tion was carried out in the calculations. This was compared to the first approximation calculation at the lower acidity. The results of these measurements and calculations are summarized in Table II.

TABLE II

COMPARISON OF FIRST APPROXIMATIONS TO K_1 AND K_3 IN 0.127 M AND 0.254 M $HClO_4$

(a) Assuming hydrogen ion dependence

$[HClO_4]$, M	$K_1 = \frac{[Ru(dt)_1^{+2}][H^+]}{[Ru^{+3}][Hdt]}$	$K_3 = \frac{[Ru(dt)_3][H^+]^2}{[Ru(dt)_1^{+2}][Hdt]^2}$
0.127	1400 ± 400	12000 ± 600
0.254	1300 ± 60	11000 ± 3000

(b) Not assuming hydrogen ion dependence

$[HClO_4]$, M	$K_1 = \frac{[Ru(Hdt)_1^{+3}]}{[Ru^{+3}][Hdt]}$	$K_3 = \frac{[Ru(Hdt)_3^{+3}]}{[Ru(Hdt)_1^{+3}][Hdt]^2}$
0.127	11000 ± 3000	740000 ± 32000
0.254	5200 ± 200	180000 ± 40000

From Table II, it is seen that the assumption of hydrogen ion dependence gives agreement in both equilibrium constants at the two acidities, whereas the assumption of no dependence does not. Therefore it must be concluded that dithioöxamide is behaving as an acid, each molecule releasing a proton on formation of the ruthenium complex. This behavior was anticipated since dithioöxamide is known to be a weak monobasic acid.[9]

Although the formation constants for the reactions as they have been written are quite small, the ruthenium is held tightly in the complex. This may be illustrated by obtaining the formation constants for the reactions

$$Ru^{+3} + dt^- \rightleftharpoons Ru(dt)_1^{+2}$$

$$K_1' = \frac{[Ru(dt)_1^{+2}]}{[Ru^{+3}][dt^-]}$$

and

$$Ru(dt)_1^{+2} + 2dt^- \rightleftharpoons Ru(dt)_3$$

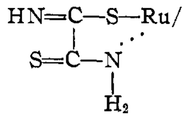
$$K_3' = \frac{[Ru(dt)_3]}{[Ru(dt)_1^{+2}][dt^-]^2}$$

Using the acidity constant of dithioöxamide evaluated at unit ionic strength,[9] $k_a = (3.78 \pm 0.04) \times 10^{-11}$, K_1' and K_3' were calculated.

$$K_1' = \frac{K_1}{k_a} = \frac{(9.3 \pm 0.3) \times 10^2}{(3.8 \pm 0.1) \times 10^{-11}} = (2.4 \pm 0.1) \times 10^{13}$$

$$K_3' = \frac{K_3}{(k_a)^2} = \frac{(8.3 \pm 0.2) \times 10^3}{[(3.8 \pm 0.1) \times 10^{-11}]^2} = (5.8 \pm 0.2) \times 10^{24}$$

Dithioöxamide has been reported to form five-membered [C–C–N–S–Metal] chelate rings with both platinum and palladium.[3–5] It seems quite likely that the ruthenium–dithioöxamide complexes involve chelate rings of the same type (I).



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[9] R. P. Yaffe and A. F. Voigt, THIS JOURNAL, **74**, 2941 (1952).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY]

The Solubility of Water in Liquid Phosphorus

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Determinations of the solubility of water in liquid phosphorus gave 3.6 ± 0.3 mg./g. at 45° and 3.9 ± 0.5 at 25°. We select 6.7×10^{-3} ml. of H_2O/1 ml. P_4 at 25° for evaluation. Published figures for H_2O in CS_2 and CCl_4 give 1.95 and 1.59 ml. of H_2O/ml. of solvent, respectively. The solubility parameter of water calculated from these data gave 26.2 for H_2O in P_4, 26.1 in CS_2 and 24.7 in CCl_4. A previously published analysis of data for H_2O in paraffins gave values close to 24.5.

In several recent investigations involving white phosphorus[1] we have found it far more convenient to protect it from air by a layer of water than by operating in a vacuum, and we have had satisfying evidence that the properties under investigation were not appreciably affected by dissolved water. We decided, however, that it would be desirable to know the solubility of water in phosphorus, both for its bearing upon past and future experiments, and for its theoretical interest, in view of the extraordinarily high solubility parameter of phosphorus and the dipole moment of water.

The procedure adopted was, briefly, to equilibrate liquid phosphorus with water, freeze it rapidly, presumably entrapping dissolved water in the solid as minute droplets, as in the case of dissolved mercury; wash off all exterior water by repeated application of cold dry methyl alcohol; melt the phosphorus and shake under methyl alcohol to extract the water, and determine its amount by the Fischer titration method.[2]

The essential details of the procedure were as follows. The phosphorus used in determinations 1–7 and 16–18 was purified by treatment with dilute acid dichromate, as previously described; that used in determinations 8–15 was distilled *in vacuo*. The methyl alcohol was Eimer and Amend C.P., anhydrous, handled so as to prevent access of water from the air. The Fischer reagent was prepared and standardized carefully by Mr. Tashinian, of our microlaboratory, to whom we express our grateful appreciation.

Five ml. of purified phosphorus was pipetted under water into a previously tared flask with ground glass cap. This was shaken in a water-bath at a stated temperature. One hour was found amply sufficient for equilibrium. The flask was then quickly chilled to freeze the phosphorus, care being taken to keep it in one compact mass and not entrap drops of the surrounding water. It was detached from the glass, and the flask cooled in ice-water, to reduce the amount of dissolved phosphorus, which can affect the reagent. The water in the flask was replaced by six washings with 50-ml. portions of precooled methyl alcohol. A seventh 50 ml. was allowed to remain in the flask. The sixth portion was

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[1] R. E. Powell, T. S. Gilman, G. J. Rotariu, Eva Schramke and J. H. Hildebrand, THIS JOURNAL, **73**, 2525, 2527 (1951).

[2] *Cf.* J. Mitchell, Jr., and D. M. Smith, "Aquametry," Interscience Publishers, Inc., New York, N. Y., 1948, p. 19.

blank tested for water to see that the washing had been adequate. All of the operations were performed in very subdued light.

The flask was next dried externally, weighed, and immersed in water at 50–55°. The melted phosphorus was vigorously swirled to allow the alcohol to extract the dissolved water from the phosphorus, the phosphorus collected and the whole cooled in ice-water for about 45 minutes. The small amount of phosphorus dissolved in the alcohol largely separated out and settled upon cooling and standing, as shown by the absence of smoking after evaporating one drop on a glass plate. This test will detect as little as 0.003 mg. of phosphorus. Any appreciable amount of it affects the Fischer reagent. Then 20 ml. of alcohol was removed in a dry, nitrogen-filled pipet into the similarly treated titration flask, an excess of Fischer reagent was then added and back-titrated with water.

The results are shown in Table I.

Table I

Solubility of Water in Phosphorus

The difference between the averages for 25 and 45° is within the error of both, hence is not significant. The figure 3.6 mg./g. corresponds to a mole fraction of water of 0.025 and a volume fraction of 0.0063.

t, °C.	No.	mg. H_2O/1 g. P_4
45	1	3.6
	2	3.6
	3	3.4
	4	2.8
	5	4.4
	6	4.3
	7	4.4
	8	4.1
	9	3.4
	10	3.0
	11	3.1
	12	4.0
		3.6 ± 0.3
25	13	3.3
	14	5.1
	15	4.6
	16	3.6
	17	3.9
	18	3.0
		3.9 ± 0.5

The senior author recently recalculated[3] the accurate figures obtained by Black, Joris and Taylor[4] for the solubility of water in a number of hydrocarbons, and showed that they were well correlated by the equation[5]

$$-\ln \varphi_2 = \varphi_1 \left(1 - \frac{v_2}{v_1}\right) + v_2\varphi_1^2(\delta_2 - \delta_1)^2/RT \quad (1)$$

where φ denotes volume fraction, v, molal volume, δ, solubility parameter, and subscript 2 the water and 1 the solvent. The values δ_2 calculated from the data were close to 24. The revision of the δ-values for hydrocarbons proposed later[6] would raise this to about 24.5. It is now interesting to see how well the same value applies to the solubility of water in phosphorus and two other non-polar liquids, carbon disulfide and carbon tetrachloride. The results are shown in Table II.

Table II

Solubility of Water, 25°

Solvent	g. H_2O/ 1000 g.	$10^4 \varphi_2$	v	$\delta_2 - \delta_1$	δ_1	δ_2
P_4	3.8	67	70	11.8	14.4	26.2
CS_2	0.14[7]	1.95	61	16.1	10.0	26.1
	0.10[8]	1.39	61	16.4	10.0	26.4
CCl_4	0.10[8,9]	1.59	97	16.1	8.6	24.7

The agreement between the δ_2-values for water calculated from the solubilities shown in Table II is probably as good as the accuracy of the data. For P_4 and CS_2, they are a little higher than the ~ 24.5 for CCl_4 and the paraffins. Despite the presence of several disturbing factors not taken into account in deriving equation 1, it evidently can serve for a rough prediction of the solubility of water in non-polar, non-hydrogen bonding liquids.

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Berkeley, California

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(4) C. Black, G. A. Joris and H. S. Taylor, *ibid.*, **16**, 537 (1948).

(5) *Cf.* J. H. Hildebrand and R. L. Scott, "Solubility of Nonelectrolytes," Reinhold Publ. Corp., New York, N. Y., 1950, p. 131.

(6) J. H. Hildebrand, *J. Chem. Phys.*, **18**, 1337 (1950).

(7) S. P. Uspenski, *Petrol. Ind.* (*Russian*), **17**, 713 (1929); *cf.* A. Seidell, "Solubilities of Inorganic and Metal Organic Compounds," D. Van Nostrand Co., Inc., New York, N. Y., 1940, p. 584.

(8) C. W. Clifford, *Ind. Eng. Chem.*, **13**, 631 (1921).

(9) C. H. Rosenbaum and J. H. Walton, This Journal, **52**, 3568 (1930).