A New Equation for Temperature Dependent Solute Impurity Diffusivity in Liquid Metals

Xuping Su, Sui Yang, Jianhua Wang, Nai-Yong Tang, Fucheng Yin, Zhi Li, and Manxiu Zhao

An equation to predict the temperature dependence of solute impurity diffusivity in liquid metals has been derived by combining the Sutherland-Einstein formula with Kaptay's unified equation on the dynamic viscosity of liquid metals. It has been demonstrated that consideration of the temperature dependence of the atomic radius of the diffusing species results in better agreement of the predicted diffusivities with the experimental data compared to when the temperature independent Goldschmidt atomic radius is used. Due to the simple-parameter nature of the equation, it could be very useful in predicting the solute impurity diffusivity in liquid metal when experimental data are scarce.

1. Introduction

Knowledge of the diffusivity of a solute in a dilute molten metallic alloy is of great benefit for various engineering fields, such as metallurgy, interfacial reaction, solidification, crystal growth, phase separation, corrosion, etc. From a theoretical standpoint, the solute impurity diffusivity in liquid metals provides the experimental basis for theories of the liquid state.

Although some efforts have been devoted to experimental study of this subject, reliable experimental data of solute diffusivities in molten metallic alloys are scarce.[1-6] Experimental measurement of diffusivity is difficult because gravity-induced convection and Marangoni convection frequently negatively affect the accuracy of the experimental results. Moreover, the diffusivity is often deduced indirectly from a measured quantity such as a concentration profile, which has a low degree of accuracy.

Xuping Su, School of Materials Science and Engineering, Jiangsu Polytechnic University, Changzhou 213164, Jiangsu, People's Republic of China and Key Laboratory of Materials Design and Preparation Technology of Hunan Province, Xiangtan University, Xiangtan 411105, Hunan, People's Republic of China; **Sui Yang**, Faculty of Materials, Optoelectronics and Physics, Xiangtan University, Xiangtan 411105, Hunan, People's Republic of China and Key Laboratory of Materials Design and Preparation Technology of Hunan Province, Xiangtan University, Xiangtan 411105, Hunan, People's Republic of China; **Jianhua Wang, Fucheng Yin, Zhi Li,** and **Manxiu Zhao**, Key Laboratory of Materials Design and Preparation Technology of Hunan Province, Xiangtan University, Xiangtan 411105, Hunan, People's Republic of China; **Nai-Yong Tang**, Teck Metals Ltd., Product Technology Centre, 2380 Speakman Drive, Mississauga L5k 1B4, ON, Canada. Contact e-mails: sxp@jpu.edu.cn and xtuys21@yahoo.com.cn.

As a result, theoretical exploration of solute diffusivity in liquid metals is of merit.

Solute impurity diffusion in liquid metals is not well understood, and the theory is not nearly as developed as that for impurity diffusion in solid metals. Some theoretical modeling has been conducted to calculate the diffusivities of solute atoms in liquid metals. The "hole" model is analogous to the vacancy mechanism in solids, and some equations[7,8] have been introduced to determine the activation energy and diffusivity for solute atoms. However, the existence of a constant activated energy for diffusion in liquid phase is questionable because there are no vacancies or interstitials which are known to associate with a relatively stable energy barrier. Another approach is the fluctuation theory[9] which considers that diffusion in liquid metals results from local density fluctuations. This approach has the inherent weakness of reliance upon disposable parameters or a presupposed average liquid state configuration. Other models, including the free volume model,[10] semi-empirical small fluctuation theory,[11] have been proposed. While some of these theories work reasonably well for some solutes in some solvents, none work well universally.[12]

Since the solute diffusivity in liquid metallic alloys is a complex function of alloy composition, temperature and pressure, it is necessary to explore some extreme cases first. For example, one can determine the temperature dependence of impurity diffusivity in an infinitely dilute solution under one atmosphere pressure. In such a system, the influence of solute concentration on the diffusivity is negligible. Based on such an understanding, an attempt has been made in this contribution to derive an equation which enables the calculation of the temperature dependent solute impurity diffusivity in molten metal.

2. Derivation of the New Equation and Comparison with Experimental Data

Unlike the diffusion process in pure liquid metals, solute diffusion involves two species which differ in size

and valence, the latter also reflects the interactions (attractive/repulsive) between the solute and the solvent. Ideally, the effects of both the size and valence should be incorporated into an equation for the prediction of the solute diffusivity. Nevertheless, it is generally agreed that the effect of size overshadows the effect of dissimilar valences.

To derive the new equation, one successful formula for describing self-diffusivity should be selected. Considering when the solute atoms are substituted by the solvent atoms, the prediction of the new equation should agree well with the available experimental data of self-diffusivity. The two most familiar models for describing liquid metals, based on the hydrodynamic theory and the kinetic theory, have been developed for the calculation of the self-diffusivity of liquid metals. The Stokes-Einstein Equation is derived from the hydrodynamic theory. It relates the diffusivity to the viscosity of the liquid metal.[13] Such an approach is valid when the solute atoms are large and the solution is dilute. The Sutherland-Einstein[14] Equation is a modified formula which refers to molten metals in which the sizes of the solute atoms and the solvent atoms are comparable. The kinetic theory is used to describe the transfer processes in liquid metals.[15] The atoms in the fluid are treated as hard spheres with an effective diameter. The Enskog Expression[16] is one of the most widely used models. Its development was based on the kinetic theory. It has been employed in evaluating the diffusivities of several liquid metals.[17] A recent investigation[18] demonstrated that the prediction of the hydrodynamic model based Sutherland-Einstein equation is more satisfactory with available experimental data than that of the hard sphere model based Enskog expression.

In this work, the Sutherland-Einstein formula serves as the starting point to derive the predictive equation. The detailed presentation is given in the following sections.

The Sutherland-Einstein equation for the self-diffusivity of a pure liquid metal is expressed as[14]:

$$D = \frac{kT}{4\pi\mu r} \qquad (Eq\ 1)$$

where k is the Boltzmann constant, T is the absolute temperature, μ is the dynamic viscosity, and r is the radius of the diffusing unit. For a molecule or atom in the case of liquid metals, r must be interpreted as some average molecular radius. For liquid metals, it is probably reasonable to use the Goldschmidt atomic diameters while using Eq 1 to estimate the value of self-diffusivity.

The size effect is an important factor in the solute diffusion in liquid metals, and that the diffusivity is inversely proportional to the size of the diffusing species.[2] Recent results studied by Cahoon et al.[19] indicated that Zn with a radius smaller than Sn diffuses more rapidly than Sn, whereas Bi and Pb with larger radii diffuse more slowly than Sn. Furthermore, Ag and Sb with radii similar to that of Sn diffuse at essentially the same rate as Sn. These results strongly support the idea of introducing atomic size to the diffusion equation. Roy and Chhabra[20] assumed that the size of diffusing species is proportional to the atomic

diameter of the metal, and that the solute diffusivity can be determined as:

$$D_{AB} = \frac{r_B}{r_A}D_{BB} \qquad (Eq\ 2)$$

where subscripts (A) and (B) represent the solute and solvent respectively, D_{AB} is the diffusivity of the solute A in the solvent B, D_{BB} is the self-diffusivity of solvent B, r_B and r_A are the atomic radius of the solvent and solute, respectively. Combining Eq 1 and 2 yields:

$$D_{AB} = \frac{kT}{4\pi\mu r_A} \qquad (Eq\ 3)$$

In order to predict diffusivity using Eq 3, an analytical expression must be developed to relate the viscosity μ of a dilute molten metallic alloy to its other physical parameters. Combining the Andrade Equation with the activation energy model, Kaptay has derived the following unified formula for predicting viscosity[21]:

$$\mu_i = C_1\frac{M_i^{1/2}}{V_i^{2/3}}T^{1/2}\exp\left(C_2\frac{T_i^m}{T}\right) \qquad (Eq\ 4)$$

Here, μ_i, M_i, V_i and T_i^m are the dynamic viscosity, the atomic mass, the absolute molar volume and the melting point under one atmospheric pressure of the given metal i, respectively. C_1 and C_2 are constants. The values of C_1 and C_2 were optimized by applying Eq 4 to over 100 experimentally measured dynamic viscosity data of 15 selected liquid metals, and were found to be $(1.80\pm0.39)\times10^{-8}$ $(J\ K^{-1}\ mol^{-1/3})^{1/2}$ and 2.34 ± 0.20, respectively. It has been shown recently on the example of the surface tension that the cohesion energy $\Delta_c U_i$ correlates with the melting point of normal metals[22]:

$$\Delta_c U_i = -qRT_i^m \qquad (Eq\ 5)$$

where q is a semi-empirical parameter determined to be $q \cong 25.4\pm2$.[23] In a dilute solution, the concentration of the solute is small, and the change in the cohesion energy of the diffusing solute is negligible. Substituting Eq 5 into 4, the following was obtained:

$$\mu_i = C_1\frac{M_i^{1/2}}{V_i^{2/3}}T^{1/2}\exp\left(-C_2\frac{\Delta_c U_i}{qRT}\right) \qquad (Eq\ 6)$$

It is clear that the interactions between the atoms of the liquid metals are involved in the unified formula for predicting viscosity. Combining Eq 2-4, the following was obtained:

$$D_{AB} = \frac{kT^{1/2}}{4\pi r_A}\frac{V_B^{2/3}}{C_1 M_B^{1/2}}\exp\left(-C_2\frac{T_B^m}{T}\right) \qquad (Eq\ 7)$$

Equation 7 takes into account both the effects on solute diffusivity of the atomic size and interactions between the atoms of the liquid metals. All the parameters on the right-hand side of Eq 7, except r_A, relate to the solvent B. To calculate the diffusivity for a given solute-solvent system

using the above equation requires knowledge of the atomic radius, atomic mass and atomic volume as well as the melting point. Atomic volumes of various solvents were calculated using the equations given by Crawley.[24] For a dilute molten metallic alloy, it is appropriate to use half of the Goldschmidt atomic diameters as the atomic radius. The values of the Goldschmidt atomic diameters are available in Smithell's reference book.[25]

The usefulness of the explicit formulation presented Eq 7 is demonstrated by making detailed comparisons with the data on solute diffusion available in the literature for a wide variety of solute-solvent systems over extended ranges of temperature. A total of 108 diffusion coefficients of the solute metals in 19 liquid metallic alloy systems were calculated to compare with the corresponding experimental values. It should be mentioned that the experimental data were reported by different authors and entailed varying uncertainty due to the different experimental conditions.[26] The buoyancy-driven convective flow in the capillary reservoir technique introduces "lid-driven" flow in the capillary that increases the "apparent" liquid diffusivity.[27] To minimize convective flow, the capillary diameter should be as small as possible to decrease the liquid fluidity.[28] However, if the diffusion capillary is less than 1 mm in diameter, the rate of diffusion will be reduced by the "wall" effect. Since the 1980s, some liquid diffusion experiments have been conducted in space to provide a reliable database for testing computer simulations and calculations of metallurgical processes.[4,29] Therefore, in this study, the experimentally measured diffusivities were taken from the open literature, and only data measured by small-sized capillaries, shear cell technique and/or under microgravity state were selected. The data assigned as D_1 calculated with Eq 7 are listed in Column 4 and Column 12 in Table 1. All the values of the parameters used are summarized in Table 2.

The performance of the equation was evaluated by determining relative difference between the measured and calculated values with three parameters of δ, Δ, and S. The definition of each parameter is presented in the following.

$$\delta = \frac{x_{\mathrm{mea}} - x_{\mathrm{cal}}}{x_{\mathrm{cal}}} \times 100 \qquad (\text{Eq 8})$$

where x_{mea} and x_{cal} are the measured and calculated diffusivities, respectively.

$$\Delta = \frac{1}{N} \sum_{i=1}^{N} |\delta_i| \qquad (\text{Eq 9})$$

where N is the number of samples.

$$S = \frac{1}{100} \sqrt{\overline{\delta_i^2}} = \sqrt{\frac{1}{N} \sum_{i=1}^{N} \left\{ \frac{(x_i)_{\mathrm{mea}} - (x_i)_{\mathrm{cal}}}{(x_i)_{\mathrm{cal}}} \right\}^2} \qquad (\text{Eq 10})$$

The parameter S corresponds to the relative standard deviation. The statistical assessment of Eq 7 was performed by computing the parameters of δ_1, Δ_1, and S_1 and the values are listed in Table 1. The experimental uncertainties for diffusivity measurements are accurate to within 5-10%.[18]

As is clear from Table 1, though some calculated values are within the range of uncertainty associated with experimental measurements, such as Au-Ag (the leading element is the solute) and Cu-Pb systems, most of the predictive data are beyond the range. For example, the prediction uncertainty for Ag-Sn is about 20% which is beyond the range of experimental measurement uncertainty. Eq 7 does not perform very well with Δ_1 and S_1 values of 16.41878 and 0.243488.

Suffice it to say that the deviations are attributed to the temperature independent atomic radius and the approximation of solute-solvent interactions. As in the dilute solution, the influence introduced by the latter is so insignificant that it can be ignored. The only way to improve the predictability of Eq 7 is to reconsider the assignment of a suitable value to size of the diffusing species, r_{A}. In this regard, the Goldschmidt atomic diameter was replaced by the effective hard sphere diameter calculated using the approach outlined by Protopapas et al.[17] Based on the repulsive intermolecular potential curve, Proptopapas et al.[17] took the average distance of the closest neighboring atoms in the liquid as the diameter of the hard spheres. The temperature dependence of the effective diameter of the hard spheres $\sigma_i(T)$ has been evaluated based on the experimentally measured diffusivities and it was found that:

$$\sigma_i(T) = 1.288 \times 10^{-8} \left(\frac{M}{\rho_{\mathrm{m}}} \right)^{1/3} \left(1 - 0.112 \sqrt{\frac{T}{T_{\mathrm{m}}}} \right) \qquad (\text{Eq 11})$$

where ρ_{m} is the mass density of the diffusing species at the melting point T_{m}, and M is the atomic mass. Substituting Eq 11 into 7, the following was obtained:

$$D_{\mathrm{AB}} = \frac{kT^{1/2}}{4\pi} \frac{(\rho_{\mathrm{A}}^{\mathrm{m}})^{1/3}}{0.644 \times 10^{-8} (M_{\mathrm{A}})^{1/3} (1 - 0.112 \sqrt{T/T_{\mathrm{A}}^{\mathrm{m}}})}$$
$$\times \frac{V_{\mathrm{B}}^{2/3}}{C_1 M_{\mathrm{B}}^{1/2}} \exp \left(-C_2 \frac{T_{\mathrm{B}}^{\mathrm{m}}}{T} \right) \qquad (\text{Eq 12})$$

Without additive parameter, Eq 12 is expressed in terms of the same physical quantities as Eq 7. The values of D_2 calculated using Eq 12 are also summarized in Column 6 and Column 14 of Table 2. An inspection of these results reveals significant improvement in the predicted values compared to when the Goldschmidt atomic radius is used. The availability of the equation considered the temperature dependence can been judged according to the success with which they are able to account for the diffusivity data with Δ_2 and S_2 values of 10.34143 and 0.170243.

As shown in Table 1, the calculated results in Column D_2 match with the experimental diffusion data better than results listed in Column D_1 for Ag-Sn, Sb-Sn, Bi-Sn, Au-Sn, Cu-Al, In-Sn, Au-Pb, Ag-Bi, Co-Cu, Ni-Cu, Ga-In, Al-Sn, Mg-Al, and Sn-Pb systems. In the cases of the Ag-Sn, Al-Sn, Mg-Al, and Sn-Pb systems, the consistency improves with increasing temperature. With a rising temperature, the liquid structure deviated farther from a crystalline structure. Consequently, Goldschmidt atomic diameters do not describe the liquid structure well. On the

Table 1 Calculated and experimental values of solute diffusion coefficients

Solu.	Solv.	T, K	D_1	δ_1	D_2	δ_2	D(Exp.)	Solu.	Solv.	T, K	D_1	δ_1	D_2	δ_2	D(Exp.)
					Diffusion coefficient, $\times 10^{-9}$ m^2 s^{-1}								Diffusion coefficient, $\times 10^{-9}$ m^2 s^{-1}		
Ag	Sn	560	2.52	19.8	2.69	12.3	3.02[a]	Mg	Al	973	3.89	−30.6	4.40	−38.6	2.7[i]
		621	3.23	17.6	3.473	9.4	3.8[a]			1073	5.08	26.0	5.79	10.5	6.4[d]
		693	4.13	35.6	4.458	25.6	5.6[a]	Ag	Pb	623	1.92	22.1	2.57	−8.8	1.74-2.95[d]
		750	4.87	29.2	5.28	19.9	6.29[a]			673	2.35	−16.6	3.16	−38.0	1.96[d]
		773	5.17	−7.2	5.61	−14.4	4.8[c]			723	2.81	29.2	3.79	−4.2	2.16-5.10[d]
		826	5.88	20.7	6.404	10.9	7.1[a]			773	3.29	−11.1	4.45	−34.3	2.36-3.49[d,j]
		1108	9.76	20.9	10.8	9.3	11.8[a]	Cu	Pb	723	3.16	8.5	3.43	0	3.43[d]
		1428	14.2	21.1	15.91	8.1	17.2[a]			773	3.71	5.7	4.03	−2.7	3.92[d]
		1683	17.6	25	19.99	10.0	22[a]			823	4.27	3.3	4.66	−5.4	4.41[d]
Al	Sn	560	2.5	−29.6	2.74	−35.8	1.76[b]			873	4.85	0.8	5.31	−7.9	4.89[d]
		650	3.61	−6.6	3.94	−14.5	3.37[b]			923	5.44	−1.29	5.97	−10.05	5.37[d]
		700	4.25	5.9	4.65	−3.2	4.5[b]	Na	Pb	625	1.45	136.9	1.74	97.4	2.75-4.12[d]
		750	4.9	17.8	5.39	7.1	5.77[b]			673	1.76	−31.3	2.12	−42.9	1.21[d]
Sb	Sn	589	2.55	2.0	2.64	−1.5	2.6[a]			853	3.08	85.1	3.79	50.4	5.25-6.15[d]
		600	2.67	19.7	2.76	15.8	3.15-3.24[a,d]			873	3.23	−41.8	3.99	−52.9	1.79-1.97[d]
		630	2.99	0.3	3.10	−3.2	3[a]	Au	Pb	633	2.00	25	2.16	15.7	2.5[k]
		743	4.27	3.0	4.47	−1.6	4.4[a]			703	2.63	17.87	2.85	7.63	3.1[k]
		800	4.95	11.4	5.2	6.12	5.36-5.67[a,d]			723	2.89	17.6	3.05	11.5	3.4[l]
		891	6.05	10.7	6.40	4.7	6.7[a]			773	3.29	12.5	3.58	3.4	3.7[c]
		700	3.77	13.40	3.94	8.50	4.14-4.41[a,d]			811	3.67	15.3	4.01	5.5	4.23[l]
		900	6.16	4.22	6.52	−1.53	6.42[a]			823	3.79	16.09	4.14	6.28	4.4[k]
		1000	7.39	1.22	7.88	−5.08	7.48[a]			973	5.38	7.8	5.92	−2.0	5.8[l]
		1100	8.63	−1.04	9.26	−7.78	8.54[a]			1123	7.04	12.9	7.81	1.8	7.95[l]
		1300	11.1	−3.96	12.05	−11.54	10.66[a]			1133	7.15	7.69	7.94	−3.02	7.7[k]
Bi	Sn	504	1.69	6.5	1.74	3.4	1.8[f]	Sn	Pb	723	2.56	1.56	2.82	−7.8	2.6[g]
		574	2.279	5.3	2.46	−2.4	2.4[f]			773	3.00	17.3	3.32	6.0	3.52[j]
		666	3.21	−9.7	3.52	−17.6	2.9[e]			823	3.46	24.3	3.85	11.7	4.3[g]
		723	3.83	−6.01	4.22	−14.69	3.6[g]			869	3.79	33.5	4.35	16.3	5.06[m]
		773	4.38	5.0	4.85	−5.24	4.6[g]			973	4.78	−5.2	5.53	−18.1	4.27-4.79[m]
		873	5.52	19.6	6.18	6.87	6.6[g]			1071	5.74	54.2	6.71	31.9	8.85[m]
		1000	7.00	14.3	7.92	1.0	8[e]	Ag	Bi	573	1.82	23.1	2.43	−7.8	2.24[d]
Au	Sn	600	2.98	0	3.21	−7.2	2.98[a]			673	2.77	86.6	3.79	36.4	5.17[d]
		700	4.22	12.6	4.57	3.9	4.75[a]	Au	Ag	1253	2.55	−3.5	2.85	−13.7	2.46[n]
		773	5.17	3.9	5.63	−4.6	5.37[h]			1300	2.83	−1.1	3.17	−11.7	2.8[n]
		826	5.88	13.9	6.42	4.4	6.7[a]			1350	3.14	1.6	3.53	−9.6	3.19[n]
		900	6.89	20.3	7.56	9.7	8.29[a]			1400	3.47	3.5	3.90	−7.9	3.59[n]
		1108	9.76	10.7	10.8	0	10.8[a]			1450	3.80	5.3	4.29	−6.8	4[n]
		1323	12.7	18.9	14.3	5.6	15.1[a]			1500	4.15	7.0	4.69	−5.3	4.44[n]
		1428	14.2	10.6	15.9	−1.3	15.7[a]			1533	4.38	8.0	4.96	−4.6	4.73[n]
Cu	Al	1000	5.25	14.3	5.79	3.6	6[d]	Co	Cu	1373	3.39	6.5	3.71	−2.7	3.61[o]
		1050	6.00	14.5	6.63	3.6	6.87[d]			1423	3.79	10.3	4.16	0.5	4.18[o]
		1100	6.78	14.7	7.51	3.6	7.78[h]			1473	4.22	13.7	4.64	3.4	4.8[o]
		1150	7.60	14.61	8.44	3.20	8.71[h]			1523	4.66	17.0	5.14	6.0	5.45[o]
		1200	8.44	14.6	9.40	2.9	9.67[h]			1573	5.13	19.7	5.66	8.5	6.14[o]
		1250	9.32	14.1	10.4	2.2	10.63[h]	Ni	Cu	1373	3.41	6.2	3.74	−3.2	3.62[o]
		1300	10.2	13.8	11.4	1.8	11.61[h]			1423	3.82	8.6	4.20	−1.2	4.15[o]
In	Sn	623	2.99	23.4	3.32	11.1	3.69[q]			1473	4.25	10.6	4.68	0.4	4.7[o]
		723	4.14	20.0	4.66	6.7	4.97[q]			1523	4.70	12.6	5.18	2.1	5.29[o]
		823	5.36	20.0	6.09	5.6	6.43[q]			1573	5.17	14.1	5.71	3.3	5.9[o]
		923	6.61	22.4	7.60	6.4	8.09[q]	Ga	In	473	2.41	27.8	2.61	18.0	3.08[p]

Table 1 continued

Solu.	Solv.	T, K	D_1	δ_1	D_2	δ_2	D(Exp.)	Solu.	Solv.	T, K	D_1	δ_1	D_2	δ_2	D(Exp.)
			Diffusion coefficient, $\times 10^{-9}$ m^2 s^{-1}								Diffusion coefficient, $\times 10^{-9}$ m^2 s^{-1}				
Sn	In	523	2.57	27.6	2.84	15.5	3.28[q]			523	3.09	21.4	3.37	11.3	3.75[p]
		673	4.43	6.5	4.97	−5.0	4.72[q]			573	3.80	16.1	4.18	5.5	4.41[p]
		873	7.07	1.70	8.11	−11.34	7.19[q]			623	4.59	10.0	5.04	0.2	5.05[p]
		1073	9.74	5.85	11.40	−9.56	10.31[q]			673	5.31	6.78	5.93	−4.38	5.67[p]
$\Delta_1(102)$			16.41878					$\Delta_2(102)$			10.34143				
$S_1(102)$			0.243488					$S_2(102)$			0.170243				

[a]Reference 2, [b]Reference 32, [c]Reference 33, [d]Reference 26, [e]Reference 34, [f]Reference 6, [g]Reference 35, [h]Reference 20, [i]Reference 36, [j]Reference 37, [k]Reference 29, [l]Reference 3, [m]Reference 27, [n]Reference 38, [o]Reference 12, [p]Reference 39, [q]Reference 4

Table 2 Values of characteristic parameters of solutes and solvents used in the present work

Metal	ρ^m, $\times 10^{-3}$ kg m^{-3}	M, kg	T^m, K	d, $\times 10^{-10}$ m	C_1, $\times 10^{-8}$ J K^{-1} mol$^{-1/3}$	C_2
Ag	9.33	107.9	1234.93	2.88	1.63	2.35
Sn	6.98	118.7	504.9	3.16	1.90	2.20
Al	2.38	26.98	933.37	2.86	1.8	2.34
Sb	6.48	121.8	903	3.22	1.8	2.34
Bi	10.05	209	544.3	3.40	1.8	2.34
Au	17.4	197	1337.43	2.88	2.18	2.03
Cu	8	63.55	1356	2.56	1.11	2.66
Mg	1.59	24.31	923	3.20	1.8	2.34
Pb	10.67	207.2	600.5	3.50	1.82	2.24
Na	0.927	22.99	370.81	3.84	1.52	2.60
Co	7.75	58.93	1768	2.50	1.8	2.34
Ni	7.9	58.69	1726	2.48	1.8	2.34
Ga	6.1	69.72	302.78	2.70	1.8	2.34
In	7.03	114.8	429.61	3.14	1.86	2.22

other hand, the temperature-dependent hard spheres are a better approximation of the solute atoms. The experimentally measured diffusivities of the Ag-Pb, Na-Pb, Au-Ag, and Sn-In systems are scattered. Nevertheless, the correspondence between the calculated results and the experimental data is reasonably good. The differences between the calculated and the experimentally measured values are believed to arise mainly from the approximation that the cohesive energy of the solute is equal to that of the solvent metal. In other words, the interactions between the solute and the solvent are believed to be equal to the interaction between the solvent atoms. However, despite this limitation, a reasonable agreement is still obtained. It should be emphasized that Chauhan et al.[18] have found that the predictions of self-diffusivity by the Eq 1 (Sutherland-Einstein equation) were noticeable improved when the Goldschmidt atomic diameter was replaced by the temperature dependent effective hard sphere diameter as proposed by Protopapas et al.[17]

3. Discussion

The performance of the present equation has been further demonstrated by making detailed comparisons with the corresponding available methods. The diffusivities calculated by the new equation obtained in the present work were compared with the predictions of three available predictive methods: Enskog Expression,[17] Liu et al.[30] and the fluid theory[20] over extended ranges of temperature. These methods have been reported in the corresponding references, and will not be detailed here. The data computed by the three methods are designated as D_E, D_H and D_F respectively and are listed in Table 3. An examination of the results presented in Table 3 reveals that the best agreement between the predicted values and the experimental data is achieved by the new equation. The deviations from the experimentally measured solute diffusivity of the predicted values by the Enskog Expression, Liu et al.'s method and the fluid theory are more significant as suggested by much larger values of Δ and S, being 32.13493 and 0.360023, 25.23921 and 0.373694, 23.16192 and 0.27244, respectively. These values should be compared to 10.34143 and 0.170243 for the predictions by Eq 12.

This is probably because the new equation takes into account the effects of atomic size and interactions between the atoms of the liquid metals during the solute diffusion process. As a result, it possesses a much better predictability. Larger deviations from the experimental results of other predictions are most likely because some important factors were not accounted for in those models. The Enskog Expression assumes that the diffusing species are hard spheres which have specific mass and volume. However, their charge was ignored in the expression. In the Enskog Expression, the calculations of reduced mass, hard sphere diameter and the radial distribution function take into account the contributions from both solute and solvent. However, only the contribution of the solvent is considered in the calculation of the packing fraction and the correlation factor. In the studies of solute in liquid Cu,[1] a comparison between experimental data and prediction by the hard sphere model indicates that the difference in size between

Table 3 Comparison of the calculated diffusivity of the new equation with three available methods

Solu.	Solv.	T, K	D_2	D_E	D_H	D_F	D(Exp.)	Solu.	Solv.	T, K	D_2	D_E	D_H	D_F	D(Exp.)
			Diffusion coefficient, $\times10^{-9}$ m^2 s^{-1}								Diffusion coefficient, $\times10^{-9}$ m^2 s^{-1}				
Ag	Sn	560	2.69	3.85	2.77	3.01	3.02[a]	Mg	Al	973	4.40	7.24	3.22	7.49	2.7[i]
		621	3.473	4.86	3.74	3.84	3.8[a]			1073	5.79	9.83	4.30	10.12	6.4[d]
		693	4.458	6.15	4.99	4.95	5.6[a]	Ag	Pb	623	2.57	5.75	1.58	3.02	1.74-2.95[d]
		750	5.28	7.23	6.02	5.92	6.29[a]			673	3.16	7.01	2.00	3.70	1.96[d]
		773	5.61	7.67	6.44	6.33	4.8[c]			723	3.79	8.36	2.44	4.44	2.16-5.10[d]
		826	6.404	8.71	7.43	7.34	7.1[a]			773	4.45	9.78	2.90	5.24	2.36-3.49[d,j]
		1108	10.8	13.77	12.62	13.98	11.8[a]	Cu	Pb	723	3.43	7.10	2.74	4.99	3.43[d]
		1428	15.91	15.28	17.85	24.04	17.2[a]			773	4.03	8.31	3.25	5.89	3.92[d]
		1683	19.99	23.52	21.41	34.00	22[a]			823	4.66	9.57	3.79	6.87	4.41[d]
Al	Sn	560	2.74	6.13	2.79	3.03	1.76[b]			873	5.31	10.87	4.34	7.92	4.89[d]
		650	3.94	8.56	4.26	4.30	3.37[b]			923	5.97	12.20	4.90	9.03	5.37[d]
		700	4.65	10.00	5.15	5.10	4.5[b]	Na	Pb	625	1.74	6.15	1.20	2.29	2.75-4.12[d]
		750	5.39	11.51	6.06	5.96	5.77[b]			673	2.12	7.55	1.50	2.77	1.21[d]
Sb	Sn	589	2.64	3.59	2.88	3.04	2.6[a]			853	3.79	13.85	2.75	4.99	5.25-6.15[d]
		600	2.76	3.74	3.03	3.17	3.15-3.24[a,d]			873	3.99	14.64	2.90	5.28	1.79-1.97[d]
		630	3.10	4.17	3.48	3.55	3[a]	Au	Pb	633	2.19	3.18	1.66	3.15	2.5[k]
		743	4.47	5.92	5.27	5.18	4.4[a]			703	2.85	4.15	2.26	4.13	3.1[k]
		800	5.2	6.86	6.21	6.12	5.36-5.67[a,d]			723	3.05	4.45	2.44	4.44	3.4[l]
		891	6.40	8.37	7.74	7.77	6.7[a]			773	3.58	5.21	2.90	5.24	3.7[c]
		700	3.94	5.24	4.57	4.53	4.14-4.41[a,d]			811	4.05	5.82	3.26	5.89	4.23[l]
		900	6.52	8.52	7.89	7.94	6.42[a]			823	4.14	6.02	3.37	6.11	4.4[k]
		1000	7.88	10.21	9.54	10.00	7.48[a]			973	5.92	8.55	4.85	9.09	5.8[l]
		1100	9.26	11.66	11.16	12.30	8.54[a]			1123	7.90	11.01	6.33	12.65	7.95[l]
		1300	12.05	13.34	14.19	17.61	10.66[a]			1133	7.94	11.17	6.43	12.91	7.7[k]
Bi	Sn	504	1.84	2.26	1.67	1.98	1.8[f]	Sn	Pb	723	2.82	5.04	2.17	3.94	2.6[g]
		574	2.46	3.08	2.53	2.71	2.4[f]			773	3.32	5.94	2.58	4.66	3.52[j]
		666	3.52	4.33	3.82	3.83	2.9[e]			823	3.85	6.89	3.00	5.43	4.3[g]
		723	4.22	5.17	4.68	4.61	3.6[g]			869	4.40	7.81	3.40	6.19	5.06[m]
		773	4.85	5.94	5.46	5.36	4.6[g]			973	5.53	9.95	4.31	8.08	4.27-4.79[m]
		873	6.18	7.53	7.04	7.03	6.6[g]			1071	6.78	11.97	5.18	10.09	8.85[m]
		1000	7.92	9.52	9.04	9.48	8[e]	Ag	Bi	573	2.43	5.89	1.14	4.07	2.24[d]
Au	Sn	600	3.21	4.03	3.40	3.55	2.98[a]			673	3.79	8.66	1.88	5.67	5.17[d]
		700	4.57	5.63	5.11	5.06	4.75[a]	Au	Ag	1253	2.85	3.66	2.27	3.12	2.46[n]
		773	5.63	6.89	6.45	6.33	5.37[h]			1300	3.17	4.10	2.55	3.55	2.8[n]
		826	6.78	7.82	7.43	7.34	6.7[a]			1350	3.53	4.67	2.87	4.03	3.19[n]
		900	7.56	9.12	8.82	8.88	8.29[a]			1400	3.90	5.20	3.18	4.53	3.59[n]
		1108	10.8	12.39	12.62	13.98	10.8[a]			1450	4.29	5.75	3.51	5.06	4[n]
		1323	14.3	13.95	16.23	20.44	15.1[a]			1500	4.69	6.33	3.85	5.61	4.44[n]
		1428	15.9	13.62	17.85	24.04	15.7[a]			1533	4.96	6.72	4.08	5.99	4.73[n]
Cu	Al	1000	5.79	8.11	4.38	10.21	6[d]	Co	Cu	1373	3.71	4.93	2.87	4.86	3.61[o]
		1050	6.63	9.42	5.06	11.86	6.87[d]			1423	4.16	5.53	3.21	5.31	4.18[o]
		1100	7.51	10.80	5.76	13.62	7.78[h]			1473	4.64	6.16	3.57	5.78	4.8[o]
		1150	8.44	12.26	6.49	15.48	8.71[h]			1523	5.14	6.81	3.93	6.26	5.45[o]
		1200	9.40	13.78	7.24	17.46	9.67[h]			1573	5.66	7.50	4.31	6.77	6.14[o]
		1250	10.4	15.36	8.01	19.54	10.63[h]	Ni	Cu	1373	3.74	5.02	2.90	4.90	3.62[o]
		1300	11.4	16.98	8.79	21.73	11.61[h]			1423	4.20	5.63	3.24	5.35	4.15[o]
In	Sn	623	3.50	4.88	3.46	3.55	3.69[q]			1473	4.68	6.27	3.60	5.82	4.7[o]
		723	4.92	6.79	5.07	5.00	4.97[q]			1523	5.18	6.94	3.97	6.31	5.29[o]
		823	6.43	8.85	6.77	6.68	6.43[q]			1573	5.71	7.63	4.35	6.82	5.9[o]
		923	8.02	10.97	8.48	8.61	8.09[q]	Ga	In	473	2.61	4.65	3.31	3.27	3.08[p]

Table 3 continued

Solu.	Solv.	T, K	D_2	D_E	D_H	D_F	D(Exp.)	Solu.	Solv.	T, K	D_2	D_E	D_H	D_F	D(Exp.)
			Diffusion coefficient, $\times 10^{-9}$ m^2 s^{-1}								Diffusion coefficient, $\times 10^{-9}$ m^2 s^{-1}				
Sn	In	523	2.94	3.94	3.65	3.39	3.28[q]			523	3.37	5.89	4.38	4.07	3.75[p]
		673	4.97	6.74	6.60	5.83	4.72[q]			573	4.18	7.23	5.53	4.96	4.41[p]
		873	8.11	10.67	10.59	10.09	7.19[q]			623	5.04	8.66	6.71	5.93	5.05[p]
		1073	11.40	13.41	14.24	15.50	10.31[q]			673	5.93	10.16	7.92	7.00	5.67[p]
$\Delta_2(108)$		10.34143		$\Delta_E(108)$		32.13493		$\Delta_H(108)$		25.23921		$\Delta_F(108)$		23.16192	
$S_2(108)$		0.170243		$S_E(108)$		0.360023		$S_H(108)$		0.373694		$S_F(108)$		0.27244	

D_2: The diffusivities calculated using the Eq 12 derivated in the present manuscript; D_E: The diffusivities predicted by Enskog Expression[17]; D_H: The diffusivities predicted by Liu's[30] method; D_F: The diffusivities predicted by fluid theory[20]; D(Exp.): The available experimental data of diffusivities
[a]Reference 2, [b]Reference 32, [c]Reference 33, [d]Reference 26, [e]Reference 34, [f]Reference 6, [g]Reference 35, [h]Reference 20, [i]Reference 36, [j]Reference 37, [k]Reference 29, [l]Reference 3, [m]Reference 27, [n]Reference 38, [o]Reference 12, [p]Reference 39, [q]Reference 4

the solute and the solvent plays an important role in the dynamic correlations. The data show that among the solute particles smaller in size and mass than the solvent atoms, the predictions are in agreement with the experimental data, those of larger mass and smaller size tend to diffuse more rapidly than predicted by the hard sphere model. Solutes larger and heavier than the solvent diffuse faster than predicted by the hard sphere model. In the Liu et al.'s method, atoms are assumed to be point charges with no volume and mass, hence, entropy considerations render the "hole" mechanism implausible.[31] Based on the fluidity model of Hildebrand, only the size effects have been accounted for, and no consideration has been given to the valence effect, namely, the interactions between the solute and the solvent. As a result, the fluidity model of Hildebrand may not be applicable to systems in which a strong interaction between the solute and solvent exists.

The equation derived in the present work contains no adjustable parameters. The equation is derived from the Sutherland-Einstein formula which stems from the hydrodynamic theory with a basic assumption that the diffusing species are spherical in shape. As a first approximation, Eq 12 assumes that the size of the flow unit is proportional to the effective atomic diameter of the metal. The true identity of the diffusing species in liquid metals is still a topic subjected to debate. Some researchers[32] believe the diffusing species are ions whereas others[2] have believed the diffusing species are atoms. The evidence for both beliefs is circumstantial. Hence, the assumption that the diffusing unit is an atom is valid. The value of the atomic diameter has been assigned equal to the average distance of closest approach for repulsive collisions in the fluid. The second approximation of the equation is that the melting point of the alloy for a dilute metallic solution is equal to the melting point of the solvent metal. The melting point of an alloy is an indication of the cohesion energy of the liquid metal, and the cohesion energy is, in turn, an approximation of the solute-solvent interaction. It is realized that these approximations carry some inherent weakness and uncertainties. Nevertheless, the excellent agreement between the predictions by the equation and the available experimental data suggest the present approach is not only simple, but also reliable.

4. Conclusions

Taking the effects of atomic diameter and the interactions between the atoms of the liquid metals into account, a new solute diffusion equation has been developed by combining the Sutherland-Einstein Equation and Kaptay's unified viscosity formula. Comparisons of the predictions of the new equation with the available experimental data indicated a satisfactory agreement between the two sets of data. The calculated results D_2 taking into consideration the temperature dependence of the atomic radius of the diffusing species match the experimental diffusion data better than data of D_1 using the temperature independent Goldschmidt atomic radius. Due to the simple-parameter nature of the equation, it could be very useful in predicting solute impurity diffusivity in liquid metals when experimental data are scarce. The range of applications shows the versatility of this simple approach.

Acknowledgments

References

1. A. Bruson and M. Gerl, Diffusion Coefficients of ^{124}Sb, ^{113}Sn, ^{110m}Ag, and ^{195}Au in Liquid Copper, *Phys. Rev. B*, 1979, **19**(12), p 6123-6129

2. A. Bruson and M. Gerl, Diffusion Coefficients of ^{113}Sn, ^{124}Sb, ^{110m}Ag, and ^{195}Au in Liquid Sn, *Phys. Rev. B*, 1980, **21**(12), p 5447-5454

3. X. Zhu and R.W. Smith, Impurity Diffusion of Gold in Liquid Lead, *Adv. Space Res.*, 1998, **22**(8), p 1253-1256

4. G. Mathiak, A. Griesche, K.H. Kraatz, and G. Frohberg, Diffusion in Liquid Metals, *J. Non-Cryst. Solids*, 1996, **205**(207), p 412-416

5. S. Suzuki, K.H. Kraatz, G. Frohberg, R. Rosu-Pflumm, and G. Muller-Vogt, Impurity Diffusion Measurements of Bi in Liquid Sn Using Stable Density Layering and the Shear Cell Technique, *J. Non-Cryst. Solids*, 2007, **353**, p 3300-3304

6. J.P. Garandet, G. Mathiak, V. Botton, P. Lehmann, and A. Griesche, Reference Microgravity Measurements of Liquid Phase Solute Diffusivities in Tin- and Aluminum-Based Alloys, *Int. J. Thermophys.*, 2004, **25**(1), p 249-272

7. D. Lazarus, Effect of Screening on Solute Diffusion in Metals, *Phys. Rev.*, 1954, **93**, p 973-976

8. A.D. LeClaire, On the Theory of Impurity Diffusion in Metals, *Phil. Mag.*, 1962, **7**, p 141-167

9. R.A. Swalin, On the Theory of Self-Diffusion in Liquid Metals, *Acta Metall.*, 1959, **7**, p 736-738

10. M.H. Cohen and D. Turnbull, Molecular Transport in Liquids, Gasses, *J. Chem. Phys.*, 1959, **31**(5), p 1164-1169

11. R.J. Reynik, A Semiempirical Small Fluctuation Theory of Diffusion in Liquids, *Trans. Met. Soc. AIME*, 1969, **245**, p 75-81

12. T. Ejima and T. Yamamura, The Properties of Liquid Metals, *Proc. 2nd Int. Conf.*, S. Takeuchi, Ed., Sept. 3-8, 1972 (Tokyo, Japan), Taylor and Francis Ltd., London, 1973, p 537-541

13. A. Einstein, *Investigation on the Theory of Brown Movement*, translated by A.D. Cowper, Dover, New York, 1956

14. W. Sutherland, A Dynamical Theory of Diffusion for Non-Electrolytes and the Molecular Mass of Albumin, *Phil. Mag.*, 1905, **9**, p 781-785

15. R. Castillo, A. Villaverdo, and J. Orozeo, Prediction of Transport Properties for Lennard-Jones Fluids and Their Binary Mixtures Using the Effective-Diameter Hard-Sphere Kinetic Theory, *J. Mol. Phys.*, 1991, **74**, p 1315-1334

16. P. Resibois and M. DeLeener, *Classical Kinetic Theory of Fluids*, John Wiley & Sons, New York, 1977

17. P. Protopapas, H.C. Andersen, and N.A.D. Parlee, Theory of Transport in Liquid Metals. I. Calculation of Self-Diffusion Coefficients, *J. Chem. Phys.*, 1973, **59**(1), p 15-25

18. A.S. Chauhan, R. Ravi, and R.P. Chhabra, Self-Diffusion in Liquid Metals, *Chem. Phys.*, 2000, **252**, p 227-236

19. J. Cahoon, Y. Jiao, K. Tandon, and M. Chaturvedi, Interdiffusion in Liquid Tin, *J. Phase Equilib. Diffus.*, 2006, **27**(4), p 325-332

20. A.K. Roy and R.P. Chhabra, Prediction of Solute Diffusion Coefficients in Liquid Metals, *Metall. Mater. Trans. A*, 1988, **19**, p 273-279

21. G. Kaptay, A Unified Equation for the Viscosity of Pure Liquid Metals, *Z. Metallkd.*, 2005, **96**, p 1-8

22. G. Kaptay, G. Csicsovszki, and M.S. Yaghmaee, Interfacial Criteria to Produce Metal Matrix Composites and Ceramic Particle Stabilized Metallic Foams, *Mater. Sci. Forum,* 2003, **414-415**, p 419-424

23. G. Kaptay, Modelling Interfacial Energies in Metallic Systems, *Mater. Sci. Forum*, 2005, **473-474**, p 1-10

24. A.F. Crawley, *Int. Met. Rev.*, 1974, **19**, p 32-48

25. C.J. Smithells, *Metals Reference Book*, Vol 1, Butterworth's, London, 1967, p 139

26. J.B. Edwards, E.E. Hucke, and J.J. Martin, Diffusion in Binary Liquid Metal Systems, *Int. Met. Rev.*, 1968, **13**, p 1-28

27. M. Klassen and J.R. Cahoon, Interdiffusion of Sn and Pb in Liquid Pb-Sn Alloys, *Metall. Mater. Trans. A*, 2000, **31**, p 1343-1352

28. H. Mueller and G. Mueller-Vogt, Investigation of Additional Convective Transports in Liquid Metals and Semiconductors During Diffusion Measurements by Means of Shear Cell Technique, *Cryst. Res. Technol.*, 2003, **38**, p 707-715

29. R.W. Smith, X. Zhu, M.C. Tunnicliffe, T.J.N. Smith, L. Misener, and J. Adamson, The Influence of Gravity on the Precise Measurement of Solute Diffusion Coefficients in Dilute Liquid Metals and Metalloids, *Ann. NY Acad. Sci.*, 2002, **974**, p 57-67

30. Y. Liu, Z. Long, H. Wang, Y. Du, and B. Huang, A Predictive Equation for Solute Diffusivity in Liquid Metals, *Scr. Mater.*, 2006, **55**, p 367-370

31. J.R. Cahoon, The Entropy Factor in Liquid Diffusion, *Metall. Mater. Trans. A*, 2003, **34A**, p 882-883

32. C.H. Ma and R.A. Swalin, A Study of Solute Diffusion in Liquid Tin, *Acta Metall.*, 1960, **8**, p 388-395

33. W. Jost, *Diffusion in Solids, Liquids and Gases*, Academic Press, New York, NY, 1952, p 479-491

34. J.R. Calhoon, Y. Jiao, K.N. Tandon, and M.C. Chaturvedi, *Proceedings of the First International Conference on Diffusion in Solids and Liquids*, A. Ochsner, J. Gracio, and F. Barlat, Ed., Aveiro, Portugal, 2005, p 75

35. K. Niwa, M. Shimoji, S. Kado, Y. Watanabe, and T. Yokokawa, Studies on Diffusion in Molten Metals, *J. Met.*, 1957, **20**, p 96-101

36. V.M.M. Lobo and R. Mills, Tracer Diffusion of Cadmium and Mercury in Mercury Over the Temperature Range 283-333 K, *Electrochim. Acta*, 1982, **27**, p 969-971

37. M. Tanigaki, N. Komatsu, M. Harada, and W. Eguchi, Diffusion Coefficients of Tin, Antimony and Silver in Lead-Bismuth Liquid Mixtures at 773 K, *J. Chem. Eng. Jpn.*, 1983, **16**, p 167-172

38. I.Y.P. Gupta, Solute Diffusion in Liquid Metals, *Adv. Phys.*, 1967, **16**, p 333-350

39. P.E. Eriksson, S.J. Larsson, and A. Lodding, Tracer Impurity Diffusion in Liquid-Metals: Indium in Gallium and Gallium in Indium, *Z. Nat.*, 1974, **29A**, p 893-896