Calculation of diffusion activation energy by thermodynamic model

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Abstract. Although self diffusion activation energy of metal is known to be strongly correlated to its melting point and heat of formation, prediction of diffusion activation energy remains a challenge and somehow an art. On the basis of the well developed quasi-chemical model, we demonstrate a general framework to estimate surface/interface diffusion activation energy using the concentration and formation energy of the interface chemical bonds. Furthermore, this framework reproduces all available diffusion activation energy data of Si on metals. We not only provide a practical method in predicting diffusion activation energy but also offer new physical insights about the interplay between chemical kinetics and thermodynamics.

1. Introduction

Diffusion activation energy data are frequently required in microstructure and phase transition research (e.g., in the glass formation process) where complicated chemical and structure parameters are involved [1-3]. However, diffusion activation energy data are scarce and the common techniques of experiment and computer simulation to derive these data are either not practical or time consuming due to wide range of changes of systems in terms of chemistry and microstructures [4, 5]. Therefore correlation methods were widely employed. Beke studied the dependence of diffusion to temperature and found that the diffusion coefficients usually obey the Arrhenius law [6]. Brown and Ashby showed the rate of diffusion at the melting point is roughly a constant for a given crystal structure [7]. In addition, melting points show strong correlation to enthalpy of formation of alloys or compounds [8]. Any guidelines derived from these different approximation methods that leading to the prediction of diffusion activation energy will advance the diffusion research in general, although the nature of chemical bond formation is largely ignored in most of the previous correlation type of models. Recent advance in chemical thermodynamic calculations offers ready descriptions of detailed solution chemistry for systems of complicated chemistry as well as for multi-component and multiphase microstructures [9]. A direct link between the thermodynamics and diffusion activation will not only generate practical prediction method but also improve current theoretical understanding of chemical kinetics in general.

We demonstrated previously [10] that interface chemistry of metal and semiconductor can be qualified by quasi-chemical model (a solution chemistry model) [11, 12]; both the heat of formation of
metal silicides and the eutectic temperatures of system consisted of the metal and semiconductors can be directly presented by the quasi-chemical model. Therefore, rather than a simple data correlation, our approach approximates the chemical bonding process, on the basis of the well developed quasi-chemical model, by calculating concentrations of different type of bonds based on the bond formation energy and solution chemical concentrations. This way, we maintain the rough physics of interface while developing correlation models.

In chemical catalysis research, factors that control chemical reaction paths and the corresponding potential energy surfaces [13, 14] are well studied and a simple linear correlation between the transition-state (TS) energy and the final-state (FS) energy of the respective elementary steps, namely, the Brønsted-Evans-Polanyi (BEP) relationship has been elucidated and applied in the analysis of surface elementary reactions. The BEP equation directly relates the change in activation energy of the reaction (a kinetic parameter) to the corresponding change of the reaction energy (a thermodynamic parameter). Liu and Hu [15] advanced the BEP method by using first principles calculations to systematically study a number of typical catalytic reactions on transition metal surfaces, and postulated that the reaction barrier can be decomposed using bond energies of all the associated reactant – surfaces and reactant – reactant pairs (or bonds). Their work directly linked the reaction barrier to the energetic of all sorts of involved chemical bonds and found that the dissociation reaction barrier is determined by the chemisorption energy at the final reaction state, in consistent with the BEP relationship.

These studies suggest that the bond energies of reactants and products may play a critical role in determining the reaction barrier and diffusion activation energy. In statistical thermodynamics, all equilibrium properties are derived by using partition functions of all energetic micro-configurations, therefore, a transition state (on an energy pathway for diffusion) has already been counted and discriminated by the partition functions. We aim to pick up the micro-configuration(s) that correspond to the transition state by reverse engineering the thermodynamic solution. Therefore, the quasi-chemical (QC) model which describes the energy and concentration of bonds of all stable and metastable micro-configurations is applied in this work. We first demonstrate such a reverse engineering technique (on QC) using the heat of formation and eutectic temperature data, and then diffusion activation energy. The resultant formulae can be used for prediction of activation energy merely from electro-negativities of the constituent elements.

2. Quasi-chemical calculation

In this section, the relationship of reaction bond energy and mole fraction of the reactant pairs of a binary system is described by the quasi-chemical model [11, 12]. The numerical results of the relationship associated with various initial component compositions are presented.

An A-B binary system contains three types of nearest-neighbor pairs, namely, A-A, B-B, and A-B. The relative amounts of the three types of pairs are determined by the energy change associated with the formation of two A-B pairs from one A-A and one B-B pair, as described in reaction (1).

\[
[A-A] + [B-B] = 2[A-B] \quad (1)
\]

Let \(X_{AA}, X_{BB}\) and \(X_{AB}\) be the mole fractions for A-A, B-B and A-B pairs, and \(X_A\) and \(X_B\) are the initial mole fractions of components A and B, respectively. When the two components are mixed, A-B pairs are formed at the expense of A-A and B-B pairs. It follows from the mass balance that:

\[
2X_A = 2X_{AA} + X_{AB} \quad (2)
\]
\[
2X_B = 2X_{BB} + X_{AB} \quad (3)
\]

The molar enthalpy change of reaction (1) is denoted by \(\omega\), the net pair bond energy. The enthalpy of mixing, \(\Delta H\), is then given as following:

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\[ \Delta H = \left( \frac{X_{AB}}{2} \right) \omega \] (4)

A “quasi-chemical equilibrium constant” for reaction (1) is obtained as

\[ \frac{X_{AB}^2}{X_A X_B} = 4e^{\frac{-\omega}{RT}} \] (5)

Substituting Eqs. (2-3) into Eq. (5) yields Eq. (6) where it indicates that the mole fraction A-B bond, \( X_{AB} \), is the function of the net pair bond energy \( \omega \), the initial component mole fraction \( X_A \) and the temperature \( T \). \( R \) denotes the gas constant.

\[ \frac{X_{AB}^2}{(2X_A - X_{AB})(2 - 2X_A - X_{AB})} = e^{\frac{-\omega}{RT}} \] (6)

The analytical solution of \( X_{AB} \) cannot be obtained from Eq. (6). Thus we perform the numerical study by plotting \(-\omega\) versus logarithm \( X_{AB} \) given \( T = 300 \) K and \( \omega = -25 \sim 0 \) kJ mole\(^{-1}\). The results are shown in Figure 1 with the initial component mole fraction \( X_A \) = 0.5, 0.6, 0.7, 0.8 and 0.9, respectively. It is noted that due to the symmetry in the composition of component A and B, the results of \( X_A = 0.1 \) and \( X_A = 0.9 \) are equal. Similarly, the result of \( X_A = 0.2 \) is same as that of \( X_A = 0.8 \), and so forth.

![Figure 1. Dependence of net pair bond energy \( \omega \) and the mole fraction of A-B bond \( X_{AB} \).](image)

3. Results

On the basis of quasi-chemical model, we examine four published data sets of formation heats, eutectic temperatures, and diffusion activation energies. Since the \( \omega \) values for these systems are not available, we use the elemental electro-negativity (\( \chi \)) to replace \( \omega \) [10]. In particular, the squared difference of electro-negativities of two constituent elements \((\Delta \chi)^2\) is used. It is noted that \((\Delta \chi)^2\) is proportional to \(-\omega\), as derived from the well-known semi-empirical Miedema’s model [16]. In this work, the Martynov-Batsanov electro-negativities (eV\(^{1/2}\)) [17] are used. In the study of the following four systems, \((\Delta \chi)^2\) is chosen as the abscissa, in consistent with the result of quasi-chemical model (Figure 1).

We first demonstrate the reverse engineering approach using the formation heats of silicides formed on the interfaces of transition metals and \( n \)-type silicon [10]. In order to obtain comparable
result, the ordinate is formulated as the logarithmic $\ln(\Delta H/\Delta \chi^2)$ where $\Delta H_i$ is the formation heat. Since the temperature is the same for this set of data which leads to a same constant for each data point, the temperature is not taken into account. The resulting trend of $(\Delta \chi)^2$ versus $(\Delta H/\Delta \chi^2)$ is shown in Figure 2. It is also found that the dependences of $X_{AB}$ and $\phi$ generated from QC model with a range of initial composition $X_A$ as shown Figure 1 can be re-scaled to well match the trend of the experimental data. Beyond this composition range, it is impossible to reproduce the trend. As an illustration, the re-scaled dependence with $X_A = 0.6$ (bold line) is plotted in Figure 2. In comparison with the results of quasi-chemical model (Figure 1), $\ln(\Delta H/\Delta \chi^2)$ is equivalent to $-\ln(X_{AB})$, which implies a strong correlation between formation heat and the A-B bond properties (concentration and energy) at micro-configurations about $X_A=0.6$.

The second system deals with the eutectic temperature of binary systems of transition metal silicides [10], since it is widely accepted for a strong correlation between diffusion and temperature [7]. In the same fashion of Figure 2, the ordinate is formulated as the logarithmic $\frac{T_{eu}}{\Delta \chi^2}$ where $T_{eu}$ is the eutectic temperature. The result is shown in Figure 3. Similarly as in Figure 2, the QC dependence with $X_A = 0.6$ (bold line) is re-scaled to fit this set of experimental data. Furthermore, since $\ln(T_{eu}/\Delta \chi^2)$ is equivalent to $-\ln(X_{AB})$, it implies a strong correlation between the eutectic temperature and the A-B bond properties at micro-configurations about $X_A=0.6$.

Inspired by the above success, we further study the diffusion of Si into metals by the reverse engineering technique. The diffusion activation energies and the corresponding average temperatures are extracted from [18] and summarized in Table 1. The ordinate is chosen as $\ln(-\frac{Q}{RT(\Delta \chi)^2})$ where $Q$ is the activation energy, $R$ the gas constant, and $T$ the average temperature. The resulting trend of $(\Delta \chi)^2$ versus $\ln(-\frac{Q}{RT(\Delta \chi)^2})$ is shown in Figure 4. Similarly, the QC dependence with $X_A = 0.6$ (bold line) is re-scaled to match this set of experimental data. Compared to Figure 1, $\ln(-\frac{Q}{RT(\Delta \chi)^2})$ is equivalent to $-\ln(X_{AB})$, implying strong correlation between the activation energy and the A-B bonding properties.

Finally, we study the reaction barrier (activation energy, $\Delta E$) in the diffusion of O, S, N on (111) surfaces of various metals (Ni, Re, Ag, Pd, Pt, Ru, Cu) [13]. Using the data listed in Table 2, we calculate $\ln(\Delta E/\Delta \chi^2)$ and plot it against $(\Delta \chi)^2$ in Figure 5. The term $(RT)$ is omitted as the temperatures

![Figure 2](image-url)  
**Figure 2.** Dependence of $\ln(\Delta H/\Delta \chi^2)$ and $(\Delta \chi)^2$ for the formation heats of transition–metal and silicon.

![Figure 3](image-url)  
**Figure 3.** Dependence of $\ln(T_{eu}/\Delta \chi^2)$ and $(\Delta \chi)^2$ for the eutectic temperatures of transition–metal silicides.
are the same for this set of data. Again, the QC dependence with \( X_A = 0.6 \) (bold line) is re-scaled to reproduce the experiment trend. Similarly, a strong correlation between the activation energy and the microscopic A-B bonding is demonstrated.

**Table 1.** Diffusion activation energies of Si into metals and the electro-negativities of metals.

| Metal | Average Temp. °C | Activation energy cal mole\(^{-1}\) | Metal Electro-negativity eV\(^{1/2}\) |
|-------|------------------|-------------------------------------|--------------------------------------|
| Ti    | 1050             | 39700                               | 1.86                                 |
| Zr    | 1100             | 55750                               | 1.7                                  |
| V     | 1100             | 61200                               | 2.22                                 |
| Nb    | 1100             | 48000                               | 2.03                                 |
| Ta    | 1000             | 34600                               | 1.94                                 |
| Cr    | 1000             | 22760                               | 2                                    |
| Mo    | 1350             | 78000                               | 1.94                                 |
| W     | 1000             | 63000                               | 1.79                                 |
| Fe    | 1000             | 22030                               | 1.67                                 |

**Table 2.** Energies of initial and transition states in the diffusion of O, S, N on (111) surfaces of various metals (Data read from Ref.[13]), and electro-negativities of each system.

| System  | Energy, eV | Electro-negativity, eV\(^{1/2}\) |
|---------|------------|-----------------------------------|
| C/Ru    | -6.69      | 2.37                              |
| C/Pt    | -6.27      | 2.37                              |
| S/Re    | -5.69      | 2.37                              |
| S/Ru    | -5.64      | 2.65                              |
| N/Ru+   | -5.55      | 2.65                              |
| O/Ru+   | -5.40      | 3.32                              |
| O/Ru    | -5.07      | 3.32                              |
| N/Ru    | -5.06      | 2.85                              |
| S/Ni    | -5.02      | 2.65                              |
| O/Ru-   | -4.79      | 3.32                              |
| S/Pt    | -4.74      | 2.65                              |
| N/Ru-   | -4.59      | 2.85                              |
| C/Cu    | -4.25      | 2.37                              |
| S/Cu    | -4.14      | 2.65                              |
| O/Pt+   | -4.08      | 3.32                              |
| C/Cu-   | -4.02      | 2.37                              |
| O/Pt    | -3.63      | 3.32                              |
| O/Pd    | -3.54      | 3.32                              |
| O/Ag    | -3.06      | 3.32                              |
| H/Pt    | -2.58      | 2.1                               |
4. Conclusions

We demonstrated, on the basis of quasi-chemical model, a general framework to formulate diffusion activation energy from solution thermodynamics. Although in this study our approach reproduced diffusion activation energy for relatively simple systems, in principle similar calculations may be carried out for complex multi-component and multiphase systems because the needed bond fraction and bond energy data can be derived from quasi-chemical model. The method offers opportunities to further understand the interplay between chemical kinetics and thermodynamics.

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