ELSEVIER

Journal of Nuclear Materials 281 (2000) 203–207

journal of nuclear materials

www.elsevier.nl/locate/jnucmat

Henrian ideality of iron in liquid uranium solvent at high temperatures

D. Das [a,*], A.S. Kerkar [a], S.R. Bharadwaj [a], S. Mukherjee [b], S.R. Dharwadkar [c]

[a] *Applied Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India*
[b] *Laser & Plasma Technology Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India*
[c] *Department of Chemistry, The Institute of Science, 15 Madam Cama Road, Mumbai 400 032, India*

Received 8 March 2000; accepted 9 June 2000

Abstract

Equilibrium vapor pressures of iron from its dilute solutions in liquid uranium were measured at high temperatures (2250–2750 K). From the Fe vapor pressure data at known compositions (x_{Fe}), Henry's coefficient ($K_{\mathrm{Fe}} = p_{\mathrm{Fe}}/x_{\mathrm{Fe}}$) of the solute was obtained as $\log K_{\mathrm{Fe}}(\pm 0.07)\ (\mathrm{Pa}) = -18975.6(\pm 1098.1)/T + 11.15(\pm 0.44)$. The behavior of $K_{\mathrm{Fe}}(T)$ is shown to be marginally different from that of the equilibrium vapor pressures of pure liquid iron ($p_{\mathrm{Fe}}{}^{\circ}$). The partial molar excess Gibbs energy of iron at infinite dilution derived from the behavior is expressed as $\Delta_{\mathrm{E}}\bar{G}^{\infty}_{\mathrm{Fe}} = -1588 + 1.25T$ (J mol^{-1}). The result is discussed in the light of the quasi-regular solution model and compared with data of the system available in the literature. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

In dilute solutions, the solute obeys Henry's law and Henry's coefficient represents the vapor pressure of a hypothetical pure state (i.e., at unit mole fraction) of the solute achieved by ideal extrapolation of the pressure data from the dilute region. Normally, the hypothetical state differs from the true pure state of the solute as, in the dilute region the solute experiences an interaction different from that in pure solute matrix. It is generally predicted in metallic alloys [1] that the difference between the two states expressed in terms of the excess Gibbs energy of the solute reduces with increase in temperature due to randomization of atomic motions by thermal energy.

In the present study this aspect is examined in the uranium–iron system by the measurement of the equilibrium vapor pressure of iron from its dilute solutions in liquid uranium at elevated temperatures (2250–2750 K). Activities of Fe have been reported from vapor pressure measurements in this system using the Knudsen effusion mass spectrometric technique [2,3] in the temperature ranges 1440–1850 and 1780–2180 K, respectively. The composition ranges covered are $x_{\mathrm{Fe}} = 0.05$–0.90 [2] and $x_{\mathrm{Fe}} = 0.003$ [3]. The activity coefficient of iron in the liquid phase as a function of temperature and composition has also been derived from the available phase diagrams [4–6].

2. Experimental

The equilibrium vapor pressure of Fe over dilute solutions of Fe in liquid uranium was measured in the temperature range of 2250–2750 K by Knudsen effusion with the forward collection technique. To verify the influence of the solute on the vapor pressure of the solvent U, p_{U} was measured at a few temperatures in the range mentioned above. The detailed description of the apparatus is reported elsewhere [7]. The liquid was contained in a single-crystal tantalum cup inside the tungsten Knudsen cell. From the reported information [8,9] of the low solubility of U and Fe in solid tantalum, it is assumed that nearly pure tantalum remains in equilibrium with the liquid alloy. The Ta activity maintained practically at unity, therefore, the vaporization was from a

---

[*] Corresponding author. Fax: +91-22 550 5151.
E-mail address: htschem@magnum.barc.ernet.in (D. Das).

PII: S0022-3115(00)00190-2

bivariant system where the composition of the liquid alloy continuously changed due to a higher volatility of Fe than U. At a defined temperature the vapor pressure measurement was carried out in a dilute state of iron in the liquid, where the variation of the Fe concentration is small within the measurement time. The alloy composition was thus controlled from kinetic restrictions.

Initially, an exploratory experiment was made to understand the region of dilution where the vaporization can be studied at a temperature with an insignificant variation in Fe concentration in the liquid maintaining dynamic equilibrium with the tantalum container. This was accomplished by measurement of the temporal variation of the vapor flux of iron at a particular temperature. With a starting alloy composition of 3 at.% Fe in about 250–300 mg liquid U, the observed variation of the vapor flux expressed as temporal pressure of iron, $p_{\mathrm{Fe}}(t)$ within the Knudsen cell at 2287 K is shown in Fig. 1. During the measurement the temperature was monitored by an optical pyrometer calibrated following an established procedure [10].

As seen in Fig. 1, the temporal pressure of Fe falls rapidly at the initial stage after which the fall is very slow over a fairly long period. The observed trend in p_{Fe} suggests a similar trend of the Fe concentration in the liquid, which should have fallen by almost the same order of magnitude as p_{Fe} by the time in which the system reached the plateau region (XX′). In the region (XX′), the sluggish change in p_{Fe} and therefore, in the Fe concentration of the liquid alloy is due to the compensation of the evaporation loss of iron atoms by its diffusion from the solid phase, i.e., Fe is dissolved in the tantalum container. There are no reported data on the ternary system Fe–Ta–U for the solid solubility of Fe in tantalum. Assuming the solubility to be a few atom percent as given in the reported binary system Fe–Ta [9], the container that was pre-equilibrated with the alloy is a quite large source for the replenishment of Fe in its highly diluted solution. Thus, the slow temporal variation observed in p_{Fe} is indicative of attaining dynamic equilibria between the solid and liquid phases.

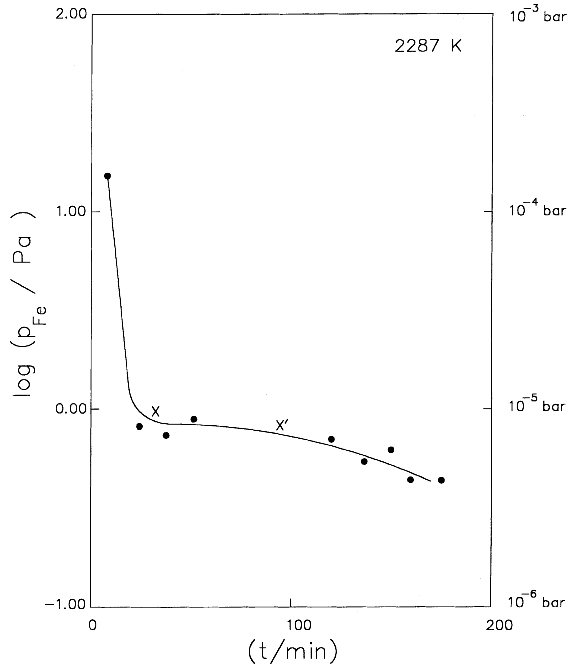

Fig. 1. Temporal variation of vapor flux of iron expressed as p_{Fe} at 2287 K. XX′ represents the plateau region where the equilibrium p_{Fe} has been measured.

In the actual runs of monitoring the vapor pressure of iron in the pseudobinary U–Fe system (of the ternary system U–Fe–Ta) at any temperature in the range of 2250–2750 K, the equilibration time for the region of slow variation was attained before collecting the effusate from the Knudsen cell. For each isothermal run this was confirmed by making target collections in two successive tantalum planchets that a showed sluggish variation of the vapor pressures calculated from the amounts of iron collected in the respective targets. The concentration of iron in the liquid alloy was measured in the cooled sample after each measurement. Vapor collection and concentration measurements of cooled samples were repeated at several temperatures within the mentioned interval.

Fe and U deposited on planchets were dissolved in acidic medium and analyzed by absorption spectroscopy (DCPAES) and fluorimetric techniques, respectively. Fe was separated out from U by solvent extraction to avoid an interference of U in the Fe analysis. The cases where Fe vapor pressures derived from two successive isothermal collections of the vapor showed inconsistency were not considered in the subsequent analysis. The frozen mass of the cooled sample consisted of U containing small amounts of Fe and Ta. The Fe and U contents in each experiment were assayed by standard procedures involving their spectrophotometric analysis. The tantalum content was established gravimetrically after filtering out the metal powder from the acid-treated mass of the frozen alloy. The acid treatment with dilute HCl readily dissolved uranium and iron while tantalum remained undissolved. Typically, the iron content in the mole fraction was in the range of 1×10^{-3}–5×10^{-4}. The tantalum contents were verified in some of the runs. The observed values of x_{Ta} at the lowest and highest temperatures of the measurement were 0.10 and 0.33, respectively. These values are in agreement with the reported values of its saturation solubility of Ta in liquid U [8].

3. Results

The vapor pressures of iron and uranium ($p_{\mathrm{Fe/U}}$) were calculated from the observed collection rates of the

Table 1
Vaporization data and Henry's coefficients (K_{Fe}) at different temperatures for iron in liquid uranium

Temperature, T (K)	Mole fraction of iron, $x_{Fe} \times 10^4$	Partial pressure of iron, p_{Fe} (Pa)	Henry's coefficient, log K_{Fe} (Pa)
2744	2.13	4.249	4.30
2646	3.35	2.917	3.94
2633	6.28	4.874	3.89
2555	10.60	5.563	3.72
2511	12.80	4.542	3.55
2380	15.70	2.606	3.22
2371	10.30	1.874	3.26
2287	11.10	0.654	2.77

metals at different temperatures with the help of the expression relating the rate of collection ($dw_{Fe/U}/dt$) under a given geometry (G), orifice area (A), and temperature (T) of the effusing cell. The expression is given by

$$p_{Fe/U} = [(dw_{Fe/U}/dt)/A]G \cdot (2\pi RT/M_{Fe/U})^{1/2}, \quad G = (r^2 + h^2)/r^2, \tag{1}$$

where, $M_{Fe/U}$ is the molar mass of Fe or U as the case may be, r the radius of the vapor collimator, and h the vertical separation of orifice to collimator in cylindrically symmetric configuration of the assembly. The measured vapor pressures of U at 2250 and 2750 K, after correcting for the ideal solubility of Ta in liquid U were found to be 0.32 and 35.28 Pa, respectively. These values are in agreement with that reported earlier by the authors [11]. This shows that the presence of iron in the dilute form practically does not influence the vaporization behavior of the solvent, i.e., liquid uranium, as expected.

The vapor pressure of iron (p_{Fe}) at different temperatures (2250–2750 K) and the correspondingly observed iron concentrations in the liquid expressed in mole fraction (x_{Fe}) are presented in Table 1. The solubility of Ta in the liquid was taken into consideration for expressing x_{Fe}. It may be noted that for some of the temperatures the vapor pressure measurements were repeated for a second time and the values of vapor pressures were reproducible within 10%. The tabulated values of p_{Fe} represent averaged figures for those cases. The values of Henry's coefficients (K_{Fe}) were calculated as $K_{Fe} = p_{Fe}/x_{Fe}$ and are given in the same table as log K_{Fe} at different temperatures. The values of log K_{Fe} versus $1/T$ were least-square fitted linearly as given by

$$\log K_{Fe}(\pm 0.07)\ (\mathrm{Pa}) = -18975.6(\pm 1098.1)/T + 11.15(\pm 0.44) \quad (2250 \leqslant T(\mathrm{K}) \leqslant 2750) \tag{2}$$

Fig. 2 shows the experimental data points along with the linear representations of Eq. (2). The figure also includes the plot (dotted line) of the vapor pressure p°_{Fe} of pure iron for comparison [12]. The ratio K_{Fe}/p°_{Fe} represents the activity coefficient of iron (γ^{∞}_{Fe}) at infinite dilution (Henry's coefficient), as the composition range of this measurement is $x_{Fe} = 10^3$–10^{-4}. Earlier reported data in the Fe–U system [2] indicates that below the composition region of $x_{Fe} = 0.1$, the solute obeys Henry's law even at lower temperatures.

The derived partial molar excess Gibbs energy of Fe in liquid uranium at infinite dilution can be represented as,

$$\Delta_E \bar{G}^{\infty}_{Fe} = -1588 + 1.25T\ (\mathrm{J\ mol^{-1}}) \quad (2250 \leqslant T(\mathrm{K}) \leqslant 2750) \tag{3}$$

According to Eq. (3), the excess quantity is positive though very small in the temperature region. In terms of γ^{∞}_{Fe} values, the positive deviation is below 10% (for example, $\gamma^{\infty}_{Fe} = 1.077$ at 2500 K), which is, however, well within the total uncertainty of the vapor pressure measurements.

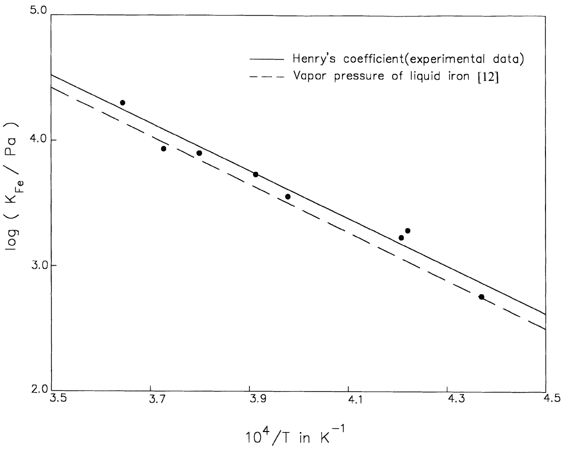

Fig. 2. Temperature dependence of Henry's coefficient (K_{Fe}) for iron in liquid uranium.

4. Discussion

The activity coefficient of iron (γ_{Fe}) in liquid uranium has been reported [2,3] from vaporization studies. According to Gardie et al. [2], the U–Fe system exhibits a negative deviation from ideality in the temperature range 1440–1850 K. We have derived the partial molar excess Gibbs energy of Fe at infinite dilution from their polynomial fits of the partial molar quantities of the components which can be represented by

$$\Delta_{\mathrm{E}}\bar{G}^{\infty}_{\mathrm{Fe}} = 1020\text{–}16.0T \ (\mathrm{J\ mol^{-1}}). \quad (4)$$

Extrapolation of this equation to higher temperatures leads to an increasingly higher negative deviation from ideality due to a high positive excess entropy associated with a small positive enthalpy. Kurosawa et al. [3] have carried out vaporization studies on U–0.3 at.% Fe alloy by a Knudsen effusion mass spectrometric method. The derived partial molar excess Gibbs energy of Fe at this composition can be given by

$$\Delta_{\mathrm{E}}\bar{G}^{\infty}_{\mathrm{Fe}} = -7304.6 - 4.307T \ (\mathrm{J\ mol^{-1}}). \quad (5)$$

The composition of 0.3 at.% Fe can be considered to be sufficiently dilute for the validity of Henry's law in metallic systems. Similar to the results shown in Eq. (4), Eq. (5) also indicates an increasingly higher negative deviation from ideality at higher temperatures. This behaviour is in contradiction with the general trend of approaching ideality at higher temperatures.

Considering solid–liquid phase equilibria in the U–Fe binary system, assessments about the partial molar quantities of Fe have been reported [4–6]. The assessment by Chiotti et al. [4] leads to the following expression for the partial molar excess Gibbs energy of Fe at infinite dilution,

$$\Delta_{\mathrm{E}}\bar{G}^{\infty}_{\mathrm{Fe}} = -864.1 - 22.76T(\mathrm{J\ mol^{-1}}). \quad (6)$$

This shows that the dilute solution of Fe in liquid uranium has a strong negative deviation from the Raoultian ideality. A similar prediction was made by Kubaschewski [5] by considering the Gibbs energy versus composition diagram for an isothermal section at 1328 K of the binary phase fields containing the intermetallic, $\mathrm{UFe_2}$.

An experimental study and phase diagram calculations of the U–Fe alloy system have been reported by Leibowitz and Blomquist [6]. Using a sub-regular solution model for the liquid phase they have derived the partial molar excess Gibbs energy of Fe at infinite dilution to be

$$\Delta_{\mathrm{E}}\bar{G}^{\infty}_{\mathrm{Fe}} = -9631\ \mathrm{J\ mol^{-1}}. \quad (7)$$

The predicted behavior of the thermodynamic property of iron in the uranium solvent at low temperatures is in contrast with the result obtained at high temperatures in the present study. The near ideality of the binary liquid observed is due to randomization of atomic motions by a high thermal energy. This type of behavior at high temperature is predicted by the quasi-regular model [1]. The negative deviation seen in the assessed results from the phase diagram analysis could be due to a strong association of the components, U and Fe, at low temperatures. The partial molar excess enthalpy and entropy values at infinite dilution derived from the results of this study using Eq. (3) are −1588 J $\mathrm{mol^{-1}}$ and −1.25 J $\mathrm{K^{-1}}$ $\mathrm{mol^{-1}}$, respectively. The negative signs of both the quantities are in accordance with the prediction made by the quasi-regular model and by other semi-empirical relationships for binary alloys reported in the literature [1,13].

The similarity in signs is due to the general validity of the fact that the enthalpic stability during alloy formation leads to a restricted accessibility of states. The opposite signs for the two thermodynamic quantities (−864.1 J $\mathrm{mol^{-1}}$ and 22.76 J $\mathrm{K^{-1}}$ $\mathrm{mol^{-1}}$, respectively) given in Eq. (6) of the reported assessment [4] could be due to the empirical nature of modeling.The expression of the excess Gibbs energy although normalized with invariants in the phase diagram appears to be insufficient in describing the two temperature coefficients, i.e., excess enthalpy and entropy. Mass spectrometric results of Kurosawa et al. [3] (Eq. (5)) also suffers from similar disparity of opposite signs of excess enthalpy and entropy terms. Eq. (4) derived from Gardie et al. [2] gives a small value of the excess enthalpy expected for a solution approaching ideality. However, a large positive excess entropy term makes the solution more non-ideal at higher temperatures. The results of the two mass spectrometric studies [2,3] characterized by increasing deviation from ideality at higher temperatures could be due to the presence of dissolved oxygen from the $\mathrm{Y_2O_3}$ container used in these experiments. This is supported by the fact that the observed vapor pressure of U [3] is lower by a factor of two than the reported and assessed values [11,14].

It is necessary to mention here that the value for the partial molar enthalpy of iron at infinite dilution ($\Delta\bar{H}^{\infty}_{\mathrm{Fe}}$) in liquid U from Miedema's model [15] is −38 kJ $\mathrm{mol^{-1}}$. Kubaschewski reported a similar value in his assessment [5] considering ideal entropy. Enthalpy values obtained from Miedema's model are generally considered as independent of temperature. While the value of $\Delta\bar{H}^{\infty}_{\mathrm{Fe}}$ at lower temperatures could be as negative as that from Miedema's model, the present experimental result suggests that it is drastically modified towards the ideal value at higher temperatures. Fe looses its stronger association with the solvent atoms once the temperature is much above the melting points of the intermetallics. The average temperature of this study is about 1000 K above the melting point of $\mathrm{UFe_2}$ (1501 K).

5. Conclusion

Phase diagram analysis and low temperature mass spectrometric data which indicate negative deviation from ideality at low temperatures are in agreement with the existence of intermetallic phases in the U–Fe binary system. However, the empirically fitted equations for the thermodynamic properties derived from these studies loose their validity at high temperatures as such equations predict increasingly larger negative deviations with increase in temperature. This experimental study has shown that the thermodynamic behavior of iron in liquid uranium solvent is nearly ideal at high temperatures as should be the normal trend.

Acknowledgements

The authors would like to thank Dr A.C. Udas of Analytical Chemistry Division and Shri V.A. Sali of Laser and Plasma Technology Division, BARC, for their cooperation in chemically analyzing the samples.

References

[1] C.H.P. Lupis, Chemical Thermodynamics of Materials, Elsevier, North Holland, 1983, p. 460.

[2] P. Gardie, G. Bordier, J.J. Poupeau, J. Le Ny, J. Nucl. Mater. 189 (1992) 85.

[3] S. Kurosawa, T. Oka, M. Yasumoto, S. Ueta, N. Morioka, N. Komada, M. Yamawaaki, J. Mass Spectrom. Soc. Jpn. 41 (1993) 329.

[4] P. Chiotti, V.V. Akhachinskij, I. Ansara, M.H. Rand (Eds.), in: The Chemical Thermodynamics of Actinide Elements and Compounds Part 5: The Actinide Binary Alloys, IAEA, Vienna, 1981, p. 114.

[5] O. Kubaschewski, Proceedings of the Symposium on Thermodynamics of Nuclear Materials held by the IAEA at Vienna, 21–25 May 1962, IAEA, Vienna, p. 219.

[6] L. Leibowitz, R.A. Blomquist, J. Nucl. Mater. 184 (1991) 47.

[7] R. Mishra, M. Ali(Basu), S.R. Bharadwaj, A.S. Kerkar, D. Das, S.R. Dharwadkar, J. Alloys Compounds 290 (1999) 97.

[8] M.S. Chandrasekharaiah, S.R. Dharwadkar, D. Das, Z. Metallkd 77 (1986) 509.

[9] L.J. Swartzendruber, E. Paul, Bull. Alloy Phase Diagrams 7 (1986) 254.

[10] D. Das, M.S. Chandrasekharaiah, High Temp. Sci. 21 (1986) 161.

[11] D. Das, S.R. Dharwadkar, M.S. Chandrasekharaiah, J. Nucl. Mater. 130 (1985) 217.

[12] M.W. Chase Jr., C.A. Davies, J.R. Downey Jr., D.J. Frurip, R.A. Mc Donald, A.N. Syverud, JANAF Thermochemical Tables Part II, 3rd Ed., J. Phys. Chem. Ref. Data 14 (1985) 1179.

[13] O. Kubaschewski, C.B. Alcock, P.J. Spencer, Materials Thermochemistry, 6th Ed., Pergamon, Oxford, 1993, p. 201.

[14] I. Barin, Thermochemical Data of Pure Substances, vol. 2, 3rd Ed., VCH, Weinheim, 1995.

[15] F.R. de Boer, R. Boom, W.C.M. Mattens, A.R. Miedema, A.K. Niessen, Cohesion in Metals, North-Holland, Amsterdam, 1988.