

Review

Selected properties of simple amalgams

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Experimental data on solubility, heat and kinetics of dissolution, diffusion and standard potentials of metals in mercury as well as the rate of the electrode process with an amalgam formation, have been collected and selected. A comparison has been made between the measured and predicted solubilities and heats of dissolution. The experimental diffusion coefficients have been analysed according to the simple Sutherland–Einstein equation; the average composition of diffusing particles in diluted amalgams have been estimated. The linear dependence between the logarithm of the rate constant of aquo-ion electroreduction on mercury and the metal solubility in mercury has been confirmed. No correlation of the dissolution rate of metals in mercury has been found.

1. Introduction

Indisputably mercury (Hg), is the metal (M), most frequently used in pure and applied electrochemistry; other applications of mercury in metallurgy, inorganic and organic synthesis, dentistry, electronics, electro-technics as well as heat transfer, seem to be less significant. From a scientific point of view, liquid mercury and amalgams are generally good models for liquid metals and alloys. For amalgams alone we have a fair collection of reliable data on thermodynamics, solubility and diffusion. Nevertheless, mercury and amalgams are not placed in the main stream of either solution chemistry or metal science.

In the present paper an essential collection and evaluation has been achieved of the following data: the type of phase diagram M–Hg, solubility of the metal in mercury, heat and kinetics of dissolution of the metal in mercury, activity and diffusion coefficients of the metal in mercury, standard potentials of amalgams, kinetics of electroreduction of M^{n+} aquo-ions on mercury electrode. Most of these features change periodically through the elements table and show mutual interrelations. When possible, the experimental data (solubility, heat of dissolution, diffusion) are compared with theoretical predictions.

2. Phase diagrams of the M–Hg systems

Phase diagrams are fundamental sources of information on alloy systems, and also amalgams. The diagrams are directly interconnected with thermodynamic and physico-chemical properties of the alloys. Thermal analysis (direct and differential) is the fundamental technique used in these determinations. In the case of amalgams, this method was supplemented by X-rays and less frequently by neutron diffraction, metallography, hardness, electrical resistivity and magnetic susceptibility measurements.

We can distinguish between five types of phase diagram for amalgams [1] given schematically in Fig. 1:

(a) with congruently melting MHg_x intermetallic compound (IC); the melting point (m.p.) of the most stable MHg_x , predominantly at a constrained pressure, is higher or equal to the m.p. of the metal; observed for Li–Cs, Mg–Ba and Lanthanides;

(b) with congruently melting IC but the m.p. of the most stable MHg_x is lower than the m.p. of the metal; observed for In and Tl;

(c) with peritectically decomposing IC or intermediate phase (IP); the m.p. of the most stable MHg_x is lower than that of the metal; observed for Actinides, Ti–Hf, Mn, Rh, Ni–Pt, Ag, Au, Zn, Cd, Sn, Pb;

(d) with a miscibility gap in the liquid state (monotectic); observed for Cu, Ga, Se, Te(?);

(e) with a limited solubility of solid metal in liquid mercury – mostly approaching the regular solution concept; observed for V–Ta, Cr–W, Re, Fe–Os, Co, Ir, B, Al, C–Ge, Sb, Bi.

For refractory elements we do not know the high-temperature parts of corresponding phase diagrams, and probably they will remain the object predictions; therefore, it is quite possible that some demonstrate the miscibility gap in a hypothetical liquid state. Eutectics may be individually observed in every type of diagram; however, they are not always detectable by an experiment.

3. Solubility of metals in mercury

Solubility is an essential fragment of a phase diagram and is substantiated as the liquidus curve. For experimental determination of solubility (S_M) of a metal (M) in mercury, various methods have been applied [1].

The oldest, most popular and also the most precise way of determining \bar{S}_M is chemical analysis of a saturated solution after decantation, filtration,

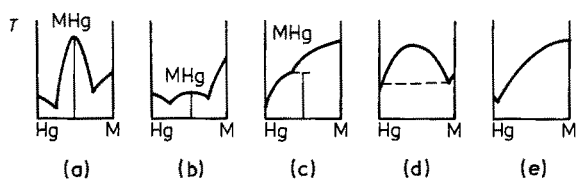


Figure 1 Schematic M-Hg phase diagrams.

centrifuging or fast cooling of a liquid phase. Decomposition of the resulting amalgam sample by completely distilling off mercury and weighting the residue sometimes produced wrong results when the metal was easy volatile or a stable IC between the metal and mercury was formed in the corresponding system. The formation of IC or IP excludes relying on the weight-loss analysis when solid metal is dipped for equilibration in mercury. The range of S_M determination by the analytical methods reported is very wide, starting at 10^{-7} and ending at 100 mol % M.

Instead of chemical analysis, the saturated liquid phase of an amalgam may be further analysed by neutron activation (Nb, Ta, Mo, W) [2], radiometry (Ge) or electroanalytical oxidation under chronoamperometric (Cu, Ge), voltammetric (Ce, Cu, Mn, Sb) or chronopotentiometric (Ga, Ni) conditions. When the preceding phase separation is effective, the precision of such analysis depends on the instrumental method used. The methods mentioned allow for determination of concentrations as low as 10^{-9} , 10^{-6} and 10^{-5} mol %, respectively.

In the previous point, thermal analysis was mentioned. This method yields valuable S_M results in the range 0.1 to 100 mol %. At temperatures below 370 K, the crystallization of oversaturated amalgams proceeds slowly, liquid segregation occurs easily and as a consequence the liquidus line on a phase diagram may be situated too high.

S_M values may also be determined by tracing various physico-chemical variables as a function of amalgam concentration. A point of sudden change on such a dependence corresponds to S_M — a border between homogeneous and heterogeneous amalgam. The most frequent physical quantity measured was the e.m.f. of galvanic cells with one or two amalgam electrodes; the metal must be less noble than mercury and more soluble than 10^{-5} , up to 100 mol %. The less frequently used techniques were based on the measurement of density (Na), magnetic susceptibility (Fe, Co), resistivity (Ga, Ge, Mg), heat of dilution (Li, Ba, Tl), diffusion coefficient (Cu), vapour pressure (Au, In, Te), kinetics of decomposition (Ce), neutron transmission (Ga) or anodic limiting current (chronoamperometry — Ln, Mn, Sb; polarography — Cu, Ln, Sb; voltammetry — Cu, Mn). All these methods were applied for very different concentrations depending on the optimum conditions of a method chosen. The quality of the results may range from extremely precise, as in potentiometry, to completely wrong, as in magnetic susceptibility.

Lastly one should mention atypical, indirect methods. When an element is poorly soluble in mercury, on the “one drop” polarographical reduction curves some irregularities occur due to crystal-

lization of the reduced element (Ge, Te). S_M is then estimated from the time and current of the undisturbed (diffusional) stage of the process; the method gives rather overstated results because times to reach an equilibrium in these systems are too short (being only a few seconds). A subsequent technique is based on potentiostatic electro-oxidation of the metal (Al, Cu, Sn) covered with thin film of mercury; S_M values obtained from a corresponding equation are, unfortunately, too high (Cu, Sn). In another method, the effect of IC precipitation by two metals in mercury was used; platinum and gold form stable compounds $PtZn_2$ and $AuZn$, respectively; S_{Pt} and S_{Au} are higher than S_{PtZn_2} and S_{AuZn} , respectively, thus platinum or gold dissolved in mercury may be titrated by reducing Zn(II) under conditions of slow rate voltammetry or current reversal chronopotentiometry. Pulse polarography may also be applied (Ni) and S_M is then estimated from the critical concentration of crystallization.

As we see, the variety of experimental methods is incomparably more extensive than for other liquid metallic solvents, mainly due to the possibility of application of all kinds of electrochemical techniques with mercury as an electrode material. In this way the concentration range 10^{-9} to 100 mol % of saturated amalgams is covered and the selected S_M values are collected in Table I. The accuracy and precision of these data are reflected by the number of digits. For some metals we know only an order of magnitude or a detection limit of a method used. It seems very interesting to compare the experimental data with those predicted by semiempirical and thermodynamical models. For many elements, even at elevated temperatures, our knowledge of S_M is limited by insufficient detectability, so searching for reliable predictions is a quite substantial undertaking.

Fig. 2 shows the dependence of $\log S_M$ at 298 K on the atomic number. One may easily observe periodical changes of the experimental S_M data. The changes within the periods of the elements are drastic while the changes within the groups (elements with the same valency electron structure) are relatively smaller. This fact may be used for S_M prediction. The graphical extrapolations and interpolations of the S_M results for adjacent metals lead to the following estimations of the orders of magnitude: B 10^{-12} ; Sc, Y 10^{-3} ; Mo 10^{-13} ; Pm 10^{-2} ; Hf 10^{-6} ; Ir 10^{-7} ; Po 10^0 ; Ac, Pa 10^{-3} ; Np, Am 10^{-2} mol % at 298 K.

Because the plot in Fig. 2 qualitatively assimilates the changes of melting enthalpy or temperature, boiling enthalpy or temperature, sublimation enthalpy, as well as hardness of elements with their atomic number, it was possible for correlations between the S_M values and these characteristic constants to be achieved independently by Kozin [9, 12] and Kerridge [13]. It is interesting that construction of analogical diagrams, $\log S_M$ against atomic number of a solute metal, for other low-melting metallic solvents (alkali metals, Pb, Bi) [13–15] is conducive to the formation of almost parallel curves, pointing out that solubility in metallic systems is primarily a function of solute features. Various solvents modify only the extent of metal dissolution.

TABLE I Comparison of the selected solubilities of elements in mercury from experiments and predictions; temperature 298 K if not otherwise stated

Element	Solubilities/mol %				
	Experimental	Predicted by Kozin [9]	Predicted in this work		
			Cellular model	Regular solution	Graphically
Li	1.3 [1]	66.5	-	-	-
Na	5.40 [1]	85.8	-	-	-
K	2.53 [1]	94.2	-	-	-
Rb	3.2 [1]	96.8	-	-	-
Cs	4.4 [1]	99.7	-	-	-
Be	3×10^{-6} [3, 4]	1.5×10^{-2}	$4 \times 10^{-7*}$	$3 \times 10^{-8*}$	-
Mg	2.7 [1]	0.86	-	-	-
Ca	1.0 – 1.5 [5, 6]	0.62	-	-	-
Sr	2.5 [1]	0.49	-	-	-
Ba	0.49 [1]	1.9	-	-	-
Sc	-	-	$2 \times 10^{-3\dagger}$	-	10^{-3}
Y	-	1.6×10^{-5}	100 (?)	-	10^{-3}
La	1.4×10^{-2} [1]	5.4×10^{-2}	-	-	-
Ce	9×10^{-3} [1]	0.45	-	-	-
Pr	1.1×10^{-2} [1]	0.16	-	-	-
Nd	6×10^{-3} [1]	5.8×10^{-2}	-	-	-
Pm	-	-	-	-	10^{-2}
Sm	2×10^{-2} [1]	4.5×10^{-2}	-	-	-
Eu	0.1 [1]	0.14	-	-	-
Gd	7×10^{-3} [1]	2.0×10^{-4}	-	-	-
Tb	1.3×10^{-3} [1]	5.2×10^{-5}	-	-	-
Dy	1.2×10^{-3} [1]	1.6×10^{-5}	-	-	-
Ho	9×10^{-4} [1]	1.6×10^{-5}	-	-	-
Er	6×10^{-4} [1]	1.5×10^{-5}	-	-	-
Tm	4×10^{-4} [1]	2.4×10^{-6}	-	-	-
Yb	0.1 [1]	0.42	-	-	-
Lu	3×10^{-4} [1]	6.1×10^{-7}	-	-	-
Ac	-	1.2×10^{-3}	-	-	10^{-3}
Th	1.5×10^{-3} [1]	7.3×10^{-5}	1×10^{-44} (?)	-	-
U	4.5×10^{-3} [1]	3.5×10^{-4}	100 (?)	-	-
Np	-	-	-	-	10^{-2}
Pu	1.5×10^{-2} [1]	-	-	-	-
Ti	2×10^{-5} [1]	9.3×10^{-5}	$5 \times 10^{-8\dagger}$	-	-
Zr	6×10^{-6} [3]	1.4×10^{-5}	100 (?)	-	-
Hf	-	3.0×10^{-9}	100 (?)	-	10^{-6}
V	10^{-10} [1]	4.8×10^{-6}	3×10^{-7}	3×10^{-5}	-
Nb	10^{-9} [2]	1.3×10^{-12}	1.6×10^{-11}	2×10^{-8}	-
Ta	10^{-8} [2]	1.7×10^{-16}	1.0×10^{-7}	7×10^{-16}	-
Cr	10^{-6} [7]	5.2×10^{-4}	3×10^{-10}	0.13	-
Mo	$\ll 10^{-6}$ [2]	2.6×10^{-13}	2×10^{-20}	8×10^{-25} [10]	10^{-13}
W	$\ll 10^{-6}$ [2]	6.8×10^{-20}	5×10^{-25}	3×10^{-20}	-
Mn	4.5×10^{-3} [1]	6.5×10^{-4}	8×10^{-4}	-	-
Tc	-	1.1×10^{-9}	6×10^{-13}	1×10^{-10}	-
Re	$< 10^{-5\dagger}$ [1]	5.9×10^{-18}	4×10^{-24}	3×10^{-19}	-
Fe	$10^{-7\ddagger}$ [1]	1.4×10^{-4}	4×10^{-10}	0.17	-
Ru	$< 10^{-7}$ [1]	1.2×10^{-11}	3×10^{-12}	5×10^{-14}	-
Os	$< 10^{-5\dagger}$ [1]	1.1×10^{-14}	6×10^{-19}	8×10^{-24}	-
Co	$10^{-7\ddagger}$ [1]	1.8×10^{-4}	1.2×10^{-7}	4×10^{-13}	-
Rh	$1 \times 10^{-4\dagger}$ [1]	1.0×10^{-8}	1.5×10^{-16}	-	-
Ir	$< 10^{-5\dagger}$ [1]	2.9×10^{-12}	2×10^{-9}	1×10^{-26}	10^{-7}
Ni	2×10^{-7} [1]	1.0×10^{-5}	8×10^{-18}	-	-
Pd	5.1×10^{-3} [1]	1.8×10^{-5}	1.5×10^{-9}	-	-
Pt	5×10^{-4} [1]	3.1×10^{-7}	0.1	-	-
Cu	1.00×10^{-2} [1]	5.7×10^{-3}	2×10^{-4}	-	-
Ag	7.6×10^{-2} [1]	4.3×10^{-2}	-	-	-
Au	0.14 [1]	1.2×10^{-2}	-	-	-
Zn	6.32 [1]	5.7	-	-	-
Cd	9.53 [1]	5.2	-	-	-
B	-	4.8×10^{-9}	-	6×10^{-25}	10^{-12}
Al	1.6×10^{-2} [1]	0.22	9×10^{-4}	4×10^{-4}	-
Ga	3.4 [1]	98.6	-	-	-
In	70.0 [1]	68.0	-	-	-
Tl	42.7 [1]	34.6	-	-	-
C	-	-	-	6×10^{-39}	-
Si	-	2.0×10^{-25}	4×10^{-11}	2×10^{-14}	-
Ge	3×10^{-7} [1]	1.1×10^{-12}	2×10^{-6}	5×10^{-6}	-
Sn	1.26 [1]	17.0	-	-	-

exceptions are expected. Unfortunately, the sublimation enthalpies of such ICs and, frequently, their molecular volumes are not known.

Thus using the model of regular solution, it is possible to calculate S_M if no IC or stable IP is formed in an M–Hg system. The following form of equation, which is valid under the assumptions that $V_M < V_{Hg}$, $S_M < 0.1$ mol % and ΔH_M^f is the energy of vaporization to gaseous valence state reported in [16], was derived from [19]

$$-\ln S_M = \frac{V_M}{RT} \left(1 + \frac{2V_M - 2V_{Hg}}{3V_{Hg} - 2V_M} \right) (\delta_M - \delta_{Hg})^2 + \frac{\Delta H_M^f}{RT} - \frac{\Delta S_M^f}{R} \quad (1)$$

where ΔS_M^f is the entropy of fusion. The results of these calculations are given in Table I, fourth column. S_{Cr} , S_{Fe} and S_{Co} predicted by this model are obviously wrong, probably due to improper magnitudes of the enthalpies of vaporization to the gaseous valence state. It is difficult to understand the serious jump between S_{Nb} (2×10^{-8}) and S_{Ta} (7×10^{-16}). S_{Os} , S_{Ir} and S_{B} seem to be too low; however, it looks quite convincing that carbon is the least soluble element in mercury. The predictions of S_M for other metals are in acceptable agreement with the experiments or predictions gathered other ways.

S_M prediction for moderately or poorly soluble metals may be derived from enthalpies of solution ($\overline{\Delta H}_M$) of liquid metal in liquid mercury at infinite dilution, foreseen by the cellular model of Miedema and co-workers [23]. Because this model takes into account the effect of chemical bonding in a liquid alloy (the difference in electronegativity, difference in electron density at the boundary between dissimilar atoms, hybridization energy) it may also be used for cases where an IC is in equilibrium with a saturated solution. If no IC or IP is formed in an M–Hg system one ought to employ the relation [24]

$$-\ln S_M = (\overline{\Delta H}_M^l + \Delta H_M^f)/RT - (\overline{\Delta S}_M^{l,ex} + \Delta S_M^f)/R \quad (2)$$

When an IC or IP (MHg_x) is formed one ought to employ the extended form: $-\ln S_M = (\overline{\Delta H}_M^l + \Delta H_M^f + x\Delta H_{Hg}^f - \Delta H_{MHg_x})/RT + (\overline{\Delta S}_M^{l,ex} + \Delta S_M^f + x\Delta S_{Hg}^f - \Delta S_{MHg_x})/R$ where $\overline{\Delta H}_M^l$, ΔH_M^f , ΔH_{Hg}^f , ΔH_{MHg_x} and $\overline{\Delta S}_M^{l,ex}$, ΔS_M^f , ΔS_{Hg}^f , ΔS_{MHg_x} are enthalpies and entropies of dissolution of liquid metal, fusion of metal and mercury, and formation of MHg_x, respectively.

If one knows the S_M value at one temperature it could be calculated at other temperatures using only enthalpic terms of Equation 2 or 3. If no experimental S_M data exist, one should estimate $\overline{\Delta S}_M^{l,ex}$ using the empirical rule of Kubaschewski [25]

$$\overline{\Delta S}_M^{l,ex} = [K'\overline{\Delta H}_M^l/(T_M^b + T_{Hg}^b)] + C' \quad (4)$$

where T_M^b and T_{Hg}^b are boiling temperatures of the metal and mercury, respectively, and K' and C' are some constants. Such a procedure was successfully applied for metals dissolved in liquid alkali metals as solvents [26]. The validity of Equation 4 for amalgams

was tested here with S_M data on more than 20 systems, well defined by experiments. $\overline{\Delta H}_M^l$ and $\overline{\Delta S}_M^{l,ex}$ were calculated using Equation 2 or 3 and fitted to Equation 4. The fitting gave the following results: $K' = 5.7$ and $C' = -48$ J mol⁻¹ at $r = 0.938$. Then S_M values were predicted by calculation with the use of Equation 2 or 3 and the estimated constants; the results are given in the third column of Table I. No calculations were performed for easily soluble metals and when $\overline{\Delta H}_M^l$ predicted in [23] was obviously incorrect as will be discussed in the next section. Probably due to erroneous values of ΔH_{MHg_x} , the predicted S_M values for Y, U, Zr, Hf, Pt are absurdly high whereas for those for Pd and Th are too low. Because S_{Ti} calculated based on experimental ΔH_{TiHg} value [27] was also over 100 mol %, we estimated S_{Ti} and S_{Sc} based on ΔH_{TiHg} and ΔH_{ScHg_3} predicted in [11]; the results of such calculations are surely nearer to the real S_{Ti} and S_{Sc} values. Similarly, in the cellular and regular solution models, the calculated S_V is unexpectedly higher than the rather more reliable (within an order of magnitude) experimental determinations.

4. Enthalpy of dissolution of metals in mercury

The heats of dissolution ($\overline{\Delta H}_M$) are experimentally determined by two methods: calorimetry [28] and from the temperature dependence of S_M [7, 9]. The first way is precise but may be only applied to the easily soluble metals. For metals poorly soluble in mercury the $\overline{\Delta H}_M$ values may be estimated by the second method; however, precision may sometimes be unsatisfactory correct. In fact dissolution of a metal in its saturated amalgam is measured this way, but when S_M is low enough, the difference between pure mercury and diluted amalgam is negligible. To satisfy the strictness of thermodynamic rules, the change in activity of the metal with change in its concentration should be taken into account. For dilute solutions the majority of investigators assume $(\partial \ln a_M / \partial \ln c_M) = 1$ [22], which is frequently called into question. When MHg_x is the saturating equilibrium phase, one may use the Equation 3 in a rearranged form for the dissolution enthalpy of solid metals in an infinite amount of liquid mercury ($\overline{\Delta H}_M = \overline{\Delta H}_M^l + \Delta H_M^f$). When pure metal is the saturating solid phase, or when the solid solubility of mercury in the metal is negligibly small, then Equation 2 is used.

Table II contains the selected experimental values of $\overline{\Delta H}_M$; they are compared with those predicted by the cellular theory [23] as well as the regular solution calculation. Comparison of these values is interesting, not only from a theoretical point of view but also as a base for giving preference to some discrepant S_M data originating from different sources. Jangg and Palman [7], Parkman [34] and Weeks [33] reported temperature dependences of S_M data of several transition metals with significantly different slopes. Moreover, Jangg and Palman [7] formulated a rule, used later by Kozin and co-workers [31] for S_M predictions, that the slopes $\Delta \ln S_M / \Delta(1/T)$, and in other ways $\overline{\Delta H}_M$ of poorly soluble metals, are almost equal if no ICs of the metal

TABLE II Selected enthalpies of solution of solid metals in liquid mercury from experiments and predictions

Element	Enthalpy $\overline{\Delta H}_M$ (kJ mol ⁻¹)		
	Experimental	Predicted by Niessen <i>et al.</i> [23]	Predicted here (regular solution)
Li	-87.4 [29]	-60	-
Na	-83.5 [29]	-38	-
K	-107.6 [29]	-43	-
Rb	-107.1 [29]	-48	-
Cs	-116.3 [29]	-53	-
Be	18 [3]*	65	57 [†]
Mg	-72 [30]	-28	-
Ca	-187.0 [29]	-175	-
Sr	-221.8 [29]	-189	-
Ba	-262.3 [29]	-215	-
La	-	-186	-
Ce	-77 [1, 31]*	~ -190*	-
Sm	-28 [1, 31]*	-	-
Th	-465 [1, 32]*	-151	-
U	-66 [1, 32]*	-30	-
Pu	-	-66	-
Ti	{ 18 [7, 27]* 169 [33, 27]*	-21	-
Zr	{ -27 [3, 27]* 128 [33, 27]*	-105	-
Hf	-	-64	-
V	{ 24 [7] 78 [34]* 103 [33]*	52	39
Nb	-	73	59
Ta	-	55	100
Cr	{ 22 [7] 188 [33]*	87	19
Mo	-	152	166 [10]
W	-	175	126
Mn	16 [30]	20	-
Tc	-	90	72
Re	-	153	120
Fe	{ 23 [7] 52 [34]*	88	18
Ru	-	87	90
Os	-	116	146
Co	{ 22 [7] 87 [34]*	56	85
Rh	few tenth negative [35]*	32	-
Ir	-	60	163
Ni	9 [30]	45	-
Pd	-33 [30]	-50	-
Pt	-46 [36]*	-9	-
Cu	-3 [30]	21	-
Ag	3 [7, 37]*	8	-
Au	8 [30]	-3	-
Zn	9.62 [30]	10	-
Cd	-2.11 [30]	4	-
B	-	-	156
Al	22 [24]	25	34
Ga	13.4 [28]	9	-
In	-5.99 [30]	0	-
Tl	-4.3 [30]	8	-
C	-	-	232
Si	-	75	98
Ge	46 [38]	39	45
Sn	14.0 [30]	7	-
Pb	9.72 [30]	11	-
As	-	26	56
Sb	33 [30]	17	-
Bi	17.7 [30]	16	-
Se	18.2 [8, 39]*	-	-
Te	10.3 [8, 39]*	-	-

*Calculated by the author, the first number denotes the source of S_M-T^{-1} and the second of ΔH_{MHg_x} .

[†] If no BeHg₂ is formed in the system.

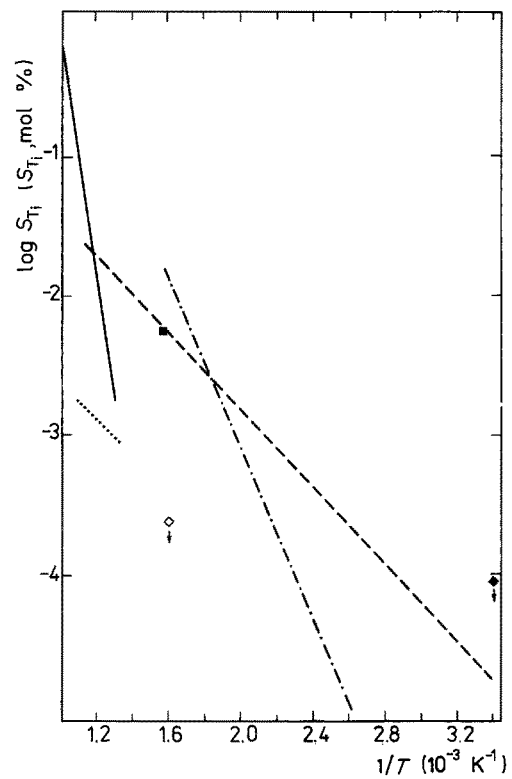


Figure 3 Dependence of $\log S_{Ti}$ on reciprocal temperature. The data sources are: (---) [7]; (◆) upper limit reported in [40]; (◇) upper limit reported in [41]; (■) [4]; (···) [42]; (—) [33]; (-·-·-) predicted in this work based on the cellular model.

are formed with mercury. Because the melting and solution effects are different for every element, their sum may be accidentally equal for some particular systems, but it ought not to be the rule. The anticipations of Miedema's group [23] reflect the full scale of variability of $\overline{\Delta H}_M$ and, finally, this picture seems to be more realistic than somewhat casual experimental data. $\overline{\Delta H}_M$ values predicted by the regular solution model are, except for Cr, Fe and Ir, in rough agreement with the predictions of the cellular model.

As mentioned previously, the slopes of $\Delta \ln S_M / \Delta(1/T)$ given earlier [7, 33, 34] are very different for Ti, Zr, V, Cr, Fe, Co. However, there are certain ranges of temperature when the S_M values given in [7] and [33] agree very well, as is schematically shown in Fig. 3 for titanium. These discrepancies might not be explained by the influence of mercury vapour pressure over the boiling point of mercury because the increasing pressure should act on the slope by decreasing it at higher temperatures because the higher the pressure the lower the solubility [22]. The opposite rule would act for metals forming ICs with mercury being stable at such high temperatures, which is not the case for the metals considered.

The high melting transition metal systems with mercury are experimentally very difficult and the only explanation of the discrepancies in $\overline{\Delta H}_M$ is the dissimilar contamination of the chemicals used, the adsorption of the solute on the sampling container walls and ineffective separation of the saturated solution from the crystals. For the liquid alkali metal solvents, one observes similar discrepancies which can sometimes be interpreted by the influence of ternary oxides, nitrides or binary carbides formed by the transition metals [15]; however, in mercury solvent no

such forms were detected. At this point one should fully agree with thermodynamic purists that the heat of dissolution estimated from the temperature dependence of S_M may be very uncertain.

The $\overline{\Delta H}_M$ values predicted by the cellular model in [23], when plotted against the atomic number, show a similar course to that of the S_M data in Fig. 2. This fact allows for the presumption that the experimental $\overline{\Delta H}_M$ data would also change in a similar way. Unfortunately, the $\overline{\Delta H}_M$ results obtained are precise, only for the easily soluble metals, therefore one should be careful about an absolute generalization of this similarity.

Let us compare the predictions in [23] with measurements of $\overline{\Delta H}_M$ for all metals in succession. For the alkali metals as solutes, the model predicts 50% less exothermic effect, whereas the experimental data are known precisely. Agreement for the alkaline earth metals is much better; and the calorimetric $\overline{\Delta H}_{Mg}$ result is not precise. The prediction of $\overline{\Delta H}_{Be}$ would indicate deficiency of the Be-Hg interactions.

No predictions are given for lanthanides, except for lanthanum, but one should expect values increasing slightly going from $\overline{\Delta H}_{Ce}$ to $\overline{\Delta H}_{Lu}$ with exceptions at Sm, Eu and Yb (stable divalent state). Owing to the significant stability of Ln-Hg compounds, the very low activity of Ln in their amalgams, the predictions at levels similar to that of lanthanum seems to be more reliable than the experimentally obtained values for Ce and Sm, which are exothermically too small because ΔH_{CeHg_4} and ΔH_{SmHg_4} are very uncertain [31]. For Actinides (Th, U), the experiments yielded, on the other hand, too high exothermic results; in particular $-\Delta H_{ThHg_4}$ [32] seems to be much overstated.

For the titanium group the predicted values are distinctly negative; the experimental results for Ti [7, 27] and Zr [3, 27] are certainly more reliable than a combination of the data [27, 33]. For V, Cr and Co, the situation is similar; Jangg and Palman [7] give probably too low values and Weeks [33] probably too high values of $\overline{\Delta H}_M$. There are many S_{Fe} data [1], but the scatter in these is significant and the temperature dependence irregular, so selection of a proper S_{Fe} data for $\overline{\Delta H}_{Fe}$ calculation may be casual. Very good agreement is observed for Mn. For the nickel group the sequence of $\overline{\Delta H}_M$ values from predictions and experiments is similar, but numerical agreement is poor. The sequence of $\overline{\Delta H}_M$ for the elements in the copper group from experiments is opposite to predictions, but the numerical values are not very different, especially for Ag. Quite good agreement is found for Zn and Cd; their experimental data are known precisely. The very high melting transition metals (Mo, W, Re, Os) are very resistive to dissolution in mercury according to the predictions, as well as qualitative observations.

The best agreement of the cellular model predictions with experiments is observed for p-electron metals and metalloids, with the exception of Sb.

5. Activity coefficients of metals dissolved in mercury

The activity coefficients are determined practically in

TABLE III Standard and related potentials of metals and their amalgams in hydrogen scale, and the activity coefficient of metals in very dilute amalgams at 298 K

Element	E_M^0 (V)	$E_{M(Hg)}^0$ (V)	Activity coefficient
Li	-3.042 [29]	-2.195 [29]	3×10^{-15} [43]
Na	-2.717 [29]	-1.958 [29]	1.3×10^{-13} [43]
K	-2.928 [29]	-1.975 [29]	6×10^{-17} [43]
Rb	-2.924 [44]	-1.970 [29]	1.2×10^{-16} [43]
Cs	-2.923 [44]	-1.950 [29]	1×10^{-15} [43]
Be	-1.97 [44]	-1.55 [45]*	$\sim 10^{-14}\dagger$
Mg	-2.356 [44]	-1.980 [29]	$2 \times 10^{-13}\dagger$
Ca	-2.840 [44]	-2.003 [29]	$4 \times 10^{-29}\dagger$
Sr	-2.890 [44]	-1.901 [29]	$3 \times 10^{-34}\dagger$
Ba	-2.920 [44]	-1.717 [29]	$2 \times 10^{-41}\dagger$
Ra	-2.92 [44]	-1.60 [46]*	$\sim 2 \times 10^{-45}\dagger$
La	-2.38 [44]	~ -1.2 [47] [‡]	$\sim 10^{-60}\dagger$
Ce	-2.34 [44]	-1.11 [48]	$10^{-62}\dagger$
Pr	-2.35 [44]	~ -1.1 [47] [‡]	$\sim 10^{-60}\dagger$
Nd	-2.32 [44]	~ -1.1 [47] [‡]	$\sim 10^{-60}\dagger$
Sm	-2.30 [44]	-1.68 [48]	$3 \times 10^{-32}\dagger$
Eu	-2.80 [44]	-1.796 [49]	$5 \times 10^{-35}\dagger$
Gd	-2.28 [44]	~ -1.1 [47] [‡]	$\sim 10^{-60}\dagger$
Yb	-2.8 [44]	-1.78 [48]	$\sim 10^{-35}\dagger$
Th	-1.83 [44]	~ -1.2 [45]*, [§]	$\sim 10^{-42}\dagger$
Cr	-0.90 [44]	-0.924 [50] [¶]	6^\dagger
Mn	-1.18 [44]	-1.127 [51]	$1.1 \times 10^{-2}\dagger$
Fe	-0.44 [44]	-0.6 [52] ^{§,}	$\sim 10^6\dagger$
Co	-0.277 [44]	-0.4 [53] ^{§,}	$\sim 10^4\dagger$
Ni	-0.257 [44]	-0.28 [54] [‡]	$\sim 6^\dagger$
Cu	0.340 [44]	0.28 [45]	$10^{2\dagger}$
Ag	0.48 [44]**	0.51 [55]*,**	0.3^\dagger
Zn	-0.763 [44]	-0.801 [29]	3.8 [43]
Cd	-0.402 [29]	-0.380 [29]	4.9×10^{-2} [43]
Al	-1.676 [44]	-1.5 [46]*	> 10 [31]
Ga	-0.529 [44]	-0.546 [46]*, ⁺⁺	2 [31]
In	-0.339 [29]	-0.297 [56]	3.0×10^{-2} [43]
Tl	-0.327 [29]	-0.294 [29]	0.12 [43]
Sn	-0.137 [44]	-0.200 [56]	32 [43]
Pb	-0.125 [44]	-0.179 [56]	23 [43]
As	0.240 [44]	-0.30 [45]*	$\sim 10^{27}\dagger$
Sb	0.17 [44]	-0.06 [57]*	$\sim 10^{11}\dagger$
Bi	0.317 [44]	0.258 [56]	16 [43]
Te	-0.42 [44]	-0.39 [46]*	$10^{-2}\dagger$

* $E_{1/2}$ polarographic potential.

† Calculated from Equation 5.

‡ Stationary potential being about the formal potential.

¶ Formal potential.

§ Irreversible.

|| $(E_{1/2}^{\text{cath.}} + E_{1/2}^{\text{anod.}})/2$.

** In acetonitrile solution.

++ In 7.5 mol dm^{-3} KCNS solution.

two ways: the vapour pressure over an amalgam, and the potential of an $M|M^{n+}|M(Hg)$ galvanic cell [31, 43]. The first method is limited to more concentrated amalgams, but the second covers effectively a range of 10^{-5} to 100 mol % M. The noble character of mercury allows for investigation of the majority of metals.

As the reference state, we assume that pure solid metal has an activity coefficient as well as its activity identically equal to 1 and then we determine its activity coefficient (f_M) in infinitely diluted liquid amalgam. Table III collects a selection of experimental data recommended in the literature [31, 43] as well as estimated by the present author based on electrochemical standard E^0 , formal E^f or reversible half-wave polarographic potential $E_{1/2}^r$ of amalgams.

$$-\ln f_M = \frac{nF}{RT} (E_{M^{n+}/M(Hg)}^0 - E_{M^{n+}/M}^0) \quad (5)$$

TABLE IV Standard rate constants (k_s) of the electrode process $M_{aq}^{n+} + ne \xrightleftharpoons{Hg} M(Hg)$ in noncomplexing electrolyte solution at 298 K

Element	k_s (cm sec ⁻¹)	Element	k_s (cm sec ⁻¹)
Li(I)	0.1 [59]	Mn(II)	4×10^{-5} [45]
Na(I)	0.4 [59]	Fe(II)	$\sim 10^{-12}$ [59]
K(I)	0.7 [59]	Co(II)	$\sim 10^{-9}$ [59]
Rb(I)	> 1 [59]	Ni(II)	$\sim 10^{-8}$ [59]
Cs(I)	0.2 [59]	Cu(II)	4×10^{-3} [65]
Ca(II)	2×10^{-3} [48]	Zn(II)	4×10^{-3} [59]
Sr(II)	3×10^{-4} [60]	Cd(II)	1 [59]
Ba(II)	2×10^{-3} [48]	Hg(II)	2 [59]
La(III)	1.3×10^{-4} [61]	Al(III)	2×10^{-3} * [66]
Ce(III)	1.6×10^{-4} [61]	Ga(III)	2×10^{-2} [59]
Nd(III)	$1 \times 10^{-3}\dagger$ [62]	In(III)	10^{-3} [59]
Sm(II)	$\sim 10^{-4}$ [60]	Tl(III)	2.6 [59]
Eu(II)	3×10^{-4} [49]	Sn(II)	0.9 [45]
Gd(III)	$\sim 10^{-3}\ddagger$ [63]	Pb(II)	1.5 [59]
Yb(II)	$\sim 10^{-4}$ [60]	Sb(III)	8×10^{-5} [59]
Cr(II)	$\sim 10^{-6}$ [64]	Bi(III)	1.3×10^{-3} [59]

* In 2% CaCl₂ + 0.2% gluconate.

† In 0.1 M LiCl.

‡ At -1.0 V versus SCE.

The activity coefficients in diluted amalgams are known with very various accuracy. For easily soluble metals with s or p electrons, the f_M values are precisely known, but for lanthanides and transition metals the estimations are based on $E_{1/2}$ where reversibility of the electrode system is seldom observed; therefore, such values should be treated with precaution, more as qualitative information.

The most impressive observation that one may obtain by analysis of f_M values in Table III, is that the activity of the metal in diluted amalgam decreases when the metal forms an IC with mercury. The more stable the IC, the lower is the f_M observed. The exceptions for Cu and Ni, which form IC, are probably due to imprecise $E_{M(Hg)}^0$ values because, for example, ΔG_{Cu} is reported as negative [31]. The stabilities of ICs formed by alkaline earths or lanthanides are so high that in 1 mol of an IC dissolved in mercury no more than one molecule is dissociated to metal and mercury atoms. All those metals with f_M values lower than unity exhibit negative deviations from Raoult's law.

The metals with f_M much higher than unity are not receptive to the formation of concentrated but homogeneous amalgams. When f_M is near to unity the amalgams are easily formed and Raoult's law is best fulfilled; however, never as for the ideal system.

6. Kinetics of discharging of metallic cations on mercury

The kinetics of electrode processes may be temporarily investigated with various electroanalytical methods [58]: d.c. and a.c. polarography, pulse polarography, voltammetry, chronopotentiometry, chronoamperometry, chronocoulometry and an a.c. bridge. The use of one of the methods is related to the magnitude of the kinetic constant and the determination precision is never better than a few per cent.

It is a well known fact that the kinetics of a red-ox process occurring even without reagent transfer through the electrode/solution interface may be slightly dependent (for example Fe(II)/Fe(III)) on the electrode

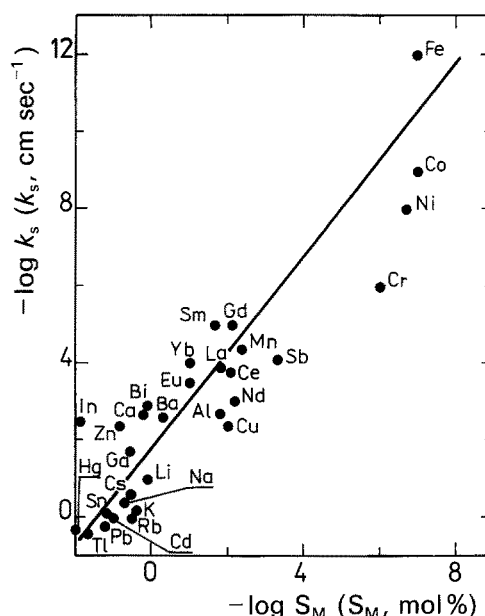
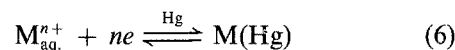


Figure 4 Dependence of $\log k_s$ on $\log S_M$ at 298 K.

material used. Consequently, the electrode material must be reflected in the electrode kinetics when in the course of the electrode process a crystal or amalgam is formed. As was pointed out by Tammamushi [59], the logarithm of the standard rate constant of the electrode process of the type



is a linear function of the logarithm of S_M but is not, as one might expect, regularly dependent on the cation M^{n+} hydration energy or the logarithm of the H₂O molecule exchange rate in the first solvation sphere. The original data of Tammamushi are supplemented by several new results (Ca, Sr, Ba, La, Ce, Nd, Sm, Eu, Gd, Yb, Cr, Mn, Cu, Hg, Al, Sn); see Table IV. Thus Tammamushi's correlation is reinforced, as may be seen in Fig. 4. This linear dependence has a purely empirical character and cannot be easily explained.

The energetics and kinetics of a cation dehydration should, at first, strongly limit the kinetics of the whole electrode process. The amalgamation energies may be significantly negative (alkali, alkaline earth, Ln and An metals) as well as positive (high melting transition metals) but they are numerically much smaller than the ion hydration effects. Later, cations of all poorly soluble metals (V, Cr, Mo, Fe, Co, Re) are reduced with significant overpotential, in spite of their moderately negative standard potentials (versus NHE).

It should be noted that the energy of amalgamation calculated from S_M values is correct only for metals weakly interacting with mercury. When a metal forms an IC with mercury, the energy of IC solvation by mercury, which is only part of the total solvation energy of the metal by mercury, may be calculated. Thus if one takes into account, instead of $\log S_M$, the total solvation energy, then the correlation analogous to that presented in Fig. 4 will be distorted. Nevertheless, for practical reasons the dependence in Fig. 4 may be effectively used to predict the order of the rate constant of the electrode process when the corresponding S_M is known, or vice versa.

TABLE V Diffusion coefficients of metals in mercury at 298 K (if not otherwise stated), radii of diffusing particles and comparison of compositions of diffusing entities and solid phases richest in Hg

Element	D_M (10^{-5} cm ² sec ⁻¹)	r_M^{eff} (10^{-8} cm)	r_M^{diff} (10^{-8} cm)	Diffusing entity in liquid Hg	Compound found in liquid Hg	Compound found in solid phase [1]
Li	0.92 ± 0.1 [74]	1.37	2.33	LiHg _{3(±1)}	LiHg ₂ [9, 31]	LiHg ₃
Na	0.84 ± 0.15 [74]	1.68	2.55	NaHg _{4(±2)}	NaHg ₄ [9, 31]; NaHg ₅₋₁₆ [76]	NaHg ₄
K	0.79 ± 0.08 (293 K) [77]	1.88	2.71	KHg _{6(±2)}	KHg ₁₅₋₁₆ [76]	KHg ₉₋₁₁
Rb	0.75 ± 0.08 [74]	2.23	2.85	RbHg _{4(±2)}	—	RbHg ₁₁₋₁₂
Cs	0.65 ± 0.1 [74]	2.40	3.30	CsHg _{6(-4,+5)}	—	CsHg ₁₂₋₁₃
Mg	0.90 ± 0.1 [60]	1.40	2.38	MgHg _{3(±1)}	MgHg; MgHg ₂ [9, 31]	MgHg ₂
Ca	0.64 ± 0.02 (283 K) [74]	1.72	3.34	CaHg _{8(±1)}	—	CaHg ₈₋₁₀
Sr	0.96 ± 0.1 (293 K) [78]	1.88	2.23	SrHg _{1½(±1)}	—	SrHg ₁₁₋₁₃
Ba	0.70 ± 0.07 (interpol.) [79]	1.98	3.06	BaHg _{6(±2)}	—	BaHg ₁₂
La	0.50 ± 0.05 [74]	1.65	4.28	LaHg _{18(-4,+8)}	—	LaHg _{6½}
Ce	0.60 ± 0.06 [80]	1.61	3.57	CeHg _{11(±3)}	—	CeHg _{6½}
Pr	0.60 ± 0.06 [81]	1.60	3.57	PrHg _{11(±3)}	—	PrHg _{6½}
Nd	0.78 ± 0.08 [82]	1.60	2.74	NdHg _{5(±2)}	—	NdHg _{6½}
Sm	0.52 ± 0.06 [74]	1.58	4.11	SmHg _{16(-6,+8)}	—	SmHg _{6½}
Tb	0.82 ± 0.08 [80]	1.56	2.61	TbHg _{4(±1½)}	—	TbHg ₄
U	0.6 ± 0.1 [83]*	1.35	3.57	UHg _{10(-4,+9)}	—	UHg ₄
Mn	0.90 ± 0.08 [74]	1.14	2.38	MnHg _{3(±1)}	—	MnHg _{2½}
Fe	1.84 ± 0.13 (?) [84]	1.12	1.16	Fe	—	Fe
Co	0.84 ± 0.04 (?) [84]	1.10	2.55	CoHg ₄ (?)	—	Co
Ni	0.65 ± 0.03 [74]	1.09	3.30	NiHg _{9(±1)}	—	NiHg ₄
Cu	1.00 ± 0.08 [74]	1.12	2.14	CuHg _{2(±1)}	—	CuHg _{0.84}
Ag	1.05 ± 0.03 [74]	1.27	2.03	AgHg _{1½(±½)}	—	AgHg _{1½}
Au	0.85 ± 0.04 [74]	1.26	2.52	AuHg _{3½(±½)}	—	AuHg _½
Zn	1.67 ± 0.06 [74]	1.23	1.28	Zn	—	ZnHg _{1/3}
Cd	1.53 ± 0.03 [74]	1.37	1.39	Cd	CdHg ₃ [9, 31]	CdHg ₃
Hg	1.60 ± 0.05 [74]	1.43	1.34	Hg	Hg	Hg
Al	1.6 ± 0.2 (interpol.) [85]	1.26	1.34	Al	—	Al
Ga	1.64 ± 0.08 [74]	1.33	1.31	Ga	—	Ga
In	1.38 ± 0.1 [74]	1.46	1.54	In	InHg ₃ [9, 31]	InHg ₆
Tl	1.05 ± 0.05 (mean value) [74]	1.51	2.03	TlHg _{1½(±½)}	TlHg _{2½} [9, 31]	TlHg _{2½}
Ge	1.70 ± 0.15 [74]	1.39	1.26	Ge	—	Ge
Sn	1.48 ± 0.04 [74]	1.48	1.45	Sn	—	SnHg _{0.12}
Pb	1.25 ± 0.04 [74]	1.54	1.71	PbHg _{1(±0.1)}	PbHg ₁ [9, 31]	PbHg ₁
Sb	1.40 ± 0.1 [74]	1.54	1.52	Sb	—	Sb
Bi	1.35 ± 0.1 [74]	1.62	1.58	Bi	—	Bi
Te	1.19 ± 0.3 (385 K) [86]*	1.59	2.95	TeHg _{6(-4,+8)}	—	TeHg

*Calculated by present author.

7. Diffusion coefficients of metals in liquid mercury

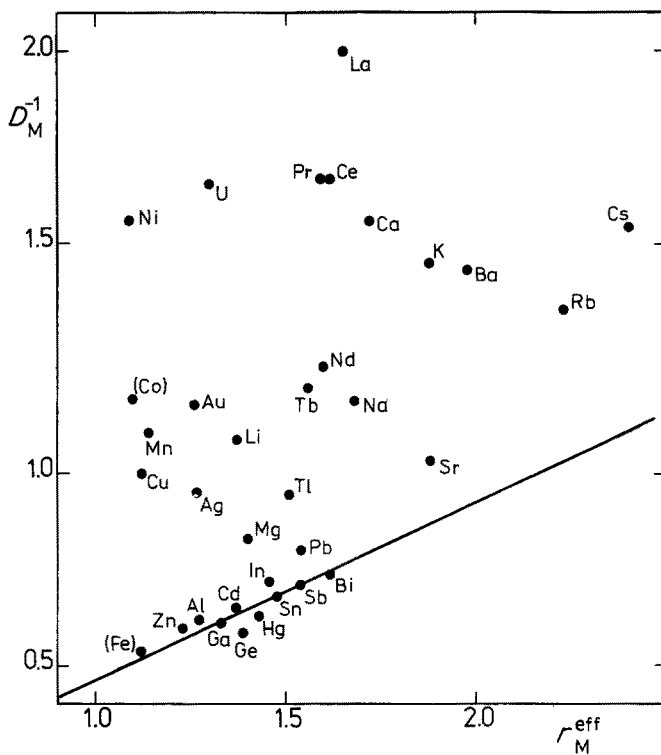
The following experimental methods may be used to determine the diffusion coefficients (D_M) of a metal in mercury: diaphragm cell, capillary reservoir, long capillary, shear cell and rotating disc techniques where metal concentration changes may be traced by chemical analysis, radioisotopes or resistivity measurements [67–72]. These methods are used mainly by physicists and metal scientists, and no one knows why [67–69] they are frequently overlooked in very useful electrochemical techniques [58]. For mercury as solvent, a fundamental part of the diffusion data was obtained from electroanalytical experiments and the results obtained are both precise and convincing; such experiments include: e.m.f. of the metal electrode covered with a fresh layer of mercury, amalgam polarography, stripping voltammetry, chronoamperometry and chronopotentiometry with the use of various electrode types [73, 74]. The fast subsequent reaction

between gold and zinc in mercury after the electroreduction of Zn(II) on a gold amalgam electrode was successfully utilized for D_{Au} determination [75].

In electroanalytical experiments, when the correct model of the process was assumed, an individual run should last no longer than 30 sec at a concentration level of 10^{-3} mol % M. In other methods, when the experimental times are significantly longer, an independent convection can produce an overestimation of results by even more than 100%. A temperature gradient as little as 0.1 K in a diffusional cell may cause a convective vortex.

For various reasons, the results of D_M reported in the literature fall into various classes of precision and accuracy. D_{Cd} and D_{Tl} have been thoroughly investigated and these most reliable results fall within intervals of $\pm 2\%$ and $\pm 5\%$, respectively. However, many elements have been subjected to only one determination and consequently the results may contain an error of $\pm 20\%$ [73, 74]. Table V contains the majority

Figure 5 Dependence of D_M^{-1} on r_M^{eff} at 298 K.



of the D_M data suggested by Galus [73, 74]. Their experimental precision has been estimated during the present work and they are supplemented with new results. D_U and D_{Te} were estimated in this work using fundamental data on the experiments described by Volkova *et al.* [83] and Dubovikov and Denisov [86], respectively. The values of D_{Fe} and D_{Co} reported by Chang and Gang [84] may be only accidentally correct, because they were derived from the voltammetric curves, where the diffusional character of the electrode process is questionable and both metals exhibit a very low solubility in mercury [1].

As may be seen in Table V, a fair number of experimental values exist and a correlation between D_M and some features of the solute metal may be sought. The starting point of analysis of the data is the Sutherland-Einstein equation [69, 87] because it expresses in the simplest and correct way the relation between the viscosity of the medium (η) (for diluted amalgams it is practically equal to the viscosity of pure mercury), temperature (T) and radius of diffusing particle (r) [88]

$$D_M = kT/4\pi r\eta \quad (7)$$

The correctness of using this equation with reference to amalgams was discussed earlier [73, 74, 89]. Equation 7 is in agreement with the modified hole theory of diffusion presented by Walls and Upthegrove [90] and is satisfied for self diffusion of mercury.

Nevertheless, many means of analysis of diffusion data in amalgams may be found in the literature according to other equations [91–95]. One should also mention the popular approach by Stromberg and Zakharova [96] and Gladyshev [97] who analysed the diffusion data using Equation 7 with a numerical coefficient of 6 instead of 4, and substituting the crystallographical radii of metallic ions at valencies not higher than +3. It must be pointed out here that Equation 7 with the coefficient 6 is only correct when

a diffusing solute particle has a radius much higher than the radius of the solvent particle [69, 87]. On the other hand, the ion valency and ionic radius in the liquid metallic state do not have equivalent in meanings.

Electrons in liquid metals are neither completely free nor localized [98], therefore the use of atomic radii is less erroneous than the use of the ionic radii of metals from their crystalline chlorides or oxides. As recently determined by Schwab and Schindewolf [99] the radius of sodium (which is easily ionized) in its amalgam is 1.63×10^{-8} cm, so it is nearer to the sodium atom radius of 1.91×10^{-8} cm than to the Na^+ radius of 0.97×10^{-8} cm. One may also quote Shimoji's statement [100] that rapid motion of electrons allows us to assume that each ion can be screened in its transport process by the electrons, so that it may be regarded as a neutral pseudo-atom.

The assumption here that the diffusing particles are metal atoms or metal atoms solvated by mercury, leads to quite reasonable results. In Fig. 5 the straight line corresponds to Equation 7 and the selected data from the experimental results lay on this line (within experimental error) if the metal does not form a stable IC with mercury. The higher affinity between mercury and the metal (see the phase diagrams, dissolution heats or activity coefficients) the higher is the departure from the law expressed by Equation 7. There is no one case of a metal not forming an IC with mercury which diffuses slower than predicted by theory; the case of D_{Co} should not be taken into account, as explained above. Instead, the underestimation of D_M for metals forming ICs with mercury may simply be explained by the existence of MHg_x molecules or labile solvates in the mercury medium.

Many years ago, Smith [91], first pointed out the diffusion of metallic solvates in mercury and formulated a quantitative dependence. The composition of the diffusing solvate may be estimated by assuming

a spherical arrangement of mercury atoms around the metal; a close packing of space with a coefficient of 0.74 [101] was taken in our calculations. The number of mercury atoms (x) in the diffusing particle was found from the equation

$$x = 0.74(r_{\text{exp}}^3 - r_{\text{M}}^3)/r_{\text{Hg}}^3 \quad (8)$$

where r_{exp} is the radius of the diffusing particle calculated from Equation 7 using experimental D_{M} , r_{M} and r_{Hg} are the effective radii and are calculated from the formula [89]

$$r_{\text{M}} = \frac{1}{2}(3V_{\text{M}}/\pi N)^{1/3} \quad (9)$$

where V_{M} is the molar volume of the metal and N is Avogadro's number.

The results of our calculation are given in the fifth column of Table V and are compared with compositions of solid-phase MHg_x being in equilibrium with diluted amalgams. One should remember the rough accuracy of the estimation of x : the smaller D_{M} the higher is the uncertainty. For the solvates significantly larger than the mercury atom the validity of Equation 7 is lost; then only an upper limit of the number of mercury atoms in the diffusing particle is reasonable. The solvate composition for many systems is equal or very similar but there are elements (like La or Sm) where the mean solvation numbers are even higher than 12 – the maximum number of contacting balls around one ball. In this way some metals lose mercury atoms going from a solid phase into a diluted amalgam, and some acquire extra mercury atoms in such a process. The uncertainty of x does not allow for more subtle analysis of the solvate structure; for example, is MHg_4 tetrahedric or square? It would also be interesting to know how labile are mercury atoms in a solvate and whether the existence of particles with different stoichiometry at a given metal concentration is possible. It seems probable that in thallium diluted amalgam some thallium atoms diffuse alone and some as TlHg_3 which gives the mean value of $\text{TlHg}_{1.3}$, as observed in the experiments. If the activation energy of diffusion is higher than the activation energy of M–Hg bond dissociation, then mercury atoms may be easily bonded to and broken from the metal in the diffusion process.

Investigations of liquid amalgams by X-rays, conductance, magnetic susceptibility and molar volume measurements [102–106] indicated the existence of intermetallic molecules in liquid amalgams in agreement with observations of the diffusion process. Some investigations of significantly concentrated amalgams showed extremes in the D_{M} –composition dependence. The minimum of D_{Tl} is observed for a composition close to Tl_2Hg_5 [107] and for D_{K} at KHg_2 [108]. Unquestionably these facts are proof of the existence of such ICs in liquid phases.

Another interesting phenomenon connected with self diffusion in liquid metals should be mentioned. Due to the disappearance of the second structure in the liquid state, a non-linear variation of $\log D_{\text{M}}$ with $\log T$ was observed for several metals including mercury [109]. For pure mercury the transition temperature is around 277 K [109, 110]. The question

arises whether the changes in the structure of mercury are reflected only in the self diffusion of mercury or also in the diffusion of various solutes in mercury. The only data which could be analysed in relation to this effect are for Ag [92], Au [92], Pb [111] and Zn [111]. The curvature of the $\log D_{\text{Pb}} - \log T$ plot deviates at about 280 K from linearity in the similar way as for mercury [110]. The break points for D_{Ag} , D_{Au} and D_{Zn} are within experimental scatter, therefore the effect of the mercury structure transition at 277 K on solute diffusion in mercury cannot be excluded; however, it is not well proved.

8. Kinetics of metal dissolution in mercury

This aspect of the amalgam formation has not been summarized before in spite of the significant amount of experimental data. One of the methods of D_{M} determination was the dissolution on rotating a metallic disc in mercury. Such a method yields reliable results when the rate of this process is limited by the diffusion of the metal in the mercury phase but not by releasing an atom from the metal crystal which then passes into the liquid mercury. The mathematical description of the dissolution was given by Berthoud [112]

$$\ln(1 - C_{\text{M}}/S_{\text{M}}) = -k_{\text{d}}AtV^{-1} \quad (10)$$

where $k_{\text{d}} = (k_{\text{s}}D_{\text{M}}/d)/(k_{\text{s}} + D_{\text{M}}/d)$, C_{M} is the metal concentration, A the surface area of solid metal, t the time, V the volume of mercury, k_{d} the dissolution rate constant, k_{s} the surface rate constant, and d the diffusion layer thickness. When $k_{\text{s}} < D_{\text{M}}/d$, $k_{\text{d}} = k_{\text{s}}$ and when $k_{\text{s}} > D_{\text{M}}/d$, $k_{\text{d}} = D_{\text{M}}/d$.

The rotation of a metallic disc in liquid mercury may be experimentally replaced by mixing or forced circulation of mercury with a constant velocity around a static metal sample. The kinetics of metal dissolution have also been investigated by electro-oxidation of finely divided metal in a heterogeneous amalgam or solid metal covered with a thin layer of mercury. The results of these investigations are collected in Table VI. Unfortunately, it is difficult to come to any general conclusion for this topic because the results are presented in various nontransferable forms and the calculated rate constants are expressed in very different units. No correlation between S_{M} , D_{M} , $\Delta\bar{H}_{\text{M}}$ or the tendency to form ICs is observed. In fact, one may only distinguish the processes controlled by the diffusion of metal in mercury or by the release of metal atoms from the surface layer of the crystal.

There are several inconsistencies in Table VI. The dissolution kinetics found for Zn [133] are claimed to be limited by diffusion but other investigators [134, 135] stated that it is a surface-controlled process. We observe similar situations for Cd ([136] contrary to [28]) and for Cu ([127, 129, 131] contrary to [128]). The dissolution of the gamma phase of Zn–Hg is faster than that of pure Zn [132]; however, the dissolution kinetics of TeHg or Cu_7Hg_6 are many times slower than pure Te [86] or Cu [127], respectively.

Atypically, the dissolution rate for nickel decreases with increasing temperature [130], nevertheless the dissolution of Ni–Hg appears to be a much slower

TABLE VI Characterization of dissolution kinetics of metals and mercury intermetallics in mercury

Substance	T (K)	Method	Results*	E_a (kJ mol ⁻¹)	Kind of process, remarks
Na-Hg [113]	293-333	Chronoamperometric oxidation of amalgam containing microcrystals	Plot of i_{ox} against t	12.1	Nondiffusional; $E_a^{hetero} \approx 4E_a^{homo}$
Ba-Hg [114]	293-333	as above	as above	19.7	Almost diffusional; $E_a^{hetero} \approx E_a^{homo}$
La-Hg [115]	298-333	as above	$2.4 \times 10^{-8} \leq k \leq 6.3 \times 10^{-8} \text{ mol dm}^{-3} \text{ sec}^{-1}$	22.6	Nondiffusional; $E_a^{hetero} \approx 2\frac{1}{2}E_a^{homo}$
Ce-Hg [116]	298-343	as above	$1.1 \times 10^{-8} \leq k \leq 3.6 \times 10^{-8} \text{ mol dm}^{-3} \text{ sec}^{-1}$	22.6	Nondiffusional; $E_a^{hetero} \approx 4E_a^{homo}$
Gd-Hg [117]	293-353	as above	$4.4 \times 10^{-5} \leq k \leq 4.1 \times 10^{-4} \text{ mol dm}^{-3} \text{ sec}^{-1}$	28.5	Nondiffusional; $E_a^{hetero} \approx 6E_a^{homo}$
U [118]	629	Sample weight loss in time in static conditions	$k = 2.2 \text{ g Hg cm}^{-2} \text{ U min}^{-1}$	-	Rates in Na or Mg amalgams are similar but in Bi amalgam is lower
U [119]	629	Sample weight loss in time in static saturated U amalgam	$k = 30 \text{ mg U cm}^{-2} \text{ U h}^{-1}$ (initially)	-	-
Mn-Hg [120]	293-323	Chronoamperometric oxidation of amalgam containing microcrystals	$3 \times 10^{-5} \leq k \leq 1.6 \times 10^{-4} \text{ mol dm}^{-3} \text{ sec}^{-1}$	40.4	Nondiffusional
Fe [121]	773	Circulating Hg in Fe loop	$R = 2.1 \times 10^{-7} D_{Fe}^{0.6} \text{ g Fe cm}^{-2} \text{ sec}^{-1}$	9.9	Diffusional
Ni [122]	478-553	Circulating Hg in Ni loop	$2.8 \times 10^{-3} \geq k \geq 2.4 \times 10^{-4} \text{ cm sec}^{-1}$	-	Nondiffusional
Ni-Hg [123]	293	Chronoamperometric oxidation of amalgam containing microcrystals	$k = 1.3 \times 10^{-7} \text{ cm}^3 \text{ sec}^{-1}$	-	-
Ni-Hg [124]	293	Chronoamperometric oxidation of amalgam containing microcrystals	$k = 3.6 \times 10^{-7} \text{ cm}^3 \text{ sec}^{-1}$	-	-
Pt [125]	293-598	Sample weight loss in time in static conditions	$8 \times 10^{-10} \leq k \leq 7 \times 10^{-7} \text{ cm sec}^{-1}$	33.5	Nondiffusional
Pt [126]	293-431	as above	$9 \times 10^{-11} \leq k \leq 8 \times 10^{-8} \text{ g Pt sec}^{-1}$	50.1	Nondiffusional
Cu [127]	295-343	Chronoamperometric oxidation of Cu covered with Hg film	$3.4 \times 10^{-3} \leq k \leq 1.1 \times 10^{-2} \text{ cm sec}^{-1}$	19.4	Nondiffusional
Cu-Hg [127]	293-323	Chronoamperometric oxidation of Cu-Hg covered with Hg film	$2 \times 10^{-4} \leq k \leq 1.1 \times 10^{-3} \text{ cm sec}^{-1}$	36	Nondiffusional
Cu-Hg [128]	293-333	Chronoamperometric oxidation of amalgam containing microcrystals	$2.1 \times 10^{-3} \leq k \leq 5.1 \times 10^{-3} \text{ sec}^{-1}$	-	Diffusional; dissolved Cu and Cu-Hg particles are simultaneously oxidized
Cu-Hg [129]	293-353	as above	$3.9 \times 10^{-5} \leq k \leq 2.8 \times 10^{-4} \text{ mol dm}^{-3} \text{ sec}^{-1}$	28	Nondiffusional
Cu-Hg [130]	298	as above	$k = 4.1 \times 10^{-6} \text{ cm}^3 \text{ sec}^{-1}$	-	-
Cu-Hg [131]	293-363	as above	Plot of i_{ox} against t	28.7	Nondiffusional
Ag [132]	332, 358	Dissolution of rotating Ag in Hg	Plot of $(1 - C/C_0)$ against (At/V)	6.7	Diffusional
Zn, Zn-Hg [132]	276-332	Dissolution of rotating Zn in Hg	as above	3.6	Mixed; dissolution of Zn-Hg γ -phase is faster than of Zn
Zn [133]	237-323	as above	Plot of J against $\omega^{\frac{1}{2}}$	3.6-6.1	Diffusional; dissolution rate depends slightly on mono-crystal orientation
Zn [133]	298	as above	as above	-	Diffusional of polycrystals
Zn [134]	303, 313	Dissolution of static Zn cylinder in rotating vessel with Hg	$k = 1.2 \times 10^{-3} \text{ cm sec}^{-1}$ at 313 K	-	Nondiffusional
Zn [135]	323	Dissolution of rotating Zn in Hg	$1.5 \times 10^{-3} \leq k \leq 7.4 \times 10^{-3} \text{ cm sec}^{-1}$	-	Nondiffusional; rate depending on mono-crystal orientation
Cd [136]	275, 293	Dissolution of rotating Cd disc in Hg	Plot of J against $\omega^{\frac{1}{2}}$	-	Diffusional
Cd [28]	293	Heat measurement of Cd dissolution in Hg	Plot of degree of dissolution against time	-	Mixed

Al [137]	293-323	Chronoamperometric oxidation of Al covered with Hg film	$2.3 \times 10^{-3} \leq k \leq 6.9 \times 10^{-3} \text{ cm}^3 \text{ sec}^{-1}$	29.3	Nondiffusional
Sn [134]	303, 313	Dissolution of static Sn cylinder in rotating vessel with Hg	$k = 1.4 \times 10^{-3} \text{ cm sec}^{-1}$ at 313 K	-	Diffusional
Sn [137]	295-333	Chronoamperometric oxidation of Sn covered with Hg film	$1.3 \times 10^{-3} \leq k \leq 2.5 \times 10^{-3} \text{ cm sec}^{-1}$	12.1	-
Sn [132]	276-303	Dissolution of rotating Sn in Hg	Plot of $(1 - C/C_s)$ against (At/V)	5.4	Diffusional
Pb [134]	303, 313	Dissolution of static Pb cylinder in rotating vessel with Hg	$k = 1.2 \times 10^{-3} \text{ cm sec}^{-1}$ at 313 K	-	Diffusional
Pb [138]	237-323	Dissolution of rotating Pb in Hg	Plot of J against ω^3	2.1-2.5	Diffusional
Sb [139]	room	Chronoamperometric oxidation of amalgam containing microcrystals as above	$k \leq 1.8 \times 10^{-4} \text{ cm}^3 \text{ sec}^{-1}$	-	Dissolved Sb and Sb particles are simultaneously oxidized
Sb [140]	293-353		$3.1 \times 10^{-3} \leq k \leq 8.3 \times 10^{-3} \text{ sec}^{-1}$	6.3	Diffusional; dissolved Sb and Sb particles are simultaneously oxidized
Te [86]	385-458	Dissolution of rotating Te disc in Hg	Plot of J against ω^3	51.1	Diffusional
TeHg [86]	418-478	Dissolution of rotating TeHg disc in Hg	Plot of J against ω^3	50.9	$J_{\text{Fe}} \approx 14J_{\text{TeHg}}$ under the same conditions

* i_{ox} = oxidation current; t = time; k = dissolution rate constant; C = concentration; C_s = solubility; A = surface; V = volume; J = dissolution rate; ω = angular velocity; R = rate of corrosion; E_a = activation energy.

process [123]. It seems that for metals forming ICs with mercury the surface dissolution of a metal by mercury in the first stage of dissolution should lead to acceleration rather than to restraining of the whole process; the dissolution of M–Hg is energetically less favourable than of pure metal. Generally speaking we do not know now whether formation of IC or IP between the metal and mercury accelerates or restrains the dissolution of the metal in mercury.

9. Other investigations

In addition to the features of simple liquid amalgams mentioned above, the changes of other thermodynamic functions (ΔG_M^{ex} [31, 43], ΔS_M^{ex} [31, 43], ΔV_M [31, 99, 105, 141]), structure factors by X-ray scattering [31, 102], electrical resistivity [31, 104, 106], magnetic susceptibility [103, 142, 143], thermoelectric power [104, 106] and viscosity [31, 107], could also be analysed. The only easily soluble metals were the subject of these investigations and any general conclusions would be premature.

The viscosity measurements indicated that an addition of Au, Cd, Sn, Pb or Bi has an insignificant influence on mercury viscosity. On the contrary, the influence of Li–Cs, Ca or Ba on the viscosity of their diluted amalgams is much stronger. If liquid amalgams contain ICs then distinctly negative values of ΔG_M^{ex} , ΔS_M^{ex} , ΔV_M are observed. The formation of an IC in a liquid amalgam phase is reflected by changes of structural parameters, the dependence of thermoelectric power on composition shows a minimum, the derivative of resistance on temperature with composition shows a maximum and the dependence of magnetic susceptibility on concentration shows a negative deviation from linearity.

10. Conclusion

The material presented in this paper is quite good base for use in the classification of simple amalgams. This will be the subject of the subsequent paper [144].

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