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

The Solubility of Mercury in Liquid Phosphorus[1]

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The fact that mercury dissolves in liquid phosphorus, already observed by others, is so remarkable, as being the only known instance of a metal dissolving by a purely physical process in a non-metallic liquid, that it invited this further study. The liquid solution is perfectly clear, but upon the rapid crystallization induced by great supercooling the mercury separates in globules so numerous and fine as to give the solid a gray-black appearance resembling that of a photographic negative. The darkening is less the higher the temperature and hence the speed of crystallization. The solubility was measured by the loss in weight of mercury after equilibration with liquid phosphorus, giving 0.29 mg. Hg per gram P_4; or 1.76×10^{-4} mole per mole or 3.7×10^{-5} cc. per cc. This is $^1/_{15}$ the value, 5.6×10^{-4} cc. per cc., calculated by the aid of regular solution theory with no allowance for the metallic nature of mercury.

In the course of the investigations on the solubility of phosphorus[3] in several solvents carried out in this Laboratory several years ago, the senior author noticed that liquid phosphorus which had been in contact with mercury and then frozen rapidly, as it does when strongly supercooled, suddenly became black. This black solid mass became quite clear on remelting. If, then, it was seeded after cooling only a little below the melting point, 44.2°, it froze to a colorless solid, but when it was more strongly supercooled it again became black on freezing, the amount of darkening increasing with the supercooling and hence with the greatly increased speed of crystallization, as set forth in the accompanying paper.[4]

Figure 1 shows a photograph of five tubes of phosphorus which had been equilibrated while liquid with the mercury seen in the bottom of each tube and then seeded after cooling to the respective temperatures marked. The one marked 0° froze spontaneously after being placed in water at 0° but doubtless before that temperature had been reached. The position of a tube in the series could be altered at will by remelting and inducing crystallization at a different temperature.

On searching the literature, we found that Thenard,[5] in 1812, had noticed the blackening and that in 1870 Blondlot[6] had attributed it to a black modification of phosphorus whose formation is catalyzed by contact with the mercury, although this interpretation was contraindicated by his own observation that after dissolving out the phosphorus from the black mass with carbon disulfide the amount of residue left upon the filter "est toujours extrêmement faible, et, chose remarquable, ne parait pas augmenter, quelles que soient la durée du contact avec le mercure et la proportion de ce dernier." This observation indicated a saturation effect, not a catalysis. However, in 1910, Gernez[7] dissolved out the phosphorus from the black mass and showed, by squeezing out globules under pressure, that the residue contained metallic mercury.

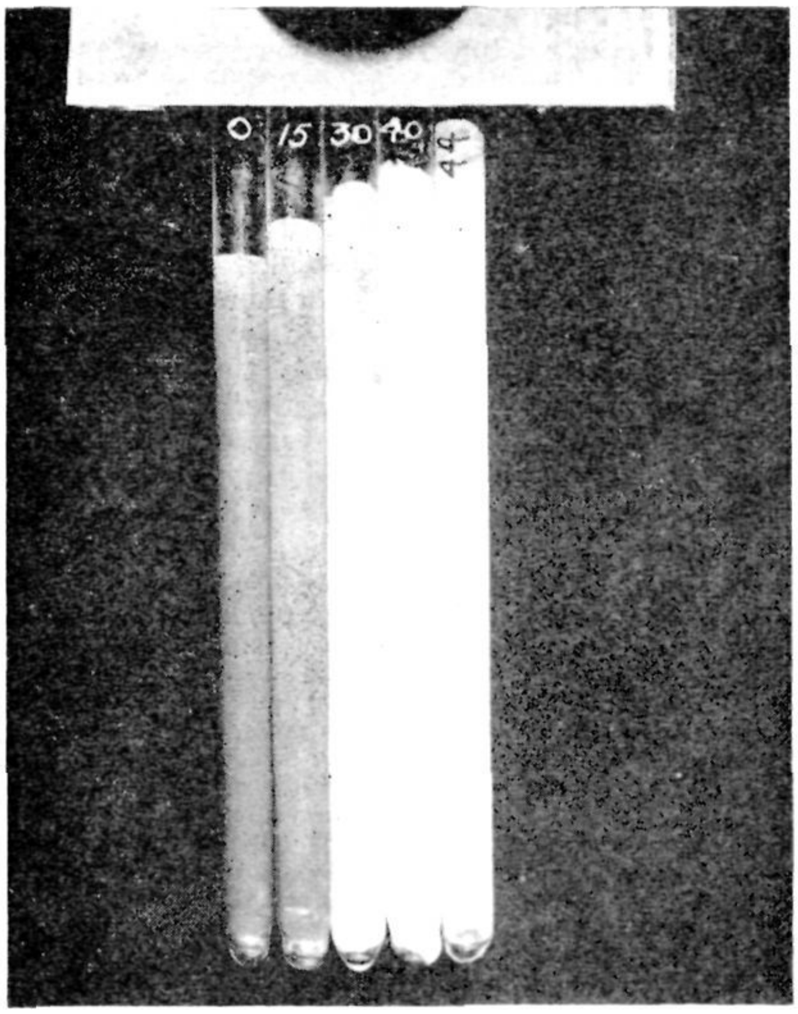

Fig. 1.—Solutions of mercury in phosphorus, frozen after supercooling to various temperatures.

That a metal should thus dissolve reversibly in a non-metallic solvent without chemical interaction appeared so unique as to invite further study. We made a calculation which showed that London forces alone could account for measurable solubility. Mercury has lower internal forces than any other metal except those of Group 1, which are too reactive to give solutions of this type, and phosphorus has higher internal forces than any non-polar, non-metallic liquid we know of. Their solubility parameters,[8] δ, (square root of energy of vaporization per cc.) are 30.7 and 14.5, respectively, at 25°. Also, the discrepancy in molal volumes, 14.8 and 70.4 cc., respectively, favors solubility in terms of the Flory–Huggins formulation.[9] And, finally, mercury is a rather poor metal if judged by its electrical conductivity. On substituting the above values in the general solubility equation

$$\ln a_2 = \ln \varphi_2 + \varphi_1 \left(1 - \frac{V_2}{V_1}\right) + \frac{\varphi_1^2 V_2(\delta_2 - \delta_1)^2}{RT} \quad (1)$$

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[1] A brief preliminary report on this work was presented at the symposium on liquid structure of the American Chemical Society in Chicago, September 4, 1950.

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[3] C. Groot and J. H. Hildebrand, THIS JOURNAL, **70**, 3915 (1948).

[4] R. E. Powell, T. S. Gilman and J. H. Hildebrand, *ibid.*, **73**, 2525 (1951).

[5] L. J. Thenard, *Ann. chim. phys.*, [1] **81**, 109 (1812).

[6] Blondlot, *Compt. rend.*, **60**, 830 (1865); **70**, 856 (1870).

[7] D. Gernez, *ibid.*, **151**, 12 (1910).

[8] See "Solubility of Nonelectrolytes," J. H. Hildebrand and R. L. Scott, Reinhold Publ. Corp., New York, N. Y., 1950.

where φ denotes volume fraction, and letting subscript 1 stand for phosphorus, and setting $\varphi_1 = 1$ and $\ln a_2 = 0$, since the mercury phase is practically pure, we get $\varphi_2 = 5.6 \times 10^{-4}$. This is equivalent to 0.40 g. of mercury per 100 g. of phosphorus at 25°. We expected, of course, to find the actual figure to be less than this because of the metallic character of mercury.

In our first attempts at measurement, we used temperatures above the melting point of phosphorus, and we greatly over-estimated the time necessary to produce saturation, with the result that some insoluble brown solid was formed and we did not obtain reproducible results. We were able, nevertheless, to verify the conclusion of Gernez that the mercury goes into solution as metal by separating the phosphorus from the liquid mercury, dissolving it out with carbon disulfide, transferring the small residue to a vessel in which a piece of gold foil was suspended, evacuating and observing the gray spots of mercury which gradually distilled onto the gold. We had thought of getting the amount of mercury dissolved in the phosphorus from the increase in the weight of the gold, but the slowness of this method, together with the uncertainty about complete recovery of the colloidal mercury which had separated upon freezing the solution, led us to turn to the following simpler procedure.

Glass tubes about 20 cm. long and 10 mm. internal diameter were bent into the form of the letter J, with the lower end closed. About 2-4 g. of carefully weighed mercury was put into each, they were filled with boiled out water, placed under water above 44° and 2.00 cc. of phosphorus pipetted under water into each, which was then closed with a cork. A number of such tubes were fixed parallel to each other in a sort of cradle mounted in a thermostat at 25°. This cradle could be slowly rocked so that the mercury globule traveled back and forth within the column of liquid phosphorus. The ratio of the contact surface to the volume of phosphorus was thus very large, the stirring was efficient and saturation resulted in a surprisingly short time. In most cases the phosphorus remained liquid; in some it had to be remelted to be sure of adequate equilibration.

After a tube had been rocked for a certain length of time, it was removed, immersed in warm water and tilted to pour out most of the solution. The remainder was dissolved in carbon disulfide and similarly decanted from the mercury. The carbon disulfide used had been shaken with mercury to remove substances which discolor a surface of mercury, present even in some of the best "C.P." material. The tube was then removed from the bath, most of the water poured off and the remainder removed by several washings with methanol. After the methanol had evaporated, the mercury was reweighed.

Table I gives the results of a number of determinations, together with the approximate time during which each tube was rocked. The last two figures, marked with an asterisk, represent weighings with a microbalance. The small fluctuations evidently come from the manipulation rather than errors in weighing. It will be seen that saturation was reached and there is no evidence of slow chemical reaction.

Table I

Solubility of P_4 in Mercury, 25°

Mg. Hg. 2 cc. P_4	Time, minutes
0.8	5
1.0	10
1.0	15
1.0	20
1.0	30
1.11*	10
0.90*	10

Extrapolating the density of liquid phosphorus to 25° from the data by Dobinski[9] between 45 and 80°, we get 1.761, and the solubility of mercury in phosphorus at this temperature is 0.285 mg. per gram; 1.76×10^{-4} mole per mole; 3.7×10^{-5} cc. Hg per cc. P_4. This is just $^1/_{15}$ of the value calculated earlier from regular solution theory with no allowance for metallic character, a quite remarkable degree of agreement.

Several determinations were made at higher temperatures, up to 100°, but no reliable conclusion can be derived from them; we can state only that the solubility appears to increase but slightly over this range.

The question arose whether the presence of water might have influenced the above results. This was answered by experiments carried out in the absence of water in a nitrogen gas atmosphere. 2 cc. of clean white phosphorus (cleaned overnight under an acid dichromate solution, and rinsed 5× with distilled water immediately before melting and using) was pipetted under water into a curved tube containing a weighed amount (about 2.5 g.) of mercury. The tube was attached to a vacuum line and the water removed completely by alternate melting of the phosphorus and evacuation of the water. Nitrogen was then admitted, the phosphorus was melted, allowed to cool slowly in air, immersed in a bath kept at 25.0° ± 0.1°C. and the tube shaken by hand for 17 min., a time sufficient, as shown by previous experience, to insure saturation. A ball joint placed horizontally in the apparatus permitted this operation. The tube was then removed quickly and submerged in the water, whereupon the phosphorus solidified and blackened. The phosphorus, with its finely dispersed mercury, was removed by washing three times with 10 cc. portions of carbon disulfide (kept over distilled mercury for 48 hours and filtered) and removing with a dropper as it dissolved. The undissolved mercury lay beneath the solidified phosphorus layer so that complete removal of the dispersed mercury was assured. The last portions of the carbon disulfide solution were removed by washing with "reagent" methanol (treated similarly as the carbon disulfide). The residual methanol was evaporated into nitrogen, and the mercury weighed again. Four determinations gave, respectively, 1.45, 1.25, 0.74, 1.28 mg. of Hg per 2 cc. of P_4. A check on the possible loss of mercury solvents was made by repeating the procedure using the same amounts of washing liquids and showed it to be negligible. These anhydrous determinations were a little more complicated and less reproducible than the ones carried out under water, but confirm the substantial accuracy of the value we report.

Acknowledgment.—This work was supported by the Atomic Energy Commission.

Berkeley 4, Calif. Received December 20, 1950

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(9) S. Dobinski, *Z. Physik*, **83**, 129 (1933).