

The Thermodynamic Properties of Phosphorus, Phosphine, and Some Phosphorus Halides

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A critical study of the equilibrium and molecular data for phosphorus and some of its compounds has been made and is described. The data are used to calculate the entropies and free energies of the substances considered.

INTRODUCTION

THE importance of phosphorus compounds in many branches of chemistry makes it desirable to have reliable values for their thermodynamic constants over a range of temperatures. Only a few reversible reactions are known whose equilibrium states have been determined, but there are a number of phosphorus compounds for which the molecular structures and energy levels have been established with sufficient certainty to permit their use for the calculation of thermodynamic quantities. It is the purpose of the present paper to present and discuss the free energies, entropies and heat contents (enthalpies) calculated from equilibrium, molecular and thermal data for a number of phosphorus compounds.

As a result of correlating the commonly used thermodynamic quantities with the analogous quantities arising in the theories of statistical mechanics,¹ the following relations, which apply to one mole of a perfect, non-degenerate gas, are obtained; these relations form the basis for the derived formulas that were used in making the calculations presented below.

$$\begin{aligned} E &= E_0 + RT^2 \partial \log Q / \partial T, \\ S &= (E - E_0) / T + R \log Q - R \log N_0 + R, \\ F &= E_0 - RT(\log Q - \log N_0), \end{aligned} \quad (1)$$

where E_0 is the arbitrarily chosen energy of the system at 0°K, F is the Gibbs-Lewis free energy, S is the entropy, N_0 is Avogadro's number, and

$$Q = \sum_{n=1}^{\infty} \exp(-\epsilon_n / kT),$$

ϵ_n being the energy of a single molecule in n th quantum state; the summation is taken over all

¹ Tolman, *Statistical Mechanics* (Oxford University Press, 1938).

accessible quantum states including translation. From these relations it follows at once that

$$H^0 - H_0^0 = RT(T \partial \log Q / \partial T + 1),$$

where the zero superscript refers to the value of H when the gas is in the standard state chosen. The free energy equation in terms of Q is also readily derived from Eqs. (1) and is

$$(F^0 - H_0^0) / T = R(\log N_0 - \log Q). \quad (2)$$

For an isothermal reaction between substances maintained in their standard states one obtains,

$$\begin{aligned} \Delta H_0^0 &= \Delta F^0 - RT \Delta(\log N_0 - \log Q) \\ &= -RT \log K - RT \Delta(\log N_0 - \log Q), \end{aligned} \quad (3)$$

and ΔH_0^0 may be evaluated if the equilibrium constants K and the Q 's are known. ΔH_0^0 is independent of T , and its constancy for a series of temperatures is a test of the consistency of the experimental K and Q values; the test is not always sufficiently sensitive, but it is quite useful in general.

The equilibrium and molecular data for phosphorus compounds which are available for use in connection with Eq. (3) are those for phosphorus vapor, phosphine and phosphorus pentachloride. Molecular data alone are available for a number of volatile phosphorus compounds, and may be used to calculate $(F^0 - H_0^0) / T$ for a moderate range of temperatures. It is unfortunate that data are not available for the calculation of the thermodynamic constants for the three well-known oxides of phosphorus, namely, P_4O_6 , P_8O_{16} , and P_4O_{10} .

The fundamental constants used in the calculations were taken from the *International Critical Tables*; this was done in order to assure consistency with the thermodynamic quantities published by other investigators.

TABLE I. ΔH_0^0 values calculated from equilibrium and molecular data.

$P_2(g) = 2P(g)$					
$T^\circ K$	1073	1173	1273	1373	1473
$-\ln K_{\text{atmos}}$	10.027	8.061	6.452	5.065	3.859
$-\Delta H_0^0$, cal.	49,400	49,600	49,900	50,200	50,500

PHOSPHORUS VAPOR

Preuner and Brockmüller² investigated the equilibria in phosphorus vapor in the temperature range 800 to 1200° and concluded that the molecules P_4 , P_2 and P were present together at measurable pressures. Later, Stock, Gibson and Stamm³ made a similar study, and their results showed that the partial pressures of monatomic phosphorus were much too small to be observed even at 1200°. It will be shown by the use of Eq. (3) that the conclusions of Stock, Gibson and Stamm are correct, and that some interfering substances must have been present in the experiments of Preuner and Brockmüller.

The emission band spectrum of P_2 has been carefully analyzed by Herzberg⁴ and by Ashley,⁵ and from their results we have derived the expression $\omega = (n + \frac{1}{2})780.76 - (n + \frac{1}{2})^2 2.98$ cm^{-1} for the vibrational energy levels; the moment of inertia of P_2 is 90.47×10^{-40} g cm^2 . The normal state of the molecule is $^1\Sigma$ while that of the atoms into which it dissociates is 4S , the dissociation energy being 5.008 electron volts (115,450 cal./mole). In Table I are presented the ΔH_0^0 values calculated by means of Eq. (3) from the data of Preuner and Brockmüller. It is evident that ΔH_0^0 is neither satisfactorily constant nor is it in agreement with the spectroscopically determined value, 115,450 cal./mole.

Table II contains the values of K_{atmos} calculated from spectroscopic data alone; it is believed that these equilibrium constants are much more reliable than those shown in Table I. It is evident that the dissociation of diatomic phosphorus is extremely slight even at 1200°.

Further evidence for the superiority of Stock, Gibson and Stamm's equilibrium data appears when the reaction $P_4(g) = 2P_2(g)$ is considered.

² Preuner and Brockmüller, *Zeits. f. physik. Chemie* **81**, 129 (1913).

³ Stock, Gibson and Stamm, *Ber.* **45**, 3527 (1913).

⁴ Herzberg, *Ann. d. Physik* **15**, 677 (1932).

⁵ Ashley, *Phys. Rev.* **44**, 919 (1933).

The P_4 molecule has a tetrahedral structure as was shown by the electron diffraction experiments of Maxwell, Hendricks and Mosely;⁶ the P-P distance is 2.21Å. Venkateswaran⁷ photographed the Raman spectrum of liquid phosphorus and found three lines corresponding to the three allowed fundamentals for a tetratomic, tetrahedral molecule. The frequencies and, in parentheses, their degeneracies are 362(2), 463(3) and 607(1) cm^{-1} . In Table III are presented the

TABLE II. Values of K_{atmos} calculated from spectroscopic data.

$$P_2(g) = 2P(g), \quad K_{\text{atmos}} = P_P^2/P_{P_2}$$

$$\Delta H_0^0 = 115,450 \text{ cal.}$$

$T^\circ K$	1073	1173	1273	1373	1473
$K_{\text{atmos}} \times 10^{20}$	0.74	91	5400	17×10^4	36×10^8
$-\ln K_{\text{atmos}}$	46.35	41.54	37.47	33.99	30.96

experimental values of K_{atmos} obtained by both Preuner and Brockmüller (PB), and Stock, Gibson and Stamm (SGS) together with the corresponding ΔH_0^0 values for the reaction $P_4(g) = 2P_2(g)$. The constancy of the ΔH_0^0 values obtained using the experimental results of Stock and co-workers is very satisfactory and is to be contrasted with the large and unidirectional variations shown by the ΔH_0^0 calculated from Preuner and Brockmüller's data.

The results of our calculations for both of the reactions considered in this section show quite definitely that the measurements of Stock, Gibson and Stamm are free from any major errors, and further that dissociation of diatomic phosphorus is very slight even at 1200°.

From existing data it is now possible to calculate a fairly reliable value for the entropy of white phosphorus, $P(w)$. Macrae and Van Voorhis⁸ studied the vapor pressures of both white and liquid phosphorus, and from their results we may write

$$4P(w) = P_4(g), \quad \Delta F_{298}^0 = 5700 \text{ cal.},$$

$$\Delta H_{298}^0 = 13,200 \text{ cal.};$$

no correction has been made for gas imperfections. The following entropies for elementary

⁶ Maxwell, Hendricks and Mosley, *J. Chem. Phys.* **3**, 699 (1935).

⁷ Venkateswaran, *Proc. Ind. Acad.* **3**, 260 (1935).

⁸ Macrae and Van Voorhis, *J. Am. Chem. Soc.* **43**, 547 (1921).

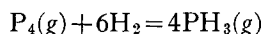
phosphorus were obtained from molecular data and the vapor pressure result.

	P(g)	P ₂ (g)	P ₄ (g)	P(w)
S ⁰ ₂₉₈ cal./deg.	38.99	52.15	66.92	10.1

Entropy determinations of the four more common modifications of solid phosphorus, namely P(w, α), P(w, β), P(red) and P(black),⁹ would add considerably to our understanding of this important element.

PHOSPHINE

The only reliable measurements of the equilibrium constants for the reaction



are those of Ipatiew and Frost.¹⁰ They worked at total pressures of from 18 to 227 atmospheres and over the temperature range 627 to 771°K. The equilibrium concentrations of phosphine were determined by chemical analysis, and the partial pressures of P₄(g) were assumed to be those in equilibrium with the red (violet) phosphorus present as a solid phase. They used the vapor pressure measurements of Smits and Bokhorst¹¹ in this connection. Since the vapor pressures of red (violet) phosphorus do not appear to be accurately reproducible, the equilibrium measurements of Ipatiew and Frost may be subject to errors on this account.

TABLE III. The values of ΔH_0^0 from molecular and equilibrium data.

	$P_4(g) = 2P_2(g), K_{atmos} = P_{P_2}^2 / P_{P_4}$				
T°K	1073	1173	1273	1373	1473
K _{atmos} (PB)	0.00855	.0329	.1053	.2763	.6579
ΔH_0^0 , cal.	48,460	49,730	51,000	52,310	53,440
K _{atmos} (SGS)	—	0.00645	.0375	.1671	.6118
ΔH_0^0	—	53,540	53,590	53,670	53,660

The infra-red and Raman spectrum of phosphine has been the subject of a number of investigations. We have chosen the frequency assignment of Sutherland¹² for our calculations. Only one moment of inertia, that about the axis

⁹ Jacobs, J. Chem. Phys. 5, 945 (1937).

¹⁰ Ipatiew and Frost, Ber. 63, 1104 (1930).

¹¹ Smits and Bokhorst, Zeits. f. physik. Chemie 91, 249 (1916).

¹² See Hibben, *The Raman Effect* (Reinhold Publishing Corporation, 1939); Yost and Anderson, J. Chem. Phys. 2, 624 (1934).

perpendicular to the symmetry axis of the pyramidal molecule, is obtainable from the infra-red bands. Stevenson¹³ has shown recently that the bond angle H—P—H is probably 93°. Table IV presents the calculated values of ΔH_0^0 . All of Ipatiew and Frost's data are not presented, but only enough to show the representative variations in ΔH_0^0 .

The variations in ΔH_0^0 are considerable. $\Delta H_0^0 = 1530$ cal. has been chosen as the most acceptable average, and it has been used to calculate the values of K and $\ln K$ shown in Table V. Greater precision in the measurements of this equilibrium is without doubt possible, and no other method seems as adequate for the estimation of ΔH since a direct determination does not appear feasible; indirect methods would unavoidably involve the large heats of formation of phosphorus and hydrogen halides or oxides. The values in Table V are consistent with the entropy measurements made by Giauque and Stephenson¹⁴ on phosphine.

PHOSPHORUS PENTACHLORIDE

Measurements of the dissociation constants for the reaction



have been made by Holland and Nernst,¹⁵ and by Fischer and Jübermann.¹⁶ In neither case were the measurements made with great pre-

TABLE IV. The dissociation of phosphine. $\omega_1(I) \parallel = 2320$, $\omega_2(I) \parallel = 970$, $\omega_3(2) \perp = 2430$, $\omega_4(I) \perp = 1118$ cm⁻¹. $I_1 = I_2 = 6.22 \times 10^{-40}$ g cm², $I_3 = 7.00 \times 10^{-40}$ g cm².

	$K_{atmos} = P_{PH_3}^4 / P_{P_4} P_{H_2}^6$				
T°K	$-\ln K_{atmos}$	ΔH_0^0 cal.	T°K	$-\ln K_{atmos}$	ΔH_0^0
627	25.08	1,110	771	28.41	3624
	25.60	1,756		28.16	3238
	25.31	1,398		28.83	3238
677	25.51	860	731	26.00	1,516
	25.90	1,381		27.24	2,398
	26.30	1,923		26.85	1,835
	26.00	1,516			

¹³ Stevenson, J. Chem. Phys. 8, 285 (1940).

¹⁴ Stephenson and Giauque, J. Chem. Phys. 5, 149 (1937).

¹⁵ Holland and Nernst, Zeits. f. Electrochemie 18, 234 (1912).

¹⁶ Fischer and Jübermann, Zeits. f. Anorg. u. angew. Chemie 235, 340 (1938).

TABLE V. *The dissociation of phosphine.* $\Delta H_0^0 = 1530$ cal.;
 $\Delta F_{298}^0 = -18,370$ cal.
 $P_4(g) + 6H_2(g) = 4PH_3(g)$

T°K	627	677	731	771
$K_{atmos} \times 10^{12}$	10	5.6	2.5	1.9
$-\ln K_{atmos}$	25.3	25.9	26.7	27.0
$P(w) + 3/2H_2(g) = PH_3(g), \Delta F_{298}^0 = -3,140$ cal.				

cision, but the results are in good agreement with each other. Electron diffraction experiments by Schomaker and Sargent¹⁷ show the PCl_5 molecule to be a trigonal bipyramid with an axial P-Cl distance of 2.12Å and an equatorial P-Cl distance of 2.03Å. Moureau, Magat and Witroff¹⁸ have investigated the Raman spectrum and find for $\omega_1, \omega_2(2), \omega_3(2), \omega_4, \omega_5(2)$ and $\omega_6(2)$ the values 100, 190, 271, 392, 449, and 495 cm^{-1} , respectively. ω_7 and ω_8 are not known; they are permitted in the infra-red but not in the Raman spectrum.

In principle it is possible to evaluate ω_7 and ω_8 from the equilibrium data. To do this conveniently the function $TB(T)$ for the reaction was defined by the relation

$$TB(T) = \Delta F^0 - T \Delta \left(\frac{F^0 - H_0^0}{T} \right)' \\ = \Delta H_0^0 - RT \ln Q_7 Q_8,$$

where Q_7 and Q_8 are partition functions of the form $(1 - e^{-hc\omega/kT})^{-1}$ for the frequencies ω_7 and ω_8 , respectively. Since

$$\Delta \left(\frac{F^0 - H_0^0}{T} \right)' = \left(\frac{F^0 - H_0^0}{T} \right)_{PCl_5} \\ - R \ln Q_7 Q_8 - \left(\frac{F^0 - H_0^0}{T} \right)_{PCl_3} - \left(\frac{F^0 - H_0^0}{T} \right)_{Cl_2}$$

and the right-hand side may be evaluated from the known energy states of PCl_5, PCl_3 and Cl_2 , it follows that $TB(T)$ may be evaluated from $\Delta((F^0 - H_0^0)/T)'$ and the equilibrium data. The following four sets of values for ω_7, ω_8 were assumed

ω_7	200	250	450	600 cm^{-1}
ω_8	500	450	600	600 cm^{-1}

¹⁷ Schomaker and Sargent, private communication.

¹⁸ Moureau, Magat and Witroff, *Comptes rendus* **205**, 276 (1937).

TABLE VI. *The dissociation of phosphorus pentachloride vapor.*
 $PCl_3(g) + Cl_2(g) = PCl_5(g)$

T°K	K_{atmos}	$-\Delta H_0^0$	T°K	K_{atmos}	$-\Delta H_0^0$
422.6	122.63	21.44	502.2	1.752	21.35
425.8	88.82	21.33	439	37.18	21.25
430.3	67.96	21.35	443	30.33	21.27
442.7	45.22	21.61	462	15.80	21.62
445.3	28.53	21.34	485	4.09	21.42
446.4	24.09	21.24	495	3.843	21.34
454.0	15.52	21.22	534	0.4767	21.35
457.9	13.42	21.26	556	0.2048	21.31
464.5	8.88	21.20	574	0.1074	21.25
471.0	8.00	21.40	613	0.0242	20.92
473.1	5.816	21.20	623	0.0234	21.21
501.9	2.175	21.54	631	0.0186	21.21
					Mean 21.32

TABLE VII. *Internuclear distances in phosphorus compounds, in Å.*

MOLECULE	P-X	P-O, P-S	$\angle X-P-X$	REFERENCE
P_2	1.88			1
P_4	2.21	—	Tetrahedral	2
PH_3	1.42	—	93°	3
PF_3	1.52	—	104	4
PCl_3	2.00	—	101	4
PBr_3	2.23	—	100	5
Cl_3PO	2.02	1.56	106	6
Cl_3PS	2.01	1.94	107	7
Cl_3PCl_2	2.03	2.12	Trigonal bipyramid	8

¹ Ashley, reference 5 of text.

² Maxwell, Hendricks and Mosley, reference 6 of text.

³ Stevenson, reference 13 of text.

⁴ Brockway and Wall, *J. Am. Chem. Soc.* **56**, 2373 (1934).

⁵ Gregg, Hampson, Sutton and Jones, *Trans. Faraday Soc.* **33**, 852 (1937).

⁶ Brockway and Beach, *J. Am. Chem. Soc.* **60**, 1836 (1938).

⁷ Beach and Stevenson, *J. Chem. Phys.* **6**, 75 (1938).

⁸ Schomaker and Sargent, reference 17 of text.

and for each set, $TB(T) + RT \ln Q_7 Q_8 = \Delta H_0^0$ was calculated at the temperatures of the equilibrium experiments. It was found that with $\omega_7 = 450$ cm^{-1} and $\omega_8 = 600$ cm^{-1} , ΔH_0^0 did not drift with temperature as Table VI shows.

FREE ENERGY TABLES

No reliable equilibrium data are available for the calculation of the free energies and heat contents of phosphorus compounds other than those described above. Fortunately there exist adequate molecular data and heats of formation for several of the important halogen-containing compounds. In Tables VI-X are assembled both the molecular and energy values for these compounds.

TABLE VIII. Frequencies, in cm^{-1} , degeneracies and symmetry numbers of phosphorus compounds.

	$\omega_{ }$	$\delta_{ }$	ω_{\perp}	δ_{\perp}	$\omega_{2 }$	$\delta_{2\perp}$	SYMMETRY NUMBER	REF.
P ₂	770	—	—	—	—	—	2	1
P ₄	372(2)	463(3)	607	—	—	—	12	2
PH ₃	2320	970	2430	1118	—	—	3	3
PF ₃	890	531	840	486	—	—	3	3
PCl ₃	511	257	480	190	—	—	3	4
PBr ₃	400	162	380	116	—	—	3	4
Cl ₃ PO	1290	267	581	193	486	337	3	5
Cl ₃ PS	748	245	539	169	430	382	3	5
Degeneracy	1	1	2	2	1	2	—	—

¹ Ashley, reference 5 of text.² Venkateswaran, reference 7 of text.³ Hibben and Yost and Anderson, reference 12 of text.⁴ Cabannes and Rousset, Ann. de physique 19, 229 (1933).⁵ Simon and Schulze, Naturwiss. 25, 669 (1937).TABLE IX. Heat content differences, $H-H_0^0$, in kcal./mole for phosphorus compounds.

T°K	P	P ₂	P ₄	PH ₃	PF ₃	PCl ₃	PCl ₅	PBr ₃	Cl ₃ PO	Cl ₃ PS
298.1	1.48	2.13	3.37	2.42	2.92	3.84	5.22	4.25	4.23	4.35
350	1.74	2.53	4.23	2.90	3.65	4.74	6.62	5.21	5.30	5.47
400	1.99	2.93	5.09	3.39	4.39	5.65	8.03	6.16	6.38	6.59
500	2.48	3.75	6.89	4.45	6.00	7.50	10.91	8.06	8.63	8.93
600	2.98	4.59	8.74	5.61	7.71	9.40	—	9.98	10.95	11.28
700	3.48	5.44	10.62	6.88	9.50	11.32	—	11.93	13.36	13.77
800	3.97	6.30	12.53	8.22	11.32	13.26	—	13.89	15.79	16.27
900	4.47	7.17	14.46	9.66	13.19	15.21	—	—	18.25	18.76
1000	4.97	8.04	16.41	11.16	15.05	17.16	—	—	20.73	21.29
1100	5.46	8.92	18.37	12.72	—	—	—	—	—	—
1200	5.96	9.80	20.32	14.36	—	—	—	—	—	—
1300	6.46	10.68	22.26	15.97	—	—	—	—	—	—
1400	6.95	11.56	24.24	17.67	—	—	—	—	—	—
1500	7.45	12.45	26.21	19.40	—	—	—	—	—	—

TABLE X. Free energies, $-((F^0-H_0^0)/T)$, and entropies of gaseous phosphorus compounds, in cal./mole deg.

T°K	P	P ₂	P ₄	PH ₃	PF ₃	PCl ₃	PBr ₃	PCl ₅	Cl ₃ PO	Cl ₃ PS
298.1	30.61	45.00	55.61	42.10	54.37	61.66	68.89	66.76	63.45	64.77
350	31.41	46.18	57.48	43.42	55.99	63.75	71.28	69.53	65.77	67.20
400	32.07	47.13	59.13	44.54	57.41	65.61	73.31	71.97	67.85	69.34
500	33.18	48.80	61.57	46.47	59.98	68.87	76.82	76.30	71.57	73.21
600	34.09	50.17	64.67	48.13	62.24	71.68	79.72	80.08	74.74	76.39
700	34.85	51.36	66.96	49.61	64.29	74.09	82.32	83.41	77.69	79.46
800	35.52	52.39	69.01	50.95	66.13	76.30	84.64	86.36	80.32	82.20
900	36.10	53.33	70.87	52.19	67.84	78.31	—	89.14	82.60	84.54
1000	36.62	54.18	72.64	53.34	69.37	80.07	—	91.56	84.76	86.81
1100	37.10	54.96	74.23	54.43	—	—	—	—	—	—
1200	37.53	55.65	75.70	55.45	—	—	—	—	—	—
1300	37.93	56.31	76.99	56.41	—	—	—	—	—	—
1400	38.30	56.92	78.32	57.34	—	—	—	—	—	—
1500	38.64	57.50	79.56	58.24	—	—	—	—	—	—
S ⁰ ₂₉₈	38.99	52.15	66.92	50.20	64.13	74.49	83.11	84.3	77.59	79.34

The values of $(F-H_0^0)/T$ and $H-H_0^0$ in Tables IX and X may be used in connection with similar tables for other substances when the free energy of a given reaction is desired. Table X contains also the standard entropies at 25° of the compounds listed, and these were used in

connection with known thermochemical¹⁹ and published entropy values to calculate the ΔF^0_{298} of formation shown in Table XI. These ΔF^0_{298} values refer to the elements in their commonly

¹⁹ Bichowsky and Rossini, *Thermochemistry* (Reinhold Publishing Corporation, 1936).

TABLE XI. *Standard free energies of formation of some gaseous phosphorus compounds at 25°.*

COMPOUND	PH ₃	PCl ₃	PCl ₅	POCl ₃
$-\Delta F_{298}^{\circ}$, cal./mole	3140	65,300	74,800	127,300

known standard states. The well-defined α white phosphorus is taken as the standard state for

this element notwithstanding the fact that the red and black modifications are the more stable at room temperature.

The free energy and entropy values given in this paper are to replace those calculated several years ago by Anderson and Yost.²⁰

²⁰ Anderson and Yost, *J. Chem. Phys.* **4**, 529 (1936).

Electric Polarization of Carboxylic Acids in Dilute Solutions of Nonpolar Solvents

I. The Relation of Electric Polarization to the Association of Carboxylic Acids in Hydrocarbon Solvents

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The association and polar character of various carboxylic acids have been studied in the solvents benzene and heptane by means of measurements of the electric polarization in very dilute solutions. The data have been analyzed by assuming an equilibrium between dimers and monomers of the acid molecules. A rather large anomalous contribution to the polarization of the dimer has been found. Possible origins of this polarization have been briefly considered.

WE may consider, as a simplified picture, that concentrated solutions of the carboxylic acids in hydrocarbons consist of a mixture of large molecular aggregates of the acid surrounded by the solvent. With dilution these aggregates break up until a state is reached where the dimer type of molecule predominates. This species persists over a large concentration range, and only at relatively low concentrations does considerable dimer dissociation take place leading to the appearance of appreciable fractions of the single species.

At present little is known of the extent and character of the dimer dissociations and still less is known of the polar character of the acid molecules which are present at low concentrations. Determinations of the dielectric constant and densities of these dilute solutions provide, through the polarizations derived from these values, a simple and effective means of studying

the molecular structure of these acids.¹ This has been carried out for a number of carboxylic acids in benzene and heptane with a view to gaining further information about the following: (1) the factors governing the dimer-monomer dissociation equilibrium, (2) the effects produced by different groups attached to the carboxyl group and by changing solvents, (3) the values of the molar polarizations and apparent moments of the single and double species of acid molecules and (4) the evidence for the existence of an appreciable "atom polarization" in the dimer.

EXPERIMENTAL

Dielectric constant differences between the solvent and the solution were measured with the heterodyne beat, parallel capacitance method. The electrical circuit has been described elsewhere.² The condenser containing the solutions

¹ The first use of polarization data in studying association in solution was by Hojendahl, "Studies of dipole-moment," Thesis, Copenhagen (1928), p. 33.

² Hobbs, Jacokes and Gross, *Rev. Sci. Inst.* **11**, 126 (1940).

* Part of thesis of Herbert A. Pohl submitted in partial fulfillment of the requirements for the Ph.D. degree in Chemistry at Duke University.