

PREFACE

This volume is concerned with the solubility of metals in mercury, and includes all of the metals and the metalloids carbon, silicon and boron. The solubility only in the seventy-six binary amalgams is considered here. The compilation of the solubility data for these binary systems includes numerous reports, such as those published by the U.S. Atomic Energy Commission from its various laboratories. The literature coverage for this volume extends through 1983.

The solubility of a metal in mercury at a given temperature is represented by the concentration of the saturated solution which is in equilibrium with the solid phase. The solid phase may be the pure metal, the metal saturated with mercury, or an intermetallic compound with mercury. This concentration also is represented by the liquidus point at the given temperature on the binary phase diagram. Clearly, the solubility also is represented by the crystallization temperature of the liquid amalgam.

Only those parts of the complete metal-mercury systems are included in which the solid metal, or a metal amalgam, appear as solid phases. In those systems where a phase diagram has been accurately determined, the equilibrium solid phase is clearly defined; the published phase diagrams for these systems are included in the Critical Evaluation, and should correctly aid the reader in assigning the solid-liquid equilibrium. However, there are some systems where there is disagreement on the equilibrium solid phase so that the solid-liquid equilibrium for these systems cannot be accurately defined. There are certain phase diagrams which have been constructed from precise data, but the liquidus data may be somewhat questionable because equilibrium may not have been attained during the short equilibration times employed. Instances of possible supersaturation in the determination of the liquidus from cooling curves are noted by the evaluators. In this volume, the emphasis is on accurate, evaluated solubility data rather than phase relations in the various systems.

Concentrations in the metal-mercury systems are mostly reported in atomic percent, at %, rather than in mole percent. The rationale for the non-SI unit is that each system is represented by the equilibrium of two atomic species, and much of the literature data on binary metallic systems are reported so.

The solubility of a number of metals in mercury, especially the refractory metals, is very low, and often below the experimental detection limit. For such systems only a selected number of data sheets were compiled for those reports which gave the highest solubility limit as determined by a well defined method. However, the solubility in these systems may be estimated by the semiempirical equations of Kozin. The first equation (1) is given by

$$\ln (100x_1) = -0.4 \left[1 + \frac{\Delta H_m (T_m - T)}{RT_m T} \right]^2 \left[\frac{\Delta H_m (T_m - T)}{RT_m T} \right]^{0.001} \quad [1]$$

where the atomic percent solubility of the metal, $100x_1$, is a function of its enthalpy of fusion, ΔH_m , and its melting point, T_m . Kozin subsequently reported (2) a second solubility equation,

$$\ln (100x_1) = - \left[\frac{\Delta H_m (T_m - T)}{RT_m T} \right]^{1.39} \quad [2]$$

Equation [2] was derived from the Schroeder relation in which the exponent is unity for ideal solutions. The exponent, 1.39, in eq. [2] results from fitting known values of solubilities in the binary amalgams to ΔH_m and T_m . It was reported by Kozin (2) that the mean standard scatter of points for systems of known solubilities is ± 0.028 at a 95% confidence level in eq. [2]. Estimates from this equation for the solubility at 298 K for some of the binary systems are near the experimental values, but there also are systems where the estimates are at great variance from experimental values. For systems of very low solubility, where experimental data are not available, eq. [2] may be applied only as a first approximation.

For some of the metal-Hg systems the data were reported only graphically; some of the liquidus covered an extensive composition range, others only a narrow composition range. Because the numerical data are of interest to many workers, the data points from these graphical presentations were visually read from the curves and are compiled on the data sheets. Admittedly, the error in abstracting such data from the curves may be large, depending on the size of the original figure.

For every system where experimental solubility data were reported, all of the data were plotted on a semilogarithmic paper (of 60 x 20 cm dimensions) as $\log(100x_1)$ vs. $(T/K)^{-1}$. The data were then evaluated by visually fitting the best curve. Evaluated solubility data are tabulated at the end of the Critical Evaluation. When at least two independent works agreed within experimental error, the solubility values were assigned to the recommended category. Values were assigned as tentative when only one reliable work was reported, or when the mean value from two or more reliable works was outside of the error limits. In this tabulation, three, two, or one significant figures is assigned for respective precisions that are better than ± 1 and $\pm 10\%$ and worse than $\pm 10\%$. There were no data that agreed to within $\pm 0.1\%$.

In a number of papers the temperature of the measurement was reported as "room temperature"; in plotting these data on the solubility curve, the temperature was arbitrarily assigned as 293 K.

Data for concentrated solutions which were reported in mol atom dm^{-3} without specifying the density were not useful for this compilation; solubilities in atom percent could not be assigned to these data.

Because of the large number of binary systems in this volume, the presentation is grouped according to the Periodic Table. The non-transition metals are given first in sequence starting from the alkali metals, followed by the transition metals in similar order. The actinides and the unstable radioactive elements are presented at the end of the volume.

Some previous compilations dealing with solubilities in selected amalgam systems (3-10) are considered incomplete, and the data in some of these references erroneous.

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REFERENCES

1. Kozin, L.F. *Tr. Inst. Khim. Nauk Akad. Nauk Kaz. SSR* 1962, 9, 101.
2. Kozin, L.F. *Fiziko-Khimicheskie Osnovy Amalgamoi Metallurgii*, Nauka, Alma-Ata, 1964.
3. Hansen, M.; Anderko, K. *Constitution of Binary Alloys*, McGraw-Hill, New York, NY, 1958.
4. Kozlovsky, M.T.; Zebreva, A.I.; Gladyshev, V.P. *Amalgamy i ikh Primenenie*, Nauka, Alma-Ata, 1971.
5. Kozlovsky, M.T.; Zebreva, A.I. *Progress in Polarography*, Vol. III, Zuman, P. and Meites, L., Eds., Wiley-Interscience, New York, NY, 1972.
6. Gavze, M.N. *Koroziya i Smachivaemost Metallov Rtutei*, Nauka, Moskva, 1969.
7. Kozin, L.F.; Nigmatova, R.Sh.; Dergacheva, M.B. *Termodinamika Binarnykh Amalgamnykh Sistem*, Nauka, Alma-Ata, 1977.
8. Jangg, G. *Metall* 1965, 19, 442.
9. Vol, A.E. *Stroenie i Svoistva Dvoynykh Metallicheskiikh Sistem*, Fizmatgiz, Moskva, Vol. I 1959; Vol. II 1962; Vol. III (with Kagan, I.K.) 1976; Vol. IV 1979.
10. Seidel, A. *Solubilities of Inorganic and Organic Compounds*, Vol. I, 3rd ed., D. Van Nostrand Company, Inc., New York, NY 1940; also Supplements to this volume.

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