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by

D. F. Bowersox
J. A. Leary

THE ENTHALPIES OF SELECTED ELEMENTS IN LIQUID PLUTONIUM

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ABSTRACT

The relative partial molar heats of solution for selected solutes in liquid plutonium have been calculated from solubility data from 700 to 1000°C by the equation

$$R \ln N_i = \Delta S_f - \Delta \overline{H}_i^*/T \quad ,$$

where R is the gas constant, N_i is the mole fraction of solute i in a saturated solution at absolute temperature T, ΔS_f is the entropy of fusion of i, and $\Delta\overline{H}_i^*$ is the sum of the heat of fusion ΔH_f of i and the excess enthalpy of solution. The entropy of fusion for these solutes was taken as 2.3 eu. The calculated relative partial molar heats of solution ($\Delta\overline{H}_i^*$ in kcal/mole) are: tungsten, 22.0; tantalum, 16.6; niobium, 11.1; vanadium, 11.0; molybdenum, 10.3; chromium, 9.5; and thulium, 9.2. These heats of solution were correlated with solubility parameters by a constant k determined from the data, so that

$$\Delta\overline{H}_i^* = \Delta H_f + k \overline{V}_i (\delta_i - \delta_{Pu})^2 \quad ,$$

where $\overline{V}_i$ is the molar volume of solute i and δ_i and δ_{Pu} are the cohesive density factors.

INTRODUCTION

The solubilities of selected elements in liquid plutonium are being studied at the Los Alamos Scientific Laboratory.[1,2] Measurements have been restricted to conditions such that the solubility of an element is constant and independent of the direction of approach to saturation at the temperatures of interest. Moreover, the data cited in this report are for binary systems whose equilibrium can be expressed by equations of the type

$$A(s) + Pu(1) = Pu(1, \text{sat'd with } A) \quad , \qquad (1)$$

where A is a solid solute element.

This report is limited to some simple eutectic-type binary systems for which solubility data are available. These are W-Pu, Ta-Pu, Nb-Pu, V-Pu, Mo-Pu, Cr-Pu, and Tm-Pu from 700 to 1000°C. Even though solubility data are available for C-Pu, Re-Pu, Mn-Pu, Zr-Pu, and Ti-Pu, this report does not discuss these systems because in several of them compound formation occurs[3] and in others there are either peritectic points[4] or solid solution formation.[5] In addition, Eq. (1) is not valid for such systems, and good estimates of the entropy and enthalpy of fusion are not available.

From the data obtained in this Laboratory,[1,2] equations containing only one empirical parameter were constructed for these binary systems. These equations were correlated with a solubility parameter based upon the cohesive densities and volumes of the solute and solvent. (This treatment is not limited to liquid plutonium, and a similar parameter should apply to other binary systems.) From this parameter, estimates of solubility were made over a wide range of concentrations from a small number of data. This approach is not a substitute for measuring solubilities when quantitative data are required; however, the estimates provide useful semiquantitative solubility approximations.

DISCUSSION

Hildebrand and Scott[6] and Wagner[7] discuss in detail the thermodynamics of solutions and alloys. In the investigation reported here, their basic equations were used to interpret the solubilities of tungsten, tantalum, niobium, vanadium, molybdenum, chromium, and thulium in liquid plutonium. These solubilities have been measured under conditions such that the dissolution of solute i in liquid plutonium can be represented by the general equilibrium reaction (Eq. 1). Each solute reported here formed a simple eutectic-type binary system with liquid plutonium.[3]

The activity of solute i in solution, with respect to an arbitrary reference state, is equal to the activity of solid i with respect to the same reference state. In other words,

$$a_i^{(s)} = a_i^{(l)} \quad . \tag{2}$$

If component i as pure supercooled liquid at the temperature of interest is chosen as the reference state, the activity of solid i is

$$a_i^{(s)} = -\frac{1}{RT}\int_{T_f}^{T} (H^l - H^s)(1/T^2)dT \quad . \tag{3}$$

In Eq. (3) R is the gas constant, T is the absolute temperature, H^l and H^s are the heat contents of liquid and solid i, and T_f is the temperature at which normal fusion occurs. The integration of Eq. (3) is exact if the heats of all phase transitions and the heat capacities, $C_p^{\,l}$ and $C_p^{\,s}$, are known as functions of temperature. In cases where the only phase transition between T and T_f is that of melting and the heat capacities of solid and supercooled liquid i are equal, Eq. (3) may be integrated as

$$R \ln a_i^{(s)} = (\Delta H_f/T_f) - (\Delta H_f/T) = \Delta S_f - \Delta H_f/T \quad , \tag{4}$$

where ΔS_f and ΔH_f are the entropy and enthalpy of fusion of solute i, respectively.

The activity of solid component i at temperature T can not be calculated from its melting point and heat of fusion. Equation (4) can be solved by relating the activity in the liquid to the mole fraction in solution, N_i. By definition the activity coefficient, γ_i, in solution is the ratio of the activity to the mole fraction of solute; i.e.

$$\gamma_i^{(l)} = a_i^{(l)}/N_i \quad . \tag{5}$$

In an ideal solution the activity coefficient is 1, and the activity is equal to the mole fraction. By combining Eqs. (2), (4), and (5), the equation

$$R \ln N_i = \Delta S_f - \Delta H_f/T \tag{6}$$

is obtained. For these simple eutectic systems, the solubilities in liquid plutonium are far less than those predicted by Eq. (6).[1,2] Evidently, the activity coefficient is much greater than unity, corresponding to positive deviations from ideality. According to Henry's law the activity coefficient is essentially constant in dilute solutions, and, as a consequence, the deviations from ideality can be computed from the solubility data.

By definition the activity is related to the partial molar free energy of mixing, $\Delta \bar{F}_i$, by the equation

$$\Delta \bar{F}_i = RT \ln a_i^{(1)} = \Delta \bar{H}_i - T \Delta \bar{S}_i \quad . \qquad (7)$$

At this point two terms should be defined. First, the relative partial molar free energy $\Delta \bar{F}_i$ is the change in the total free energy upon mixing 1 mole of pure substance i with an infinite quantity of a solution of the given composition. For fixed values of temperature and pressure,

$$\Delta \bar{F}_i = \bar{F}_i - F^o_i \quad , \qquad (8)$$

where $\bar{F}_i$ is the final relative partial molar free energy and F^o_i is the relative partial molar free energy of component i in the initial standard state. $\Delta \bar{F}_i$ can be measured. It is equivalent to the work done on the system when the process of mixing 1 mole of solute i with an infinite quantity of a solution of given composition is reversible and isothermal and the pressure-volume work is negligible.

The second factor to be defined is the relative integral molar free energy of the solution, F^M, defined as

$$\Delta F^M = F_m - \left(N_i F^o_i + N_B F^o_B\right) = \left(\bar{F}_i - F^o_i\right) N_i + \left(\bar{F}_B - F^o_B\right) N_B = N_i \Delta \bar{F}_i + N_B \Delta \bar{F}_B \quad , \qquad (9)$$

where F_m, the total free energy of the solution, is equal to the relative partial molar free energies of the components multiplied by their respective mole fractions, N_i and N_B. Thus ΔF^M is the work required for the reversible and isothermal formation of one mole of solution from N_i mole of pure substance i and N_B mole of pure substance B. The pressure-volume work, once again, is considered negligible.

Each of the component parts of Eq. (7) can be treated as consisting of an ideal and an excess term. For example,

$$\Delta \bar{S}_i = \Delta \bar{S}_i^{id} + \Delta \bar{S}_i^{xs} \quad . \qquad (10)$$

The ideal partial molar entropy is given by the equation

$$\Delta \bar{S}_i^{id} = -R \ln N_i \quad , \qquad (11)$$

so that Eq. (7) can be rewritten as

$$RT \ln a_i^{(1)} = \Delta \bar{H}_i - T(-R \ln N_i + \Delta \bar{S}_i^{xs}) \quad . \qquad (12)$$

At equilibrium Eqs. (2), (4), and (12) may be combined as

$$R \ln N_i = (\Delta \bar{S}_i^{xs}) - (\Delta H_f + \Delta \bar{H}_i/T \quad . \qquad (13)$$

A plot of R ln N_i versus 1/T will yield a curve with slope $(\Delta H_f + \Delta \bar{H}_i)$ and an intercept equal to $(\Delta S_f + \Delta \bar{S}_i^{xs})$. At very low concentrations of i, $\Delta \bar{H}_i$ should be a constant; the plot becomes a straight line under these conditions.

Equation (13) will be evaluated by first considering the entropy terms, $(\Delta S_f + \Delta \bar{S}_i^{xs})$, and then calculating the sum of the enthalpy terms from the data. From the least-squares equations, the intercept varies from 1.2 to 6.0 eu.[1,2] The extrapolation is a rather large one, and the variation indicates that it may be an inaccurate one as well. If changes in entropy are considered as measures of changes of randomness in the system, as is often claimed in statistical mechanics, then the entropy term should remain about the same for all the solutes under consideration. Searcy, in fact, reports that the excess entropy term in dilute solutions of fairly similar components should be zero.[8]

Hildebrand and Scott define a regular solution by the statement: "A regular solution is one involving no entropy change when a small amount of one of its components is transferred to it from an ideal solution of the same composition, the total volume remaining the same."[6] If the solutions under consideration are assumed to be regular, i.e. if $\Delta \bar{S}_i^{xs}$ is zero, Eq. (13) becomes

$$R \ln N_i = \Delta S_f - (\Delta H_f + \Delta \bar{H}_i)/T \quad . \qquad (14)$$

For convenience, the enthalpy terms in Eq. (14) will be combined to a single term so that

$$R \ln N_i = \Delta S_f - \Delta \bar{H}_i^*/T \quad , \tag{15}$$

where $\Delta \bar{H}_i^*$ is the sum of the enthalpy terms, called the relative partial molar heat of solution of solute i in liquid plutonium.

Before proceeding, the restrictions on Eq. (14) will be summarized:

1) The activity coefficient is constant over the temperature and concentration range of interest.
2) The heat capacity of the solid solute is equal to that of the supercooled liquid solute at a given temperature.
3) Fusion is the only phase change that occurs between the temperature of interest and that of the melting temperature of the solute.
4) The solution is regular; i.e. the excess entropy is zero.

To estimate solubilities in regular solutions, Hildebrand and Scott[6] derived the equation

$$R \ln N_i' = \Delta S_f - \Delta H_f + \bar{V}_i (\delta_i - \delta_B)^2 \alpha_B^2/T \quad , \tag{16}$$

Where N_i' is the estimated mole fraction of solute, $\bar{V}_i$ is the molar volume of solute i, and α_B is the volume fraction of the solvent, which is usually assumed to be 1 in dilute solutions. The solubility parameters, δ_i and δ_B, are calculated from the heat of vaporization, ΔH_v; and the molar volume, for example, the parameter for solute i, is

$$\delta_i = \left((\Delta H_v - RT)/V_i\right)^{\frac{1}{2}} \quad . \tag{17}$$

CALCULATIONS

Hultgren, et al. estimate the entropies of fusion for all these solute elements as 2.3 eu.[9] This value was used with the solubility data to calculate $\Delta \bar{H}_i^*$ values from Eq. (15) for tungsten, tantalum, niobium, vanadium, molybdenum, chromium, and thulium in liquid plutonium.[1,2] The average $\Delta \bar{H}_i^*$ values for each element are given in Table I.

Table I

The Relative Partial Molar Enthalpies of Selected Elements in Liquid Plutonium

Element	$\Delta \bar{H}_i^*$, kcal/mole
W	22.0 ± 0.1
Ta	16.6 ± 0.1
Nb	11.1 ± 0.1
V	11.0 ± 0.1
Mo	10.3 ± 0.1
Cr	9.5 ± 0.1
Tm	9.2 ± 0.2

Table II

The Thermodynamic Properties of Selected Elements

Element	Melting Point, $^{\circ}K^{a}$	Heat of Fusion ΔH_f (kcal/mole)[a]	Entropy, eu[a]	Molar Volume, V (cc/mole)[b]	Cohesive Density, δ (cal/cc)[b]
W	3650	8.4	2.3	9.6	145
Ta	3269	7.5	2.3	10.8	136
Nb	2740	6.3	2.3	10.8	127
V	2190	5.1	2.3	8.5	119
Mo	2890	6.7	2.3	9.4	128
Cr	2176	5.0	2.3	7.3	108
Pu	913	...	...	...	81

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[a] See Ref. 9.

[b] See Ref. 6.

The melting points, heats of fusion, entropies, molar volumes, and the cohesive density factors of these elements are listed in Table II. The enthalpy term of Eq. (16) can be expressed as

$$\Delta \bar{H}_i^{*\prime} = \Delta H_f + \bar{V}_i (\delta_i - \delta_{Pu})^2 \quad , \tag{18}$$

where $\Delta \bar{H}_i^{*\prime}$ is the relative molar heat of solution estimated by Eq. (16). Values of $\Delta \bar{H}_i^{*\prime}$, which were calculated from the data in Table II, are given in Table III. These can be equated with the $\Delta \bar{H}_i^*$ values previously derived from the experimental data by the use of a solubility constant for each solute. In other words,

$$\Delta \bar{H}_i^* = \Delta H_f + k \bar{V}_i (\delta_i - \delta_{Pu})^2 \quad , \tag{19}$$

where k is an empirical constant. Values of k are given in Table III. The reasons for variations in k are unknown.

Table III

Solubility Parameters and Correlation Constants for Selected Elements with Liquid Plutonium

Element	Solubility Parameter, $\Delta \bar{H}_i^{*\prime}$ [a]	Correlation Constant, k [b]
W	47.7	0.35
Ta	40.2	0.28
Nb	29.2	0.21
V	17.6	0.47
Mo	27.3	0.17
Cr	10.3	0.85

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[a] Calculated by the equation

$$\Delta \bar{H}_i^{*\prime} = \Delta H_f + \bar{V}_i (\delta_i - \delta_{Pu})^2 \quad ,$$

where $\Delta \bar{H}_i^{*\prime}$ is calculated from the thermodynamic values given in Table II.

[b] Calculated by the equation

$$k = \frac{\Delta \bar{H}_i^{*} - \Delta H_f}{\bar{V}_i (\delta_i - \delta_{Pu})^2} \quad ,$$

where $\Delta \bar{H}_i^{*}$ is the experimentally measured value given in Table I.

CONCLUSIONS

Solubilities undoubtedly are related to factors such as the molar volumes, cohesive densities, and the electronic configurations. In most of these cases the differences are not significant; the atomic size and electronegativity changes for example, within these elements, are small. No interrelations with the changes in solubility could be found. The changes in electronic configuration are undoubtedly difficult to evaluate. Such changes could cause variations in the empirical constant k in Eq. (19). The cohesive energy in the solutes, which is partially reflected in the melting temperatures and the heats of fusion, evidently affects the solubility. In general, the solubilities decreased with increasing melting points and with increasing heats of fusion.

It should be possible to extend this study by employing Eq. (14) for other systems, and particularly for other liquid metal solvents. This could eventually lead to a systemization of the properties of the solutes in various solvents. Other areas of interest include systems with more components, such as those commonly found in liquid-metal technology.

REFERENCES

1. D. F. Bowersox and J. A. Leary, "The Solubilities of Carbon, Tantalum, Tungsten, and Rhenium in Liquid Plutonium," J. Nucl. Mater. 21, 219 (1967).
2. D. F. Bowersox and J. A. Leary, "The Solubilities of Selected Elements in Liquid Plutonium II. Titanium, Vanadium, Chromium, Manganese, Zirconium, Niobium, Molybdenum, and Thulium," J. Nucl. Mater., in press.
3. F. W. Schonfeld, "Plutonium Phase Diagrams Studied at Los Alamos," in The Metal Plutonium, Eds. A. S. Coffinberry and W. N. Miner, University of Chicago Press, Chicago, 1961, pp. 240-254.
4. D. M. Poole, M. G. Bale, P. G. Mardon, J. A. C. Marples, and J. L. Nichols, "Binary Alloys," in Plutonium 1960, Eds. E. Grison, W. B. H. Lord, and R. D. Fowler, Cleaver-Hume Press, London, 1961, pp. 277-278.
5. J. A. C. Marples, J. Less-Common Metals 2, 331 (1960).
6. J. H. Hildebrand and R. L. Scott, The Solubility of Nonelectrolytes, 3rd Ed., Rheinhold Publishing Corporation, New York, 1950.
7. C. Wagner, Thermodynamics of Alloys, Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1952.
8. A. W. Searcy, Lawrence Radiation Laboratory Report No. UCRL-16256 (1965).
9. R. Hultgren, R. L. Orr, P. D. Anderson, and K. K. Kelley, Selected Values of Thermodynamic Properties of Metals and Alloys, John Wiley and Sons, Inc., New York, 1963, pp. 25-339.