The heat of formation of manganese dioxide was obtained by two solution methods involving the use of sulfuric acid–ferrous ammonium sulfate solutions, both with and without the use of hydrogen peroxide. Agreeing results were obtained, the weighted mean of which is $\Delta H_{298.16} = -124{,}640 \pm 200$ cal. per mole.

BERKELEY, CALIFORNIA RECEIVED DECEMBER 4, 1942

[CONTRIBUTION NO. 471 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

Heats of Dilution and Relative Heat Contents of Aqueous Solutions of Lanthanum Chloride and Lanthanum Sulfate at 25°

BY C. C. NATHAN,[1] W. E. WALLACE[2] AND A. L. ROBINSON

The heat of dilution of dilute solutions of electrolytes has been the subject of many investigations in recent years.[3] Extrapolation of such measurements to infinite dilution and comparison of the limiting slopes so obtained with the predictions of the Debye–Hückel theory[4,5] has been a matter of considerable interest. Earlier studies did not include electrolytes of higher valence type than 2–2. In this paper are presented measurements on lanthanum chloride and sulfate. From these data relative apparent and relative partial molal heat contents have been calculated. All measurements were made at 25 ± 0.02°. With the chloride the range of concentrations extended from 0.1 to 0.00006 molal, while with the sulfate the range was 0.025 to 0.000015 molal.

Materials.—The sulfate and chloride were prepared from a supply of lanthanum oxide procured from the Eastman Kodak Co. The analysis indicated a product of high purity containing less than 0.01% of other rare earths and heavy metals.

Lanthanum chloride was prepared by dissolving the oxide in hydrochloric acid and precipitating the highly soluble salt by saturation with dry hydrogen chloride gas at 0°. The hydrated product was freed of water and excess hydrogen chloride by heating at 230° in a stream of dry hydrogen chloride gas. Heating the chloride directly in the presence of air results in the loss of hydrogen chloride, as well as water, and the formation of basic chlorides.[6] Determinations of the lanthanum and chloride content of the anhydrous salt indicated its purity to be 99.7% or better.

Lanthanum sulfate was prepared from the hydrated lanthanum chloride by repeated digestion with sulfuric acid until all the hydrogen chloride had been driven off. The excess sulfuric acid was removed by heating the sample in an electric furnace maintained at 650°. This temperature is somewhat critical since at lower temperatures the lanthanum acid sulfates are not completely converted to the normal sulfate, while at higher temperatures the normal sulfate itself is decomposed into oxides of lanthanum and sulfur.[7] The anhydrous lanthanum sulfate was then dissolved in seven times its weight of ice-water, the salt being added in small portions to the water while agitating with a mechanical stirrer. The small amount of residue was filtered from the solution, and the filtrate slowly warmed to 35° while stirring continuously. The enneahydrate, $La_2(SO_4)_3 \cdot 9H_2O$, crystallized[8] from the solution between 30 and 35°. The crystals were washed with water, then with acetone and dried at 50° until free of the odor of acetone. Determinations of the lanthanum, sulfate and water contents of the salt indicated a purity equal to or greater than 99.6%.

Procedure.—The dilutions were carried out in the apparatus and manner described by Wallace and Robinson.[9] The only significant change in apparatus was the replacement of the old pipets of gilded brass with new ones of monel metal. The volumes of the new pipets were 10.351 and 10.389 ± 0.005 ml., and the amounts of water in the two sides of the calorimeter were respectively chosen as 1000 and 1003 ± 1 ml. in order to give equal dilution ratios on both sides of the calorimeter. This ratio was 96.6.

The most concentrated solutions of sulfate and chloride were prepared directly by dissolving a weighed sample in a known volume of water. Other solutions were made by volumetric dilutions of the strongest. The concentrations were expressed on a weight basis with the aid of density data determined at 25 ± 0.2°. Equations relating density to molarity are

$$d^{25} = 0.9971 + 0.227\,c \text{ for } LaCl_3 \text{ below 0.1 molar} \quad (1)$$

$$d^{25} = 0.9971 + 0.584\,c \text{ for } La_2(SO_4)_3 \text{ below 0.025 molar} \quad (2)$$

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[1] From a thesis submitted by Charles C. Nathan in partial fulfillment of the requirements for the degree of Master of Science at the University of Pittsburgh, 1942.

[2] Research Fellow in Chemistry under a grant made by the Carnegie Institution of Washington and the Buhl Foundation of Pittsburgh.

[3] (a) E. Lange and A. L. Robinson, *Chem. Rev.*, **9**, 89 (1931); (b) E. A. Gulbransen and A. L. Robinson, THIS JOURNAL, **56**, 2637 (1934); (c) T. F. Young and P. Seligmann, *ibid.*, **60**, 2379 (1938); (d) A. L. Robinson and W. E. Wallace, *ibid.*, **63**, 1582 (1941); *Chem. Rev.*, **30**, 195 (1942).

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[5] G. Scatchard, THIS JOURNAL, **53**, 2037 (1931).

[6] J. N. Friend, "A Textbook of Inorganic Chemistry," Vol. IV, Charles Griffin and Company, Limited, London, 1917.

[7] J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. V, Longmans, Green and Company, London, 1931.

[8] Leopold Gmelin, "Handbuch der anorganischen Chemie," Deutschen Chemischen Gesellschaft, Berlin, 1924.

[9] W. E. Wallace and A. L. Robinson, THIS JOURNAL, **63**, 958, (1941).

TABLE I

LANTHANUM CHLORIDE

Moles/1000 g. H_2O			Calories				Cal./mole salt	
$10^5 m_1$	$10^5 m_2$	$10^5 m_3$	$-q_{1\rightarrow 2}$	$\Delta q_{1\rightarrow 2}$	$-q_{3\rightarrow 2}$	$\Delta q_{3\rightarrow 2}$	$-\Delta H_{1\rightarrow 2}$	$-\Delta H_{3\rightarrow 2}$
9670	99.91	198.9	1.001	+0.017	0.126	−0.035	986 ± 21	78 ± 8
9670	99.91	198.9	0.922	− .062	.105	− .056		
9670	99.91	198.9	.955	− .029	.223	+ .062		
9670	99.91	198.9	1.069	+ .085	.167	+ .006		
4855	50.20	99.91	0.436	− .002	.0635	+ .0144	849 ± 14	53 ± 7
4855	50.20	99.91	.417	− .021	.0426	− .0065		
2440	25.24	50.20	.1818	+ .0039	.0196	+ .0040	710 ± 7	30 ± 6
2440	25.24	50.20	.1765	− .0014	.0106	− .0050		
1225	12.68	25.24	.0700	+ .0016	.0082	+ .0032	547 ± 3	25 ± 5
1225	12.68	25.24	.0684	.0000	.0043	− .0007		
615.5	6.371	12.68	.0276	+ .0017	.0007	− .0009	432 ± 2	10 ± 3
615.5	6.371	12.68	.0273	+ .0014	.0018	+ .0002		
				LANTHANUM SULFATE				
2388	24.38	48.54	1.070	−0.011	0.412	+0.052	4480 ± 100	843 ± 3
2388	24.38	48.54	1.145	+ .064	.418	+ .058		
1191	12.25	24.38	0.624	+ .006	.214	− .013	4890 ± 110	857 ± 11
1191	12.25	24.38	.582	− .032	.205	− .022		
596.9	6.160	12.25	.327	− .016	.109	− .009	5520 ± 80	949 ± 15
596.9	6.160	12.25	.357	+ .014	.121	+ .003		
596.9	6.160	12.25	.330	− .013	.117	− .001		
596.9	6.160	12.25	.350	+ .007	.119	+ .001		
299.5	3.095	6.160	.1896	+ .0085	.0608	+ .0104	5960 ± 50	918 ± 26
299.5	3.095	6.160	.1815	+ .0004	.0544	+ .0040		
299.5	3.095	6.160	.1792	− .0019	.0508	+ .0004		
299.5	3.095	6.160	.1856	+ .0045	.0595	+ .0091		
150.3	1.561	3.095	.0919	+ .0014	.0230	+ .0004	5785 ± 90	698 ± 28
150.3	1.561	3.095	.0878	− .0029	.0202	− .0024		

Results computed from equation (1) are in agreement with similar data obtained by Jones and Bickford.[10]

Experimental Results and Treatment of Data

Relative Apparent Molal Heat Contents.— The treatment of data is identical with that described in earlier publications.[3d,9]

The experimental heats of dilution are given in Table I. Dilutions between m_1 and m_2 are the "long chord" dilutions; dilutions between m_3 and m_2 are the "short chord" dilutions.[3d] From the short chord heat effects, given in Column 6, analytical expressions for ΦL_2 were derived following the method of Young.[3c,11] It was assumed that the slope, $\partial \Phi L_2/\partial m^{1/2}$, varied linearly with $m^{1/2}$ in this low concentration range. The slope equations on integration give the following relations for the relative apparent molal heat contents

$$\Phi L_2 = 3129m^{1/2} + 41{,}121m \text{ cal./mole LaCl}_3 \quad (3)$$

$$\Phi L_2 = (4.804 \times 10^5)m^{1/2} - (0.9628 \times 10^7)m \text{ cal./mole La}_2(\text{SO}_4)_3 \quad (4)$$

The probable errors for the limiting slopes (S^0) are ±930 for the chloride and ±1.81 × 10^5 for the sulfate. Equations (3) and (4) are valid for values of $m < 0.002$ and 0.0005, respectively. Figures 1 and 2 show the short chords and their analytical representations. Modifications of equations (3) and (4), using theoretical values for the limiting slopes (7010 and 27,750, respectively) do not give

TABLE II

DATA USED IN THE EVALUATION OF THE RELATIVE APPARENT HEAT CONTENTS

m_1 moles/1000 g. water	m_2 moles/1000 g. water	$\Delta H_{1\rightarrow 2}$ cal./mole salt	$\Phi L_2(m_2)$ cal./mole salt	$\Phi L_2(m_1)$ cal./mole salt
		Lanthanum Chloride		
0.09670	0.0009991	986	140	1126
.04855	.0005020	849	91	940
.02440	.0002524	710	60	773
.01225	.0001268	547	40	587
.006155	.0000637	432	28	460
		Lanthanum Sulfate		
0.02388	0.0002438	4480	5152	9632
.01191	.0001225	4890	4139	9029
.005969	.00006160	5520	3178	8698
.002995	.00003095	5960	2375	8335
.001503	.00001561	5785	1645	7430

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[10] G. Jones and C. F. Bickford, THIS JOURNAL, 56, 602 (1934).

[11] (a) T. F. Young and O. G. Vogel, *ibid.*, 54, 3030 (1932); (b) T. F. Young and W. L. Groenier, *ibid.*, 58, 187 (1936).

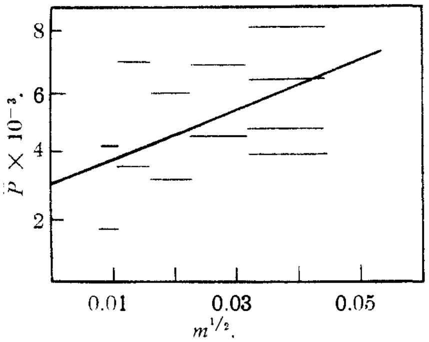

Fig. 1.—Short chords ($P = -\Delta H_{3\rightarrow 2}/\Delta m^{1/2}$) and equation (3) for $LaCl_3$.

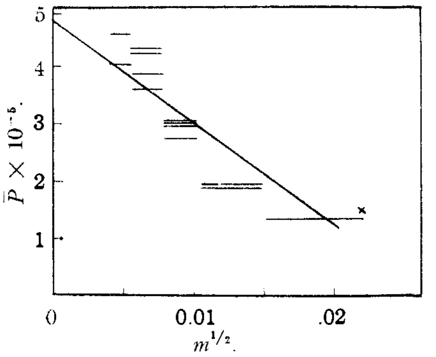

Fig. 2.—Short chords ($\bar{P} = -\Delta H_{3\rightarrow 2}/\Delta m^{1/2}$) and equation (4) for $La_2(SO_4)_3$: x represents two chords.

agreement with the experimental results within the estimated limits of experimental errors[3d]; this is particularly true for lanthanum sulfate.

From equations (3) and (4) the relative apparent molal heat contents at the final concentrations of the long chord dilutions (m_2 in Table I) may be computed. These ΦL_2 values when combined with the long chord heats of dilution ($\Delta H_{1\rightarrow 2}$ in Table I) yield values for ΦL_2 at the initial concentrations, $\Phi L_2(m_1)$. These data are presented in Table II. The ΦL_2 values of column 5 of Table II for lanthanum chloride can be represented by an analytical expression for concentrations greater than 0.002 m. The equation is[12]

$$\Phi L_2{}^{12a} = 6194m^{1/2} - 8305m \text{ cal./mole } LaCl_3 \quad (5)$$

An attempt to derive a similar equation for lanthanum sulfate was unsuccessful, apparently because of the extremely rapid change of slope between 0.001 and 0.006 m. For this salt ΦL_2 values above 0.0005 m were read from a curve constructed from a large scale plot of the $\Phi L_2(m_1)$ values of Table II.

An estimate was made of the errors introduced in the ΦL_2 values by the extrapolations involved in obtaining equations (3) and (4). This was done by comparing the values calculated from the equations and those obtained when extrapolating to the theoretical limiting slopes. From such considerations the maximum extrapolation error for lanthanum chloride is estimated to be 25 cal./mole and for lanthanum sulfate, 400 cal./mole. ΦL_2 values at several concentrations are given in Table III and the experimental and analytical values are shown in Fig. 3. Deviations of the experimental heat effects from the calculated values, obtained in the manner described above, are shown in columns 5 and 7 of Table I.

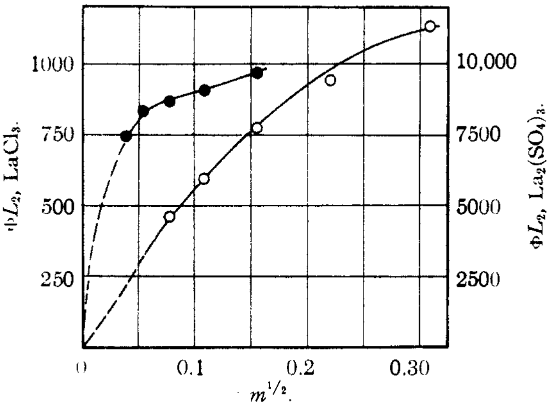

Fig. 3.—ΦL_2 (calories per mole salt) *vs.* $m^{1/2}$, circles show ΦL_2 (m_1): ○, $LaCl_3$; ●, $La_2(SO_4)_2$. Dashed curves represent Equations (3) and (4).

Relative Partial Molal Heat Contents.—These were derived from the relative apparent molal heat contents by use of Rossini's equations[13]

$$\bar{L}_1 = -\frac{m^{3/2}}{2(55.506)}\frac{d(\Phi L_2)}{dm^{1/2}} \quad (6)$$

$$\bar{L}_2 = \Phi L_2 + \frac{m^{1/2}d(\Phi L_2)}{2dm^{1/2}} \quad (7)$$

For the chloride the analytical expressions for ΦL_2 were substituted into the above equations giving the relations

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[12] In the derivation of this equation a value for ΦL_2 at $m = 0.001$ computed from equation (3) was included. This was done in an effort to secure a consistent representation of the data in the concentration range wherein both equations (3) and (5) are effective.

[12a] It is admittedly awkward to represent the ΦL_2 values by two equations which intersect in a discontinuity at $m = 0.00384$. It would be desirable to have a single analytical representation over the entire concentration range. A cubic equation in $m^{1/2}$ using the limiting slope of equation (3) gave poor agreement with the experimental results. A cubic equation using the theoretical value of the limiting slope was suggested by the referee

$$\Phi L_2 = 7010m^{1/2} - 12{,}900m + 8720m^{3/2}$$

This equation gives an excellent representation of our data except in the region below 0.002 m, the region of the short chord dilutions. This equation gives an inflection at about 0.2 m, whereas the experimental data indicate an inflection at about 0.004 m. The most satisfactory detailed representation of the data seems possible with the use of equations (3) and (5).

[13] F. D Rossini, *J. Research Natl. Bur. Standards*, **4**, 313 (1930).

$$\bar{L}_1 = -28.186m^{3/2} - 740.84m^2 \quad \text{cal./mole } H_2O \qquad (8)$$

$$\bar{L}_1 = -55.796m^{3/2} + 149.62m^2 \quad \text{cal./mole } H_2O \qquad (8a)$$

$$\bar{L}_2 = 4694m^{1/2} + 82{,}242m \quad \text{cal./mole } LaCl_3 \qquad (9)$$

$$\bar{L}_2 = 9291m^{1/2} - 16{,}610m \quad \text{cal./mole } LaCl_3 \qquad (9a)$$

Equations (3) and (4) intersect at $m^{1/2} = 0.062$; the intersection of (8) and (8a) is at $m^{1/2} = 0.031$; and (9) and (9a) intersect at $m^{1/2} = 0.047$. Representation of the ΦL_2 values by two equations replaces the inflection at about 0.004 *m* by a discontinuity, which is of course an approximation. In a region of overlap ($m^{1/2} = 0.055 - 0.068$) the deviation of either equation (3) or (5) from the apparently "best" curve is not greater than 20 cal./mole, which is the estimate of uncertainty in the original data. From graphical considerations we believe equations (8) and (9) to be satisfactory for calculating $\bar{L}$ values below 0.002 *m* and equations (8a) and (9a) useful above 0.01 *m*. From 0.002 to 0.01 *m* $\bar{L}$ values may be obtained graphically by interpolation.

For lanthanum sulfate below 0.0005 *m* the equations for the $\bar{L}$'s are

$$\bar{L}_1 = -4328m^{3/2} - 1.735 \times 10^5m^2 \text{ cal./mole } H_2O \qquad (10)$$

$$\bar{L}_2 = 7.207 \times 10^5m^{1/2} - 1.9256 \times 10^7m \quad \text{cal./mole } La_2(SO_4)_3 \qquad (11)$$

Above 0.0005 *m*, $\bar{L}$ values were derived from the large-scale plot of ΦL_2 *vs.* $m^{1/2}$, using slopes obtained with the aid of the differentiated form of the Lagrange interpolation formula.[14]

$\bar{L}$ values at several concentrations are given in Table III.

TABLE III

RELATIVE PARTIAL MOLAL HEAT CONTENTS

	$LaCl_3$			$La_2(SO_4)_3$		
m	$\Phi\bar{L}_2$ cal./mole salt	$-\bar{L}_1$ cal./mole H_2O	$\bar{L}_2$ cal./mole salt	$\Phi\bar{L}_2$ cal./mole salt	$-\bar{L}_1$ cal./mole H_2O	$\bar{L}_2$ cal./mole salt
0.00005		.....	..	2916	0.0_2109	4130
.0001	35	0.0_4356	55	3841	$.0_2259$	5280
.0005	91	$.0_3500$	146	5926	.0125	7535
.001	140	$.0_2163$	231	6045	.0213	8250
.005	...	.....	..	8620	.0640	9310
.01	536	.0408	763	9110	.108	9660
.02	710	.0980	986	9450	.288	10280
.05	970	.249	1147			
.1	1129	.268	1277			

Discussion of Results.—The Debye–Hückel limiting slopes, $(\partial\Phi L_2/\partial m^{1/2})_{m \to 0}$, are 7010 and 27,750 for the chloride and sulfate, respectively. The experimental limiting slopes are (equations (3) and (4)) 3129 and 480,400. The differences between theory and experiment seem to be entirely beyond the limit of experimental error. Studies of the heats of dilution of 1–1, 1–2, 2–1[3c] and 2–2[3d] valence types all indicate an approach to the limiting law, although in some cases this approach first becomes evident at concentrations below 0.001 *m*. Even the cadmium halides,[3d] weaker electrolytes, show qualitative agreement with theoretical predictions at low concentrations. The behavior of the lanthanum salts, therefore, is unusual. *p*H measurements indicated that the possible influence of hydrolysis on the heats of dilution was negligible. The *p*H's of chloride and sulfate solutions were 4.7 and 5.2, respectively, at 0.025 *m* and increased steadily with dilution toward the value for the water used, 6.4; our results for lanthanum chloride solutions agree with the values reported by other investigators.[10]

Shedlovsky and MacInnes[15] have computed activity coefficients of lanthanum chloride in dilute aqueous solutions at 25° from e. m. f. measurements of cells with transference in the concentration range 0.0006 to 0.03 *m*. The results of their calculations show that even in the most dilute solutions the activity coefficients do not approach the theoretical limiting slope. The activity coefficients decrease less rapidly with concentration than would be expected from the interionic attraction theory. This behavior, they point out, is opposite to that which would result from ion pair formation. Various extensions of the Debye–Hückel equation proved inadequate to account for the behavior of these solutions. In the same concentration range the relative partial molal heat contents ($\bar{L}_2$) are lower than the predictions of the theory. The temperature coefficient of the activity coefficient is therefore less than the expectation from theory and, so far as the activity coefficients are concerned, the salt is approaching the behavior of a strong electrolyte at higher temperatures.

Jones and Bickford[10] measured the conductance of lanthanum chloride solutions at 25° between 0.00025 and 1.0 *m*. The experimental limiting slope of the conductance *vs.* $c^{1/2}$ curve was 20% greater than the value predicted from the Onsager equation. Their data revealed an inflection point at about 0.005 *m* and some significance may be attached to the fact that the apparent heat contents also show an inflection point at approximately the same concentration, 0.004 *m*.

No measurements of the properties of lanthanum sulfate solutions seem to be available.

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(14) T. R. Running, "Empirical Formulas," John Wiley and Sons, Inc., New York, N. Y., 1917, p. 108.

(15) T. Shedlovsky and D. A. MacInnes, THIS JOURNAL, **61**, 200 (1939).

The disagreement of calculated and experimental limiting slopes for the heat contents of this salt is very pronounced. In some respects the results are similar to those given by the bivalent sulfates.[3d] Below 0.0005 *m* for calcium, magnesium and cadmium sulfates, the slopes of the $\partial(\Phi L_2)/\partial m^{1/2}$ *vs.* $m^{1/2}$ curves showed a definite tendency to decrease toward the theoretical values. Slight evidence for a similar behavior by lanthanum sulfate is observable in a plot of the short chords. It would be desirable to extend these measurements to lower concentrations to verify this point, but this does not seem feasible with the apparatus and technique available at present.

Summary

Heats of dilution at 25° have been reported for lanthanum chloride between 0.00006 and 0.1 *m* and for lanthanum sulfate between 0.00002 and 0.025 *m*. Relative partial molal heat contents have been computed for the concentration intervals studied.

The results in dilute solutions fail to reveal an approach to the Debye–Hückel theory even at the lowest measured concentrations.

RECEIVED AUGUST 17, 1942

[CONTRIBUTION FROM THE BUREAU OF PLANT INDUSTRY, U. S. DEPARTMENT OF AGRICULTURE]

Polymorphism of Phosphoric Oxide*

BY W. L. HILL, G. T. FAUST[1] AND S. B. HENDRICKS

Phosphoric oxide, or phosphorus pentoxide, is a component of several phase systems that have great significance in the chemistry of fertilizer manufacture, and accurate knowledge of its behavior in the pure condition is a prerequisite to a complete understanding of complex systems of more immediate practical importance. Thus far the polymorphous nature of phosphoric oxide has been deduced largely from vapor pressure measurements.[2,3,4] These data show that this compound exists in at least two crystalline modifications that melt to different liquids. The low-temperature or volatile form, the one with which the chemist is familiar, was found to change at 260° or above into a high-temperature modification having a negligible vapor pressure below about 400°. Recent crystal structure investigations showed that the low-temperature polymorph belongs to the rhombohedral division of the hexagonal system[5] and that a high-temperature form obtained by heating hexagonal crystals belongs to the orthorhombic system.[6] These later will be referred to as the H and O forms, respectively. Published vapor pressure data for the H form are for the most part in very good agreement, but results obtained by different workers on high-temperature preparations differ considerably. Existence of a third crystalline form was suggested,[2] but in the absence of adequate microscopic examination of the materials no definite conclusions could be drawn.

The authors approached the problem with a view toward (1) the preparation and identification of the different modifications, (2) the measurement of their optical constants, (3) a study of the phase transformations by the quenching method, and (4) the use of the new findings as a guide to an interpretation of the vapor pressure data.

Experimental Method

Materials.—The starting material was the H form obtained as an exceptionally good reagent grade of phosphorus pentoxide. Sampling was done in a dry chamber of the conventional type, dried with phosphorus pentoxide and provided with long rubber gloves for manipulations. On opening a fresh bottle of the reagent the leathery surface layer of partially hydrated oxide was removed, thus exposing the dry material below. The sample was then taken in successive small quantities, so that any small residual lumps from the surface layer could be recognized and discarded.

High-temperature crystalline modifications were prepared by heating P_2O_5 in closed glass tubes. In order to

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* Not copyrighted.

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(2) J. M. A. Hoeflake and F. E. C. Scheffer, *Rec. trav. chim.*, **45**, 191–200 (1926).

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