THE DIFFUSION OF HYDROGEN IN B.C.C. V–Ti SOLID SOLUTIONS

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Abstract—Recent data for the variation of the diffusivity of hydrogen in b.c.c. V–Ti solid solutions with Ti-concentration and temperature have been analyzed in terms of the cell model for such ternary solid solutions. The data have been shown to be compatible with this model and a simple cell energy spectrum involving H-metal interactions which are linearly dependent upon the Ti-concentration.

It is shown that the interaction energies deduced from the kinetic behavior of the system are in good accord with thermodynamic data for the V–H and Ti–H terminal solid solutions.

Keywords: Diffusion, hydrogen, interstitial body-centered cubic, V–Ti-solid solutions.

1. INTRODUCTION

Recent years have witnessed a large volume of research effort involving the diffusion of hydrogen through binary substitutional solid solutions. Recent reviews [1, 2] of this area reveal that much of the work has been centered on face-centered cubic (f.c.c.) solutions, and, further that the bulk of this effort has been directed toward H-diffusion in Pd-based substitutional systems. Much less effort has been devoted to (body-centered cubic) b.c.c. solutions.

The present short paper represents an effort to apply current kinetic ideas of H-diffusion to the b.c.c. V–Ti solution. The kinetics of H-diffusion in this "binary matrix" have been studied in some detail, and the thermodynamic properties of the V–H and Ti–H terminal systems are well known.

It is clear that classical rate theory is not directly applicable to much of the data for H-diffusion in many H–metal systems since the energy of the localized vibrations of a proton is often greater than kT at room temperature. At high temperatures, and especially in the f.c.c. metals, the classical theory is a useful approximation. In the case of the metals Nb, V, and Ta, the lowest excitation energy of vibration of a proton is about 120 meV, corresponding to ~1400 K [3]. However, the quantum mechanical modifications to the classical theory (Le Claire [4], Alefeld [5]) have lead to useful approximations for these b.c.c. metals. An excellent discussion has been given by Kehr [6]. This approach leads to a diffusivity relation which has the same form as the classical Arrhenius equation [7] and in general leads to adequate descriptions of the isotope effect, the activation energy, and the prefactor in the Arrhenius expression for H-diffusion in the b.c.c. metals.

In this paper we will treat the matter somewhat pragmatically by using the modified quantum approach and justify this by the fact that it is phenomenologically in accord with H-diffusion behavior above room temperature. This point will be discussed more fully later.

2. EXPERIMENTAL DATA

Experimental data for H-diffusion in the V–Ti binary matrix are available from the electrotransport measurements of Pine and Cotts [8] and the resistivity measurements of Tanaka and Kimura [9]. The data of Pine and Cotts span the temperature range 310–480 K and Ti-concentrations θ_u (mole fraction of
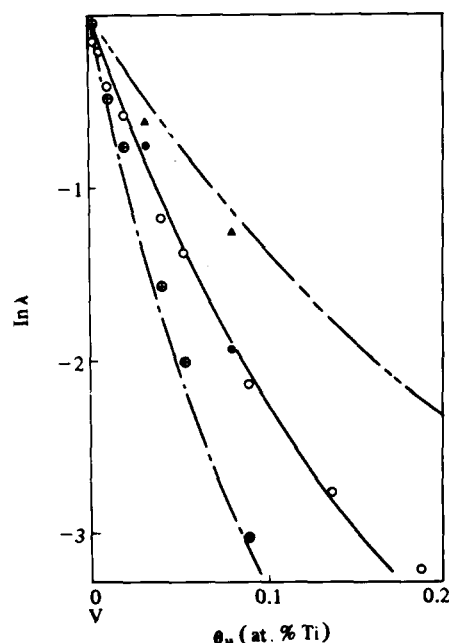

Fig. 1. Variation of the diffusivity ratio λ for H in V–Ti solutions with the Ti-concentration (θ_u).
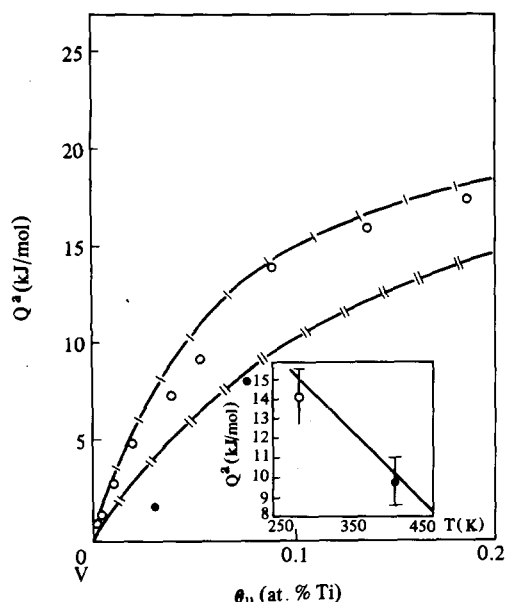
Fig. 2. Variation of the apparent activation energy for the diffusion of H in V–Ti solid solutions, Q^a, with Ti-concentration (θ_u). The inset diagram shows Q^a as a function of T: the solid line is calculated from the model.

Ti) of 0.03 and 0.08. The data of Tanaka and Kimura extend up to $\theta_u = 0.19$ and were taken in the temperature range 196–365 K. The experimental data are illustrated in plots of $\ln \lambda$ (diffusivity ratio) vs θ_u (Fig. 1) and Q^a vs θ_u (Fig. 2), where Q^a is the apparent activation energy determined from the Arrhenius relationship for the diffusivity D:

$$D = D_o \exp(-Q^a/kT), \qquad (1)$$

where D_o is the usual pre-exponential factor. All the measurements for a given θ_u are in excellent accord with the representation (1) in the range of measured temperatures. The diffusivity ratio λ is the ratio of the H-diffusivity D^{v-u-i} in the V–Ti–H system to the diffusivity D^{v-i} in the V–H binary system. The nomenclature V = major substitutional element (in this case V), U = minor substitutional element (in the case Ti), and i = interstitial, will be used. The symbols ▲ (433 K) and ● (333 K) are calculated from the values of D_o and Q^a given by Pine and Cotts [8] and ○ (333 K) and ⊕ (273 K) are taken from the actual data points given by Tanaka and Kimura [9]. The values of D^{v-i} are taken from the "best" values from the data compilation of Völkl and Alefeld [10]. The variation of Q^a with θ_u is given in Fig. 2. The Q^a-values refer, of course, to the entire temperature span of the data sets for each individual θ_u-value. The solid lines in Figs 1 and 2 correspond to calculations which will be explained in section 4 of the report.

3. DIFFUSIVITY CALCULATION

The experimental results embodied in Figs 1 and 2 will be interpreted in terms of the cell model for

$V–U–i$-ternary solid solutions. In accord with neutron scattering data [3], the H-atoms will be assumed to occupy the tetrahedral sites in the b.c.c. lattice in V and V–Ti-solutions. In the cell model diffusion occurs by the motion of H-atoms from given tetrahedral sites into nearest-neighbor tetrahedral sites. If this process can adequately be represented by the formalism of classical rate theory, it is easy to show that the diffusivity ratio λ is given by [2, 11]:

$$\lambda = \exp\left(\frac{Q^o}{kT}\right) \sum_{n=0}^{n=z} \left(\frac{n_i^n}{N_i}\right)$$
$$\times \left\{ \sum_{m=0}^{m=z} \left(\frac{N_m}{N}\right) \exp\left(-\frac{\langle Q \rangle}{kT}\right)\right\}. \qquad (2)$$

In this equation the indexes n and m label neighboring interstitial sites such that n is the cell in which a given jump is initiated and m is a cell in which the diffusion jump terminates (recipient cell). Each tetrahedral site has $z = 4$ lattice atoms and the indexes n, m give the numbers of U atoms in the shell z neighbors. The quantity Q^o is the value of Q^a for $\theta_u = 0$ (i.e. V–H), n_i^n is the number of i (i.e. H) atoms in cell n, N_i the total number of i-atoms in the volume element of crystal considered and N_m/N is the fraction of recipient cells in the state m ($N = N_v + N_u$, the total number of lattice atoms). N_m is given by [12]:

$$N_m = \frac{Nz!}{(z-m)!m!} (1 - \theta_u)^{(z-m)} \theta_u^m. \qquad (3)$$

The energy $\langle Q \rangle$ is written as

$$\langle Q \rangle = Q^o - \sigma_i^n + Q_{nm}, \qquad (4)$$

where σ_i^n is the energy required to insert an i-atom from a reference state into a cell of index n and Q_{nm} are the elements of the "barrier matrix", which essentially defines the maximum energy of the saddle point configuration with respect to Q^o. These energies are illustrated by the energy diagram in Fig. 3. A major problem in the thermodynamics of solid solutions relates to the dilation of the $V–U$ "parent" lattice as the U-concentration (θ_u) is changed. The
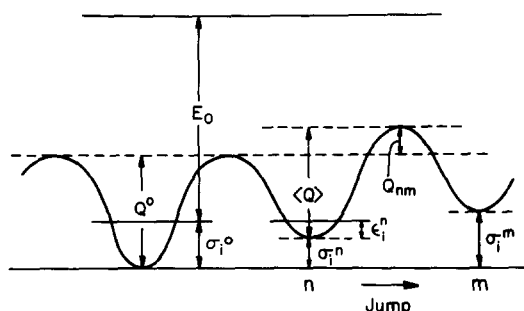

Fig. 3. Schematic energy level diagram for the cell model. The symbols are explained in the text.

quantities σ_i^n and Q_{nm} are clearly functions of θ_u. When the "infinite dilution limit" (i.e. $\theta_i \ll 1$) applies, this "volume" problem may be attacked in several ways. In many previous reports [2] the spectrum σ_i^n has been regarded as independent of θ_u in a so-called quasi-rigid lattice in which the specific volume of the $V-U$-lattice is held constant and the calculated thermodynamic behavior of the quasi-rigid lattice system is compared to the properties of constant-pressure (experimental) systems by using a series of correction terms derived from classical thermodynamics and involving the elastic properties of the $V-U$-matrix [13]. This treatment, although formally correct, suffers from a general lack of input elastic information, especially when complications due to Zener relaxations at grain boundaries occur at high temperatures [14]. An alternative procedure is to write the cell energy spectrum in a form such that the σ_i^n are dependent upon θ_u. In this work the simple linear form

$$\sigma_i^n = n\sigma_i^\circ + f_i^n \sigma_i' + \rho\theta_u \qquad (5)$$

has been selected. The term $\rho\theta_u$, where ρ is a constant, takes lattice dilation into account and $f_i^n = 2n(n-1)/(z-1)$ is the probability of finding a $U-U$ nearest-neighbor pair in a cell of index n and σ_i' is the energy associated with such a pair. The energy σ_i° is the energy to transfer an i-atom from the reference state into a cell for which $n = 0$. Note that this energy does not simply correspond to site occupancy in the $V-i$ binary system, but to any cells for which $n = 0$. Placing eqns (3), (4) and (5) into (2) and rearranging yields gives

$$\lambda = \frac{[Q_z(P,T)]^{-1}}{2} \sum_{n,m}^z P_{nm} \exp\left(-\frac{Q_{nm}}{kT}\right), \qquad (6)$$

where the P_{nm} are $(N_n N_m)/N^2$. The P_{nm} have been given previously [11] in tabular form. The quantity $Q_z(P,T)$ is the cell partition function [2]:

$$Q_z(P,T) = Tr\left\{\delta_{nm}\left(\frac{N_n}{N}\right)\exp\left(-\frac{\sigma_i^n}{kT}\right)\right\}. \qquad (7)$$

Note that this partition function for the constant-pressure ensemble is written $Q_z(P,T)$ in contrast to the designation $Q_z(V,T)$ used in previous reports [2] for the constant-volume representation.

The remaining problem is to select a form for the barrier matrix $\hat{Q}_{nm}$. Several forms of this quantity have been discussed in previous discussions of H-diffusion in Pd-based binary matrices [2, 11]. In order to abbreviate the present discussion, it is noted that data-fitting procedures, to be described in a later section, have given, in the case of V-Ti-H systems, a simple and somewhat surprising result; namely that all $Q_{nm} \approx 0$. This leads to the simple form for λ:

$$\lambda = [Q_z(P,T)]^{-1} \qquad (8)$$

and

$$Q^a \equiv -k\left[\frac{\partial \ln D^{v-u-i}}{\partial 1/T}\right]_P = Q^\circ - \frac{Q_z'(P,T)}{Q_z(P,T)}, \qquad (9)$$

where

$$Q_z'(P,T) = Tr\left\{\delta_{nm}\left(\frac{N_n}{N}\right)\sigma_i^n \exp\left(-\frac{\sigma_i^n}{kT}\right)\right\}. \qquad (10)$$

Equations (9) and (10) will provide the basis for the discussion of the results shown in Figs 1 and 2.

4. DISCUSSION

The uppermost line in Fig. 1 (-·······-) is calculated from eqn (8) using the values of σ_i', σ_i°, Q_{nm} and ρ deduced from a least-squares regression to all the data using intervals of 0.5 kJ/mole. The "best" values of these parameters are $\delta_i^\circ = -6.25$ kJ/mole, $\sigma_i' = 0$, $Q_{nm} = 0$ and $\rho = 6.0$ kJ/mole. The upper line is computed for $T = 433$ K corresponding to the data points ($\blacktriangle$). The central line (———) is constructed for $T = 333$ K corresponding to the data points ($\bigcirc$, $\bullet$), and the lowest line (-×-×-) is at $T = 273$ K, corresponding to the data of Kanaka and Kimura [9] ($\oplus$). It can be seen that the simple diffusivity eqn (9) is in good accord with the experimental variation of λ with both T and U-concentration.

The values of σ_i° (-6.25 kJ/mole) and ρ (6.0 kJ/mole) deduced from the variation of λ with θ_u and T may now be used to calculate Q^a using eqn (9). The results are shown in Fig. 2. The uppermost curve in Fig. 2 (-|-) is calculated at 280 K corresponding to the mean temperature of the data of Tanaka and Kimura ($\bigcirc$). The lower line (-||-) corresponds to 395 K, the mean temperature of the data of Pine and Cotts ($\bullet$). The variation of Q^a with θ_u is in good accord with the experimental data.

The inset diagram in Fig. 2 shows the calculated variation of Q^a at $\theta_u = 0.1$ with temperature. The variation is virtually linear. The symbols show the experimental values taken from the curves of Fig. 2 for $\theta_u = 0.1$. If the model adequately describes H-diffusion in these systems then it is clear why the Arrhenius plots of $\ln D$ vs $1/T$ are linear, within experimental scatter, since if Q^a is a linear function of T then $[\partial \ln D/\partial(1/T)]$ is not dependent upon temperature even though Q^a may vary strongly with temperature.

As a further check on the self-consistency of the parameters σ_i° and ρ, we may now calculate the difference in the partial enthalpies $\bar{H}_i$ of the terminal systems. In the Ti-H binary system $\bar{H}_i$ is simply $E_0 + z\sigma_i^\circ + \rho(\theta_u = 1)$ where E_0 is the ground state energy. For the V-H system $\bar{H}_i = E_0$ and thus the difference is $\delta\bar{H}_i(\text{Ti-V}) = z\sigma_i^\circ + \rho = -19$ kJ/mole. Now Kleppa et al. [15] have measured the relative partial enthalpy $\Delta\bar{H}_i$ of H in V-H at 573 K. Their value is -31.98 kJ/mole. The values of $\Delta\bar{H}_i$ for H in

Ti at two temperatures (971 and 713 K) have also been given by Kleppa et al. [16]. A linear extrapolation of these values gives $\Delta \bar{H}_i = -52.98$ kJ/mole for the Ti–H system at 573 K. Thus, the experimental value of $\delta \bar{H}_i = \delta (\Delta \bar{H}_i) = -21.0$ kJ/mole. This value is (probably fortuitously) close to the value calculated from σ_i^0 and ρ.

A final question may be posed in regard to the physical significance of the parameters σ_i^0 and ρ. It is clear that ρ must be related to the elastic properties of the $V–U$ matrix. This relation may be derived in the following manner. The chemical potential μ_i of the i-species can be written in the form [12]:

$$\mu_i = E_o + kT \ln \frac{\theta_i}{Q_z(PT)}. \tag{11}$$

It is easy to show [17] that this chemical potential can be written in terms of the quasi-rigid lattice partition function $Q_z(V, T)$ and the elastic properties of the $V–U$ matrix in the form:†

$$\mu_i = E_o + kT \ln \frac{\theta_i}{Q_z(V, T)} + \int_0^{\theta_u} \frac{\Delta V B \bar{V} i}{V_s} d\theta_u, \tag{12}$$

where ΔV is the difference in the partial molar volumes, $\Delta V = \bar{V}_u - \bar{V}_v$, $\bar{V}_i$ is the partial molar volume of the H-atoms, B is the bulk modulus of the $V–U$-matrix and V_s is the molar volume of the $V–U$-binary solution. Equating these chemical potentials (the analog of $(\partial G/\partial \mathrm{Ni})_{P,T} = (\partial F/\partial \mathrm{Ni})_{V,T}$) yields

$$\frac{Q_z(P, T)}{Q_z(V, T)} = \exp \left\{ -\frac{1}{kT} \int_0^{\theta_u} \frac{\Delta V B \bar{V}_i}{V_s} d\theta_u \right\}. \tag{13}$$

The ratio $Q_z(P, T)/Q_z(V, T)$ is obtained from the definition (7) by writing $\sigma_i^1 = n\sigma_i^0 + \rho\theta_u$ for the constant-pressure partition function and $\sigma_i^n = n\sigma_i^0$ for the quasi-rigid lattice. This gives

$$\frac{Q_z(P, T)}{Q_z(V, T)} = \exp \left(-\frac{\rho\theta_u}{kT} \right)$$

and, since the integral in eqn (13) for $\theta_u \ll 1$ can be evaluated [17] in the form $\bar{V}_i \Delta V B_0 \theta_u / V_v^0$, where V_v^0 is the molar volume of V, then

$$\rho = \frac{\bar{V}_i \Delta V B_0}{V_v^0}, \tag{14}$$

where B_0 is the value of B for pure V.

The value of ΔV may be taken from the X-ray lattice parameter determinations of Pietrokowsky and Duwez [18] ($\Delta V = 0.64 \times 10^{-6}$ m^2/mole) and $\bar{V}_i$ from the work of Maeland [19] ($\bar{V}_i = 1.65 \times 10^{-6}$ m^3/mole). The bulk modulus of V and V–Ti solutions at 298 K has been measured by Katahara et al. [20] ($B_0 = 1.58 \times 10^{11}$ N/m^2). Inserting these data into eqn (14) yields $\rho = 18.59$ kJ/mole. This estimate of ρ is larger than the value of $\rho = 6.0$ kJ/mole obtained from the analysis of the kinetic data. This is perhaps all that can be expected in view of the simple nature of the linear model of eqn (5) and the uncertainties inherent in the measurements of ΔV and $\bar{V}_i$ (both ΔV and $\bar{V}_i$ are taken from composition regions where $1 \gg \theta_u$, θ_i).

It may be stated that the values of σ_i^0 and ρ are in general in good accord with both the variation of λ and Q_a with T and θ_u, and with the thermodynamic data for the V–H and Ti–H "end systems".

The fact that the "best" value of $\sigma_i' = 0$ is not surprising. Similar analyses of thermodynamic and kinetic data for ternary (noble metal)–H systems have given the same result [2].

The fact that the diffusion data are consistent with $Q_{nm} = 0$ is somewhat surprising in view of the relatively large positive lattice dilation accompanying the insertion of Ti into the V lattice. It suggests that this system should be a prime candidate for embedded atom calculations [21, 22].

A few concluding remarks on the validity of the assumptions underlying the approach taken in this work are appropriate. The central point concerns eqn (2) which describes H-atom diffusion in terms of elementary "jumps" from a spectrum of differing sites. As the short discussion in the introduction outlined, it is difficult to describe these "jumps" in terms of classical rate theory, even though the latter assumption has often been made. Both Pine and Cotts [8] and Tanaka and Kimura [9] discuss their data in terms of conventional trapping models and Steward [23], for example, has given a classical calculation of the isotope effect for H in Nb.

The discussion of Alefeld [5], who used the dynamic formulation of classical rate theory to study diffusion at low temperatures, is especially clear. It leads to a form for the jumping rate Γ which has the appearance of an Arrhenius law, but with a slightly temperature-dependent frequency factor. In the quantum mechanical limit at low temperatures $(h\nu_{A,S} \gg kT)$ jump rate becomes [6]

$$\Gamma = \frac{kT}{h} \exp \left[-\frac{E - \frac{1}{2}h[m\nu_A - l\nu_S]}{kT} \right], \tag{15}$$

where E is the potential energy difference between the saddle point and the minimum configuration and the "hop" is taken as m degenerate localized frequencies ν_A of a H-atom in the minimum configuration and l such modes at the saddle point, ν_s. All the lattice vibrations in both configurations are assumed to be

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† In deriving this equation [17] note that we must write $\Delta V < 0$ since the pressure needed to compress the solid to its original volume is positive. The actual value of ΔV is positive in the case of V–Ti solutions since the lattice dilation is positive, but the change in volume occurring when the dilated lattice is compressed to its volume at $\theta_u = 0$ is $-\Delta V$.

the same. The activation energy E is thus perturbed by the zero-point energies of the localized proton degrees of freedom. Schaumann, Völkl and Alefeld [24, 25] have pointed out that for H in Nb, V and Ta, $h\nu_{A,S} \gg kT$ and the isotope effect in the activation energy is similar to that given by eqn (15).

It is not clear why the modified classical rate theory apparently conforms to much of the observed kinetic data for H in the b.c.c. group V metals at temperatures above 280 K. The literature concerning the diffusion of the light interstitials at low temperatures is large and it is clearly not the intent of this short report to pursue this matter in more depth. Let it suffice to say that the observations on H-diffusion in the V–Ti system are in good agreement with the statistical mechanical cell model in which the elementary jumps are taken to be describable in terms of the reasoning behind eqn (15).

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