method from purified silver oxalate were superior to electrodes prepared from silver oxide for making silver–silver oxalate electrodes.

The silver–silver oxalate and mercury–mercurous oxalate electrodes have been compared.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF CALIFORNIA]

The Solubility Relations of White Phosphorus

BY CORNELIUS GROOT AND JOEL H. HILDEBRAND

White phosphorus, P_4, has an extraordinarily high internal pressure, as measured in the liquid state, higher than iodine and sulfur, and so far exceeding the internal pressures of the usual nonpolar solvents that its solutions show enormous deviations from Raoult's law, so great that even with carbon disulfide, one of its best solvents, unmixing to two liquid phases, one of them supercooled, occur below −6°. Its solutions, therefore, put maximum strain upon the theory of deviations from Raoult's law. The three solutions for which data existed were discussed by the senior author[1] in 1935 in the light of the theory of regular solutions. It was shown that the solubility of the liquid and solid phases can be correlated by aid of the equation for regular solutions

$$RT \ln (a_2/x_2) = v_2\phi_1^2(\delta_2 - \delta_1)^2 \qquad (1)$$

where a_2 is the activity of the phosphorus referred to its own pure liquid; x_2 its mole fraction in saturated solution, V_2 its liquid molal volume, ϕ_1 the volume fraction of the solvent, and δ_2 and δ_1 the square roots of the internal pressures of the phosphorus and solvent, respectively, defined by $\delta_2 = \Delta E^V/V \cong a/V^2$, ΔE^V being the molal energy of vaporization of the pure liquid. We shall designate δ as the "solubility parameter." In a solution saturated with solid P_4, $a_2 = a_2^s$, the activity of the solid form, which can be calculated from its melting point, $T_m = 317.4$°K., its heat of fusion, ΔH^F, and the difference in heat capacity of the liquid and solid. Since the publication of the earlier paper we have secured more accurate values than we then had for the heat terms. Young and Hildebrand[2] obtained $\Delta H^F = 601$ cal./mole (earlier value, 625 cal./mole) and $c_p^s = 21.46 + 2.872 \times 10^{-2}\,t$ and $c_p = 24.47 - 9.521 \times 10^{-3}t - 3.927 \times 10^{-5}t^2$. These values give, for example, $a_2^s = 0.865$ at 0° and 0.941 at 25°. The remarkably small heat of fusion of P_4 is responsible for a correspondingly small temperature coefficient of solubility, and gives room for the appearance of a liquid–liquid curve with carbon sulfide beginning at −6°, far below the melting point of P_4, 44.2°.

The present investigation was undertaken in order to extend the study to additional common typical solvents; carbon tetrachloride, a symmetrical molecule, and normal heptane, a linear molecule.

We first experimented with a procedure designed to measure solubilities at different temperatures with a single filling of an apparatus consisting of two connecting bulbs with a cylindrical tube, or "tail" attached to one. The apparatus was charged with a solvent and an excess of phosphorus. After saturation, the solution was decanted into the other bulb and the phosphorus was melted and transferred to the tail tube when its volume could be measured. The difference between this and the total phosphorus present gave the amount dissolved. Unfortunately, the molten phosphorus had a tendency to stick to the glass, making it often impossible to collect for a volume measurement, therefore the method was abandoned in favor of an analytical method. We report only the values for acetone solutions although it should be remarked that the points we obtained for benzene solutions agreed with those of Christomanos within the errors evident for both sets. The method adopted consisted in saturating a solution with solid P_4 in an apparatus similar to that described by Negishi, Donally and Hildebrand,[3] sealing off little bulbs of saturated solution and analyzing the contents. For liquid P_4, the little bulbs were filled with both liquid phases and sealed off, the cloud points were determined and the contents analyzed. The method of analysis[4] consisted in treating with a solution of copper nitrate, which gives copper phosphide and phosphorous acid, oxidizing to phosphoric acid with concentrated nitric acid saturated with bromine and determining as ammonium phosphomolybdate.[5] Due attention was paid to careful manipulation and to the precautions necessary to prevent oxidation, to retard the formation of red phosphorus, to ensure saturation, and to secure reasonable accuracy of analysis. These details can be learned by private correspondence with either author by anyone interested.

The solvents were of high purity from commercial sources and boiled within narrow limits.

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[1] (a) J. H. Hildebrand, THIS JOURNAL, **57**, 866 (1935); (b) "Solubility of Non-Electrolytes," Reinhold Publishing Corp., New York, N. Y., 1936, Chap. X, see also, (c) J. H. Hildebrand and T. F. Buehrer, THIS JOURNAL, **42**, 2213 (1920), for consolute temperatures with liquid phosphorus.

[2] F. E. Young and J. H. Hildebrand, *ibid.*, **64**, 839 (1942).

[3] G. R. Negishi, L. H. Donally and J. H. Hildebrand, THIS JOURNAL, **55**, 4793 (1933).

[4] E. H. Brown, H. H. Morgan and E. R. Rushton, *Ind. Eng. Chem., Anal. Ed.*, **9**, 524 (1937).

[5] W. F. Hillebrand and G. E. F. Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1929.

The phosphorus was purified by distillation in vacuum.

The experimental results are summarized in Table I. Only the means of the two or more determinations at each temperature are given. The root-mean-square deviations seldom exceeded 2%. Table II gives values in mole per cent. at 5 temperatures smoothed out by aid of a plot of log x_2 against $1/T$, x_2 being the mole fraction of P_4. The table includes also values for solutions in carbon disulfide by Cohen and Inouye,[6] and in benzene and ether by Christomanos.[7] We obtained values for acetone by the first method described above, but due to the inaccuracy of the method and the small solubility of P_4 in acetone, we give only the smoothed out values shown in Table II. In Fig. 1 are plotted values of log x_2 *vs.* $10^4/T$.

TABLE I

SOLUBILITY OF PHOSPHORUS

n-C_7H_{16}			CCl_4		
t°C.	g./100 g. solvent	No. detns.	t°C.	g./100 g. solvent	No. detns.
		Solid			
0	0.86	8	0	0.64	12
25	1.49	7	25	1.27	6
32.9	1.89	9	32.9	1.58	4
40.0	2.16	7	40.0	1.82	2
41.0	2.21	4	41.0	1.94	4
42.0	2.23	8	42.0	1.89	12
		Liquid			
33.0	1.94	2	25	1.32	4
40.4	2.23	2	42	1.89	4
42.0	2.26	2	45	1.96	2
46.0	2.40	2	48	2.09	4
50.0	2.62	2	51	2.19	2
63	3.27	2	52	2.28	2
71	3.72	4	59	2.56	2
78	3.83	2	72	3.16	2
84	4.50	4	91	4.10	2
100	5.66	2	94	4.23	2
131	7.58	2	100	4.55	2

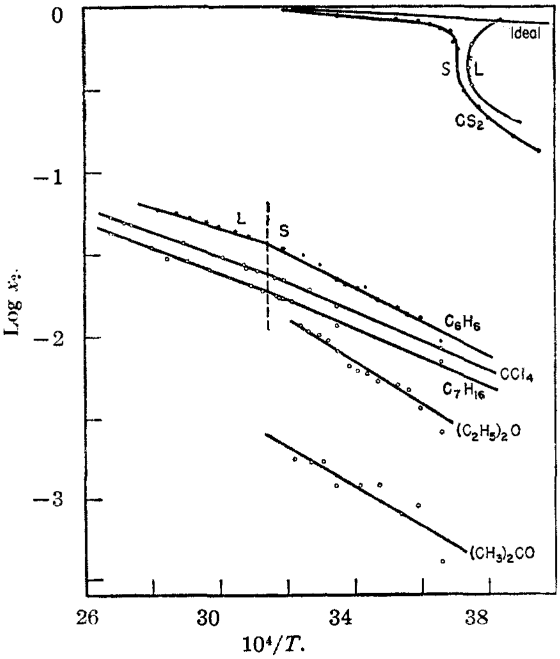

Fig. 1.—Solubility of white phosphorus, P_4.

TABLE II

SOLUBILITY OF P_4, MOLE PER CENT. SMOOTHED OUT VALUES

T, °C.	$(CH_3)_2$-CO	$(C_2H_5)_2O$	C_7H_{16}	CCl_4	C_6H_6	CS_2
−10 Solid						21.9
0 Solid	0.05	0.32	0.72	0.84		72.7
25 Solid	.14	0.83	1.24	1.58	2.27	89
40 Solid	.22	1.34	1.73	2.19	3.27	
50 Liquid			2.09	2.63	4.07	
75 Liquid			3.02	3.80	5.62	
δ_1 for solvent, 25°		7.45	7.43	8.58	9.16	9.92

The points by Christomanos for benzene and ether do not fall very closely upon the curves and the slopes for solid phosphorus are steeper than the slopes of our curves for carbon tetrachloride and heptane, although one would expect that all the curves for solid P_4 should fall below the extrapolated curves for liquid P_4 by about the amount of log x_2^i, where x_2^i is the ideal solubility, indicated at the top of Fig. 1.

The greater slope for benzene is rather puzzling, because solid and supercooled liquid P_4, at the same temperature, if they both consist of approximately pure phosphorus, with solid of the same crystal energy, would differ by the same free energy, regardless of the solvent. Figure 1 shows that the difference in slope between the solid and liquid curves for solutions in heptane and carbon tetrachloride agree within the limits of error with each other and with the slope of the "ideal" line. The considerably greater difference between the two branches for the solutions in benzene could be explained (1) by the presence of benzene, in solid or as compound, in the solid phase; (2) as a crystal form of P_4 of different energy; or (3) as inaccuracies in the measurements by Christomanos. We can offer at present only the following remarks concerning these possibilities. (1) We distilled away the benzene from a phosphorus solution till the solid phase that separated appeared dry; this, upon melting, yielded no further benzene. (2) Christomanos published photographs showing that the crystals separating from benzene solution have a very different appearance from those ordinarily obtained. This we verified, but are unable at present to say whether they represent a different crystal system or merely a different habit. If the latter, it is is difficult to see how their energy could be sufficiently different to account for the slope of the line in Fig. 1, particularly since solid P_4 above its transition point, −77°, is doubt-

(6) E. Cohen and K. Inouye, *Z. physik. Chem.*, **72**, 411 (1910).

(7) A. C. Christomanos, *Z. anorg. allgem. Chem.*, **45**, 132 (1905).

less rotating, on the evidence of its small entropy of fusion. This problem invites further investigation. The third possibility appears real because of the scattering of the experimental points. We regret that our investigation had to be terminated before we could redetermine these points by the more reliable method which we finally adopted.

We may note, first, that the solvent powers of the non-polar solvents for P_4 increase in the order of their internal pressure as measured by their δ-values, added to Table II. Ether is a poorer solvent, probably by reason of its polarity, and acetone very much poorer, for the same reason.

We now proceed to a quantitative test of Equation 1, extending to the new data the method used in the original paper[1] on P_4. We shall examine the degree of uniformity of δ_2 for P_4 calculated from the solubility data for different solutions. For the molal energies of vaporization over the range of these experiments we use the following expressions, based upon the best data available

P_4	$15{,}135 - 8.87T$	n-C_7H_{16}	$13{,}490 - 17.9T$
C_6H_6	$12{,}100 - 15.4T$	CS_2	$8{,}810 - 9.6T$
CCl_4	$10{,}990 - 12.9T$	$(C_2H_5)_2O$	$10{,}960 - 17T$

The molal volumes have been computed from the density expressions given in "I.C.T." and are reproduced for certain temperatures in Table III, along with δ-values.

TABLE III

	Molal volumes, v.				Solubility parameter			
	0°	25°	40°	75°	0°	25°	40°	75°
P_4	69.4	70.4	70.9	72.3	13.5	13.3	13.2	12.9
CS_2	58.8	60.6	61.8	...	10.27	9.92	9.70	...
C_6H_4	...	89.3	91.1	95.1	...	9.16	8.94	8.4
CCl_4	94.2	97.2	99.0	103.5	8.90	8.58	8.38	7.92
n-C_7H_{16}	143.0	147.5	150.2	157.6	7.76	7.43	7.24	6.78
$(C_2H_5)_2O$	100.6	104.5	107.2	...	7.92	7.56	...	...

Table IV gives values of δ_2 for P_4 calculated from the solubilities at 25°, Table II, by means of Equation 1, using the δ_1 values in Table III. The values of δ_2 in the case of benzene and carbon tetrachloride, 14.9 and 14.5, are as nearly alike as should be expected, in view of all the factors involved, including experimental errors, and the simplifying assumptions made in deriving Equation 1.

TABLE IV

VALUES OF THE SOLUBILITY PARAMETER OF PHOSPHORUS, δ_2, WITHOUT ENTROPY CORRECTION AND δ_2, WITH ENTROPY CORRECTION

	δ_2, 0°C.	δ_2, 25°C.	δ'_2, 25°C.
CS_2	15.0	..	..
C_6H_6	..	14.9	15.2
CCl_4	15.0	14.5	14.9
C_7H_{16}	13.9	13.5	14.3
$(C_2H_3)_2O$	14.6	13.9	14.4

Yost and Russel[8] have calculated the heat of vaporization of solid P_4 at 298° K· to be 13,200 cal. Subtracting the heat of fusion[2] gives the heat of vaporization of the liquid, 12,600 cal. at 25° and $\Delta E^V = 12{,}010$ cal. We plotted the vapor pressure measurements of P_4 made by different investigators and fitted them by the empirical equation

$$\log p_{mm} = 18.3351 - 33.08.7/T - 3.462 \log T$$

from which we calculate $\Delta E^V = 12{,}490$ at 25°. From this and $v_2 = 70.4$ cc. we get $\delta_2 = 13.3$. This is considerably less than the value of 14.5 derived from the solubility of P_4 in carbon tetrachloride. In the course of a careful reexamination of the solubilities of sulfur and iodine by the senior author, to appear in the third edition of "Solubility of Non-Electrolytes," co-author, R. L. Scott, a similar discrepancy has been found. It is therefore preferable, where data exist, to calculate a δ_2-value from solubility data rather than from $\Delta E^V/v$; the value so derived can be used to correct solubilities in various solvents and to predict approximate solubilities in new solvents, provided the specific interactions do not occur such as are illustrated by the brown iodine solutions.

The fact that δ_2 calculated from the heptane solutions has a lower value is no surprise in view of the size and shape of the heptane molecule. A similar deviation exists for solutions of iodine, sulfur and stannic iodide in heptane and octane.[1b] An approximate allowance for the effect of relative molal volumes upon the entropy of the solution may be made by means of an equation for the entropy of solution of molecules of different size in terms of free volumes.[9] If the free volumes are assumed proportional to the molal volumes, this yields, for the partial molal entropy of transfer of component 2 from pure liquid to solution

$$-\Delta\bar{S}_2/R = \ln \phi_2 + \phi_1(1 - v_2/v_1)$$

where ϕ_1 and ϕ_2 denote the volume fractions of the respective components.

Combining Equations 1 and 2, to take account of the effects of non-ideal behavior of both heat and entropy of solution, we may write

$$\ln a_2^s = \ln \phi_2 + \phi_1 \left(1 - \frac{v_2}{v_1}\right) + \frac{\phi_1^2 \, v_2 \, (\delta_2 - \delta_1)^2}{RT} \quad (3)$$

The values of δ'_2 in Table IV were calculated by aid of this equation. It can be seen that the discrepancy between the values obtained from the heptane solutions and those from the carbon tetrachloride solutions is thus considerably reduced.

The solubility of P_4 in carbon disulfide at 25° is so nearly ideal that an accurate value of δ_2 cannot be calculated from it, but at 0° and lower the deviation, due to the peculiar S-shape of the curve in Fig. 1, is sufficient to permit this to be done. It was shown in the first paper that Equation 1 serves to account not only for the shape of the curve for solid P_4 in carbon disulfide, but also for the liquid-liquid curve, which is nearly tangent to it. The agreement shown in Table IV between the results for carbon disulfide and carbon tetrachloride solutions at 0° is striking, despite the enormous difference in the solubility of P_4 in these two solvents; the mole-fractions are, respectively, 0.727 and 0.0084.

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(8) D. M. Yost and H. Russel, Jr., "Systematic Inorganic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1944, p. 180.

(9) *Cf.* J. H. Hildebrand, *J. Chem. Phys.*, **15**, 225 (1947).

One other point remains to be mentioned, the variation of solubility with temperature. Both δ_1 and δ_2 decrease with temperature, but ordinarily at different rates, and both are subject to more or less uncertainty. In a calculation of solubility by this theory, since $(\delta_1 - \delta_2)$ appears in the role of an exponent, an error of one unit in $(\delta_1 - \delta_2)$ appears as an error of a factor of ten in the calculated solubility. This exponential form, which gives the equations their wide applicability, also greatly increases the disturbing effects of approximations in the theory and experimental errors in the parameters. As a practical measure for interpolating or extrapolating solubilities, one may employ the procedure used by Hildebrand and Negishi.[10] The values for $\delta_2 - \delta_1$ calculated from solubilities for two or more temperatures were plotted against temperature and a straight or nearly straight line drawn through them, giving points for other temperatures.

Summary

1. The solubility of white phosphorus, P_4, has been measured from 0 to 130° in normal heptane and from 0 to 100° in carbon tetrachloride. Rough measurements of its (small) solubility in acetone are also reported int he range 0 to 40°.

2. These results, together with data from the literature for the solvents carbon disulfide, benzene and ether, are analyzed in terms of present solubility theory for solutions of non-electrolytes. The very different solubilities of phosphorus in carbon disulfide and in carbon tetrachloride are correlated by means of the ordinary equation, with benzene solutions showing only small divergence. Heptane solutions diverge moderately in the same direction as previously found with other solutes, but the correlation is improved by taking into account the entropy of mixing molecules of significantly different size.

Berkeley 4, California Received June 15, 1948

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[10] J. H. Hildebrand, This Journal, **59**, 2083 (1937); J. H. Hildebrand and G. R. Negishi, *ibid.*, **59**, 330 (1937).

[Contribution from the Chemistry Laboratories of The Ohio State University]

Phase Studies of Some Group 4a Tetrachloride–Aromatic Ether Systems

By Harry H. Sisler, Wilbur J. Wilson, Betty J. Gibbins, Harry H. Batey, Barbara Pfahler and Robert Mattair

The results of studies of compound formation by the tetrachlorides of carbon, silicon, germanium and tin with diphenyl ether and with anisole have been reported.[1] The present work was undertaken with the objective of expanding these studies to include various other aromatic ethers with the hope of obtaining information which would serve to answer some of the questions raised by the work on anisole and diphenyl ether. As this work progressed the previously reported data on the anisole systems seemed more and more anomalous. It was decided, therefore, to study the anisole systems again. We regret to report that the previously recorded results on the anisole systems, which were carried out by a co-worker of one of the authors in another laboratory, and published jointly with him, have been shown to be unreliable[1] (ref. 1, pp. 1517–1518). The new results, which have been obtained by four of us, are reported in this paper. In addition, the binary systems of phenetole with each of the group 4a tetrachlorides, methyl *m*-cresyl ether with each of the group 4a tetrachlorides, methyl *o*-cresyl ether with germanium tetrachloride, and *n*-propyl phenyl ether with germanium tetrachloride have been studied and are discussed below.

Experimental

Preparation of Materials.—The carbon tetrachloride was purified by fractionation in a five-foot column packed with glass helices at atmospheric pressure. Silicon tetrachloride from Eimer and Amend, germanium tetrachloride from the Eagle-Picher Lead Co., and tin tetrachloride from Baker and Adamson were similarly purified by fractionation at atmospheric pressure, protected from moisture by drying tubes filled with drierite. In each case a constant boiling middle fraction was taken and its purity checked by taking its freezing point.

Anisole, phenetole, methyl *m*-cresyl ether, methyl *o*-cresyl ether, and *n*-propyl phenyl ether, obtained from the Eastman Kodak Co., were dried by allowing them to stand over sodium wire, and were purified by fractional distillation. In each case a constant boiling middle fraction was retained and its purity checked by taking its freezing point.

Procedure.—The systems were studied by the freezing point method, the freezing points being determined by means of cooling curves. The cell used in these experiments was similar to that in previously reported studies.[1] The thermocouple well was filled with a mixture of carbon tetrachloride and chloroform to minimize convection effects. The stirrer in the cell consisted of a stainless steel wire coil attached to an iron cylinder coated with nickel; the stirrer was operated by means of an air-cooled solenoid which was wired through a motor driven interrupter, thus allowing continuous stirring. Weighed quantities of the components of the system being studied were introduced from a Lunge pipet, the pipet having a ground-glass surface of the same taper as the opening. While the sample was being introduced, another opening was open to the atmosphere through a drying tube filled with drierite. A copper–constantan thermocouple attached to a Leeds–Northrup Micromax self-recording potentiometer was used to measure the temperatures and record the cooling curves.

The various mixtures were cooled in a solid carbon dioxide–carbon tetrachloride–chloroform-bath, or in liquid air, depending upon the freezing point for the particular mixture. The rate of cooling was modified further by surrounding the cell with one or more test-tubes of larger

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[1] Sisler and Cory, This Journal, **69**, 1515 (1947).