ses on the reaction of Re(-I) with copper(II) sulfate or oxygen, it is probable that the first product of oxidation is Re(+I), followed by formation of Re(IV) with excess oxidant.

Attempts to prepare a solid compound of Re(-I) by reduction of K_2ReCl_6 by potassium gave only rhenium metal. No indication of volatility of Re(-I) or of reaction of Re(-I) with carbon monoxide was found.

Pasadena, California Received December 12, 1949

[Contribution from General Electric Research Laboratory]

The Solubility of Iron in Mercury at 25–700°

By A. L. Marshall, L. F. Epstein and F. J. Norton

Various developments involving the contact of iron with mercury over extended temperature ranges rendered necessary a study of the equilibrium solubility relationships.

The primary difficulty in this solubility determination is to secure initial, preliminary *wetting* of the iron by mercury. Iron broken under mercury will show wetted surfaces at the fracture. This wetting is lost after exposure to air.

Experimental

To have pure iron wetted by pure mercury with no other amalgamating material present, all oxide must be removed, the iron must be degassed and no access of oxygen allowed. The stringent requirements of attaining and maintaining exclusion of oxygen to a high degree were met by the following experimental arrangements.

Twenty mil pure Swedish iron was arranged as a cylinder in a quartz vessel in a vacuum system. The iron was heated by high frequency and degassed in a good vacuum[1] at about 800°, then fired in hydrogen. The hydrogen was purified by being passed through degassed, activated charcoal at liquid air temperatures.

When pure liquid mercury at room temperature was admitted suddenly to such a piece of hot iron, complete wetting occurred. This is permanent for many months if air is not admitted to the iron.

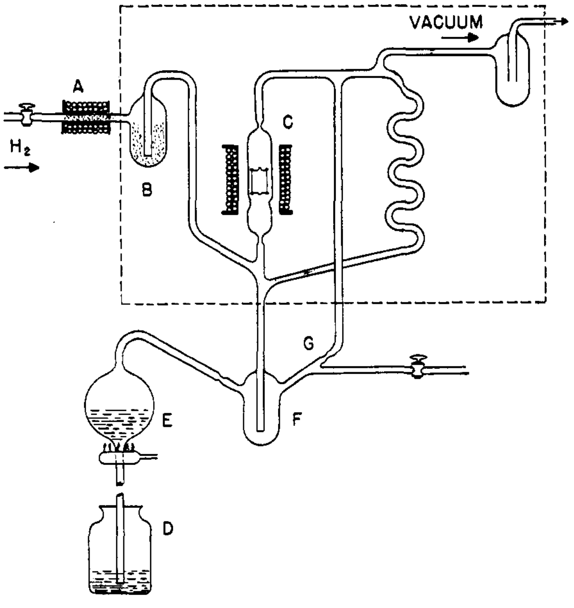

Fig. 1.—Apparatus for heating iron cylinder in pure hydrogen and in vacuum.

The arrangement for heating iron in very pure hydrogen, then admitting mercury, is shown in Fig. 1. The portion enclosed by dotted lines was in a bake-out oven so all of the glassware and the iron could have a preliminary bake out in a good vacuum at 450°. At A, the point of admission of hydrogen, is a furnace with platinized asbestos in the line to assure reaction of traces of oxygen. At B is the degassed, activated charcoal which had liquid air on when the hydrogen was admitted. This removed the traces of air and also traces of other impurities in the hydrogen. The high frequency heating coil C surrounded the iron sample which was in the form of a thin cylinder. The thickness was such to give uniform heating by high frequency. Small prongs bent out at the extremities of the cylinder supported it in the quartz container with minimum contact. The quartz bulb holding the iron cylinder had graded seals at top and bottom. These led to the rest of the apparatus which was of Nonex glass.

Redistilled mercury of good purity initially was distilled again from the barometric reservoir E into F, after bake out and evacuation. Then on sealing off at G, nitrogen pressure raised the mercury over the iron sample.

The various by-passes enabled the sample bulb to be sealed off in a good vacuum at top and bottom. The quartz container had two sections with a constricted neck between. The upper one held the wetted iron and the lower the pure mercury. On rocking the container the mercury passed over the iron and back.

The sample container was placed in a steel bomb of one inch wall thickness, steel wool keeping the bulb in position. Mercury was placed in the bomb on the outside of the container so the pressure at high temperatures would be equalized inside and out. The steel bomb was then welded shut.

After various periods of agitation in an oscillating constant temperature furnace, the furnace was left in a slanted position so all of the mercury drained down off the iron into the lower section of the container. All this was done at the temperature of the experiment. Then on cooling down to room temperature any iron separating out from the mercury was in contact with quartz only. In the analysis, all the iron—in the mercury and on the wall—was determined.

Another point of interest is that at room temperature, mercury passed over wetted iron attained its equilibrium solubility in a few seconds.

In general, runs were made for several hours at temperature, and one run was made for one month. This gave the same result as shorter runs.

After equilibration the sample bulb was opened, the iron cylinder removed and the mercury slowly distilled in vacuum away from the bulb, and weighed. The residue was washed from the bulb with acid and iron determined.

This was done by oxidizing the iron and determining it by the red color which develops with KCNS. This colorimetric determination was made on the General Electric recording spectrophotometer.[2] The absorption

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[1] F. J. Norton and A. L. Marshall, *Trans. Am. Inst. Min. Met. Eng.*, **156**, 351 (1944).

[2] J. L. Michaelson and H. A. Liebhafsky, *General Electric Review*, **39**, 455 (1936).

band at 4600 Å. was calibrated by known, standard iron solutions and the amount of iron in the mercury thus determined.

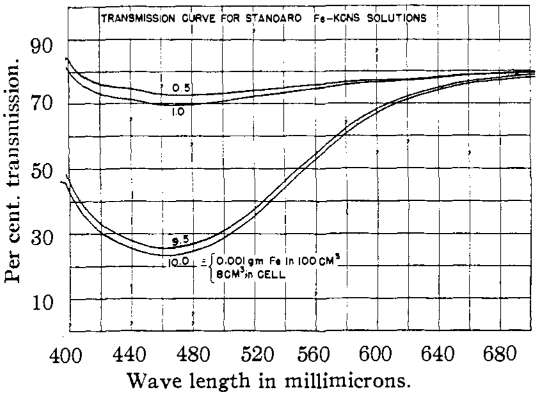

Fig. 2.—Recording spectrophotometer calibration curves for Fe–KCNS solutions.

The curves from a typical calibration on the spectrophotometer are given in Fig. 2. Table I lists the experimental values.

TABLE I

EXPERIMENTAL VALUES

EQUILIBRIUM SOLUBILITY OF IRON IN MERCURY

°C	Parts per million (g. Fe per 10^6 g. Hg)	°C.	Parts per million (g. Fe per 10^6 g. Hg)
25	0.013	500	0.105
25	.015	500	.225
25	.017	500	.270
250	.037	700	1.0
250	.066	700	1.2
425	.105		

The blank of the mercury was 0.0015 p. p. m. Fe.

These data were fitted by the method of least squares to the equation

$$\log_{10} m = -3.821 + 277.2/T + 3.614 \times 10^{-3}\, T \ldots \quad (1)$$

m = parts per million Fe in solution in Hg
T = degrees absolute Kelvin

The smoothed values for solubility derived from this equation are given in Table II.

TABLE II

EQUILIBRIUM SOLUBILITY OF IRON IN MERCURY

°C.	Fe in parts per million (grams Fe per 10^6 grams Hg)
25	0.015
100	.019
200	.030
300	.054
400	.11
500	.21
600	.45
700	.96

Figure 3 gives the experimental points. The smooth curve is that for the equation given. It should be noted that this equation yields a minimum in the solubility at 2.2°. Consequently, it should not be used for extrapolation below this temperature, and in fact, it is recommended that its use be confined strictly to the region covered by the experimental data, 25 to 700°.

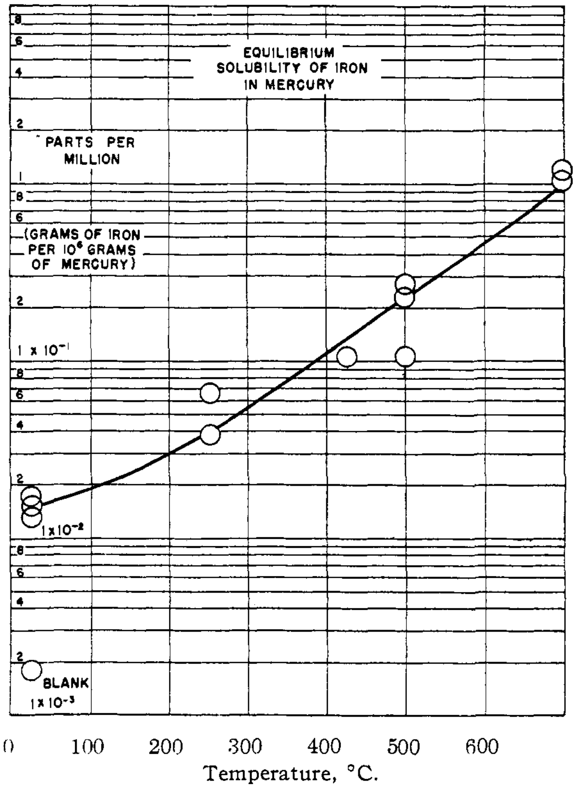

Fig. 3.—Equilibrium solubility of iron in mercury (parts of iron per million parts mercury).

Discussion

As has been shown[3,4] when a small amount of constituent separates the heat of solution ΔH can be calculated from the equation

$$\Delta H_S = -R\,(\partial \ln x/\partial(1/T))_P \quad (2)$$

In the extremely dilute solutions considered here, the mole fraction x of iron in solution is related to m by the equation

$$x = 3.592 \times 10^{-6}\, m \quad (3)$$

Though the mercury pressure at 700° becomes about 50 atmospheres, the effect of this pressure on solubility is small and may be neglected here, for data of this precision.

By differentiation of Eqn. (1), Eqn. (4) is derived and expressed in cal. per mole

$$\Delta H_S = 1.653 \times 10^{-2}\, T^2 - 1268 \quad (4)$$

The following values in Table III may then be computed, to illustrate the wide deviation from ideality.

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[3] K. K. Kelley, Contributions to the Data on Theoretical Metallurgy, V. Heats of Fusion of Inorganic Substances, Bulletin 393, p. 4, U. S. Bureau of Mines, Washington, 1936.

[4] D. H. Andrews and J. Johnston, *J. Inst. Metals*, **32**, 385 (1924).

TABLE III

°C.	Heat of solution, ΔH_S cal./mole
25	202
100	1034
200	2433
300	4163
400	6223
500	8614
600	11335
700	14388

Now

$$RT \ln x + RT \ln \gamma = -T \int_{T_0}^{T} (H^S - H^L)(1/T^2)\mathrm{d}T \quad (5)$$

γ is the activity coefficient of iron in Hg, T_0 is the melting point of iron (1803°K.), and H^S and H^L are the heat contents of solid and liquid iron, respectively, at the temperature T. Extrapolating Kelley's equations[5] for the heat capacities and heats of transition of the various forms of iron down into the range of these measurements, it follows that approximately

$$4.576T \log_{10} x + 4.576\, T \log_{10} \gamma = -4332 - 21.145T - 3.19 \times 10^{-3}T^2 + 9.256\, T \log_{10} T \quad (6)$$

Combining these equations, the computed activity coefficients of Fe in Hg are given by Table IV.

TABLE IV

°C.	γ (activity coefficient of Fe in Hg)	°C.	γ (activity coefficient of Fe in Hg)
50	$0.6 \times 10^{+5}$	400	$2.5 \times 10^{+5}$
100	1.0	450	2.3
150	1.6	500	1.9
200	2.1	550	1.6
250	2.5	600	1.3
300	2.7	650	1.2
350	2.7	700	0.8

It will be noted that the Fe–Hg system shows large positive deviations from Raoult's law, even in extremely dilute solutions. Contrary to the usual behavior of simple systems, the system does not become more uniformly nearly ideal as the temperature is raised, but γ passes through a maximum. This can be explained on the assumption of a negative entropy of mixing amounting to about −24 cal./mole-deg.; *i. e.*, the solution is much less random ("mixed up") than would be expected from simple theory. It is conceivable that this is due to a tendency toward compound formation even in the dilute solutions considered here. Other hypotheses for the nature of the deviations from ideality are also possible.

Summary

The equilibrium solubility of pure iron in pure mercury was determined over the temperature range 25 to 700° C., and an equation developed to express the results.

SCHENECTADY, N. Y. RECEIVED DECEMBER 27, 1949

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[5] K. K. Kelley, Contributions to the Data on Theoretical Metallurgy, II, High-Temperature Specific-Heat Equations for Inorganic Substances, U. S. Bureau of Mines Bulletin, 371, 26, Washington, D. C., 1934.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Particle Size Distribution in Sulfur Hydrosols by Polarimetric Analysis of Scattered Light

BY MILTON KERKER[1] AND VICTOR K. LA MER

The particle size of monodispersed sulfur hydrosols has been determined in this Laboratory by light scattering methods based upon the angular positions of the higher order Tyndall spectra,[1,2,3] the polarization ratio of the scattered light[4] and the optical transmission.[5,6] The results are consistent with the theory of scattering by homogeneous spheres developed by G. Mie.[7]

This paper will (a) extend the polarization ratio method to a range of larger sizes, (b) present a fourth method of size determination, namely, that of phase angle, (c) analyze the size distribution of mixtures of sols and (d) determine the degree of monodispersity of the sulfur hydrosols prepared in this Laboratory.

I. Experimental

A schematic diagram of the light scattering apparatus constructed is shown in Fig. 1. The collimated beam from a high pressure mercury vapor lamp is rendered monochromatic by Corning glass filters. The beam is linearly polarized by a Glan–Thompson prism which can be rotated 180° and whose azimuth can be read to the nearest tenth of a degree.

The scattering cell is cylindrical (75 mm. diameter) except for a small plane window through which the incident beam enters. The refraction of the scattered light on leaving the cell is corrected by a cylindrical lens in the observing system. There is a slot for the insertion of a quarter wave plate of quartz in the path of the scattered light. A second Glan–Thompson prism is used

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[1] Clarkson College of Technology, Potsdam, N. Y.

[2] Johnson and La Mer, THIS JOURNAL, **69**, 1184 (1947).

[3] (a) Kenyon and La Mer, *J. Coll. Sci.*, **4**, 163 (1949); (b) Barnes, Kenyon, Zaiser and La Mer, *ibid.*, **2**, 349 (1947).

[4] Sinclair and La Mer, *Chem. Revs.*, **44**, 245 (1949).

[5] Barnes and La Mer, *J. Coll. Sci.*, **1**, 79 (1946).

[6] La Mer and Barnes, *ibid.*, **1**, 71 (1946).

[7] G. Mie, *Ann. Physik*, **25**, 377 (1908).