. Elving, Ind. Eng. Chem., 41, 2864 (1949).

(5) R. R. Dreisbach and S. A. Schrader, ibid., 41, 2897 (1949).

(6) W. Ramsay and S. Young, J. Chem. Soc., 47, 640 (1885).

(7) C. D. Hurd and F. D. Pilgrim, J. Am. Chem. Soc., 55, 757 (1933). (8) Prof. J. O. Halford in a private communication has called the authors' attention to the explosion hazard involved if this reaction is not carried out at high dilution. Heavy-walled bomb tubing should be used and the concentration of C<sub>1</sub>O<sub>2</sub> should not exceed 1.5 molar.

To avoid distillation of acetic acid from the hot vapor chamber to the cold manometer, a small differential manometer was interposed between them. In our adaptation, the sample bulb is connected to a small mercury manometer. Both are contained in a thermostated oil-bath having a plate glass window through which the manometer may be observed. The small manometer is connected to a large manometer outside the oil-bath by a tube fitted with a 3-way stopcock. As the bath is coming to temperature, the pressure in the connecting tube between the manometers is regulated, by pressure or vacuum connections to the stopcock, so that the mercury in the two arms of the small manometer remains at about the same level. A half hour at constant temperature was found sufficient for attaining vapor-liquid equilibrium. The small manometer is read by a telescopic cathetometer outside the bath. The large manometer is read by a steel scale graduated in 0.5 mm., readily estimated to 0.1 mm. by a parallax-eliminating mirror-reading device. Both manometers were constructed of 22 mm. i.d. tubing, large enough to eliminate errors aris-ing from differences in capillary depression and meniscal shape. A small amount of sample always distilled from shape. A small amount of sample always distilled from the sample bulb to the mercury surface in the small manometer during the runs. Manometer measurements were corrected for the weight of this layer which never amounted to more than 0.2 mm. mercury equivalent. The total pressure in the sample bulb was obtained as the algebraic sum of the two manometer heights and was reduced to mm. of mercury at 0° and normal gravity. Corrections for the vapor pressure of mercury were applied where necessary. The constant temperature bath was regulated by a con-

tinuously operating electronic control and was reliable to within 0.01° at all temperatures at which measurements were made. Temperatures were measured by means of a platinum resistance thermometer calibrated by the National Bureau of Standards.

The entire apparatus was tested by measuring the vapor pressure of water up to 100°. The results obtained showed an average deviation of less than 0.25 mm. from the values given by Osborne and Meyers.<sup>9</sup>

Vapor pressures of the two acids were obtained by successive equilibrations at a series of six to twelve temperatures, each higher than the preceding, and then spotting in about an equal number of points at decreasing temperatures in the same range. Self-consistency between both sets of readings was taken as indicating that equilibrium was reached. At the conclusion of such a run, about 80% of the sample in the bulb was distilled out through the attached breakable seal and sealed off. A new series of vapor pres-sures was taken on the remaining 20%. Consistency of the observed vapor pressures between the 20% sample and the total sample was taken as indicative of the purity of the sample and of the absence from the system of permanent gases. The vapor pressures observed for  $CH_3COOH$  and  $CD_3-COOD$  are listed in Tables I and II.

On fitting to an Antoine equation in the form

$$\log P_{\rm mm} = A - B/(C+t)$$

the following values were obtained

	CH3COOH	$CD_3COOD$
$\boldsymbol{A}$	7.4275	7.4397
В	1558.03	1556.17
C	224.79	224.82

for pressures expressed in mm. of Hg. The tables

(9) N. S. Osborne and C. H. Meyers, J. Research Natl. Bur. Standards, 13, 1 (1934).

<sup>(1)</sup> To whom inquiries concerning this article should be addressed: Department of Chemistry, Miami University, Oxford, Ohio.

	VAPOR PRESSURE	OF ACETIC ACIE	)
°C.	Obsd. vapor Total sample	pressure, m.m. 20% sample	Calcd. vap. press.
29.80	20.0		20.3
40.25	35.2		35.3
51.08	60.1		60.1
55.54	74.1		73.9
60.93	94.5		94.1
65.50		115.0	114.8
71.04	145.1		144.7
75.50		173.3	173.3
80.41	210.3		210.2
85.69		256.7	256.6
90.59	307.0		307.1
95.66		367.4	367.7
100.29	431.2		431.2
105.45		512.4	512.4
110.00	594.0		593.9
115.12		697.5	697.9
118.41	772.4		772.2
122.44		871.1	871.8
1 <b>2</b> 3.86	9 <b>0</b> 9.5		909.5
126.45		980.1	981.0

TABLE I

#### TABLE II

D----

	VAPOR FRESSURE OF ACETIC-a <sub>3</sub> ACID-a	
°C.	Obsd. vapor pressure, mm. Total 20% sample sample	Calcd. vap. press.
24.34	15.6	15.6
30.42	22.0	22.0
40.27	37.1	37.1
50.27	60.7	60.7
55.39	77.1	77.1
60.04	94.8	94.8
60.06	95.1	94.9
65.11	118.2	118.1
69.85	144.2	144.2
74.83	176.6	176.4
75.32	179.6	179.8
80.18	217.0	217.5
84.82	258.8	259.4
89.92	312.8	312.9
90.10	315.2	314.9
94.95	374.0	374.3
99.89	443.8	443.8
103.97	508.9	509.0
104.73	522.0	521.9
109.80	615.3	615.4
114.59	715.3	715.8
114.86	721.0	721.8
116.61	761.3	761.9
118.88	815.7	816.6
119.52	832.3	832.4
121.21	876.0	876.0
122.44	908.7	908.8
1 <b>24</b> .39	962.3	96 <b>2</b> .4

also give the vapor pressures calculated from these equations for the temperatures observed. The average deviation observed from calculated values is less than 0.25 mm. The computed normal boiling points are: for CD<sub>3</sub>COOD, 116.53°; for CH<sub>3</sub>COOH, 117.89°. The uncertainty in both boiling points, estimated by a propagation of the average deviation in vapor pressure, is  $\pm 0.01^{\circ}$ .

It is of interest to compare the vapor pressure difference (CH<sub>3</sub>COOH minus CD<sub>3</sub>COOD) obtained by the differential method employed by Wilson<sup>2</sup> and Halford and Anderson<sup>3</sup> with that obtained by subtracting the independent measurements of this research. Table III lists the vapor pressure difference obtained by these authors at a number of temperatures compared with corresponding data from the present research.

# TABLE III

Difference	IN	VAPOR	Pressure	OF	Ordinary	AND
	De	UTEROA	CETIC ACID I	N MI	м.	
		VD of C	H COOH	N N	P of CD COC	חו

	V.P. of CH <sub>3</sub> C	OUH minus V.P. c	
°C.	Wilson <sup>2</sup>	According to Halford- Anderson <sup>3</sup>	This research
21.0	0.7	0.6	0.7
35.8	1.6	0.9	1.1
41.7	2.1	1.3	1.8
48.6	2.9	1.8	<b>2.5</b>
54.6	3.7	2.4	3.2
59.7	4.7	2.8	4.1
65.9	6.0	3.4	5.6
74.3	8.3	4.7	7.2
83.6	11.8	6.5	10.4

The results of this research fall everywhere between those of the earlier authors. Halford and Anderson stated in effect that they were uncertain of the adequate purification of their material. They do not report the deuterium content of their deuteroacid. Wilson reports a m.p. of  $15.75^{\circ}$ for his deuteroacid compared to  $15.92^{\circ}$  for ours. Our acid, known to contain 95% deuterium melts  $0.68^{\circ}$  lower than the ordinary acid. Since CD<sub>3</sub>-COOD and CH<sub>3</sub>COOH surely form solid solutions, it seems unlikely that an additional 5% of deuterium would lower the m.p. by as much as  $0.17^{\circ}$ more. There is thus considerable reason to believe that Wilson's acid was less pure than ours.

Attempts were made to prepare  $CH_3COOD$ for a study of its vapor pressure. The most successful method was similar to that employed by Engler,<sup>10</sup> and involved the hydrolysis of  $CH_3COCl$ with D<sub>2</sub>O, followed by treatment of the crude hydrolysate with  $CH_3COOAg$  in order to remove dissolved DCl.

Lewis and Shutz<sup>11</sup> failed to find evidence of methyl-carboxyl hydrogen exchange in CH<sub>3</sub>COOD, but later work by Herman and Hofstadter<sup>12</sup> indicates that exchange may occur. In view of the conflicting evidence it was thought advisable to investigate the possibility of exchange before proceeding with the vapor pressure measurements.

The infrared spectrum of one portion of a sample of  $CH_3COOD$  was obtained. Another portion of the same sample was sealed in a glass tube, held at 100° for two days, and then examined by the infrared spectrometer. Parts of the resulting spectra are reproduced in Fig. 1. Comparison of the two spectra shows an unequivocal increase in absorption in the O-H\*\*O region and decrease in the O-D\*\*O region. W. C. Child of this Laboratory has

(10) W. Engler, Z. physik. Chem., B32, 471 (1936).

(11) G. N. Lewis and P. W. Shutz, J. Am. Chem. Soc., 56, 493 (1934).

(12) R. C. Herman and R. Hofstadter, J. Chem. Phys., 6, 538 (1938).



Fig. 1.—Part of the infrared spectrograms of fresh "CH<sub>3</sub>-COOD" and the same material heated in glass at 100° for two days. The principal bonds ascribed to hydrogen bond and deuterium bond absorption are marked. The decrease in hydrogen bond and increase in deuterium bond absorption on heating indicates an exchange between methyl hydrogen and carboxyl deuterium.

carried out a similar experiment using  $CH_3CH_2$ -COOD with similar results.

Apparently then there is no stable compound of formula  $CH_3COOD$  under the conditions obtaining in our vapor pressure apparatus, and the question of its vapor pressure has no clearly definable meaning. No attempt was made to investigate the exchange equilibrium nor to make measurements of vapor pressure on the equilibrium mixture.

**Liquid Density.**—The liquid density of CD<sub>3</sub>-COOD was measured using a weight dilatometer similar to that of Gibson and Loeffler,<sup>13</sup> but dif-

(13) R. E. Gibson and O. H. Loeffler, J. Am. Chem. Soc., 61, 2515 (1939).

fering from the cited design in having its only opening through the capillary tip. The thermal expansion and volume of the dilatometer were determined by a calibration run using water. The observed liquid densities are shown in Table III.

TABLE	III
<b>T</b> 1 <b>N N N N</b>	***

LIOUID ]	DENSITY	OF	ACETIC-d <sub>3</sub>	ACID-d
----------	---------	----	-----------------------	--------

°C	Density, Obsd.	g /cc. Calcd.	Temp., °C.	Density, Obsd.	g./cc. Calcd.
28.70	1.1091ª	1.1091	74.80	1.0528	1.0528
29.86	1.1075	1.1077	79.77	1.0466	1.0467
34.84	1.1013	1.1016	84.98	1.0402	1.0402
39.75	1.0956	1.0955	89.90	1.0340	1.0341
44.52	1.0898	1.0897	94.85	1.0278	1.0279
49.81	1.0833	1.0833	99.98	1.0213	1.0213
54.85	1.0772	1.0772	105.05	1.0148	1.0149
59.40	1.0716	1.0717	109.51	1.0090	1.0091
64.77	1.0650	1.0651	113.32	1.0041	1.0042
69.88	1.0588	1.0588			

<sup>a</sup> Determined independently by pycnometer.

The above data were fitted to a cubic polynomial in temperature ( $t = {}^{\circ}C$ .) by means of least squares, the result being

$$\frac{1.1450 - (1.2807 \times 10^{-3})t + (1.218 \times 10^{-6})t^2 - (7.84 \times 10^{-9})t^2}{(7.84 \times 10^{-9})t^3}$$

with an average deviation of  $0.7 \times 10^{-4}$  g./cc. The densities calculated from this equation are also listed in Table III.

Acknowledgment.—The authors wish to express their appreciation to R. H. Burris for carrying out the mass spectrographic analyses, to W. C. Child for testing the vapor pressure apparatus by measurement of the vapor pressure of water, and to D. W. Johnson for measuring the infrared spectra. We are indebted to E. I. du Pont de Nemours and Co., Inc., for financial aid.

# THE STANDARD POTENTIAL OF SILVER–SILVER CHLORIDE ELECTRODE IN ETHANOL

# By L. M. MUKHERJEE

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The standard potential of silver-silver chloride electrode in spectroscopically pure and dry ethanol has been determined with the help of two types of cells without junction, one of which involves a metallic contact. The value +0.00977 volt of the potential (in molar scale) so obtained for the reaction AgCl  $+ 0.5H_2 \rightarrow Ag + Cl_{EtOH}H^+_{EtOH}$ , not only differs in magnitude but also in sign from those reported by previous workers. The discrepancy is perhaps ascribable to the presence, however small, of accidental impurities and/or moisture in the alcohol. In the spectroscopically pure alcohol used in this work the presence of the above was scrupulously guarded against.

#### Introduction

Suitable reference electrodes for electro-chemical work in the non-aqueous solvents offer special problems and hence they cannot be easily made. In this paper, silver-silver chloride electrode has been used as a reference in connection with certain measurements in ethanol as solvent. For this purpose, its standard potential in this medium in terms of hydrogen electrode as zero, was determined. The value so obtained has been compared with those reported by previous workers.  $1-\delta$ 

Apparatus and Method.—The following two types of cells were set up: Cell A.

Pt, H<sub>2</sub>; HCl/EtOH; AgClAg+

- (2) H. S. Harned and M. H. Fleysher, ibid., 47, 82 (1925).
- (3) J. W. Woolcock and H. Hartley, Phil. May., [7] 5, 1133 (1928).

<sup>(1)</sup> P. S. Danner, J. Am. Chem. Soc., 44, 2832 (1922),

Nov., 1954

$$\begin{split} E^{\circ} &= E_{\rm obs} + 2k \log C - \frac{2ku\sqrt{2C}}{1 + A\sqrt{2C}} - \\ 2k \log \left(1 + 0.07034C\right) + \frac{2k}{2.303} \left[ \left(\frac{\epsilon^2 z^2 N}{DRTa}\right)^3 \left(\frac{1}{2} x_{\rm S(ka)} - 2Y_{\rm S(ka)}\right) + \left(\frac{\epsilon^2 z^2 N}{DRTa}\right)^5 \left(\frac{1}{2} x_{\rm S(ka)} - 4Y_{\rm S(ka)}\right) \right] \end{split}$$

and Cell B4

C.,

$$E_{\text{obs}} = \Delta E^{\circ} + 2k \log \frac{C_{\text{HC1/3tOH}}}{C_{\text{HC1/3t20}}} + 2k \log \frac{I \pm \text{HC1/2tOH}}{Y_{\pm \text{HC1/H20}}}$$

where  $E^{\circ}$  is the standard reduction potential of the silver-silver chloride electrode and  $\Delta E^{\circ}$  represents the difference in the standard potentials of this electrode in water and ethanol. All other symbols in the above equations are the same as those used by Harned and Owen.<sup>5</sup>

The alcohol used was purified by refluxing commercial rectified spirit twice over pure NaOH; the distillate was then subjected to a short reflux over pure Na metal and subsesubjected to a short find over point we have a paratus having CaCl<sub>2</sub> guard tubes.<sup>6</sup> The e.m.f.'s were recorded at  $35 \pm 0.25^{\circ}$  with the help of a Leeds and Northrup type-K potentiometer in combination with a Hartmann and Braun galvanometer. The hydrogen electrode assembly consisted of a platinum foil coated with platinum black, and cautiously purified electrolytically prepared hydrogen gas (  $p \sim$ 1 atm.). The train of purifiers includes a heated copper gauze, lead acetate solution, concd. NaOH soln., concd.  $H_2SO_4$  and finally, purified alcohol. The silver-silver chloride electrode was prepared by the method of Noyes and Ellis' using aqueous and non alcoholic solutions as was done by Nonhebel and Hartley.<sup>8</sup> Before use the electrodes were checked in 0.1 N aqueous KCl solution and the pair of elec-trodes used in cell B was tested for zero e.m.f.; the hydrogen electrodes used in this cell was vere purified simultaneously to secure uniformity. For use in alcoholic systems, the electrodes were washed thoroughly with alcohol.

Solutions of HCl in ethanol were prepared by absorbing in the solvent, in almost complete absence of air, HCl gas obtained by treating G.R. quality NaCl (E. Merck, oven-dried at 105–110°) with concd.  $H_2SO_4$  and dried by passing through concd.  $H_2SO_4$ . Solutions of high concentrations, e.g., I to 2 molar, often give out fumes of HCl and are, therefore, unsuitable. The present work covers a range of concentrations from 0.000084 to 0.13018 molar. The experimental solutions were prepared by proper dilution with alcohol of the stock solution of HCl. The latter was standarchield by taking aliquot portions of rICI. The latter was stand-ardized by taking aliquot portions of it in water or in a known excess of aqueous KOH solution and then titrating the solu-tions thus obtained either pH-metrically or volumetrically using phenolphthalein, against aq. KOH or aq.  $H_2SO_4$  as the case may be. The concentration of the solutions has been calculated in terms of molerity and not moleility as the been calculated in terms of molarity and not molality, as the latter involves a precise knowledge of the density of the solutions.

**Results and Discussions.**—The value, +0.00977volt (see Table I), obtained as the standard potential of silver-silver chloride electrode in molar scale, *i.e.*, +0.02190 volt in molal scale, in ethanol was computed by the extrapolation procedure outlined by Harned<sup>9</sup> with the help of the extended form of Debye-Hückel equation<sup>10</sup> for activity co-effi-The latter is supposed to provide correccient.

(4) F. Daniels, "Outlines of Physical Chemistry," 7th Ed., John Wiley and Sons, Inc., New York, N. Y., 1950, p. 471.

(5) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Am. Chem. Soc. Monograph Series, Reinhold Publ. Corp., New York, N. Y., 1943.

(6) L. M. Mukherjee, Science and Culture (India), 19, 314 (1953).

(7) Arthur A. Noyes and J. H. Ellis, J. Am. Chem. Soc., 39, 2532 (1917).

(8) G. Nonhebel and H. Hartley, Phil. Mag., [6] 50, 729 (1925). (9) H. S. Harned, J. Am. Chem. Soc., 60, 33€ (1938)

(10) T. H. Gronwall, V. K. LaMer and K. Sandved, Physik Z., 29, 358 (1928)



Fig. 1.—Mean activity of HCl aq. used = 0.0975.

tions for all the probable complications such as the large and specific salt effects owing to the low dielectric medium used in the present study. The value of a as finally chosen by trial to fit the condition of extrapolation comes out to be 6.2 Å. which is somewhat different from the value 5.9 Å. employed previously for extrapolation with the help of a less comprehensive equation for activity co-efficient, viz.

$$\log y_{\pm} = -\frac{1}{2.303} \frac{u\sqrt{2}\sqrt{C}}{1 + A\sqrt{2}\sqrt{C}} - \log\left(1 + 0.07034C\right)$$

The actual magnitude and sign of the standard potential of silver-silver chloride electrode obtained in this work are not in accord with that reported by Woolcock and Hartley<sup>3</sup> who realized the same to be  $-0.0883 \pm 0.0003$  volt. The results of Harned and Fleysher<sup>2</sup> also differ from the value re-corded in this paper. The negative sign attached to their value suggests the electrode process (AgCl + $e^- \rightarrow Ag + \widetilde{Cl}^-$  to be non-spontaneous. This is difficult to explain and could not be confirmed in the present set of measurements. Moreover, a cell of the type Ag-AgCl, 0.1 N LiCl/EtOH; Hg<sub>2</sub>Cl<sub>2</sub>-Hg was found to register an e.m.f. of +0.04750 volt (at  $25^{\circ}$ ), *i.e.*, the value expected for the same set up in aqueous solution, assuming, of course, that the nature of the electrode process and the sign of the standard potentials of the respective electrodes, *i.e.*, Ag–AgCl and Hg–Hg<sub>2</sub>Cl<sub>2</sub>, remain the same as in water.

In connection with the present work it was observed that reproducible and steady values of e.m.f. could be secured if and only when the samples of alcohol used were almost the same in quality. The purity and dryness were tested by means of ultra-

	TABLE I <sup>a</sup>	
HCl/EtOH conen., M	E.m.f. obs. (v.) cor. to one atm. Hydrogen press. (ref. cell A)	Mean activity coeff. of HCl ± <i>i.e.</i> , in molar scale
0.000084	0.50820	0.9890
.000149	. 47955	.9541
.000771	. 39620	. 8890
. 001030	.38175	.8751
.001290	.37100	.8539
.001780	. 35700	. 8061
.003530	. 32500	.7431
.006154	. 29920	. 6946
.009070	.27940	.6878
.011834	. 27035	.6194
.015130	.26590	. 5316
.021790	.24395	. 5520
.037241	. 22160	.4975
.037400	. 22105	. 4958
.065090	. 19555	. 4607
. 130180	. 16320	. 4234
<b>n</b> o : ,		

 ${}^{a}E^{\circ}$  in molar scale (ref. cell A) = +0.00977 volt;  $E^{\circ}$  in molar scale (ref. cell B; see fig. 1) = +0.21245 volt.

violet spectrophotometry which was adopted throughout as a routine.<sup>6</sup> It is not unlikely that the reported discrepancies might be attributable to alcohol whose quality was not rigorously defined by the previous workers. The influence of traces of water in alcohol often referred to by some workers as the cause of the observed discrepancies was also looked into. It has been shown that about 0.02 molar solution of HCl in ethanol could retain up to about 1.3% by vol. of water without any noticeable change in the observed e.m.f.; solutions of lower concentrations are, however, much more sensitive to addition of water.

**Conclusion.** 1. The standard reduction potential of silver-silver chloride in ethanol is found to be +0.00977 volt in molar scale (*i.e.*, +0.02190volt in molal scale), the nature of the electrode process, as suggested thereby, is in agreement with that in aqueous medium, viz., AgCl  $+ \epsilon \rightarrow Ag +$ Cl<sup>-</sup>. 2. The experimental value of mean activity co-efficients of HCl in alcoholic solutions have been correlated with the Debye-Hückel equation taking into account the extended terms introduced in it. 3. Reproducibility and steadiness of the e.m.f. values of such systems seem to depend primarily on the state of purity and dryness of the medium which must be rigorously defined.

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# OXYGEN TRANSFER BETWEEN CARBON DIOXIDE AND CARBON MONOXIDE IN THE PRESENCE OF CARBON

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Radioactive carbon,  $C^{14}$ , was used as a tracer to study oxygen transfer reactions between  $CO_2$  and CO in the presence of different carbons in the temperature range from 650 to 900°. The reaction was dependent as much upon the physical state of the "carbon" as upon composition and the presence of catalytic agents. Oxygen transfer, between carbon and oxidizing and reducing gases, is a probable reaction step in the gasification of carbon that explains many observations of the kinetics of the gasification reaction. The tracer technique is discussed as a tool for testing theories on the mechanism of these reactions between gases and solids.

Adsorption and degassing experiments<sup>2</sup> show that carbon adsorbs oxygen in chemically bonded structures that decompose upon heating to liberate oxides of carbon. It has been found that a degassed sugar carbon reduces carbon dioxide to carbon monoxide at 600°, the extra oxygen of the dioxide remaining on the carbon.<sup>3</sup> Experiments in flowing systems have shown that carbons, previously reduced in a stream of hydrogen, have a limited capacity at about 600° for reducing carbon dioxide to carbon monoxide and that the oxygen deposited on the carbon can be removed by a stream of hydrogen to form water.<sup>4</sup> Radioactive

(3) A. F. Semechkova and D. A. Frank-Kamenetsky, Acta Physicochim., U.R.S.S., 12, 879 (1940).

(4) J. D. F. Marsh, Inst. Gas Engrs., Commun. No. 393, 1951.

carbon has been used as a tracer to show that, when carbon dioxide is reduced by carbon, the carbon of the dioxide remains in carbon monoxide in the gas phase.<sup>5</sup>

These observations show that carbons react with oxidizing and reducing gases to form, or to remove, chemically bonded oxygen on the carbon surface. These reactions occur at measurable rates at temperatures below those required for the breakage of carbon to carbon bonds in the gasification reaction so that the oxygen transfer reactions involved in the oxidation and reduction of the carbon surface may be studied under such conditions that there is negligible complication resulting from simultaneous gasification reactions. Availability of a radioactive tracer,  $C^{14}$  in  $CO_2$ , enabled measurement of rates of oxygen transfer between  $CO_2$  and CO over carbon in a system at

(5) F. Bonner and J. Turkevich, J. Am. Chem. Soc., 73, 561 (1951).

<sup>(1)</sup> Explosives Department, E. I. du Pont de Nemours & Co., Gibbstown, N. J.

<sup>(2)</sup> H. H. Lowry and G. A. Hulett, J. Am. Chem. Soc., 42, 1408 (1920).

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dynamic equilibrium so that interpretation of data would not be complicated by effects of heat release or of changes in gas composition. Study of these oxygen transfer reactions was considered important because of their relation to the gasification of solid fuels, a process of increasing importance for the production of synthesis and fuel gases.

#### **Apparatus and Procedure**

Apparatus consisted of equipment for flowing various proportions of carbon dioxide and carbon monoxide through a bed of granular carbon and for estimating the proportions of radioactive carbon in the components of effluent gas. Radioactivity measurements were made on the gas samples by use of a mica window Geiger-Mueller counter, Victoreen V.G. 10A, with a 2.5 mg. per cm.<sup>2</sup> window. The gas flowed through a cylindrical cell,  $1^{3}/_{8}$  in. in diameter and  $1^{1}/_{8}$  in. deep, under the counter window.

<sup>1</sup>/<sub>8</sub> in deep, didd the control window. Radioactive carbon dioxide was made by decomposition of barium carbonate with lead chloride.<sup>6</sup> The barium carbonate, containing C<sup>14</sup>, was obtained from the Isotopes Division, U. S. Atomic Energy Commission. One millicurie of the carbonate was sufficient, diluting with non-active carbon dioxide, to produce 250 l. of carbon dioxide giving about 3000 counts per minute.

The sample of carbon, 7 g. nominal weight and sized between 8 and 20 mesh U. S. Standard sieves, was held in a  $1/2^{"}$  i.d. Vycor tube set vertically in an electrically-heated furnace. A packing of crushed porcelain and quartz wool served as a sample support and to preheat the entering gas. Temperature was measured by a thermocouple set in the middle of the bed. Calibration indicated constant temperature within  $\pm 2^{\circ}$  throughout the bed.

The sample was preconditioned in non-radioactive gas for three hours under the temperature, gas composition and flow conditions of the experiment. A gas flow of 34 cc. per minute, N.T.P., was used except as otherwise indicated. After preconditioning, gas containing carbon dioxide tagged with C<sup>14</sup> was substituted for the non-active gas. When radioactivity measurements on the entering and effluent gas streams indicated complete flushing of the system, counting rates on effluent gas, before and after removal of CO<sub>2</sub>, were made to determine the distribution of radioactive carbon.

Analysis of Data.—Analysis of the data required quantitative relations between counts per unit time and the specific radioactivity and concentration of tagged components. Calibration experiments showed that, under the conditions of the present investigation, dilution at constant pressure with inactive  $CO_2$ , CO or  $N_2$  reduced the number of counts per minute in proportion to the ratio of the original to the new volume. Some deviation from this relation might have been expected,<sup>5.7</sup> but none was observed. Specific radioactivities of individual gas components were calculated from observed numbers of counts per minute, on the basis of inverse proportionality with the volume of diluted gas, as the number of counts per minute above background that would have been observed had the counting cell been filled at normal temperature and pressure with the given component alone.

The gas metered into the reaction system had radioactive carbon in the carbon dioxide only. No significant amount of radioactivity was found on the solid carbon following an experiment and the specific radioactivity of the effluent gas was the same as that of the entering gas as long as the temperature was low enough so that gasification was negligible. Exit gases were found to have radioactivity in both the carbon dioxide and the

(6) N. Zwiebel, J. Turkevich and W. W. Miller, J. Am. Chem. Soc., 71, 376 (1949).

(7) J. T. Kummer, Nucleonics, 3, 27 (1948).

carbon monoxide, the relative amounts depending on the carbon sample and experimental conditions.

These findings were consistent with an assumption that reaction occurred at the carbon surface as

$$\operatorname{CO}_2 \xrightarrow{1}{\swarrow} (0) + \operatorname{CO}$$

The symbol (O) is used to represent an atom of oxygen held on the carbon surface in a chemically bonded structure. For a given state of the solid surface the rates of the forward and reverse reactions are proportional to the partial pressures of the gases entering the reactions. These rates will be represented by  $k_1p_{CO_2}$  and  $k_2p_{CO}$ , respectively. Since the samples were brought to equilibrium with respect to oxygen transfer in the gas mixture to be used in each experiment, these rates were equal.

$$k_1 p_{\rm CO_2} = k_2 p_{\rm CO} \tag{1}$$

The radioactive carbon remained in the gas phase either in the carbon dioxide or the carbon monoxide. The sum of the partial pressures of these gases, each multiplied by its specific radioactivity, was the same for entering and effluent gases. The partial pressure of each gas component, multiplied by the ratio of specific radioactivities of the given component and the original carbon dioxide, was treated as the equivalent partial pressure of radioactive gas and will be designated here by an appropriate symbol with an asterisk. The conservation of radioactivity in the gas phase can be expressed with such symbols as

$$p_{\rm CO_2}^* + p_{\rm CO}^* = p_0^* \tag{2}$$

The transfer of radioactivity from the  $CO_2$  is a first-order process.<sup>8</sup> It satisfies a rate equation of the form

$$\frac{d(p_{CO_1}^*)}{d(W/F)} = -k_1 p_{CO_2}^* + k_2 p_{CO}^*$$
(3)

where the ratio, W/F, of sample weight to gas flow rate at the temperature and pressure of the experiment, is used as a measure of contact time.

Equations 2 and 3, when all of the radioactivity is initially in the  $CO_2$ , lead to the following solution

$$k_1 + k_2 = -(F/W) \ln \left\{ 1 - \frac{p_{\rm co}^*/p_0^*}{p_{\rm co}/p_0} \right\}$$
 (4)

The numerator of the last term in the logarithmic factor is the fraction of the total radioactivity found in the CO, while the denominator is the fraction of CO in the mixture of  $CO + CO_2$ , and hence the value toward which the numerator approaches with increasing time. Equations 1 and 4, giving the ratio and the sum of rate constants, were used to calculate the forward and reverse constants,  $k_1$  and  $k_2$ , respectively, from the gas composition and observed change in distribution of radioactivity.

Table I gives experimental data for various materials. Figure 1 shows the effect of gas composition and temperature upon the reaction rate for the high temperature coke listed in Table I. Figure 2 gives similar data for Graphite II.

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

TABLE I

 $k_2$ 

0.13

0.49

0.36

5.6

14.2

2.5

5.9

27.7

 $\begin{array}{c} 0 & 7 \\ 3 & 3 \end{array}$ 

	DATA	ON OXYGEN	TRANSFER
Material	Ash, %	Temp., °C.	Carbon monoxide, %
Porcelain		810	53
Porcelain		915	50
Graphite I	<0.005	900	56
Activated coccnut char	0.9	650	55
Activated coconut char	0.9	900	77
Coke	10.0	800	50
Leached coke		800	53
$Coke + 6\% K_2CO_3$		800	60
$Porcelain + 6\% K_2 CO_3$		800	55
$\rm Porcelain ~+~6\%~K_2CO_3$		900	55



Fig. 1.—The effect of gas composition and temperature upon the reaction rate for high temperature coke.

#### Discussion

Graphite I proved as unreactive as porcelain. Graphite II was equally pure but more reactive. The high temperature coke was more active than either graphite, but less active than an activated coconut char. Potassium carbonate, which is known to catalyze the gasification reactions, was added in amount of 6% by weight to the porcelain and the high temperature coke. Enhanced transfer rates were found. Iron is also known to catalyze the gasification reactions. A sample of the high temperature coke was treated with chlorine at  $620^{\circ}$ . Though considerable ferric chloride distilled from the coke, samples so treated appeared more active than the original coke. The chlorine must have had some effect other than removal of iron.

These data show that oxygen is transferred between carbon dioxide and carbon monoxide in a heterogeneous reaction at rates that depend upon the nature of the solid, upon the presence of catalytic agents, and upon the gas composition. The physical state of the carbon seems as important as chemical composition and catalysis. Graphite I was hard and gritty; Graphite II had a typically soft unctuous feel. The coke had a coarser pore structure than that of the graphites. Addition of 6% of potassium carbonate was more effective on the high temperature coke than on porcelain. The difference may be due either to differences in



F/W

8.8

9.7

11.2

16.2

16.2

17.5

17.0

17.2

8.7

9.6

(cc. g.  $^{k_1}$  min.  $^{-1}$ )

0.15

0.49

0.46

6.8

47.6

2.5

6.7

41.5

0.8

4.0

Fig. 2.—The effect of gas composition and temperature upon the reaction rate for Graphite II.

porosity or to an effect of carbon as the substrate. The ratio of the rate constants,  $k_1$  and  $k_2$ , is given by the ratio of partial pressures of CO and CO<sub>2</sub>, equation 1. The individual values depend further upon an effect of gas composition on the state of oxidation of the carbon surface. These constants are given in Figs. 1 and 2 for the high temperature coke and for Graphite II in various mixtures of CO and CO<sub>2</sub> and at various temperatures.

Data for the high temperature coke may be represented by the equations

$$k_1 = \dot{\kappa}_{10} e^{-43,100/RT} \tag{5}$$

and

$$k_{10} = 5.70 \times 10^9 p_{\rm CO} \tag{6}$$

where  $p_{CO}$  is measured in atmospheres. The lines drawn through the data of Fig. 1 are given by these equations. Data for graphite may be represented by the equations

$$k_1 = k_{10} e^{-58,900/RT} \tag{7}$$

and

$$k_{10} = \frac{1.86 \times 10^{12} p_{\rm CO}}{p_{\rm CO} + 1.91 p_{\rm CO_2}} \tag{8}$$

as shown in Fig. 2.

It may be assumed that the activity of the sample depends upon the activity of oxygen adsorbed upon its surface and upon the activity of surface available for oxidation. These activities may be assumed to be proportional to the fractions,  $\theta$  and  $1 - \theta$ , of surface or of active centers that are, or are not, occupied by chemically bound oxygen. Equation 1 then becomes

$$k_1'(1 - \theta)p_{\rm CO_2} = k_2'\theta p_{\rm CO} \tag{9}$$

$$k_1'(1 - \theta) = \frac{k_1' p_{\rm CO}}{p_{\rm CO} + (k_1'/k_2')p_{\rm CO_2}}$$
(10)

$$k_{2}'\theta = \frac{\kappa_{1}' p_{\rm CO2}}{p_{\rm CO} + (k_{1}'/k_{2}')p_{\rm CO2}}$$
(11)

If  $k'_1$  equals  $k'_2$ , equation 10 agrees with equation 6 for the coke when the sum of partial pressures of CO and CO<sub>2</sub> is 1 atmosphere. Equation 10 similarly agrees with equation 8 for the graphite if the ratio of  $k'_1$  to  $k'_2$  is 1.91.

The assumptions of equation 9 may be questioned in that different points, or active centers, on the surface of a solid may be expected to differ in activity. The assumed linear dependence of activity upon fractional coverage must be no more than a first approximation. Tracer techniques provide a tool for investigating such relationships. The present investigation confirms the approximate linear relationship, though it lacks the high precision needed to establish the exact form.

Evidence here reported and data of the present investigation show that gases, such as  $CO_2$  and  $H_2O$ , can bring about the oxidation of a carbon

surface and that such gases as CO and  $H_2$  can reduce the oxidized carbon surface. These reactions are measurably fast below temperatures needed for gasification of the carbon by the same oxidizing gases. The chemically-adsorbed oxygen weakens adjacent carbon to carbon bonds so that at higher temperatures thermal rupture of the weakened bonds liberates oxygen in combination with carbon. Reducing gases may hinder this gasification reaction since they preferentially remove the oxygen in a reduction reaction. Oxygen transfer also explains the approach to equilibrium, with respect to the water-gas shift, which is observed in the product of many gasification systems.

There is nothing in the experimental data that identifies oxygen, first placed upon the carbon by reduction of steam, with oxygen that later appears in the products of gasification obtained under conditions of high gasification rates. On the other hand, conventional treatment of heterogeneous reaction kinetics data involves approximations that limit discrimination between proposed reaction mechanisms. More critical examination with new tools and concepts will be needed to establish the reaction mechanism, but it should be recognized that oxygen transfer between carbon and oxidizing and reducing gases is a preliminary step that qualitatively, if not quantitatively, explains the kinetics of the gasification reactions.

# THE PREPARATION AND INFRARED SPECTRA OF THE OXIDES OF NITROGEN<sup>1</sup>

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Improved laboratory preparations of several oxides of nitrogen are described, convenient for accurate and quantitative preparation of pure samples. The analysis of mixtures of these compounds by infrared spectroscopy is discussed, with critical identification of the bands which are useful.

The many interesting reactions of the oxides of nitrogen have been the subject of study by numerous chemists since their discovery. During our investigation of the kinetics of some of their reactions,<sup>2</sup> we have found it necessary to prepare and purify a number of these materials. Moreover, since we use infrared absorption bands to follow the concentration of one or more of these compounds during the course of a reaction, we have been interested in their infrared spectra under various conditions.

Although many preparations can be found in the literature,<sup>3</sup> the oxides of nitrogen are not easy to obtain in known amounts and in a pure state free from water and other oxides of nitrogen. The

methods we describe in this paper have proved convenient and reliable, and should be useful to other investigators working with these compounds.

To use the infrared spectra of these molecules for identification or analysis, one needs reliable spectral data for each pure compound. In many cases these are available in the literature, but in some cases they are not. Particular care must be exercised because, in a mixture of these compounds (such as one usually encounters in kinetic studies), an absorption band of one molecule is frequently found overlapped by one of another molecule.

A brief discussion of the preparation of  $O_3$  and preparation and spectral properties of HNO<sub>3</sub> has been included. Ozone is used in the preparation of N<sub>2</sub>O<sub>5</sub>, and since a good deal of trouble is often experienced in removing the last traces of water in the N<sub>2</sub>O<sub>5</sub> preparation, the infrared spectrum of HNO<sub>3</sub> is of particular interest. Much of our work in the preparation of these compounds has

<sup>(1)</sup> This research was supported by the Bureau of Ordnance, U. S. Navy.

<sup>(2)</sup> G. R. Cowan, D. L. Rotenberg, A. Downie, B. Crawford, Jr. and R. A. Ogg, Jr., J. Chem. Phys., 21, 1397 (1953); R. E. Nightingale, G. R. Cowan and B. Crawford, Jr., *ibid.*, 21, 1998 (1953).
(3) D. M. Yost and H. Russell, Jr., "Systematic Inorganic Chemis-

<sup>(3)</sup> D. M. Yost and H. Russell, Jr., "Systematic Inorganic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1946.

been directed toward the removal and exclusion of water.

#### **Chemical Preparations**

All the oxides are prepared from commercially available tank gases on a vacuum line. Nitric oxide has been used as the basic starting material for all of the oxides discussed because its pressure can be measured with an ordinary mercury manometer. Once pure NO has been prepared,  $NO_2$ may be obtained quantitatively by reaction with  $O_2$ , and  $N_2O_5$  quantitatively by the oxidation of  $NO_2$  with  $O_3$ . Halocarbon grease<sup>3</sup> has proven to be the most satisfactory ubriaget for storage of a storage to be the most satisfactory

lubricant for stopcocks and ground joints in our vacuum system. Although it absorbs  $NO_2$  (and perhaps other gases) over a period of time, it has the advantage that it contains no hydrogen, and thereby cannot react to give water. Also, it does have fairly satisfactory mechanical properties.

properties. Nitric Oxide.—Commercial tank nitric oxide contains considerable amounts of  $N_2$ ,  $NO_2$ ,  $N_2O_3$  and  $N_2O$ . The first three of these are quite easily removed; nitrogen can be pumped off while the oxides are held at liquid nitrogen temperature, and NO<sub>2</sub> and N<sub>2</sub>O<sub>3</sub> can be removed by distillatemperature, and  $NO_2$  and  $N_2O_3$  can be removed by distilla-tion from a trap surrounded by solid  $CO_2$ , at which tempera-ture they have a negligible vapor pressure. Removal of nitrous oxide is more difficult, and there is no convenient way to separate it completely from nitric oxide. However, their boiling points are some 60° apart and fractionation is practical. We, in fact, fractionated two or three times and tent only the most weltile third of our existing applied kept only the most volatile third of our original sample. This procedure was possibly unnecessarily extravagant, but it did give a product in which the N<sub>2</sub>O pressure was reduced to less than 0.5% and which was sufficiently pure for our purposes.

The purified nitric oxide was a pale straw-green liquid which froze to a light grey-blue solid. Any small amount of N<sub>2</sub>O remaining was detected by the very intense infrared band at 2240 cm. -1

The fractionation was carried out on the vacuum line shown in Fig. 1, the procedure being as follows.



Fig. 1.—Apparatus for the purification of nitric oxide.

After the system has been evacuated down to the cylinder head, gas is let into the line up to stopcock 3 to about one atmosphere. Liquid nitrogen is then placed around C and 3 is opened. Most of the oxides condense rapidly, but the presence of nitrogen makes the last few centimeters go slowly so that it is best to draw the last of the gas through C by carefully opening stopcock 5 and pumping. Finally it is opened wide and the nitrogen all pumped off. This proce-dure is repeated three or four times so that we have 3-4 liter-atm. of frozen oxides in C. At this point the conden-

sate will be blue, particularly around the top, due to  $N_2O_3$ . Stopcocks 1, 2 and 5 are closed and the liquid nitrogen around C is replaced rapidly by a Dry Ice-accone-bath, being itself transferred to D. Nitric and nitrous oxides then distil over into D leaving behind the NO<sub>2</sub>, N<sub>2</sub>O<sub>3</sub> and water. It is important that the Dry Ice-bath reach considerably higher around C than did the liquid nitrogen, for the  $NO_2$  and  $N_2C_3$  condense at the top of the cold surface and in order that they may be retained efficiently, the Dry Ice-bath must completely cover them. This distillation is repeated if necessary until there is no trace of the characteristic deep blue color of  $N_2O_2$  in the condensate. The second

(3a) This may be obtained from Halocarbon Products, Inc., North Bergen, New Jersey.

fractionation is done from D to E rather than from D to C so that the condensate may be kept isolated while the im-

so that the condensate may be kept isolated while the in-purities are pumped away. We are left with a mixture of NO and N<sub>2</sub>O at liquid ni-trogen temperature in either D or E. The refrigerant is lowered so that it does not quite touch the container, which remains, however, within the Dewar. The oxides evapor-ate slowly into the line until, at about 1/4 atmosphere, the manometer remains steady for some time while the nitric oxide is melting. The evaporation is carried out above this pressure, as one gets better thermal equilibrium if the con-densate is liquid rather than solid. In this way, the  $N_2O$  is retained at the temperature of the boiling NO instead of distilling off from the warmer parts of the condensate. As the pressure rises the gas is bled off into bulbs A and B and evaporation is continued until both contain almost an atmosphere. The remaining condensate is discarded. The gas is recondensed and the process repeated until the NO is sufficiently free of  $N_2O$ . The final product is distilled into where it is stored.

B where it is stored. Nitrogen Dioxide—Dinitrogen Tetroxide.— $NO_2$  (in equi-librium with  $N_2O_4$ ) is prepared by treating NO with  $O_2$ . This reaction is third order and quite slow at low pressures. If excess oxygen is undesirable, it may be removed by freezing the  $NO_7$ - $N_2O_4$  in a container which allows a large surface to come in contact with the refrigerant; if the cold surface is too small, the presence of the uncondensed  $O_2$  makes condensation of the  $NO_2$  very slow. The  $O_2$  is then pumped off.

The oxygen used in the preparation of nitrogen dioxide is prepared from commercial tank O<sub>2</sub> by removal of nitrogen and water. A quantity of oxygen is condensed, about  $\frac{2}{3}$ , of the condensate slowly pumped away, and a bulb of  $O_2$ 

of the condensate slowly pumped away, and a burlo of  $O_2$ is collected, leaving some to retain any water. Ozone.—Dry ozone is prepared behind a safety-glass explosion screen in the apparatus shown in Fig. 2. The ozonizer is similar to that described by Henne and Peril-stein.<sup>4</sup> Extreme precautions are necessary to exclude water, which readily reacts with N<sub>2</sub>O<sub>5</sub> to give HNO<sub>3</sub>.



Fig. 2.—Apparatus for the preparation of ozone.

Prior to the preparation the system is pumped out for some time and bulb F, which ultimately is to contain the Some time and burb F, which distinguish to contain the  $O_3$ , is flamed to remove adsorbed moisture. Sufficient oxygen is condensed in A by liquid N<sub>2</sub>. The liquid N<sub>2</sub> is lowered so that the O<sub>2</sub> boils off slowly, flushing out the line; any N<sub>2</sub> will come off in the first portion. The ozonizer is then turned on. Oxygen passes through the P<sub>2</sub>O<sub>5</sub> trap, B, the flow meter, C, and into the ozonizer. Trap D is cooled with a Dry Ice-acetone-bath to remove any water or N<sub>2</sub>O<sub>5</sub> produced by residual N<sub>2</sub> and the O<sub>2</sub>-O<sub>2</sub> mixture is condensed produced by residual N<sub>2</sub>, and the O<sub>3</sub>-O<sub>2</sub> mixture is condensed in E. A positive flow of gas must be maintained through F and the Dry Ice trap G, or moisture will be condensed in E from the atmosphere.

When enough  $O_3$  has been collected, with some liquid  $O_2$ in A to retain any water, the stopcock between D and E is In A to retain any water, the subjects between D and E is closed, the positive flow through G being maintained by slow-ly boiling off some of the  $O_2-O_3$  from E. The  $O_3$  is now con-centrated by allowing the oxygen to boil off slowly. The last fraction will be richest in  $O_3$ , but it is advisable to leave a little of the oxydensate in E to rate on eavy matter. The a little of the condensate in E to retain any water. The ozonized  $O_2$  gas in the liter bulb will be a pale blue and should be used within a short time as it decomposes fairly rapidly.

Nitrogen Pentoxide.—If comparatively small amounts of  $N_2O_5$  are needed and if the presence of excess ozone and oxygen can be tolerated, the preparation may be carried out directly in a storage bulb or absorption cell by the re-

(4) A. L. Henne and W. L. Perilstein, J. Am. Chem. Soc., 65, 2183 (1943).



WAVE NUMBER (cm-1).

Fig. 3.—The more intense infrared bands of the oxides of nitrogen. The pressures indicated for NO<sub>2</sub> and N<sub>2</sub>O<sub>4</sub> are incorrect; these should read: 8.1 mm. NO<sub>2</sub> and 0.8 mm. N<sub>2</sub>O<sub>4</sub> in 265 mm. N<sub>2</sub>.

action  $2NO_2 + O_3 \rightarrow N_2O_5 + O_2$ . Direct reaction between  $O_a$  and NO is unadvisable because of the explosive violence of this reaction.

Larger quantities are obtained by successive preparations of small amounts. Ozonized oxygen is added cautiously to an excess of NO<sub>2</sub> in a long-necked flask which permits a large area to be refrigerated. Following the reaction, the mixture is frozen down with Dry Ice, the oxygen pumped off, and the reaction vessel allowed to warm up again. This procedure is repeated until the brown color of gaseous NO<sub>2</sub> has been removed completely.

Nitric Acid.—Anhydrous nitric acid was prepared for the purpose of studying its infrared spectrum. The preparation is carried out essentially as was done by Redlich and Nielsen<sup>5</sup> by vacuum distillation of a mixture of concentrated HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>. This is followed by several fractional distillations from more H<sub>2</sub>SO<sub>4</sub> at low temperature on the vacuum line. The product is colorless.

## Infrared Spectra

We have examined the spectra of the oxides of nitrogen in the rock-salt region, 650-2500 cm.<sup>-1</sup>, to find absorption bands suitable for analytical purposes. The results of our search are shown in Fig. 3; the region above 2500 cm.<sup>-1</sup> has not been included since there are no strong bands to be found there. The spectra in Fig. 3 should be useful in showing the positions, relative intensities, and shapes of the infrared bands of each molecule. Easy methods for determining such things as the amount of N<sub>2</sub>O in an NO sample, or a small amount of water in N<sub>2</sub>O<sub>5</sub>, become immediately apparent.

Spectra of these compounds have been reported in the literature<sup>6</sup> and in most cases we have little

(5) O. Redlich and L. E. Nielsen, J. Am. Chem. Soc., 65, 654 (1943).

- (6) The following selected references give a more complete discussion of the infrared spectra of the oxides of nitrogen:
- N<sub>2</sub>O: E. K. Plyler and E. F. Barker, *Phys. Rev.*, 41, 369 (1932);
   W. S. Richardson and E. B. Wilson, *J. Chem. Phys.*, 18, 694 (1950).

NO: A. L. Smith, W. E. Keller and H. L. Johnston, *ibid.*, **19**, 189 (1951).

NsOs: Very little is to be found in the literature. An infrared band

to add. We have, however, gone to considerable trouble to obtain the spectrum of  $N_2O_5$  free from water and have made an interesting observation with our fast scanning instrument.<sup>7</sup>

We have used silver chloride windows on our infrared cells when working with NO<sub>2</sub>,  $N_2O_4$ ,  $N_2O_5$  and HNO<sub>2</sub> since these materials attack sodium chloride, particularly when the gases are wet. In order to eliminate the possible reaction of  $N_2O_5$  or  $O_3$  with the common sealing compounds used to fasten the silver chloride windows onto the Pyrex absorption cells, we have welded the silver chloride directly to the glass. A small amount of silver chloride was placed around the rim of the cell end and heated vigorously with a gas-oxygen flame until the silver chloride wetted the glass. Some free silver was formed, but this caused no trouble. The cell end was then heated evenly almost to redness and the silver chloride window was dropped on as firmly and evenly as A few small cracks between the window and the possible. cell were filled in with more AgCl by heating a small area at a time with a tiny flame until the cell was vacuum tight.

Figure 4 shows one portion of the spectrum of  $N_2O_5$  on which we have focused our attention. The strong band at 1240 cm.<sup>-1</sup> quite definitely belongs to  $N_2O_5$ . A band just above it at 1315 cm.<sup>-1</sup> also has been assigned to  $N_2O_5$ . However, if one prepares  $N_2O_5$  in an infrared absorption cell as described above, and looks at this region with the

at about 1300 cm.  $^{-1}$  has been assigned to N<sub>2</sub>O<sub>8</sub>. L. H. Jones,

R. M. Badger and G. M. Moore, *ibid.*, **19**, 1599 (1951).
 NO<sub>2</sub>: M. K. Wilson and R. M. Badger, *Phys. Rev.*, **76**, 472 (1949).

- No. R. M. Son and R. M. Bargel, Phys. Rev. D, 112 (1919).
   N. G. B. B. M. Sutherland, Proc. Roy. Soc. (London), 141, 342 (1933).
- N2Os: Gas-phase infrared work is incomplete. There is mention of some isolated bands in the work of Ogg, et al. R A. Ogg, W. S. Richardson and M. K. Wilson, J. Chem. Phys., 18, 573 (1950); R. A. Ogg, ibid., 770 (1950). For infrared studies on crystalline N2Os see, J. C. Decius, ibid., 21, 1116 (1953).
- HNO<sub>2</sub>: L. H. Jones, R. M. Badger and G. M. Moore, *ibid.*, **19**, 1599 (1951).
- HNO<sub>1</sub>: H. Cohn, C. K. Ingold and H. G. Poole, *J. Chem. Soc.* (London) 4272 (1952).

O: M. K. Wilson and R. M. Badger, J. Phys. Chem., 16, 741 (1948).
 (7) P. J. Wheatley, E. R. Vincent, D. L. Rotenberg and G. R. Cowan, J. Opt. Soc. Am., 41, 665 (1951); G. R. Cowan, E. R. Vincent

and B. Crawford, ibid., 43, 710 (1953).

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Fig. 4.—A portion of the spectrum of  $N_2O_5$  as taken with an infrared fast-scanning spectrometer.

fast-scanning spectrometer, the band at 1315 cm.<sup>-1</sup> is initially very weak while the one at 1240

cm.<sup>-1</sup> assumes its full intensity immediately. Then the smaller band begins to grow to a constant value, while the stronger band decreases slightly. Since nitric acid has a strong band at 1315 cm.<sup>-1</sup>, this band is probably due to a trace of water in the N<sub>2</sub>O<sub>5</sub> preparation. The final amount of HNO<sub>3</sub> formed in a typical run (~0.4 mm.) could arise from only 0.1% of water in the reactants.

It has been reported<sup>8</sup> that  $N_2O_5$  also has a band in the 860 cm.<sup>-1</sup> region. We have observed only a very weak band centered at 880 cm.<sup>-1</sup>. Nitric acid shows a strong band centered at 880 cm.<sup>-1</sup>, and in our  $N_2O_5$  samples the ratio of the optical densities of the 1315 and 880 cm.<sup>-1</sup> bands are the same, within the error of measurement, as in the spectrum of pure nitric acid. We therefore believe that this HNO<sub>3</sub> band was that assigned to  $N_2O_5$  at 860 cm.<sup>-1</sup>.

(8) R. A. Ogg, Jr., J. Chem. Phys., 18, 770 (1950).

# NOTES

## LIGHT-SCATTERING DURING THE FORMATION OF GELATIN GELS

By George L. Beyer

Communication No. 1645 from Kodak Research Laboratories, Eastman Kodak Company, Rochester, N. Y. Received April 8, 1954

Previous measurements of light-scattering during the transition of colloidal solutions to the gel state have attempted to derive the increase of particle size from the depolarization of scattering<sup>1</sup> or from the intensity of scattering.<sup>2</sup> These methods were able to give only qualitative observations of the changes occurring. The present paper concerns the application of a new method by which lightscattering may be used to study the early stages of the sol-gel transition, and which permits the calculation of absolute particle dimensions.

A recent report of Boedtker and Doty<sup>3</sup> on the light-scattering of gelatin solutions included some observations on the behavior of these systems at low temperatures. They found that dilutions of aggregates formed at low temperatures were surprisingly stable at constant temperature, and allowed straight-line extrapolation of the 90° scattering to zero concentration. Such extrapolation appears to offer a means of determining the absolute average size of the aggregate particles present in the undiluted solution.

The present author confirmed the stability of these dilutions, and applied this dilution method to the determination of the average size of the aggregates present in gelatin solutions in various stages of gelation. The measurements reported

(1) P. K. Katti, J. Chem. Phys., 20, 1980 (1952).

(2) M. Prasad and K. D. V. Doss, J. Coll. Sci., 4, 349 (1949).

(3) H. Boedtker and P. Doty, Technical Report No. 1, Part (a) issued under Office of Naval Research Contract N50ri-07654, NR-330-025, Dec. 15, 1952.

here used a fractionated gelatin which had a molecular weight from light-scattering of 103,000, with an intrinsic dissymmetry of 1.06, and an intrinsic viscosity of 0.36. These results were obtained at  $40^{\circ}$ , and all experiments were made at the isoelectric *p*H of 4.7, in solutions 0.05 molar with respect to each of the following: acetic acid, sodium acetate and potassium chloride. Details of the molecular weight measurements for various gelatin fractions will be presented in a later paper. The first experiments were made with solutions at three different gelatin concentrations stored at 2° for 18 hours, then brought to  $10^{\circ}$  and held at this temperature for 4 hours before dilutions were prepared. Extrapolation of both the 90° scattering and the dissymmetry of scattering produced apparent straight lines (see Fig. 1) from which the following values were calculated.

### TABLE I

Gelatin concn., g./ml.	Aggregate wt. (cor. for dissym.)	R, Â., for coil
0.0050	$5.0 imes10^6$	2100
. 0020	$0.61 imes10^6$	790
.0010	$0.31 imes10^6$	590

Both the aggregate weight and the root-meansquare end-to-end distance, R, remained constant within 10% over a 2-hour period. These results show the great dependence of the aggregate size on the gelatin concentration during the aggregation process. A random coil configuration has been assumed for the shape of the aggregate in the calculations above. An estimate of the shape of the aggregate was gained from measurements of the distribution of scattered light over a series of angles between 45 and 135° for five gelatin concentrations prepared by dilution of the aggregates obtained as



Gelatin concn.,  $\sigma$ ./ml.  $\times$  10<sup>2</sup>. Gelatin concn., g./ml.  $\times$  10<sup>2</sup>. Fig. 1.—Light scattering by gelatin aggregates at 10°:  $\bigcirc$ , c = 0.0010 g./ml.;  $\bullet$ , c = 0.0020;  $\triangle$ , c = 0.0050.

above at 0.0050 g./ml. These data were then plotted by the Zimm<sup>4</sup> grid method, and extrapolated to zero angle and zero concentration. The aggregate weight so obtained is independent of the particle shape and can be compared with the values calculated by the dissymmetry method assuming various configurations. Spherical and rod-shaped aggregates do not give reasonable results, but corrections assuming a monodisperse coil give an aggregate weight only 60% of that found by the grid method. A polydisperse coil model with the distribution of molecular weights assumed by Doty<sup>5</sup> improves the agreement to 70%. It is concluded that the aggregate has a coil configuration, but that a broader distribution of particle sizes would have to be assumed to give good agreement between the methods. The uncertainty in extrapolation both by the dissymmetry and the grid methods is sufficient to make such further calculations of questionable value. Although linear plots of 1/(z - 1) have better theoretical justification for the extrapolation of the dissymmetry, z, to infinite dilution, the fit obtained is no better than that shown in Figs. 1 and 2. The resulting aggregate weights and dimensions, R, differ from those listed by 11% or less, and the relationships between aggregate weight and R, and between aggregate weight and viscosity are changed only slightly.

The first stages of gelation have been studied for a solution containing 0.005 g./ml., which was cooled from 40 to 15.0°. The turbidity of this solution increases rapidly at first, then appears to approach a maximum value, which is not reached even after 24 hours. Similar increases of the inherent viscosity,  $\{\eta\}$ , also occur, but both are difficult to interpret in terms of the structure of the aggregate from measurements at a single concentration. The dilution method allows a continuous measure of the aggregate weight and size, as is illustrated by the data of Fig. 2, and the results in Table II, which were obtained with dilutions of the aggregate at various stages.

The dimensions calculated for all these aggregates are proportional to the square root of the aggregate weight within experimental error. This result suggests that the aggregates closely approach a Gaussian distribution of segments for which this proportionality is expected.<sup>6</sup> The

- (4) B. H. Zimm, J. Chem. Phys., 16, 1093 (1948).
- (5) P. Doty and R. F. Steiner, ibid., 18, 1211 (1950).
- (6) A. M. Bueche, J. Am. Chem. Soc., 71, 1452 (1949).



Gelatin concn., g./ml.  $\times$  10<sup>2</sup>. Gelatin concn., g./ml.  $\times$  10<sup>2</sup>.

Fig. 2.—Light scattering during gelation; dilutions from c = 0.0050 g./ml. at 15°:  $\bigcirc$ , 30 min.;  $\bigcirc$ , 60 min.;  $\triangle$ , 140 min.;  $\blacktriangle$ , 300 min.;  $\Box$ , 500 min.;  $\blacksquare$ , 1500 min.

	1	TABLE II		
Time at 15.0°, min.	Aggregate wt. (cor. for dissym.)	Av. no. of moles/ aggreg.	R, Å., for coil	$\{\eta\}\$ for $c = 0.005$
30	$1.78  imes 10^{5}$	1.73	420?	0.464
60	$2.10 imes10^{5}$	2.04	455	. 512
140	$2.75 imes10^{b}$	2.63	540	. 60
300	$3.70 imes10^{5}$	3.60	650	.74
500	$4.80  imes 10^5$	4.66	750	
1500	$9.30 \times 10^{5}$	9.05	1040	1.08

relation between the aggregate weight and the inherent viscosity of the 0.005 g./ml. solution closely follows an equation of the form  $\{\eta\} = 3.6 \times 10^{-3}$  (Agg. wt.)<sup>0.41</sup>. A more significant relationship would be expected if the viscosity data also were extrapolated to zero concentration. The results of this preliminary study of gelation do not appear to follow the kinetic mechanism proposed by Stockmayer<sup>7</sup> for the polymerization of multifunctional monomers, since the latter would expect a greater rate of reaction for larger aggregates.

(7) W. H. Stockmayer, J. Chem. Phys., 11, 45 (1943).

# THE SURFACE TENSION OF POTASSIUM

# By W. Primak and L. A. Quarterman

Chemistry Division, Argonne National Laboratory, Lemont, Illinois Received May 19, 1954

An attempt to determine the surface tension of liquid potassium was first made by Quincke many years ago, when he devised the drop method for determining surface tension,<sup>1</sup> by dropping potassium from a capillary tube in an atmosphere of carbon dioxide dried by sulfuric acid. Despite his expressed uncertainty of the result (he remarked the drops were of unusual size, developed a white coating as they formed, and would occasionally ignite), it has been widely quoted and even subjected to the refinements of corrections calculated for the drop method.<sup>2,3</sup> Quarterman and

(1) G. von Quincke, Ann. Physik (Poggendorff), 135, 621 (1868).

(2) W. A. Roth and K. Scheel, "Landolt-Börnstein Physikalischchemische Tabellen," Vol. I, Edward Brothers Publ. Co., Ann Arbor, Mich., 1943, 5th Ed., p. 200.

(3) "International Critical Tables," Vol. IV, McGraw-Hill Book Co., New York, N. Y., 1928, p. 440.

#### Notes

			TABLE I			
SURFACE	TENSION	OF POTAS	SSIUM BY	THE	DROP-WEIGHT	Method

Total no. of drops	Cooling rate, deg./sec.	Length of freezing curve, sec.	Heat capacity, cal./deg.	Wt. of drops, g.	$\frac{r}{V^{1/a}}$	Harkins- Brown function	Surface tension, d./cm.
91	0.0097 .0098	2410 2610	1.10 1.10	$\begin{array}{c} 1.78 \\ 1.94 \end{array}$	0.105 .102	0.87 .87	120 130
252	.0062	6460	1.60	4.41	. 109	.86	110
484	. 0093 . 0141	$\begin{array}{c} 5850\\ 4115\end{array}$	<b>3.06</b> <b>3</b> .06	$11.5\\12.2$	. 098 . 096	.87 .88	150 150

Primak<sup>4,5,6</sup> observed that the behavior of liquid potassium in glass capillary tubes did not conform to the high surface tension obtained by Quincke (37 mg./mm.) and indicated instead a surface tension between 86 and 95 d./cm. Some theoretical evidence has become available through the work of Skapski<sup>7</sup> and Oriani.<sup>8</sup> Oriani's final relation may be written

$$\sigma = T \frac{d\sigma}{dT} + \frac{L_0 \rho^{2/2}}{\omega f N^{1/2} M^{2/2}}$$

where  $\sigma$  is the surface tension, T is the temperature (about 350°K.), M is the atomic weight (39.1),  $\rho$ is the density (about 0.83), N is the Avogadro number  $[6.02(10^{23})]$ , f is a packing factor (1.09),  $L_0$  is approximated<sup>8</sup> by the heat of sublimation<sup>9,10</sup>  $[8.72(10^{11}) \text{ ergs/g. atom}], \omega$  is Oriani's correlation factor (5.4-6.2). The mean value of  $d\sigma/dT$  for rising and falling temperatures obtained by the authors<sup>6</sup> (-0.02) seems low and an examination of the data for other metals suggests it may be as high as -0.1. With these numbers, Oriani's relation indicates the surface tension of potassium should lie between 81 and 126 d./cm. Additional experimental evidence for a much lower value of the surface tension than Quincke's was obtained by Quarterman and Primak<sup>11</sup> during the course of their determination of the heat of reaction of graphite and potassium.<sup>12</sup> It was hoped to refine the method into a precise determination but, since the opportunity to do this has not arisen, it seems desirable to publish the past observations.

During the course of one of the experiments the calorimeter<sup>13</sup> was assembled with a ground capillary (o.d. 4.44 mm., i.d. 0.60 mm.) leading from the potassium still and condenser to the calorimeter cup. As the potassium distilled into the calorimeter (maintained now at 110° by an airbath) the drops were counted visually. After a series of drops had been delivered, the weight of potassium was determined from the heat transfer coefficient, the length of the freezing curve (airbath maintained at 50°), and the known heat of fusion.<sup>9</sup> The heat transfer coefficient was ob-

(4) ANL-4232, (1948), p. 55.

(5) ANL-4359, (1949), p. 60.

(6) L. A. Quarterman and W. L. Primak, J. Am. Chem. Soc., 72, 3035 (1950).

(7) A. S. Skapski, J. Chem. Phys., 16, 389 (1948).

(8) R. A. Oriani, ibia., 18, 575 (1950).

(9) L. G. Carpenter and C. J. Steward, *Phil. Mag.*, 27, 551 (1939).
(10) E. F. Fiock and W. H. Rodebush, *J. Am. Chem. Soc.*, 48, 2525 (1926).

(11) ANL-4526, (January 1951), p. 85.

(12) L. Quarterman and W. Primak. J. Am. Chem. Soc., 74, 806 (1952).

(13) Reference 12, Fig. 1.

tained from the slope of the cooling curve just prior to freezing and the heat capacity determined electrically as previously described<sup>12</sup> (air-bath at 92°, potassium at 82°). Three sets of determinations were achieved in filling the cup. There evidently was not a sufficiently high concentration of potassium vapor present in the cup during the baking out process, for the potassium did not wet the flat portion of the tip between the i.d. and the o.d., the drops forming from the i.d. The surface tensions were computed with the use of the Harkins-Brown function,<sup>14</sup>  $\phi(r/V^{1/3})$ , (the needed values were obtained by a graphical extrapolation) by the formula  $\sigma = gm/2\pi r\phi = 5180 m/\phi$  where g is the acceleration due to gravity, m the weight of a single drop, and r the capillary radius. The results are given in Table I.

The results of the present determinations are only approximate for a number of reasons: the exact tip dimensions were uncertain since slight wetting at the edge may have occurred; the drop size was in a range which Harkins and Brown consider poor for drop-weight determinations, and a range for which the Harkins-Brown function is not well known; the accuracy of the freezing method used to determine the weight of potassium was probably no better than 10% because of the use of an air-bath as a thermostat; the drops were delivered in an irregular manner in a series of spurts. These would be expected to lead to high results. Accordingly the results of Table I are taken to confirm the previous surface tension values obtained by the authors using the capillary rise method.

It is now taken as certain that the results reported by Quincke for the surface tension of potassium are wrong by about a factor of 4, and that the correct value is about 95 d./cm. (within 10%).

(14) W. D. Harkins and F. E. Brown, J. Am. Chem. Soc., 41, 519 (1919).

# SPARK-IGNITION ENERGIES IN HYDROGEN-BROMINE MIXTURES

#### BY TOM D. BROTHERTON AND ROBBIN C. ANDERSON Defense Research Laboratory and Department of Chemistry, The University of Texas, Austin, Texas Received July 6, 1964

In connection with a series of studies of hydrogen-bromine flames, measurements have been made of spark ignition energies. The system is of interest as one differing quite markedly from the hydrocarbon fuels which have commonly been studied,<sup>1,2</sup> and offering possibilities for comparisons of experimental data with calculations from theoretical equations such as that of Lewis and von Elbe.<sup>3</sup>

#### Experimental

The ignition vessel was made of horosilicate glass. The central section was a large glass cylinder 3 inches long and 2.29 inches wide. Its volume was 515 ml. At each end a section of 1.25 inch glass tubing was connected to the cylinder by a spherical ground-glass joint. Each end section had a side-arm which was provided with a vacuum stopcock. One of these was connected with a vacuum pump and the other with a hydrogen line. At one end another side-arm was provided as a holder for an ampoule of liquid bromine which could be broken to introduce bromine vapor into the system.

Each end-section was also fitted with a short side-arm about 3 cm. long ending in a spherical ground-glass joint The side-arm was packed with glass wool. and a cap. Just before ignition of a mixture the caps were removed. The glass wool plugs served to prevent for a short time ap-preciable diffusion of air into the system and also acted as safety valves, which blew out if the pressure in the reaction vessel increased sharply.

The electrodes were mounted in 1 cm. glass tubes extending axially down the end-pieces to the center of the large cylinder. The electrodes were of 0.025 inch tungsten wires with blunt ends. The distance between ends was about 1 to 3 mm. (because of problems of corrosion and leakage, the electrodes could not be mounted to give a variable gap). Connection to the external electric circuit was provided by soldering on 1/8 inch copper rods.

The whole ignition vessel was mounted in an air-bath, which was maintained at 50° for mixtures containing less than 54 mole % bromine, and at 60° for mixtures richer in bromine.

After successively flushing the vessel with hydrogen and evacuating it, the vessel was thoroughly evacuated. The bromine ampoule was then broken and the bromine vaporized. Thirty minutes after vaporization, the pressure of the bromine gas was measured. Hydrogen was then slowly admitted until a predetermined partial pressure was reached. The final pressure was always greater than atmospheric pressure by a few mm. A period of two hours was allowed for mixing of the gases by thermal diffusion.

Immediately prior to ignition, the spherical caps covering the glass-wool plugs were removed. Thus, all ignition tests were conducted at atmospheric pressure, which averaged about 746 mm. All mixtures were ignited within a few moments after removal of the caps, usually within two minutes.

There was some initial reaction between the electrodes and the gases in the vessel, but after the formation of a dark coating, no further reaction was observed. A high-pressure mercury vapor lamp was mounted above the electrodes to provide an abundance of ion-pairs in the region of the electrode gap.

The power supply was a Hi Volt Power Supply manufactured by the Condenser Products Company, Chicago, Illinois. The output voltage was continuously variable from 0 to 12,000 volts. Maximum ripple at the output terminal was 1.5%. To further reduce the ripple, a 0.05  $\mu$ f. condenser was connected to ground.

The high voltage terminal was connected to a voltage-divider circuit consisting of a 10 megohm and a 101.4 megohm resistor. A third very high resistance (1010 ohms) was placed in the circuit to permit very slow charging of the variable capacitance.

The capacitance of the circuit was continuously variable from 50 to 250  $\mu\mu f$ . with air dielectric and 100 to 500  $\mu\mu f$ . with carbon tetrachloride dielectic. The capacitance was with carbon tetrachloride dielectic. The capacitance was calibrated in place. The energy of the spark discharge was calculated from the capacitance and the potential before discharge

For high-energy spark discharges, capacitance and po-

(1) See B. Lewis and G. von Elbe, "Combustion, Flames, and Explosions of Gases," Academic Press, Inc., New York, N. Y., 1951, p. 391 et seq.

(2) H. F. Calcote, C. H. Gregory, C. M. Barnett and R. B. Gilmer. Ind. Eng. Chem., 44, 2656 (1952).

(3) B. Lewis and G. von Elbe, J. Chem. Phys., 16, 803 (1947). See also ref. 2, p. 351.

tential could be measured simultaneously by replacing the 10<sup>10</sup> ohm resistance by a copper rod. For low-energy spark discharges, this was not possible, for multiple sparks often passed between the electrodes. For these discharges, a method similar to that employed by Calcote<sup>2</sup> was adopted. A series of tests for a given composition and a fixed electrode gap distance were run, alternately measuring the breakdown voltage and the minimum capacitance required for ignition.

In determining the minimum ignition energy of a mixture, the capacitance was first set to the minimum value. The potential was then slowly increased to the breakdown value. If ignition did not occur with the first discharge, after an interval of at least 10 seconds a second discharge was passed. If ignition had not occurred after the passage of at least 4 discharges, the capacitance was increased and the process repeated. The hydrogen and bromine used were the best grades

commercially available.

### Results

The averaged results of the experimental de-termination of the spark ignition energies for gaseous hydrogen-bromine mixture are plotted in Fig. 1. The ignition energy descends from a value of 34 millijoules at 42% bromine in a parabola-like curve similar to those obtained for the spark ignition of other combustible mixtures.<sup>1,2</sup>





Since it was not feasible to vary the spacing of the electrodes, the values of Fig. 1 do not represent minimum ignition energies in all cases, spacings greater than the quenching distances being necessary to observe the true minima.<sup>1</sup> However, data on the minimum tube diameters for flame propagation<sup>4</sup> show that the quenching distance is larger

(4) T. D. Brotherton, V. D. Phillips and R. C. Anderson, 4th Symposium on Combustion, Williams and Wilkins Company, Maryland, 1953, p. 701.

A distinct change in the behavior of the hydrogen-bromine system occurred just beyond 69% bromine. At  $\epsilon$  composition of 71% bromine, flame propagation was quite slow, but was approximately spherical. At a composition of 74%bromine, spherical propagation of the flame did not occur. Instead, flat, ribbon-like tendrils of flame moved about at random for as long as two seconds after a discharge of sufficient energy had occurred. Similar results were obtained with mixtures of 76, 78 and 80% bromine. The averaged minimum energy for these 4 mixtures can be joined by a smooth curve; but since a phenomenon different from that encountered with leaner mixtures is clearly involved, no attempt is made to link them with the ordinary ignition values.

### Discussion

Kokochashvil.<sup>5</sup> found that the minimum pressure for self-ignition for hydrogen-bromine mixtures at temperatures of 470, 523 and 571° occurred at a composition of 67% bromine. The experimental ignition energies reached an apparent minimum at 68 or 69% bromine, a value in general agreement with the results on minimum pressures.

Values calculated using the equation of Lewis and von Elbe<sup>3</sup> and the data on burning velocities<sup>6</sup> and limiting tube diameters<sup>4</sup> previously reported did not show good agreement with experimental For 40% bromine, the calculated value values.<sup>7</sup> was 298 millijoules, giving a ratio of  $H_{\text{calc}}/H_{\text{exp}} =$ 7.4. For 48% bromine, the calculated value was 160 millijoules, giving a ratio of  $H_{calc}/H_{exp} = 22$ , even though the gap spacing was such that this experimental value should be very close to the true minimum spark ignition energy. However, it may be noted that similar variations have been observed with other systems—e.g., propane and air<sup>1</sup>—which have low heat release and low burning velocities.

There are, however, strong indications that the ignition process involves a thermal mechanism. In a diffusion-controlled mechanism of ignition, the limiting factor would be the ratio of the rate of production of atoms to the rate of diffusion of these atoms. Minimum requirements for ignition might then be expected to be found for compositions in the range of 50% bromine, or less, because these are the ranges in which atomic concentrations for bromine and hydrogen respectively reach maxima and which could give most effective ignition. For a thermal mechanism of ignition, the rate of generation of heat by reaction would have to be counterbalanced against losses by heat flow. The first should be at a maximum for equimolar

(5) V. I. Kokochaszivili, J. Phys. Chem. (U.S.S.R.), 23, 15, 21 (1949); ibid., 24, 268 (1950).

(6) S. D. Cooley and R. C. Anderson, J. Am. Chem. Soc., 74, 739 (1952).

(7) Details of these calculations are reported in Report No. 335, T. D. Brotherton and R. C. Anderson, 25 August, 1953, University of Texas, Austin, Defense Research Laboratory. mixtures, but the second should decrease in excess bromine; so optimum conditions for ignition could

conceivably occur in mixtures with excess bromine. The authors wish to express their appreciation for the support of this work by the Defense Research Laboratory, operating under contract NOrd-9195 with the Bureau of Ordnance, US Navy Department.

# TEMPERATURE COEFFICIENTS OF VIS-COSITY OF SOME HALOGEN SUBSTITUTED ORGANIC COMPOUNDS

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Any attempt to correlate the viscous properties of liquids with liquid structure necessitates the use of accurate viscosity measurements made on purified compounds over a wide temperature range. Present day literature data on viscosity-temperature relationships is not very extensive. In an effort to contribute to such data, the viscosities of the following organic liquids were determined over a wide temperature range: dibromomethane, dichloromethane, diiodomethane; *o*-dichlorobenzene, *m*-dichlorobenzene, *p*-dichlorobenzene; 1,2,3trichlorobenzene, *p*-chlorobenzene, 1,2,4trichlorobenzene; *p*-chlorophenol, *o*-chlorophenol.

Measurements for o-, m- and p-dichlorobenzenes were made using a Hoeppler precision viscometer. The temperature in the Hoeppler was maintained within 0.2°. Measurements of absolute viscosities with this instrument are reliable to 0.2%. The Cannon-Fenske modification of the Ostwald type viscometer was used for the remaining viscosity measurements. All measurements were made in a thermostatically regulated bath of water-glycerol mixture. It was always possible to maintain the bath to within 0.05° of the given temperature. Readings were taken on a 0-100° stem corrected thermometer, graduated in tenths of a degree.

TABLE I

# DENSITIES AND VISCOSITIES AS A FUNCTION OF TEMPERATURE

Compound	°C.	Density	Viscosity, centi- poises
Dibromomethane	0	$2.54852^a$	1.3405
	15	$2.50986^a$	1.0672
	25	2.4815	
	30	$2_{-4693}$	0.9413
	40	2.4426	0.8566
	50		0.7870
	60	2.3907	0.7225
	70		0.6749
	80	2.3430	0.6265
Dichloromethane	-3.4		0.5436
	0	1.36174°	0.5424
	15	$1.33479^{a}$	0.4625
	<b>20</b>	$1.3255^{a}$	
	25	1.3160	
	30	1.3071	0.4088

TABLE I	(Contir	nued)			120	1.1687	
	m		Viscosity,		130	1.1552	0.4350
Compound	°C.	Density	centi- poises		140	1.1439	
Diadamatha	10.0	0.000.48	poneee				
Diiodomethane	12.2	3.3394		<i>p</i> -Dichlorobenzene	55	1.2495	
	15	3.3326°		·	55.4		0.8394
	<b>20</b>	$3.3212^{a}$			65	1.2400	
	<b>25</b>	3.3073			69.3	-	0.7202
	30	3.2939	2.4138		75	1 2343	0=0=
	40	3.2691	2.1115		70 4	1.2010	0 6678
	50		1.8483		15.1 95	1 9145	0.0078
	60	3.2169	1.6550		00	1.2140	0 6922
	70		1 4471		89	1 0010	0.0233
	80	3 1744	1 3221		95	1.2019	
	100	3 1168	1 1451		99.4		0.5629
	120	3 0708	0.0875		110	1.1814	
	150	3.0708	0.9075		116.4		0.5093
	100		0.8174		120	1.1692	
o-Dichlorobenzene	-8		2.3051		130	1.1572	0.4510
	3		1 8494		140	1.1448	
	10		1 6230				
	20	1 2056	1.0203	$p ext{-Chlorophenol}$	44.6	1.2571	6.50
	20	1.0000	1 2047		50.4	1.2506	5.06
	21 1	1 9000	1.3947		60.4	1.2406	3.65
	25	1.2998			70.2	1.2303	2.77
	31.9		1.2018		80.3	1.2198	2.18
	35	1.2883			90.2	1 2097	1 77
	41.6		1.0616		00.2	1 2004	1 50
	45	1.2770			00.2	1.2001	1.00
	50.4		0.9627	a-Chlorophenol	0	1 2716	12 1
	55	1.2657		0-Chiefophenoi	48	1 2647	9 21
	58		0.8819		10.0	1.2594	7 00
	65	1.2549			20.0	1.2094	1.09
	68.8		0 7956		20.0	1.2470	4.00
	75	1 2437			30.0	1,2300	0.20
	78.0	1.2101	0 7186		40.0	1.2233	2.45
	95	1 9295	0.1100		50.0	1.2113	1.91
	00 4	1,2020	0 6664		60.0	1.1996	1.56
	88.4 07	1 0004	0.0004		70.0	1.1877	1.29
	95	1.2224			80.0	1.1759	1.11
	99.6		0.5804		90.0	1.1640	0.95
	110	1.2035					
	120	1.1910		1,2,3-Trichlorobenzene	40.0	1.4533	19.9
	121		0.5011		50.0	1.4407	16.8
	130	1.1793	0.4800		60.0	1.4284	14.4
	140	1.1673			70.0	1.4158	12.7
	0		1 5400		80.0	1.4030	11.1
<i>m</i> -Dichlorobenzene	-8		1.7493		90.0	1.3912	9.85
	3		1.3980		98.0	1.3812	9.06
	10		1.2750				
	<b>20</b>	1.2884		1,3,5-Trichlorobenzene	64.0	1.3865	8.93
	23.3		1.0450		70.0	1.3780	8.41
	25	1.2819			80.0	1.3644	7.57
	32.8		0.9551		90.0	1 3542	6.94
	35	1.2705			99.0	1 3430	6 42
	40.4		0.8807		00.0	1.0100	0.1
	45	1.2585		1.2.4-Trichlorobenzene	0	1.4827	32.9
	50.0		0.7948	- ,, -	10.0	1.4698	25.7
	55	1 2468	0.0010		20_0	1 4569	20.8
	58.9	1,2400	0 7350		30.0	1 4441	17 2
	00.2 65	1 9240	0.1009		40.0	1 4313	14 7
	00 60 1	1,2049	0 6504		50.0	1 4196	12.8
	09.1 75	1 0004	0.0094		60.0 60.0	1 4057	11.9
	/5 70 0	1.2234	0.0050		70.0	1.4007	0.90
	78.8		0.6056		70.0	1.0901	9.09 0 0 <del>7</del>
	85	1.2127			80.0	1.3802	ð.ðí 0.00
	88.3		0.5683		90.0	1.3675	8.03
	95	1.1990			98.0	1.3575	7.44
	99.9		0.5310	<sup>a</sup> Values taken from "Ph	usico-Che	mical Cons	tants of Pure
	110	1.1803		Organic Compounds," by	J. Timm	nermans, F	lsevier Pub.
	115.8		0.4815	Co., Houston, Texas, 1950.		•	

ENERGIES OF ACTIVATION FOR	VISCOUS FLOW	
Compound	$E_{vis}$ , cal./mole	Temp. range, °C.
Dibromomethane	1798.6	
Dichloromethane	1489.5	
Diiodomethar.e	2550.6	
o-Dichlorobenzene	2373	
<i>m</i> -Dichlorobenzene	2087	
$p ext{-Dichlorobenzene}$	2317	
Mean $E_{vis}$ , cal./:	mole	
1,2,3-Trichlorobenzene	3130	0-98
1,2,5-Trichlorobenzene	<b>22</b> 90	64-99
1,2,4-Trichlorobenzene	<b>2</b> 860	40-98
<i>p</i> -Chlorophenol	3150	45-99
o-Chlorophen ol	2380	0-90

TABLE II

readings, differing by not more than 0.05% of the mean value, were obtained.

The density of each liquid was determined at selected temperatures by gravimetric procedure. Weighings were made on an analytical balance whose absolute error is less than 0.2 mg.

In Table I, the densities and viscosities of the compounds studied are given as a function of temperature. When the logarithm of the viscosity is plotted as a function of  $1/T \times 10^3$ , dibromomethane, dichloromethane, diiodomethane, o-dichlorobenzene, m-dichlorobenzene and p-dichlorobenzene yield linear graphs, and hence show normal behavior for unassociated liquids. The values of the slopes,  $E_{\rm vis}$ , are given in Table II. The trisubstituted benzenes and the chlorophenols show definite deviation from linearity, indicating some

# TABLE III

Source and Purity of Compounds

Compound	Source	Purity	B.p., °C. determined	B.p., °C. from lit.
Dibromomethane	Eastman #1903	98% (min.)		
Dichloromethane	Eastman #342	98% (min.)		
Diiodomethane	Eastman #167	98% (min.)		
o-Dichlorobenzene	Dow Chemical	99.28%		
<i>m</i> -Dichlorotenzene <sup>a</sup>			172.5 - 173.0	173
<i>p</i> -Dichlorobenzene	Dow Chemical	99.56%		
1,2,3-Trichlorobenzene			215.5-216.5	218-219
1,3,5-Trichlrobenzene			205.5-206.5	208.5, 207.5, 206.5
1,2,4-Trichlorobenzene			210-211	213, 212-213, 210
o-Chlorophenol			174.5-175.0	175-176, 174-175
p-Chlorophenol			217 - 218	219.7, 218.3-218.9
-				218.

<sup>a</sup> Prepared from pure *m*-chloroaniline by diazotization, followed by Sandmeyer reaction. Purified by washing with concentrated sulfuric acid, then with water; dried over calcium chloride and distilled.

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The efflux times were recorded with an accuracy of 0.1 second. With proper carc, the error in loading was reduced to less than 0.001%. Successive runs were made until three consecutive association. Mean activation energies of flow were calculated for these compounds, as shown in Table II. Table III indicates the source and purity of the substances used.



