Diffusion Equation for Solute Atoms under a Temperature Gradient

Ryuichi Habu

Technical Research Center, SKY Aluminum CO., LTD., Fukaya 366-8511, Japan

By combining Wirtz's equation and the phenomenological diffusion equation for carbon under a temperature gradient, $J_C = -(D_C N_C / RT) [\nabla(\mu_C)_T + {}^*Q_C \nabla T / T]$, Shewmon proposed the relation, ${}^*Q_C = -\varepsilon_C^m$, where, *Q_C and ε_C^m are the heat of transfer and the migration enthalpy of carbon in α -iron. In this paper, it is pointed out that (1) the vector space in which Wirtz's and the phenomenological diffusion equation are defined is not the same, (2) hence, it is not allowed theoretically to combine directly these two equations to obtain the relation, ${}^*Q_C = -\varepsilon_C^m$. Showing a correct equation to be combined with Wirtz's equation, the correct diffusion equation for solute atoms under a temperature gradient is derived.

(Received April 30, In Final Form September 13, 1999)

Keywords: thermal diffusion, interference, heat of transfer, reduced heat of transfer, temperature gradient, phenomenological equation

I. Introduction

Shewmon annealed iron-carbon alloys for a long time in a constant temperature gradient until carbon diffusion stopped⁽¹⁾. After the annealing, Shewmon measured the carbon distributions along the temperature gradient, and as the result, it was shown that carbon atoms segregate toward the higher temperature side of the diffusion specimens. To interpret these results, Shewmon applied the phenomenological diffusion equation⁽¹⁾⁽²⁾.

$$J_C = -\frac{D_C N_C}{RT} \left[\nabla(\mu_C)_T + \frac{{}^*Q_C}{T} \nabla T \right]. \quad (1)$$

Here, suffix C stands for diffusor (carbon). J_C denotes the diffusion flux, D_C the diffusion coefficient, μ_C the chemical potential, and N_C concentration of carbon. The quantity, *Q_C , is called the reduced heat of transfer or simply the heat of transfer of carbon. R and T express the gas constant and a local temperature in an irreversible system, respectively.

Shewmon firstly suggested the relation ${}^*Q_C = -\varepsilon_C^m$, where ε_C^m is the migration energy of carbon in α -iron⁽¹⁾⁽²⁾. Shewmon limited the application of his suggested relation to interstitial solute atoms in BCC crystals. However, this relation has been widely accepted and the range of its application has been expanded into solute atoms other than interstitial solute atoms, and into crystals other than BCC.

Voronkov applied the relation, ${}^*Q_C = -\varepsilon_C^m$, to diffusion of point defects (self-interstitial atoms and vacancies) during melt-growth of silicon single crystals. As a considerably large temperature gradient exists in the crystal growth end, the temperature gradient is considered to affect diffusion of point defects during crystal growth. Referring to Shewmon's paper and using eq. (1), Voronkov proposed a diffusion equation which describes the distribution of crystal defects which have grown by

the agglomeration of point defects during melt-growth of silicon single crystals.⁽³⁾ However, he ignored the second term in the right hand side of eq. (1), due to his considering that the values of $\varepsilon_{I,V}^m$ are sufficiently small, so that the second term is negligible for point defects in silicon crystals.

Borg and Diens applied the relation, ${}^*Q_I = -\varepsilon_I^m$, to a self-interstitial atom⁽⁴⁾. However, they gave ${}^*Q_V = \varepsilon_V^m$ to a vacancy due to their considering that movement of a vacancy causes a mass flow reverse to that of the movement of a self-interstitial atom⁽⁴⁾.

Wijaranakula adopted the view of Borg and Diens to diffusion of point defects and he calculated the distribution of point defects which were frozen into silicon crystals during melt growth⁽⁵⁾.

Recently, Ebe discussed saturation of point defects in growing silicon crystals starting from eq. (1), however, he adopted the relation $|{}^*Q_{I,V}| \leq \varepsilon_{I,V}^m$ ⁽⁶⁾.

Habu gave an alternative interpretation to Shewmon's experimental results, and proposed ${}^*Q_C \approx -h_C$, where h_C denotes the partial molar enthalpy of carbon⁽⁷⁾⁽⁸⁾.

Brown *et al.* used diffusion equations with ${}^*Q_{I,V} = -h_{I,V}$ to describe diffusion of point defects in silicon crystals during melt-growth⁽⁹⁾.

As described above, there are disagreements among the equations hitherto proposed to describe diffusion of point defects or solute atoms under a temperature gradient. These equations are roughly divided into two groups. The first group includes the equations of Voronkov, Wijaranakula and Ebe. Their theories were developed in line with Shewmon's view. The other group includes the equations of Habu and Brown *et al.*, proposing ${}^*Q_{I,V} = -h_{I,V}$.

The object of this paper is to clarify these disagreements, and to give a correct diffusion equation under a temperature gradient.

II. Outline of the Phenomenological Diffusion Equations

1. Basic equations

According to de Groot, the phenomenological diffusion equations for a continuous, n -component system with a temperature gradient are expressed as⁽¹⁰⁾:

$$J_i = \sum_{k=1}^n \alpha_{ik} X_k + \alpha_{iu} X_u, \quad J_q = \sum_{k=1}^n \alpha_{uk} X_k + \alpha_{uu} X_u, \quad (2a)$$

$$X_k = F_k - T \nabla (\mu_k / T), \quad X_u = -\nabla (T) / T, \quad (2b)$$

$$\alpha_{iu} = \sum_{k=1}^n \alpha_{ik} Q_k^*, \quad (2c)$$

where, J_i is the diffusion flow flux of component i , and J_q is a heat flow flux. T is a temperature, μ_k the chemical potential of component k , and F_k an external force acting on a unit mass of component k . The quantities α_{ik} ($i, k = 1, 2, \dots, n$) are phenomenological coefficients, α_{ii} corresponding to, for instance, the heat conductivity, or the electrical conductivity, while the coefficients α_{ik} ($i \neq k$) describe the coupling phenomena between irreversible processes i and k . The quantity X_k is called the generalized force, and corresponds to the driving force that enhances diffusion of component k . Similarly, X_u is force for heat conduction.

The quantity Q_k^* is the heat of transfer for component k . It has been verified that Q_k^* corresponds to the heat transported by a unit mass of diffusion flow of component k under a uniform temperature⁽¹⁰⁾. This means that if diffusion flow of matter occurs in a diffusion system with a uniform temperature, the diffusion flow incurs a temperature difference in the diffusion system. Such effect is known as the Dufour effect and is actually observed for gas diffusion. This effect is the cross (coupling) effect between a diffusion flow of matter and a heat flow. In general, the cross term must be small compared to the main term of the diffusion. Hence, Q_k^* can not take a large value, in principle⁽¹⁰⁾.

We will now consider solute diffusion in a 2-component system (1; solvent, 2; solute) with a temperature gradient.

Ignoring the effects of the external forces on diffusion flows, and the coupling between diffusion flows of the 2 components, a diffusion equation for the solute can be derived from eqs. (2a)–(2c):

$$J_2 = \alpha_{22} X_2 + \alpha_{2u} X_u \\ = -\alpha_{22} \left[T \nabla (\mu_2 / T) + Q_2^* \frac{\nabla T}{T} \right]$$

Since μ_2 / T is a function of N_2 (concentration of solute 2) and T , the differentiation is carried out by N_2 and T , keeping T and N_2 constant, respectively⁽¹¹⁾.

$$J_2 = -\alpha_{22} \left[\nabla (\mu_2)_T + T \frac{\partial (\mu_2 / T)}{\partial (1/T)_{N_2}} \frac{\partial (1/T)}{\partial T} \nabla T + \frac{Q_2^*}{T} \nabla T \right] \\ = -\alpha_{22} \left[\nabla (\mu_2)_T + \frac{(Q_2^* - h_2)}{T} \nabla T \right]. \quad (3)$$

Here, h_2 is the partial molar enthalpy of the solute. The first term in the square bracket of eq. (3) gives the driving force for usual diffusion. The term, $-h_2 \nabla T / T$ is the potential gradient which gives rise to the drift motion of the solute along the temperature gradient. The remaining term, $Q_2^* \nabla T / T$, gives rise to the thermal diffusion of the solute.

When $\nabla T = 0$, eq. (3) must agree with Fick's first law.

$$J_2 = -\alpha_{22} \nabla (\mu_2)_T = -D_2 \nabla N_2$$

Hereafter $\mu_2 = \mu_2^0(T) + RT \ln N_2$ is assumed for simplicity. Then,

$$-\alpha_{22} \nabla (\mu_2^0(T) + RT \ln N_2)_T = -\alpha_{22} \frac{RT}{N_2} \nabla N_2,$$

$$\therefore \alpha_{22} = \frac{D_2 N_2}{RT}. \quad (4)$$

Here, D_2 is the diffusion coefficient of the solute. Substituting eq. (4) into eq. (3), the diffusion equation for the solute is expressed as:

$$J_2 = -\frac{D_2 N_2}{RT} \left[\nabla (\mu_2)_T + \frac{(Q_2^* - h_2)}{T} \nabla T \right] \quad (5)$$

2. The linear transformation for the phenomenological diffusion equations

The phenomenological equations can be transformed into another expression by a linear transformation. Prigogine introduced a linear transformation⁽¹²⁾:

$$J'_k = J_k, \quad J'_q = J_q - \sum_{k=1}^n h_k J_k. \quad (6)$$

J'_q is called the reduced heat flow flux. It is important that J'_q contains not only a heat flow but also diffusion flows of matter. By this transformation, eqs. (2a)–(2c) are transformed into⁽¹²⁾⁽¹³⁾:

$$J'_i = \sum_{k=1}^n \beta_{ik} X'_k + \beta_{iu} X'_u, \quad J'_q = \sum_{k=1}^n \beta_{uk} X'_k + \beta_{uu} X'_u, \quad (7a)$$

$$X'_k = F_k - \nabla (\mu_k)_T, \quad X'_u = -\nabla (T) / T, \quad (7b)$$

$$\beta_{iu} = \sum_{k=1}^n \beta_{ik}^* Q_k. \quad (7c)$$

Here, *Q_k is called the reduced heat of transfer for component k , and relates to the coupling between diffusion flow of component k and the reduced heat flow.

The diffusion equation for a 2-component system which is derived from eqs. (7a)–(7c), and corresponds to eq. (5) can be obtained as the following.

$$J'_2 = -\beta_{22} \left[\nabla (\mu_2)_T + \frac{^*Q_2}{T} \nabla T \right], \\ = -\frac{D_2 N_2}{RT} \left[\nabla (\mu_2)_T + \frac{^*Q_2}{T} \nabla T \right].$$

By comparing this with eq. (1), it is apparent that eq. (1) is defined on the basis of the reduced heat flow flux. Therefore, *Q_c in eq. (1) must be understood as the reduced heat of transfer for carbon in α -iron.

3. Correlation between *Q_k and Q_k^*

The quantity *Q_k must be correlated with Q_k^* by the linear transformation, eq. (6). This correlation has already been established as the following⁽⁷⁾⁽¹²⁾⁽¹³⁾.

$$^*Q_k = Q_k^* - h_k. \quad (8)$$

This relation was first verified by Prigogine, and verified again by the present author and reported in the previous paper⁽⁸⁾.

Now, attention must be paid to the fact that *Q_k can have a large value, different from Q_k^* . The quantity, *Q_k , corresponds to the reduced heat transported by a unit mass of component k under a uniform temperature. However, since $J'_k (= J_k)$ accompanies the heat transportation, $-h_k J_k$ due to eq. (6), *Q_k seems to have a value as large as $-h_k$. This is the reason why *Q_k can have large value, and is the background of eq. (8). However, the heat transported here is not actual heat but so-called reduced heat.

III. Disagreements between Shewmon's and Habu's theories

1. Wirtz's equation

Shewmon developed his theory by combining eq. (1) with Wirtz's equation, which deals with dependence of atomic jumps upon a temperature gradient⁽¹⁾⁽¹⁴⁾.

According to Wirtz, the probability of a successful atomic jump from an initial site at temperature T to a final site at temperature $T + \Delta T$ is proportional to⁽¹⁴⁾:

$$\exp\left(-\frac{H_0}{RT}\right) \exp\left(-\frac{H_i}{R(T+\Delta T/2)}\right) \exp\left(-\frac{H_f}{R(T+\Delta T)}\right). \quad (9)$$

Here, H_0 , H_i and H_f are the quantities of energy which must be absorbed at or on the planes of the original, intermediate and final sites, respectively.

Similarly to eq. (9), the probability of the reverse jump is proportional to:

$$\exp\left(-\frac{H_f}{RT}\right) \exp\left(-\frac{H_i}{R(T+\Delta T/2)}\right) \exp\left(-\frac{H_0}{R(T+\Delta T)}\right). \quad (10)$$

The condition under which the diffusion of the solute atoms stops in a specimen placed in a temperature gradient is given as the condition that the frequency of atomic jumps of the solute atoms from the higher to the lower temperature sites is equal to that of the reverse jumps. Then, the condition is given as:

$$\frac{N_{T+\Delta T}}{N_T} = \exp\left(\frac{-H_0+H_f}{RT}\right) \exp\left(\frac{-H_f+H_0}{R(T+\Delta T)}\right). \quad (11)$$

Here, N_T and $N_{T+\Delta T}$ are atomic densities of the solute atoms on the higher and lower temperature site, respectively. From eq. (11), Wirtz derived the following equation⁽¹⁴⁾:

$$\frac{1}{N(z)} \frac{dN(z)}{dz} = -\frac{(H_0-H_f)}{RT^2} \frac{dT(z)}{dz}. \quad (12)$$

Here, z is a coordinate taken along the temperature gradient.

Attention must be paid to the fact that even though the effect of a temperature gradient on atomic jumps of solute atoms is taken into account to derive eqs. (9)–(12), however, the effect of a heat flow upon atomic jumps is not taken into consideration. This is the important point to bear in mind during the later discussion.

2. Shewmon's theory

To interpret his experimental results, Shewmon adopted eq. (1). Substituting $\mu_c = \mu_c^0(T) + RT \ln N_c$ into eq. (1), the carbon distribution under the condition $J_c = 0$ is expressed as⁽¹⁾⁽²⁾:

$$\frac{1}{N_c} \frac{dN_c}{dz} = -\frac{^*Q_c}{RT^2} \frac{dT}{dz}. \quad (13)$$

By integrating eq. (13), Shewmon obtained the value of *Q_c from the carbon distribution. The experimental value of *Q_c was obtained as $^*Q_c = -100 \pm 8 \text{ kJ/mol}^{(1)}$.

Equations (12) and (13) give the same distribution of solute (carbon) atoms in a temperature gradient, under the condition $J_c = 0$. Therefore, Shewmon derived the following relation by combining eqs. (12) and (13)⁽¹⁾,

$$(H_0-H_f) = ^*Q_c. \quad (14)$$

Shewmon interpreted eq. (14) as meaning that *Q_c relates to the energetics of atomic jumps. From the fact that the experimental value of *Q_c agreed well with the theoretical value of the energy necessary to insert an interstitial carbon atom into a interstitial site of BCC α -iron, and the fact that the theoretical value was close to the value of the migration energy of interstitial carbon atoms in α -iron, $\varepsilon_c^m = 108 \text{ kJ/mol}$, Shewmon suggested that⁽¹⁾:

$$^*Q_c = -\varepsilon_c^m. \quad (15)$$

Finally, the diffusion equation for solute atoms under a temperature gradient can be given as:

$$J_2 = -D_2 \nabla N_2 + \frac{D_2 N_2 \varepsilon_2^m}{RT^2} \nabla T. \quad (16)$$

Shewmon considered the application of eq. (15) was limited to diffusion of interstitial solute atoms in BCC crystals⁽¹⁾. However, eq. (15) has been widely accepted, and its range of application was extended to include diffusion of solute atoms or point defects in crystals other than BCC, and is now the leading theory in this field⁽²⁾.

3. Habu's theory

Habu proposed an alternative interpretation of the results of Shewmon's experiment. Habu started his analysis from eq. (5) instead of eq. (1)⁽⁷⁾⁽⁸⁾.

By substituting $\mu_c = \mu_c^0(T) + RT \ln N_c$ into eq. (5), the diffusion equation for carbon atoms in a temperature gradient is obtained.

$$J_C = -D_C \nabla N_C - \frac{D_C N_C (Q_C^* - h_C)}{RT^2} \nabla T. \quad (17)$$

Assuming $J_C = 0$ for eq. (17), the equation that corresponds to eq. (13) is obtained:

$$\frac{1}{N_C} \frac{dN_C}{dz} = -\frac{Q_C^* - h_C}{RT^2} \frac{dT}{dz}. \quad (18)$$

Since Q_C^* can not have a large value, Habu assumed that Q_C^* is close to the minus value of h_C , which assumption was confirmed and reported in the previous paper⁽⁸⁾.

The value of $-h_C$ in α -iron calculated utilizing thermodynamic database SGTE with THERMO-CALC was $-108 \text{ kJ/mol}^{(8)}$. The experimental value obtained by Shewmon was $-100 \pm 8 \text{ kJ/mol}^{(1)}$. These two values agree with each other in the limit of experimental error. This agreement results in:

$$Q_C^* \approx 0. \quad (19)$$

This is consistent with the theoretical requirement for the value of Q_C^* .

IV. Discussion

1. Diffusion equation for solute atoms under a temperature gradient

Equations (1) and (13) are correct equations, however, eq. (14) is not correct. Equation (14) is obtained by combining Wirtz's equation, eqs. (12) and (13). However, this combination is not allowed from a theoretical viewpoint.

Table 1 summarizes differences among eqs. (12), (13) and (18). Above all, the differences listed in the first row of the table are especially important. Equations (12) and (13) are defined in different vector spaces, respectively. Thus, it is not allowed to combine these two equations to obtain eq. (14).

Even though Wirtz did not specify the heat flow flux when he formulated eq. (12), it is natural to understand that he intuitively assumed an ordinary heat flow flux. On the other hand, it is clear that eqs. (1) and (13) are defined using the reduced heat flow flux.

The equation to be combined with eq. (12) is eq. (18) but not eq. (13). However, the effect of a heat flow upon diffusion of solute atoms is not taken into consideration

in the case of eq. (12). Therefore, $Q_C^* = 0$ is necessary to compare for eq. (18) with eq. (12). By comparing eq. (12) with eq. (18) assuming $Q_C^* = 0$, the relation thus obtained is:

$$(H_0 - H_f) = -h_C. \quad (20)$$

The assumption for eq. (18), $Q_C^* = 0$, is consistent with eq. (19), $Q_C^* \approx 0$. This relation, $Q_C^* \approx 0$, is determined from the comparison between Shewmon's experimental value and the thermodynamic calculation⁽⁸⁾. The database used for the calculation is accumulated experimental work on the iron-carbon phase diagram. Thus, eqs. (17)–(19) are quite compatible with the experimental facts. Therefore, the correct diffusion equation for carbon atoms under a temperature gradient is:

$$J_C = -D_C \nabla N_C + \frac{D_C N_C h_C}{RT^2} \nabla T$$

Since $Q_C^* = 0$ is assumed for the above equation, this equation is an approximate one. The correct and accurate diffusion equation for carbon atoms in a temperature gradient is eq. (17).

It is important that there is no assumption which restricts the application of eq. (17) to carbon in α -iron. Equation (17) is a general equation applicable to all kinds of diffusors under a temperature gradient.

2. Meaning of Wirtz's equation

To clarify meaning of Wirtz's eq. (12), imagine solutes are self-interstitial atoms. From eq. (20) and since the partial molar enthalpy of self-interstitial atoms is equal to formation enthalpy of these atoms, *i.e.*, $h_I = \varepsilon_I^f$, then, Wirtz's eq. (12) can be written as:

$$\frac{1}{N_I} \frac{dN_I}{dz} = \frac{\varepsilon_I^f}{RT^2} \frac{dT}{dz}. \quad (21)$$

By integrating:

$$\frac{dN_I}{N_I} = d(-\varepsilon_I^f/RT) \quad \therefore N_I(T) = N_0 \exp(-\varepsilon_I^f/RT).$$

This means that Wirtz's eq. (12) gives a distribution of self-interstitial atoms that agrees with the Arrhenius plot. If the effect of a heat flow upon diffusion is ignored, a distribution of self-interstitial atoms must converge to their Arrhenius plot. This is consistent with our

Table 1 Differences among Wirtz's equation, Shewmon's and Habu's theories.

	Wirtz's equation eq. (12)	Shewmon's theory eq. (13)	Habu's theory eq. (18)
Heat flow flux used to define the equations	Ordinary heat flow flux	Reduced heat flow flux	Ordinary heat flow flux
Effect of a heat flow upon atomic jumps	Not taken into consideration	Taken into consideration	Taken into consideration
$\frac{1}{N_C} \frac{dN_C}{dz} =$	$-\frac{(H_0 - H_f)}{RT^2} \frac{dT}{dz}$	$-\frac{Q_C^*}{RT^2} \frac{dT}{dz}$	$-\frac{(Q_C^* - h_C)}{RT^2} \frac{dT}{dz}$

knowledge.

If eq. (15), $(H_0 - H_f) = -\varepsilon_I^m$, is permitted instead of eq. (20), ε_I^f in eq. (21) is replaced by ε_I^m . Thus, the distribution of self-interstitial atoms deviates from the Arrhenius plot. Furthermore, the distribution can not approach to the Arrhenius plot even when a temperature gradient becomes very small. This is apparently improper, hence, it can be said that eqs. (14) and (15) are not correct.

3. Final distribution of carbon under a temperature gradient

Since $Q_C^* \approx 0$, eq. (18) can be approximated as:

$$\frac{1}{N_C} \frac{dN_C}{dz} = \frac{h_C}{RT^2} \frac{dT}{dz}.$$

$$\frac{1}{N_C} \frac{dN_C}{dT} = \frac{h_C}{RT^2} \left(\because \frac{dN_C}{dz} = \frac{dN_C}{dT} \frac{dT}{dz} \right).$$

The later equation means that h_C can be interpreted as being the heat of solution of carbon in α -iron⁽¹⁵⁾⁽¹⁶⁾. Hence, carbon must be distributed in proportion to its solubility limit curve in the final stage of the diffusion ($J_C = 0$) under a temperature gradient. This was confirmed and reported in the previous paper⁽⁸⁾.

The value of the heat of solution of carbon in α -iron has been experimentally measured, and reported to be 100 kJ/mol and 108 kJ/mol⁽¹⁷⁾⁽¹⁸⁾. This value is very close to the experimental value of Q_C^* for α -iron. Therefore, the carbon distribution Shewmon observed can be understood as being the distribution of carbon along its solubility limit curve⁽⁸⁾.

If $Q_C^* = -\varepsilon_C^m$ is assumed, the final distribution of carbon has no relation to its equilibrium distribution. Since ε_C^m (108 kJ/mol) is accidentally close to h_C (108 kJ/mol), the distribution does not deviate from its equilibrium one. However, from a theoretical viewpoint, this difference can not be overlooked.

4. Contradiction caused by the relation $Q_V^* = +\varepsilon_V^m$

If $Q_V^* = +\varepsilon_V^m$ is assumed for vacancies⁽⁴⁾, diffusion of vacancies must occur in a direction reverse to that of self-interstitial atoms. This means that if diffusion of self-interstitial atoms and vacancies occur simultaneously in a specimen placed in a temperature gradient, the specimen must move as a whole toward the high temperature side of the temperature gradient.

If $Q_V^* = +\varepsilon_V^m$ is applied to vacancies in a silicon crystal, since a considerably large temperature gradient exists in a crystal growth end during melt-growth, the vacancies must diffuse toward the low temperature side of the crystal. Thus, the flow of vacancies occurs in a direction that increases the degree of thermal excess of vacancies inside the crystal. This conflicts with the principles of thermodynamics⁽⁸⁾.

5. Concluding remarks

As shown above, many contradictions result from $Q^* = -\varepsilon^m$. Such confusion firstly comes from the mis-

take taking the reduced heat of transfer, Q_2^* , for the heat of transfer, Q_2^* . The origin of this mistake is a lack of understanding about the linear transformation of the phenomenological diffusion equations.

Equations (7a)–(7c) are derived from eqs. (2a)–(2c) by the linear transformation given in eq. (6). And Q_k^* can be correlated with Q_k^* as shown in eq. (8). If the correlation $Q_k^* = Q_k^* - h_k$ is taken into the consideration, it is clear that eq. (1) and eq. (5) are equivalent each other.

Then, when we use the phenomenological equations, we have to be very careful to the vector space on which equations are formulated. Often different authors study the same process using another equivalent phenomenological equations so that the identity of their results is not always clear⁽¹²⁾. The confusion described above is due to the same situation.

V. Summary

The phenomenological diffusion equation for solute atoms under a temperature gradient can be given as:

$$J_2 = -\frac{D_2 N_2}{RT} \left[\nabla(\mu_2)_T + \frac{Q_2^*}{T} \nabla T \right].$$

Shewmon proposed the relation $Q_C^* = -\varepsilon_C^m$ (ε_C^m migration enthalpy of the solute). Habu claimed another relation $Q_C^* \approx -h_2$ (h_2 partial molar enthalpy of the solute). The disagreement between the above two relations is surveyed and followings are pointed out.

(1) The phenomenological diffusion equation is defined on the basis of the reduced heat flow flux.

(2) Wirtz's equation that Shewmon used to obtain his relation is thought to have been defined using a usual heat flow flux.

(3) The combination of Wirtz's equation and the phenomenological diffusion equations can not be allowed since the heat flow fluxes on which these equations are defined are not the same.

(4) The correct equation which can be compared with Wirtz's equation is:

$$J_2 = -\frac{D_2 N_2}{RT} \left[\nabla(\mu_2)_T + \frac{Q_2^* - h_2}{T} \nabla T \right], \quad Q_2^* \approx 0,$$

where Q_2^* is the heat of transfer of the solute. Thus $Q_C^* \approx -h_2$ is concluded.

REFERENCES

- (1) P. G. Shewmon: *Acta Metall.*, **8** (1960), 605–611.
- (2) P. G. Shewmon: *Diffusion in Solid*, McGraw-Hill Book Company, New York, (1963), Chap. 7.
- (3) V. V. Voronkov: *J. Cryst. Growth*, **59** (1982), 625–643.
- (4) R. J. Borg and G. J. Diens: *An Introduction to Solid State Diffusion*, Academic Press, Santiago, (1988), Chap. VI-3.
- (5) W. Wijaranakula: *J. Electrochem. Soc.*, **139** (1992), 604–616.
- (6) T. Ebe: *J. Cryst. Growth*, **203** (1999), 387–399.
- (7) R. Habu: *Jpn. J. Appl. Phys.*, **36** (1997), 2800–2801.
- (8) R. Habu and W. Yamada: *Mater. Trans., JIM*, **39** (1998), 351–356.
- (9) R. A. Brown, D. Maroudas and T. Sinno: *J. Cryst. Growth*, **137** (1994), 12–25.
- (10) S. R. de Groot: *Thermodynamics of Irreversible Processes*, Inter-

- science Publisher Inc., New York, (1952), Chap. 4.
- (11) R. Haase: *Thermodynamics of Irreversible Processes*, Dover Publications, Inc., New York (1990), §4-8.
- (12) I. Prigogine: *Introduction to Thermodynamics of Irreversible Processes*, Interscience Publisher Inc., New York, (1952), Chap. 4.
- (13) S. R. de Groot: *Thermodynamics of Irreversible Processes*, Interscience Publisher Inc., New York, (1952), §44.
- (14) K. Wirtz: *Physikalische Zeitschrift*, **44** (1943), 221-231.
- (15) P. G. Shewmon: *Trans. Amer. Inst. Min. Eng.*, **212** (1958), 642-647.
- (16) L. Darken and R. Gurry: *Physical Chemistry of Metals*, McGraw-Hill Book Company, New York, (1953), Chap. 16.
- (17) J. C. Swartz: *Trans. Metall. AIME*, **245** (1969), 1083-1092.
- (18) J. Chipman: *Metal Trans.*, **3** (1972), 55-64.

Erratum

Material Transactions, JIM, Vol. 39 (1998), No. 3 pp. 351-356
 “Heat of Transfer for Carbon in Iron-Carbon System”
 R. Habu and W. Yamada

In the above paper, the authors discovered mistakes after the publication. The collections are as followings.

Line 5 from the bottom of the page 352A to line 4 on the page 352B, ‘minus’ should be inserted ahead of α_{11} , *i.e.*, $\alpha_{11} \rightarrow -\alpha_{11}$.

Equation (7) in the line 5 on the page 352B, ‘minus’ in the right hand side of the equation should be deleted.

Equation (9) in the page 352B, $J'_u = J_u - \sum_{k=1}^n h_k j_k$ is to be replaced by $J'_q = J_q - \sum_{k=1}^n h_k j_k$.

Equation (10) in the page 352B, $X'_k = -\nabla T/T$ is to be replaced by $X'_u = -\nabla T/T$.