117. *The Solubilities of Copper, Manganese, and Some Sparingly Soluble Metals in Mercury.*

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In this work the solubilities of metals of atomic numbers 22—29 and of molybdenum, tungsten, and uranium have been investigated directly. The analytical method is sufficiently sensitive to give consistent and positive results for copper and manganese only. It fixes, however, the upper limit of solubility of the other metals. The only earlier work by a direct method is that of Richards and Garrod-Thomas (*Z. physikal. Chem.*, 1910, **72**, 179). They filtered saturated amalgams of copper and of iron through chamois leather thrice, distilled most of the mercury off, removed the rest by volatilisation, and determined the metals colorimetrically; copper was also determined gravimetrically. For copper they got a mean value of 0·0024 g. per 100 g. of mercury, the order of which was supported by electrometric measurements. For iron the value was 0·0013 g. They doubted whether this small value was genuine, as it was unsupported by electrometric measurements.

The only other work on the solubilities of these metals has been done by electrometric methods by Tammann and Kollmann (*Z. anorg. Chem.*, 1927, **160**, 242) and by Tammann and Hinnüber (*ibid.*, p. 249). The former prepared dilute amalgams of iron, cobalt, nickel, and copper and determined the *P.D.*'s between increasingly diluted amalgams and the calomel electrode; the potential fell at first quickly with dilution but eventually attained a constant value from which the solubility of the metal in the mercury was calculated. The latter workers found this method unsuitable for the other metals examined, and made several modifications of it. The values they obtained in the combined experiments were (in g. per 100 g. of mercury at 18°) Fe $1{\cdot}0 \times 10^{-17}$, Co $1{\cdot}7 \times 10^{-1}$, Ni $5{\cdot}9 \times 10^{-4}$, Cu $3{\cdot}2 \times 10^{-3}$, Mn $2{\cdot}5 \times 10^{-4}$, Cr $3{\cdot}1 \times 10^{-11}$, and U $1{\cdot}4 \times 10^{-4}$. Definite data for the upper limits of the solubilities of vanadium, molybdenum, and tungsten could not be obtained; the values, however, must be very small. These authors suggested that Richards and Garrod-Thomas's value for copper, which was two-thirds of theirs, was possibly due to oxidation of copper during filtration in the latter's work, with consequent retention by the chamois leather of copper oxide.

The solubility in mercury of a metal which is sparingly soluble is clearly unlikely to be a definite quantity. The metals under discussion, unlike zinc, tin, lead, and bismuth, are known to form aggregates not only with themselves but also with mercury. The sizes of the particles may accordingly vary from atomic dimensions upwards, and the quantity which passes a filter would then depend upon the factors controlling the distribution of particle sizes and the diameter of the filter-pores. Until the sizes of particles in mercury have been determined, the term " solubility " must be a very loose one. Nevertheless, there is a possibility that with some metals there may be a sharp distinction between the sizes of the smallest particles and the others, and this would be revealed by filtration experiments. In the experiments to be described, chamois leather was used as a filter at first; later, a filter-crucible of sintered glass was found to be more convenient and to give much more consistent results. Results with some metals, especially with copper, obtained with the two different filters were strikingly different. The filter used had a base of sintered Jena glass, 3 cm. in diameter and 3 mm. thick with a porosity described by Schott and Gen. as " 5—7." Under the reduced pressure caused by a water-pump, an amalgam of a sparingly soluble metal was quickly separated into a filtrate in the Buchner funnel and a semi-solid paste on the glass filter. In all experiments on which reliance was placed, the base of the filter was completely covered with this paste and the filtrate passed through it at least three times. The uncertainty of the results obtained with a chamois leather filter was partly that some of the apertures in it were unduly larger than others and partly that the filtrate could not always be passed through a thick layer of paste to ensure the retention of much that might otherwise pass through.

The filtrate was examined for soluble metal by being shaken with a few drops of $N/10$-permanganate acidified with dilute sulphuric acid. If none is there shaking breaks up the mercury into a mass of small bubbles. If some is present, then, since all but nickel and tungsten are more reactive in mercury than mercury itself (Russell, J., 1929, 2398), they react first with permanganate. An excess of the latter ensures complete removal from the mercury. It is then simple to remove mercuric ions from the solution and determine the metal volumetrically.

EXPERIMENTAL.

Solubility of Copper.—Experiments with chamois leather. These showed entirely different values of the solubility according as the copper amalgam was prepared (i) by electrolysis or displacement by a more reactive metal or (ii) by shaking into mercury the finely divided copper from the reduction of copper sulphate by acidified bivalent vanadium ions. In the former case, an amalgam containing 0·2—5 g. of copper in 200 g. of mercury gave a paste which was retained by the leather and a filtrate which gave a concentration of copper from 0·0032 to 0·10% depending upon the nature of the leather, the original concentration of the amalgam, and the time the amalgam had stood between preparation and filtration. There were, however, no significant regularities. The minimum value, which was obtained many times, is the only one of interest; it represents the best that chamois leather can do; it is equal to the mean value of Tammann and Hinnüber. In the latter case, frequently the whole of the amalgam passed repeatedly through the same chamois leathers as had before been used in obtaining minimum values of the solubility; apparent solubilities as high as 0·78% were obtained. Very concentrated amalgams prepared in the same way usually developed a thin paste which was retained by the leather. It was different in appearance and in touch from the other pastes. In presence of this paste the solubility varied from 0·3 to 0·01%. These divergent results, although of significance in an investigation of particle size in mercury, promised little for exact solubility determinations. The chamois leather method was accordingly abandoned.

Final results. Copper amalgams were prepared in three ways: (*a*) by electrolysing 1—5 g. of copper into 200 g. of mercury, (*b*) by complete displacement of about 2 g. of lead or bismuth in 200 g. of mercury with the equivalent mass of copper from acidified copper sulphate, (*c*) by the vanadium-reduction method already mentioned. In (*a*), analysis of the copper–mercury complex (to be described in a later paper) showed that most of it existed as a new compound Hg_5Cu_8. In (*b*) most of it existed as the well-known compound HgCu. In (*c*) the copper was heavily mercurised at first but, in a few days, became converted into a new compound, rich in mercury, Hg_7Cu_4. These different associations with mercury might be expected to lead to different values of the solubility. The amalgam was then passed through the ground-glass filter until the whole of its base was covered with a thick layer of paste. [This occurred the first time with amalgams made by methods (*a*) and (*b*).] The filtrate was then passed thrice through its paste, weighed, shaken with acidified permanganate till bubbles appeared, and then shaken with a further 5 c.c. of $N/10$-permanganate. Mercuric ions were next completely removed by a method to be described, a freshly-made paste of cuprous iodide was added to the copper solution, and copper finally determined by the potassium iodide–thiosulphate method.

Although mercuric ions in small amount do not interfere with the determination of quantities such as 10 c.c. of $N/10$-copper sulphate, an excess of mercuric ions led to inaccurate results when the quantities, as here, were of the order of 1 or 2 c.c., even when a paste of cuprous iodide was added as catalyst. Mercuric ions were removed simply as follows. A 2% amalgam of cobalt was vigorously shaken with the solution containing the cupric and mercuric ions. It reduced the latter quantitatively to metal and slightly reduced some of the cupric to cuprous ions. The latter could be re-oxidised by a few drops of $N/10$-permanganate, but the end-point was not easily seen in presence of the cobaltous ions. It was found simpler to make a general correction for the error introduced by the method. Known quantities of copper, of the order of those to be determined, were accurately electrolysed into mercury, removed from it by oxidation with excess of acidified permanganate, and the resulting solution vigorously shaken with the cobalt amalgam. To the decanted liquid and its washings, were added potassium iodide, a paste of cuprous iodide, and starch, and the liberate iodine was titrated with $N/10$-thiosulphate. The following results were obtained: Copper taken, 0·0495, 0·0111, 0·0098, 0·0067, 0·0041 g.; found, 0·0463, 0·0101, 0·0088, 0·0061, 0·0038 g. respectively. To bring the experimental to the true results increases of 7, 10, 11, 10 and 8% respectively were thus necessary. A correction of 10% was adopted.

Experimental results at 20° under different conditions are included in the table.

Method of making amalgam.	Time between preparation and filtration.	Copper found, g.	Mercury, g.	Solubility (g. per 100 g. of mercury).
(*a*)	5 mins.	0·0035	170	0·0020
(*a*)	36 hours	0·0035	170	0·0020
(*a*)	7 days	0·0035	170	0·0020
(*a*)	30 mins.	0·0094	450	0·0021
(*a*)	1 day	0·0175	850	0·0020
(*b*)	1 day	0·0101	530	0·0019
(*b*)	4 days	0·0097	475	0·0020
(*c*)	30 mins.	0·0315	370	0·0851
(*c*)	30 mins.	0·0042	215	0·0020
(*c*)	1 day	0·0056	290	0·0019

The results obtained are constant : 0·0020% with an error of 5% may be taken as the solubility. The only high value of this table, the eighth, was obtained as might have been expected from the results with chamois leather, when filtration occurred with insufficient paste to cover the base of the filter. When paste made by methods (*a*) or (*b*) was placed there before amalgams (*c*) were filtered, as in the two last results, the normal result was obtained.

Attempts were made to diminish the solubility by adding to different saturated copper amalgams in about 500 g. of mercury : (i) the insoluble paste from a filtered amalgam of iron, (ii) the insoluble paste from a filtered amalgam of the compound ZnCu, (iii) 1 g. of zinc, then allowing the amalgams to stand for 1 day and determining the solubility in the ordinary way. In every case a solubility of 0·002% (within the limits of experimental error) was obtained. In the first case it was expected that the insoluble iron complex would sorb the very small amount of soluble copper. After filtration through the mixed pastes, however, 470 g. of mercury gave 0·0097 g. of copper and 460 g. gave 0·0090, leading to values 5% greater and less respectively than the mean value adopted. (In these experiments any soluble iron would not interfere with the copper determination because, although it would be oxidised to ferric ions on its removal from the amalgam, it would be reduced to ferrous ions by the cobalt amalgam, and thus not react with potassium iodide.) It is shown later, however, that iron is quite insoluble in mercury. In the second and third cases, it was expected that possible compound formation between copper and the compound ZnCu or between copper and zinc would convert the soluble copper into insoluble compound. Earlier work (this vol., p. 856) has shown, however, that despite the fact that insoluble copper is, without difficulty, converted into insoluble copper compound, there is some dissociation of the latter into free copper sufficient to give the ordinary value of the solubility.

Solubility of Manganese.—An amalgam of 1 g. of metal in 200 g. of mercury was prepared by the method of Russell, Evans, and Rowell (J., 1926, 1872). It furnished a paste on the glass filter through which the filtrate passed without difficulty. The weighed filtrate was shaken with excess of acidified *N*/10-ferric sulphate to oxidise the manganese, the mercuric ions were removed by shaking this solution with zinc amalgam, and manganese was determined volumetrically as permanganate after oxidation by sodium bismuthate and nitric acid. The second part of the method was checked by reducing 20 c.c. of *N*/10-permanganate with zinc amalgam, and re-oxidising the solution with sodium bismuthate to give accurately 20·0 c.c. of *N*/10-permanganate standardised against *N*/10-ferric sulphate. The insoluble paste was then added to various masses of mercury and refiltered after different times of standing from 1 hour to 7 days. All experiments gave approximately the same values for the solubility. Typical experiments were :

Manganese found, g.	0·0022	0·0088	0·0080	0·0075
Mercury, g.	200	900	850	670
Solubility (g. per 100 g. mercury)	0·00110	0·00098	0·00094	0·00112

The mean value is taken as 0·001% with an error of 10%. In presence of zinc, this small value was found not to be diminished. To a manganese amalgam containing 0·1 g. in about 700 g. of mercury was added 1 g. of zinc. This is more than sufficient to form any possible complex with the manganese. (This was shown by oxidising the amalgam with acidified *N*/10-ferric sulphate. In the solution obtained, no manganese ions were detected. This showed that the more reactive free zinc was present in the amalgam.) The solubility of manganese was determined in the ordinary way, the soluble zinc which also passed the filter not interfering with the determination. The ordinary value of the solubility was found. Thus 0·0075 g. of manganese was found in 680 g. of mercury : this gives a value of 0·0011%.

Solubilities of Titanium, Vanadium, Chromium, Iron, Cobalt, Nickel, Molybdenum, Tungsten, and Uranium.—Separate amalgams of these metals containing approximately 0·2 g. of metal in about 200 g. of mercury were obtained by electrolysis : those of titanium, vanadium, and uranium by the methods of Groves and Russell (J., 1931, 2385), of molybdenum and tungsten by the methods of Jackson, Russell, and Merrill (J., 1929, 2389 and 2394), and those of the other metals by standard methods. After two days' standing, it was presumed that the mercury was saturated with the soluble metal. After filtration through its own paste on the ground-glass filter, the filtrate in every case broke into a mass of small bubbles of mercury on being shaken with a few drops of acidified $N/10$-permanganate or ferric sulphate solution, indicating that the amount of second metal present must be very small. In each case the amalgam was then shaken with 5 c.c. of $N/10$-permanganate, the mercuric ions removed by shaking with zinc amalgam, and the liquid tested qualitatively for second metal. In no case was any detected. The sensitiveness of the test employed was then determined by ordinary methods to fix an upper limit for the solubility of the metal. The values for the percentage solubilities obtained were : Titanium $< 1 \times 10^{-5}$, vanadium $< 5 \times 10^{-5}$, chromium $< 5 \times 10^{-5}$, iron $< 1 \times 10^{-5}$, cobalt $< 8 \times 10^{-5}$, nickel $< 2 \times 10^{-5}$, molybdenum $< 2 \times 10^{-5}$, tungsten $< 1 \times 10^{-5}$, uranium $< 1 \times 10^{-5}$.

Discussion of Results.

The percentage solubilities determined in this work are compared with those of other workers in the table.

Metal.	This work.	Tammann, Kollmann, and Hinnüber.	Richards and Garrod-Thomas.
Copper	0·0020	0·0032	0·0024
Manganese	0·0010	0·00025	—
Titanium	$<1 \times 10^{-5}$	—	—
Vanadium	$<5 \times 10^{-5}$	Very small	—
Chromium	$<5 \times 10^{-5}$	$3·1 \times 10^{-11}$	—
Iron	$<1 \times 10^{-5}$	1×10^{-17}	0·0013
Cobalt..............	$<8 \times 10^{-5}$	0·17	—
Nickel..............	$<2 \times 10^{-5}$	$5·9 \times 10^{-4}$	—
Molybdenum	$<2 \times 10^{-5}$	Very small	—
Tungsten	$<1 \times 10^{-5}$	Very small	—
Uranium	$<1 \times 10^{-5}$	$1·4 \times 10^{-4}$	—

The agreement, it is seen, is not good. For copper there is agreement about the order of the result, but the direct (filtration) methods evidently give lower results than the electrometric method. For manganese the direct method gives a value four times larger than that obtained by the electrometric, but with three other metals, *viz.*, cobalt, nickel, and uranium, the values got are much smaller; this is especially so with cobalt which has been carefully done many times by the direct method. There is agreement that the solubilities of the remaining metals are all exceedingly small. It is evident also that Richards and Garrod-Thomas were right in their conjecture that the solubility of iron was not their determined value but very much smaller.

It is noteworthy that copper and manganese alone have measurable solubilities when investigated by the filtration method. Regarded as a pre-transition element, the latter has an abnormally high solubility. Regarded as a metal of the B sub-group of the periodic classification, the former has an abnormally low one. Since none of the many intermetallic compounds formed in mercury has an appreciable solubility in mercury, it might be argued that the low solubilities of the metals examined in this work are due to compound formation with mercury. The high value for copper would then be explained by the fact established in earlier work (this vol., p. 856), that the copper–mercury compound dissociated to a small extent into uncombined copper. The argument may be true for copper but is not generally applicable. There is no evidence that manganese dissociates from its compound with mercury into free manganese. There is positive evidence, on the other hand, that iron often does not form a compound with mercury (this vol., p. 843).

The work on solubilities is being continued by other methods in order to throw light on particle-sizes in mercury.

Summary.

1. The solubilities of metals of atomic numbers 22—29 and of molybdenum, tungsten, and uranium in mercury have been determined by preparing an amalgam of each metal, separating the solid from the liquid phase by filtration through a filter of sintered Jena glass, removing the metal from the mercury by oxidation with potassium permanganate or ferric sulphate, and determining it volumetrically.

2. Copper and manganese alone of these metals have solubilities greater than 1 in 10^7, their values being 0·0020 and 0·0010% respectively. These values seem quite definite, and are not appreciably influenced by the presence in the amalgams of certain third metals or intermetallic compounds.

3. Upper limits for the solubilities of the other metals examined are given.

4. The solubilities determined are not in good agreement with those previously obtained by other workers by electrometric methods.

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