see if the previously unexplained magnetic behavior of the heavy transition metals[5] can be accounted for entirely on the basis of Kotani's calculations.

Experimental.—Ammonium hexabromoösmate(IV) was prepared from metallic osmium through the tetroxide by the method of Gilchrist.[6] Reagents of analytical grade were used throughout and a spectroscopic analysis of the osmium showed it to be free of other platinum metals. The magnetic susceptibility was measured by the Gouy method with the sample tube suspended inside a large Dewar flask for temperature control.[7] The magnet was a large electromagnet with truncated conical pole pieces and a gap of 2.00 inches. The field strength was varied from 0 to 8,000 oersteds and was measured by means of a calibrated fluxmeter. The susceptibility of powdered cupric sulfate, $CuSO_4 \cdot 5H_2O$, was measured to test the operation of the apparatus. The value of $\mu_{eff.}$ for cupric ion in this salt was found to be 1.94. This may be compared with reported values of 1.923[8] and 1.920[9] for the same salt.

The susceptibility of ammonium hexabromoösmate(IV) was measured at temperatures of 25.1, −36.3, −47.2, −87.4, −147.4 and −180.2°, and it was found that the susceptibility of osmium(IV), corrected for the diamagnetism of ammonium and bromide ions,[10] was 980×10^{-6} (±2%) c.g.s. units over this entire range. Both the temperature dependence and field strength dependence were zero within the experimental error over the range of values used.

Acknowledgment.—We gratefully acknowledge the helpful advice and encouragement given so generously by Raleigh Gilchrist and Irvin L. Cooter, of this Bureau.

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NATIONAL BUREAU OF STANDARDS
WASHINGTON 25, D. C.

Liquid Solution of Gallium in Yellow Phosphorus[1,2]

BY ROBERT G. ARMSTRONG[3] AND GEORGE J. ROTARIU

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The first example of a metal dissolving in a non-metallic liquid by a pure physical process, that of mercury in yellow phosphorus, was discovered by Hildebrand in 1950.[4] The subsequent solubility work[5] revealed that the regular solution theory was able to deal with this system, with an allowance made for the metallic nature of the mercury. One would expect the metallic nature of the mercury to lead to a larger excess free energy and therefore to a smaller solubility; this was indeed the case.

We have investigated the system of liquid gallium in yellow phosphorus at 45° with the aim of finding a second system in which a liquid metal dissolves in a non-metallic liquid. Although the theory predicts a solubility of 10^{-30} g. Ga/3 cc. P_4, it was felt that enough gallium might dissolve (if this system could not be handled by the theory) to make its presence detectable. The pertinent physical constants are summarized in Table I; the data are taken from reliable sources.[6]

TABLE I

PHYSICAL CONSTANTS

	P_4	Hg	Ga
M.p., °C.	44.1	−38.9	29.75
B.p., °C.	280.5	357	1983
d_{25}	1.76	13.55	5.9
V_{25}	70.4	14.8	11.8
Resistivity (micro-ohms cm.)	10^{11}	95.8	27
δ_{25}	14.5	30.7	74

Gallium has been reported[7] to form a phosphide, GaP, but only under extreme conditions; when $Ga(OH)_3$ is heated in a P_4 vapor atmosphere (diluted with H_2) at 500°, the orange-yellow GaP is formed. We have found that liquid gallium (Alcoa, 99.95%) could be kept in contact with liquid phosphorus at 45° almost indefinitely with no discoloration of the shiny metallic surface of gallium and with no trace of an orange-yellow substance. We did find that a trace of a substance of this color was formed when the mixture was kept at 98° for 15 minutes. Since our work was to be done at 45° or lower it seemed unlikely any phosphide would form.

We conclude, on the basis of the following evidence, that gallium metal dissolves in yellow phosphorus by a physical process, to the extent of 0.01 to 0.1 μg. of gallium per ml. of P_4 at 45°.

Ga Metal Dissolves.—(1).—When samples of phosphorus (saturated with Ga; filtered through a medium porosity scintered glass disc) were burned in air and the residue excited by a 110 v. a.c. carbon arc, the 4033 Å. Ga I emission line (Gaertner Monochrometer) was observed. Similar tests with the water and phosphorus used failed to reveal any line at 4033 Å.

(2).—Metallic beads of gallium metal were isolated from six samples of Ga-saturated P_4. The freezing and washing away of the P_4 with CS_2 of such samples revealed the presence of tiny metallic-like beads (45–260 × magnification) which could be rolled about and indented with a needle probe. These beads were supercooled with ice to 0°, frozen with Dry Ice and remelted at about 30° with an electric wire. It should be pointed out that traces of Ga_2O_3 are undoubtedly present in suspended or dissolved form also in the P_4, although we have never observed any white or gray residue with this procedure. Positive 8-hydroxyquinoline tests[8] confirmed the presence of gallium. These metallic beads were also isolated by a high vacuum distillation (10^{-5} mm.) of the P_4 at 55°.

Solubility between 0.01–0.1 μg. Ga/ml. P_4. (1).—The upper limit of 0.1 μg. is given by the failure of observing any absorption at 392.5 mμ for the gallium-quinolinol present when tested according to the procedure of Moeller and Cohn[9] with the Beckmann Model DU Spectrophotometer. These authors have shown that the minimum detectable limit is 0.1 μg. of gallium per ml. of $CHCl_3$ extracting solvent. These samples which did not show an absorption spectra, when evaporated to dryness and the residue examined spectrographically, *did* reveal the 4033 Å. Ga I line.

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(2) Presented at the 125th Meeting of the American Chemical Society, Kansas City, Mo., March, 1954.

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This upper limit is given support by the fact that Ga-saturated P_4 solutions do not, upon solidification at 25°, exhibit the "blackening" effect shown by the Hg–P_4 system.[5] Further, when P_4 saturated with Hg was diluted 100× with more P_4, it also failed to reveal any trace of "blackening." Since the solubility of Hg in P_4 is 0.5 mg./cc. P_4,[5] it is unlikely that more than 5 μg. of Ga dissolves per cc. of P_4.

(2).—The lower limit of 0.01 μg. is given by the fact that the residues mentioned above when examined spectrographically *did* reveal the 4033 Å. Ga I emission line. Owens[10] found that as little as 0.025 μg. of aluminum on such electrodes could be detected spectrographically. Assuming that gallium has the same sensitivity of detection under these conditions as aluminum, we can say that the amount of Ga per cc. of P_4 is about 0.01 μg.

Microscopic examination (up to 900×) of thin sections (approx. 1 mm.^{2} in area, under immersion oil) of solid P_4 saturated with Ga failed to reveal any distinct difference between them and those of pure solid P_4. We estimate there is about 5×10^{-11} g. of Ga per section (*i.e.*, about 10^{-12} mole of Ga = 10^{11} atoms of Ga). This small amount if distributed evenly would be difficult to detect since the P_4 contains tiny entrapped bubbles of water and has in addition the slicing marks on its surface. One has difficulty in spotting the difference even with the Hg–P_4 system where the Hg solubility is some 1000× that of the Ga. Thus the size of the Ga particles present and frozen out must be below the lower detectable limit of the microscope. The possibility that the liquid Ga exists in colloidal form of particle size larger than this limit is therefore precluded.

Our earlier attempts to determine the amount of Ga were; unsuccessful; these included a micro-balance loss-in-weight procedure and the polarographic procedure of Zeltzer.[11] These failures were undoubtedly due to the small amount of Ga present in our P_4 samples. The use of large samples of P_4 is inadvisable due to the fire hazard in case of an accident.

The inability of the regular solution theory to predict the solubility of 0.01–0.1 μg. Ga/ml. P_4 at 45° may be due to the extremely large differences in molar volumes of the two substances and to the metallic character of the Ga.

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Some Metal Complexes of Kojic Acid

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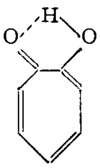
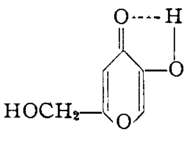
Introduction

There has been in progress in this Laboratory an investigation of the metal complexes of tropolone and its derivatives.[2,3] It was found that tropolone[2] and the alkyltropolones[3a] form metal complexes of much greater stability than those of β-diketones of comparable acidity. The benzotropolones[3b] were found to form complexes whose stabilities are intermediate between the simple tropolones and the β-diketones. Several factors[3a] were proposed as possibly contributing to the unusual stabilities of the metal tropolonates. Among these was the size of the chelate ring.

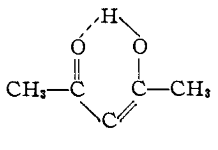
Tropolone (I) and kojic acid (II) both form five-membered chelate rings with hydrogen or a metal, while acetylacetone (III), a typical β-diketone, forms a six-membered ring.



I



II



III

If the size of the chelate ring is the major contributing factor to the stability of the metal complexes of tropolone, it would be expected that the metal kojates would also exhibit stabilities appreciably greater than those of metal derivatives of β-diketones of comparable acidity. Since kojic acid has been shown to react with a large number of metal ions[4] and is readily available, it was chosen as a representative compound for study.

Experimental

The kojic acid was a gift from the Corn Products Refining Company and was purified by sublimation: stout, white needles, m.p. 154–156°; reported[5] 154°.

Potentiometric titrations and calculations of constants were done as described previously.[3a] An orange powder, m.p. > 250°, precipitated when methanolic solutions of kojic acid and uranyl acetate were mixed. *Anal.* Found: C, 26.72; H, 2.13. Calcd. for $UO_2(C_6H_5O_4)_2$: C, 26.09; H, 1.83; calcd. for $UO_2(C_6H_5O_4)_2 \cdot {}^1/_2H_2O$: C, 25.66; H, 1.97. Purification was difficult because of the extremely low solubility of the material.

The negative logarithm of the acid dissociation constant (pK_D) of kojic acid in 50% aqueous dioxane was found to be 9.40. Formation constants of the metal complexes are given in Table I.

TABLE I

FORMATION CONSTANTS OF METAL KOJATES

Metal ion	log K_1	log K_2	log $K_{av.}$
UO_2^{++}	10.1	7.4	8.8
Cu^{++}	9.3	7.2	8.3
Zn^{++}	7.4	5.8	6.6
Ni^{++}	7.1	5.5	6.3
Co^{++}	6.8	5.2	6.0
Cd^{++}	6.6	4.7	5.7
Ca^{++}	4.4	2.7	3.6

Discussion

Calvin and Wilson[6] demonstrated for a variety of compounds containing a carbonyl group and an hydroxyl group (so situated as to make the formation of a six-membered chelate ring possible) that there exists a linear relationship between pK_D's for the hydrogen compounds and log k_{av}'s for the copper complexes. The hydroxy aldehydes divided themselves into three major groups classified according to the aromatic ring system of the molecule. A fourth group, forming the most stable copper derivatives, consisted of β-diketones and β-keto esters. When the pK_D of kojic acid is plotted on the same graph[6] with the hydroxy aldehydes, β-diketones and β-keto esters, it is found that copper kojate is of the same order of stability as the copper derivatives of β-diketones and β-keto esters, but much more stable than the copper derivatives of

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