Application of the Dzugutov Scaling Law for Atomic Diffusion to Binary Liquid Alloys —A Hard-Sphere Description

Isao Yokoyama, Hiroki Yokoyama* and Yoshio Waseda**

Department of Kampo Pharmaceutical Sciences, Nihon Pharmaceutical University, Kitaadachi-Gun 362-0806, Saitama, Japan
**Tsukuba Research Laboratory, Tokuyama Corporation, Tsukuba 300-4247,Ibaraki, Japan*
***Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan*

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ABSTRACT

The Dzugutov scaling law relating the diffusion coefficient and the excess entropy of a liquid has been tested for 29 binary alloys in the equiatomic composition using a hard-sphere model. At first, no volume change on mixing is assumed but the Dzugutov scaling law is found to hold very well for 29 binary alloys. Next, we examine 13 binary alloys in which the effect of volume variation on mixing is taken into account. When volume change on mixing is not so significant, the scaling law still works well and the formalism provides a reasonable description of the interdiffusion coefficients of alloys. The relation between the coefficients of interdiffusion and self-diffusion was also considered and then the viscosity coefficient and the surface tension of liquid alloys have been estimated in terms of the modified Stokes-Einstein relation.

Keywords: Scaling law, Dimensionless diffusion coefficient, Excess entropy, Hard-sphere model, 50-50 binary alloys

1. INTRODUCTION

Dzugutov /1, 2/ has proposed a universal scaling relationship between the diffusion coefficient and the excess entropy in condensed matter. The Dzugutov scaling law enables us to find a very important relation between the dynamic behavior of liquids and their static thermodynamic quantity. Following his proposal, several investigations /3-6/ have been made to understand how the atomic diffusion depends on the structure and thermodynamics of a liquid. The essential points proposed by Dzugutov are as follows. First, the short-range repulsive interaction governs the transfer of energy and momentum in a liquid and this interaction can be approximated by binary hard-sphere collisions. Second, the rate of the cage diffusion in a liquid can be described by the frequency of the local structural relaxations, which is proportional to the number of accessible configurations in the system. Therefore, the scaled diffusion coefficient D^* is proportional to the quantity of $\exp(S_E)$, where S_E is the excess entropy (the total entropy minus the ideal gas contribution) per atom expressed in units of k_B. In the original Dzugutov paper the excess entropy was approximated by the two-body approximation (hereafter denoted by S_2 in this paper). Dzugutov demonstrated the validity of the scaling law for several model liquids, including Pb, Cu, Lennard-Jones and hard-sphere systems. In all cases, a simple pair potential was employed in computer simulations.

One of the present authors (I.Y.) /3-5/ examined the Dzugutov scaling law using the experimental data of structure and self-diffusion /3/, and compared with the calculated values of the self-diffusion coefficient for the hard-sphere model liquid /4/. These studies clearly indicate that the Dzugutov scaling law is well accepted for 17 simple liquid metals near the melting point and also holds very well for the hard-sphere liquid over a wide range of thermodynamic states when the excess entropy is used in place of the pair correlation entropy in the formula originally proposed by Dzugutov /1/.

On the other hand, Hoyt *et al.* /6/ performed a comprehensive test of the Dzugutov scaling law using the interatomic potentials derived from the embedded atom method (EAM) for Ag, Au, Cu, Ni, Pd, Pt, Ni_3Al and AuPt. The angular dependent Stlinger-Weber form was also used to study for Si. One of their conclusions is that the S_2 approximation is not completely reliable when utilizing EAM potentials. It is suggested another important point of the results obtained by Hoyt et al /6/ that the individual scaled diffusivities of Al and Ni in the Ni_3Al alloy lie well off the relationship found in the original work of Dzugutov. Therefore, Hoyt *et al.* /6/ newly formulated a scaling function for a binary mixture by using the results of Jacucci and McDonald /7/ by applying the Enskog theory collision frequency/8/. Except for Si, the Dzugutov scaling law is found to be valid for all EAM systems studied. However, the least squares fit to the EAM data yielded a slope of 1.06 with an uncertainty of ± 0.07. The intercept differs from the original Dzugutov value due to the different reference state used for the entropy calculations (see Fig.2 of Ref./6/). This is an important point to be noticed in evaluation of the real diffusion coefficient.

The purpose of the present work is to test the validity and usefulness of the Dzugutov scaling law for a large number of binary alloys on the basis of a hard-sphere model in which the total ionic volumes are supposed not to change on alloying. Such hard sphere model has been widely employed for liquid metals and alloys, for example, Umar *et al.* /9/ discuss the relationship between the excess volume and the excess entropy of mixing in liquid alloys. It should be noted in the present calculation that the liquid system is assumed to be ideal in the sense of no strong short-range order, similar to the idea of Dzugutov/1, 2/ for two binary cases.

2. THEORETICAL BACKGROUND

2.1. Hard-Sphere Model

Let us consider a binary liquid where c_i is the concentration of species i and N is the total number of hard-spheres. For a binary liquid with c_1N hard-spheres of diameter σ_1 and c_2N hard-spheres of diameter σ_2, the mean volume ω and mean diameter σ_{12} of a sphere are given in the following form.

$$\omega = \frac{\pi}{6}(c_1\sigma_1^3 + c_2\sigma_2^3) = \frac{\pi}{6}\sigma_{12}^3 \, . \tag{1}$$

If $N\Omega$ is the total volume containing the spheres, then the packing fraction ξ is given by

$$\xi = \omega / \Omega \, . \tag{2}$$

The extension of the Enskog theory /8/ with respect to collision frequency to a binary mixture has been discussed by Jacucci and McDonald /7/. The self-diffusion coefficient of a particular species of 1 in a binary system is given by

$$D_1 = \frac{3k_BT}{16\pi}\left[c_1\sigma_1^2 g_{11} n_1 \left(\frac{m_1 k_B T}{4\pi}\right)^{1/2} + \right. \\ \left. \frac{1}{4} c_2 (\sigma_1 + \sigma_2)^2 g_{12} n_2 \left(\frac{m_1 m_2 k_B T}{2\pi(m_1 + m_2)}\right)^{1/2} \right]^{-1} , \tag{3}$$

where m_1 and m_2 are the mass of the two particles and their contact radial distribution functions are given by g_{11} and g_{12}, respectively. Incidentally, the number densities of n_1, and n_2 are missing in Re./7/, so that we add such information in Eq.(3).The expression for D_2 can be readily obtained from Eq.(3) by interchanging the species labels. The two terms within square brackets represent the contributions to D_1 arising, respectively, from 1-1 and 1-2 collisions. The contact distribution functions of additive hard spheres in a binary liquid can be easily evaluated, when using the Carnahan-Starling results /10/, as follows.

$$g_{11} = \left[(1 - \frac{\xi}{2}) + \frac{1}{4}\pi c_2 n_2 \sigma_2^2 (\sigma_1 - \sigma_2) \right] (1 - \xi)^{-3} \, , \tag{4a}$$

$$g_{12} = \frac{\sigma_2 g_{11} + \sigma_1 g_{22}}{\sigma_1 + \sigma_2} = g_{21} \, , \tag{4b}$$

where ξ is given in Eq.(2). It may be noted that Jacucci and McDonald /7/ have used the Percus-Yevick results in Eqs.(4a) and (4b).

Two problems should be noted in application of Eqs.(3) and (4) to the system of interest. First, an appropriate choice must be made for the equivalent hard-sphere diameter. In the present work, we have chosen diameters so as to obtain the experimental entropy of pure liquid metals. The second difficulty is the fact that the Enskog method itself becomes less adequate at high densities. Alder, Gass and Wainwright /11/ suggested from the results of molecular-dynamics on pure hard-sphere liquids that the true diffusion coefficient differs from the Enskog case at intermediate densities and shows distinct and negative deviation as the packing fraction increases. Accordingly, we consider a density- dependent correction factor /11/ in describing the diffusion coefficient of the hard-sphere liquids as

$$D_i = C_{AGW}(\xi) D_{i(TE)}, \tag{5}$$

where $D_{i(TE)}$ is the Thorne-Enskog result(Eq. (3))and $C_{AGW}(\xi)$ is a density- dependent correction factor. For dense hard-sphere liquids we also assume that the correction factor has the same dependence on packing fraction as that observed by Alder, Gass and Wainwright /11/ in the case of the pure liquid. On the other hand, the relevant scaled diffusivity of species 1 in a binary liquid can be written as

$$D_1^* = \frac{D_1}{\chi_1}, \tag{6}$$

where the scaling factor is given by

$$\chi_1 = 4\sigma_1^4 g_{11} n_1 \left(\frac{\pi k_B T}{m_1}\right)^{1/2} + 4\sigma_{12}^4 g_{12} n_2 \left(\frac{\pi(m_1+m_2)k_B T}{2m_1 m_2}\right)^{1/2} \tag{7}$$

A scaling variable for species 2 can be defined by simply interchanging index 1 and 2 in Eq.(7). The scale factor now includes the mixed species radial distribution functions g_{12} and g_{21} which are important for liquids exhibiting chemical short-range order and it contains the effective hard-sphere diameter σ_{12} which is necessary in treating liquids with significant atomic size mismatch. We can then define a single scaled diffusion coefficient for a binary liquid in the following way as given by Ref./6/:

$$D^* = \left(\frac{D_1}{\chi_1}\right)^{c_1} \cdot \left(\frac{D_2}{\chi_2}\right)^{c_2}. \tag{8}$$

The total excess entropy of ion disorder alone, on the other hand, is given by

$$S_E = c_1 S_1^E + c_2 S_2^E, \tag{9}$$

where S_i^E is the excess entropy of species i.

Now we define D_E^* as

$$D_E^* = 0.049 \exp(S_E / k_B). \tag{10}$$

The Dzugutov scaling law states that there exist a strong correlation between D^* and D_E^*.

2.2 Excess Entropy of Pure Liquid Metals

Details of the Gibbs-Bogoliubov technique with the hard-sphere theory for liquid metals and alloys have been given in literature /12-14/ and the entropy is simply written as follows.

$$S = S_{hs} + S_{elec}, \tag{11}$$

where S_{hs} denotes the hard-sphere entropy and is given in the following form for pure liquid metals.

$$S_{hs} = S_{gas} + S_\xi. \tag{12}$$

Here S_{gas} is the ideal gas contribution, and S_ξ is the excess entropy due to the finite packing of the hard-spheres. We use the Carnahan-Starling expression /10 /

$$\frac{S_\xi}{k_B} = \frac{\xi(4-3\xi)}{(1-\xi)^2}. \tag{13}$$

S_{elec} in Eq.(11) denotes the electronic contribution as given by

$$S_{\text{elec}} = \frac{1}{3}\pi^2 n_{\text{F}} k_{\text{B}}^2 T , \tag{14}$$

with n_{F} being the density of electron states (two per orbital)at the Fermi level. Typically, for simple metals, S_{elec} is known to be only a few percent of the size of S_ξ so that its accurate determination is not essential. For this reason, the free-electron result is employed in this work.

$$S_{\text{elec}} = z(\pi k_{\text{B}} / k_{\text{F}})^2 T , \tag{15}$$

where z is the valence and k_{F} is the Fermi wavenumber. Therefore, the excess entropy of ion disorder alone is given by

$$S^{\text{E}} = S - S_{\text{gas}} - S_{\text{elec}} = S_\xi . \tag{16}$$

The result of Eq.(16) does not yet apply to metals until the hard-sphere diameters $\sigma_{\text{i}}(T)'s$ defining S_ξ have been determined. In this work we use Eq.(16) for determining the hard-sphere diameters, $\sigma_{\text{i}}(T)'s$ as a function of temperature T, so as to reproduce the measured entropy for pure liquid metals S_{expt}. For this purpose Eq.(13) can be rewritten as follows:

$$\begin{aligned} \frac{S_\xi}{k_{\text{B}}} &= 3 - \frac{2}{1-\xi} - \frac{1}{(1-\xi)^2} \\ \frac{1}{1-\xi} &= -1 + \sqrt{4 - S_\xi / k_{\text{B}}} . \end{aligned} \tag{17}$$

On the other hand,

$$\frac{S_\xi}{k_{\text{B}}} = \frac{S_{\text{expt}}}{k_{\text{B}}} - \frac{S_{\text{gas}}}{k_{\text{B}}} - \frac{S_{\text{elec}}}{k_{\text{B}}} \tag{18}$$

is obtained from Eq.(16). Now taking the experimental data of Hultgren *et al.* /15,16/ as S_{expt} in Eq. (18),we can obtain the value of $\frac{S_\xi}{k_{\text{B}}}$. This is inserted into Eq. (17) and the value of the packing fraction ξ of the pure liquid metal is extracted. Therefore, σ_{i} is determined by $\sigma_{\text{i}} = (6\xi\,\Omega_{\text{i}} / \pi)^{1/3}$, where Ω_{i} is the specific volume for the pure liquid at the temperature indicated. The density data of Allen /17/ were used for further calculation and this process includes linear extrapolation of density values from the melting point to the desired temperature. When two metals are mixed at the same temperature, the hard-sphere diameters are assumed not to vary. It should be mentioned that the hard-sphere diameter used in the present work always corresponds to the realistic packing fraction which reproduces the structural data of X-ray or neutron diffraction /14/. In cases when the temperature of the alloy is below the melting temperature of the constituent metal, the corresponding value has to be considered in the super-cooled liquid state. For this purpose we have followed the work of Umar et al. /9/ in assuming that the entropy of fusion is temperature-independent.

The dimensionless diffusion coefficients D* and D_{E}* were calculated for alloys in the equiatomic composition listed by Wilson /18/ for which the experimental entropy and (excess) density data are available. The relevant data for NaK were taken from the results of Faber /19/.

2.3 Interdiffusion

The coefficient of interdiffusion , D_{12}, can be written in the form /7/

$$D_{12} = k_{\text{B}} T \left(\frac{c_2}{m_1} + \frac{c_1}{m_2}\right) \int_0^\infty Z_{12}(t)\,dt . \tag{19}$$

The function $Z_{12}(t)$ is the normalized autocorrelation function /20/ and Eq. (19) provides a simple relation for calculating the interdiffusion coefficient from the results of molecular-dynamics. According to Jacucci and McDonald /7/, Eq. (19) is rewritten as follows:

$$D_{12} = c_2 D_1 + c_1 D_2 + k_{\text{B}} T \left(\frac{c_2}{m_1} + \frac{c_1}{m_2}\right) \int_0^\infty Q(t)\,dt , \tag{20}$$

where $Q(t)$ is a sum of all cross-correlations of the type $\langle v_{\text{i}}(0) \cdot v_{\text{j}}(t) \rangle$, with i ≠ j.The last term of Eq.(20) depends on the differences between the species 1 and 2 and it is small when two species are not too different. In such case, D_{12} appears to be the following simple sum of the self-diffusion coefficients of two constituents.

$$D_{12} \approx c_2 D_1 + c_1 D_2 . \qquad (21)$$

For the system Ar-Kr, Jacucci and McDonald /7/ find that the interdiffusion coefficient can be described over the side composition range within about 10% deviation from the linear relation of Eq.(21).

2.4 Viscosity Coefficient and Surface Tension

According to Iida and Guthrie /21/, the modified Stokes-Einstein formula is in excellent agreement with self-diffusivity data in liquid metals. The formula is given as follows.

$$D = \frac{k_B T}{\varsigma (V/N_A)^{1/3} \eta} , \qquad (22)$$

where D is the diffusion coefficient, V is the total volume, N_A is the Avogadro number, η is the viscosity coefficient and ζ is a constant taking a value between 5 and 6 in cgs units. The radius r of a diffusing particle can be obtained on the basis of the hard-sphere model. From the definition of the packing fraction, we obtain

$$\left(\frac{V}{N_A}\right)^{1/3} = \left(\frac{4\pi}{3\xi}\right)^{1/3} r . \qquad (23)$$

Equations (22) and (23) were originally obtained for pure liquid metals, but we tried to extend Eqs. (22) and (23) to a binary liquid. Substituting Eq. (23) into Eq. (22) with the values of ζ, we obtain

$$\frac{1}{C_L} \cdot \frac{k_B T}{2\pi\sigma_{12} D_{12}} \leq \eta_{12} \leq \frac{1}{C_H} \cdot \frac{k_B T}{2\pi\sigma_{12} D_{12}} \qquad (24)$$

in which C_L and C_H are given by:

$$C_L = \frac{3}{2\pi} \cdot \left(\frac{4\pi}{3\xi}\right)^{1/3} ,$$

$$C_H = \frac{2.5}{2\pi} \cdot \left(\frac{4\pi}{3\xi}\right)^{1/3} .$$

The values of C_L and C_H are determined from ξ for alloy. For example, with $\xi = 0.463$ near the melting points, we have $C_L \approx 1.00$ and $C_H \sim 0.83$. Then, Eq. (24) becomes

$$\frac{k_B T}{2\pi\sigma_{12} D_{12}} < \eta_{12} \leq 1.20 \times \frac{k_B T}{2\pi\sigma_{12} D_{12}} . \qquad (25)$$

Equation (25), which was previously suggested by Yokoyama /22/ from a different aspect of viscosity, indicates that the modified Stokes-Einstein formula is equivalent to the Surtherland-Einstein equation/21/, when the hard sphere diameter is employed for a diffusing atom.

On the other hand, it is known that there is a correlation between the shear viscosity coefficient η and the surface tension γ /23/:

$$\frac{\gamma}{\eta} = \left(\frac{15}{16}\right)\left(\frac{k_B T}{m}\right)^{1/2} . \qquad (26)$$

Connecting Eq. (26) with the modified Stokes-Einstein relation given by Eq.(24), we obtain

$$\frac{1}{C_L} \cdot \frac{15 k_B T (k_B T/m)^{1/2}}{32\pi\sigma_{12} D_{12}} \leq \gamma_{12} \leq \frac{1}{C_H} \cdot \frac{15 k_B T (k_B T/m)^{1/2}}{32\pi\sigma_{12} D_{12}} , \qquad (27)$$

where $m = c_1 m_1 + c_2 m_2$.

Since D_{12} is evaluated from Eq.(21), η_{12} and γ_{12} can be evaluated from Eqs. (24) and (27).

3. RESULTS

The input data are given in Table 1 for simple alloys together with the extracted packing fractions and the effective diameters. Table 2 provides information for compound- forming alloys. The data of volume were taken from the paper of Umar *et al.* /9/. The calculated results of C_{AGW}, D^*,S_E/k_B, and D^*_E are summarized in Tables 3 and 4. As seen from the last columns of Tables

Table 1

Input data of the present calculation for simple alloys($c_1 = c_2 = 0.5$). These 19 alloys are considered simple in the sense that they do not form compounds in the solids. $\Omega_0 \equiv c_1\Omega_1 + c_2\Omega_2$, where $c_1 = c_2 = 0.5$. $\sigma_i(m) = \sigma_i(\mathrm{au})\cdot a_\mathrm{B}$, and $\Omega_i(\mathrm{m}^3) = \Omega_i(\mathrm{au})\cdot a_\mathrm{B}^3$ where a_B is the Bohr radius ($a_\mathrm{B} = 0.529177\times10^{-10}(\mathrm{m})$).

Alloy	T (K)	Ω_1 (au)	Ω_2 (au)	Ω_0 (au)	ξ_1	ξ_2	σ_1 (au)	σ_2 (au)
AgAu	1350	131.10	127.80	129.45	0.4257	0.4504	4.7414	4.7905
AuCu	1300	127.40	88.62	108.01	0.4538	0.4325	4.7975	4.1832
BiCd	773	239.40	161.00	200.20	0.4028	0.4291	5.6895	5.0909
BiSn	608	234.50	191.80	213.15	0.4337	0.4435	5.7913	5.4565
CdSn	773	161.00	194.61	177.81	0.4292	0.4184	5.0913	5.3776
CdPb	773	161.00	222.20	191.60	0.4292	0.4270	5.0913	5.6588
CdTl	673	158.80	205.20	182.00	0.4441	0.4383	5.1260	5.5588
CdZn	800	161.50	113.70	137.60	0.4249	0.4275	5.0795	4.5279
InZn	700	188.90	111.60	150.25	0.4240	0.4432	5.3481	4.5543
NaK	373	278.30	537.80	408.05	0.4267	0.4128	6.0984	7.5125
PbSn	773	222.14	194.61	208.38	0.4271	0.4185	5.6587	5.3780
SnZn	700	193.40	111.60	152.50	0.4288	0.4432	5.4105	4.5543
BiHg	594	234.10	175.00	204.55	0.4363	0.4169	5.7996	5.1843
BiPb	700	237.20	220.10	228.65	0.4156	0.4375	5.7314	5.6868
CdIn	723	159.90	189.40	174.65	0.4364	0.4207	5.1079	5.3389
HgSn	423	169.70	188.60	179.15	0.4490	0.4717	5.2599	5.5386
HgZn	608	175.50	109.80	142.65	0.4146	0.4578	5.1797	4.5789
CdHg	600	157.20	175.20	166.20	0.4553	0.4158	5.1513	5.1817
PbZn	926	226.50	116.30	171.40	0.4053	0.4093	5.5969	4.4965

Table 2

Input data for the present calculation for compound- forming alloys ($c_1 = c_2 = 0.5$). These 10 alloys form compounds in the solid phase or they are considered in some other way more complex (see Wilson /18/). $\Omega_0 = c_1\Omega_1 + c_2\Omega_2$, where $c_1 = c_2 = 0.5$. $\sigma_i(m) = \sigma_i(\mathrm{au})\cdot a_\mathrm{B}$, and $\Omega_i(\mathrm{m}^3) = \Omega_i(\mathrm{au})\cdot a_\mathrm{B}^3$ where a_B is the Bohr radius ($a_\mathrm{B} = 0.529177\times10^{-10}(\mathrm{m})$).

Alloy	T (K)	Ω_1 (au)	Ω_2 (au)	Ω_0 (au)	ξ_1	ξ_2	σ_1 (au)	σ_2 (au)
CuZn	1200	87.76	122.50	105.13	0.4414	0.3736	4.1980	4.4379
AlMg	1000	128.00	173.70	150.85	0.4232	0.4087	4.6945	5.1373
BiMg	973	245.80	172.90	209.35	0.3693	0.4125	5.5760	5.1453
CdSb	773	161.00	208.30	184.65	0.4291	0.4247	5.0909	5.5283
HgK	600	175.20	573.00	374.10	0.4159	0.3426	5.1821	7.2108
HgNa	648	176.80	297.80	237.30	0.4082	0.3501	5.1656	5.8395
MgPb	823	168.60	223.60	196.10	0.4287	0.4196	5.1682	5.6377
MgSn	1043	174.90	199.50	187.20	0.4031	0.3844	5.1255	5.2712
MgZn	923	171.50	116.30	143.90	0.4194	0.4098	5.1598	4.4983
SbZn	823	209.20	114.10	161.65	0.4182	0.4242	5.5079	4.5215

Table 3

Simple alloys ($c_1 = c_2 = 0.5$) without volume change on mixing ($\delta \Omega = 0$). These 19 alloys are considered simple in the sense that they do not form compounds in the solids. The values of ξ, D^*, S_E and D^*_E are obtained from Eqs. (2),(8), (9) and (10), respectively. The values of C_{AGW}, which are dependent on packing fraction ξ, are obtained by the chord approximation using molecular dynamics of Alder et al. /11,20/.

Alloy	T (K)	ξ	C_{AGW}	D^* (10^{-3})	S_E (k_B)	D^*_E (10^{-3})	D^*/D^*_E
AgAu	1350	0.4379	0.990	1.086	-3.732	1.173	0.93
AuCu	1300	0.4451	0.947	0.924	-3.821	1.073	0.86
BiCd	773	0.4134	1.136	1.695	-3.362	1.698	1.00
BiSn	608	0.4381	0.988	1.075	-3.736	1.168	0.92
CdSn	773	0.4233	1.077	1.444	-3.484	1.503	0.96
CdPb	773	0.4279	1.049	1.305	-3.555	1.401	0.93
CdTl	673	0.4408	0.972	1.015	-3.782	1.116	0.91
CdZn	800	0.426	1.061	1.353	-3.523	1.446	0.94
InZn	700	0.4311	1.030	1.184	-3.652	1.271	0.93
NaK	373	0.4175	1.111	1.510	-3.419	1.605	0.94
PbSn	773	0.4231	1.078	1.455	-3.467	1.529	0.95
SnZn	700	0.4341	1.013	1.116	-3.692	1.221	0.91
BiHg	594	0.428	1.049	1.320	-3.533	1.432	0.92
BiPb	700	0.4261	1.060	1.373	-3.533	1.431	0.96
CdIn	723	0.4279	1.049	1.321	-3.565	1.387	0.95
HgSn	423	0.4609	0.852	0.677	-4.146	0.775	0.87
HgZn	608	0.4312	1.029	1.165	-3.712	1.197	0.97
CdHg	600	0.4345	1.010	1.156	-3.698	1.214	0.95
PbZn	926	0.4067	1.163	1.829	-3.221	1.956	0.94

Table 4

Compound-forming alloys ($c_1 = c_2 = 0.5$) without volume change on mixing ($\delta \Omega = 0$). These 10 alloys form compounds in the solid phase or they are considered in some other way more complex (see Wilson /18/). The values of ξ, D^*, S_E and D^*_E are obtained from Eqs.(2),(8), (9) and (10), respectively. The values of C_{AGW}, which are dependent on packing fraction ξ, are obtained by the chord approximation using molecular dynamics of Alder *et al.* /11,20/.

Alloy	T (K)	ξ	C_{AGW}	D^* (10^{-3})	S_E (k_B)	D^*_E (10^{-3})	D^*/D^*_E
CuZn	1200	0.4019	1.177	2.052	-3.263	1.875	1.09
AlMg	1000	0.4149	1.127	1.678	-3.358	1.706	0.98
BiMg	973	0.3871	1.220	2.427	-2.993	2.456	0.99
CdSb	773	0.4266	1.057	1.349	-3.535	1.429	0.94
HgK	600	0.3598	1.276	2.791	-2.856	2.818	0.99
HgNa	648	0.3717	1.265	2.903	-2.840	2.863	1.01
MgPb	823	0.4235	1.075	1.326	-3.490	1.495	0.89
MgSn	1043	0.3931	1.202	2.350	-3.022	2.385	0.99
MgZn	923	0.4155	1.123	1.619	-3.335	1.745	0.93
SbZn	823	0.4203	1.095	1.454	-3.441	1.570	0.93

3 and 4, the degree of agreement between D^* and D_E^* is remarkable. The log of D^* versus S_E/k_B is plotted in Fig. 1 for 19 simple alloys and in Fig. 2 for 10 compound- forming alloys. These two figures show a close variation as a function of $\neg S_E/k_B$ in the dimensionless diffusion coefficients D^* and D^*_E. However, if the results are plotted without the correction factor $C_{AGW}(\xi)$, poor agreement should be cited.

Table 5 shows numerical results of ξ, σ_{12} and C_{AGW} when the measured excess volume $\delta\Omega$ on alloying is incorporated into calculation. The volumes of alloys are estimated by applying percentage deviations shown in the table to the pure metal volume data already calculated, i.e., $\Omega = \Omega_0(1+\delta\Omega/\Omega_0)$ where $\Omega_0 = c_1\Omega_1 + c_2\Omega_2$, with Ω_1 and Ω_2 being the specific volumes for pure liquid metals at the same temperature. It needs to be remembered that the experimentally determined excess volumes are not always known accurately (see also the caption to the table of Ref./9/). As mentioned in Ref. 9, the percentage excess volumes are of prime importance, yet these are often quoted by Wilson /18/ (his data are given in the table) to one-figure accuracy only. The results of D^*, D^*/D^*_E, D_{12}, η_{12} and γ_{12} for 13 alloys are summarized in Table 6. All these alloys listed in Tables 5 and 6 have small volume changes on alloying. As seen from the fourth column of Table 6, the degree of agreement between D^* and D^*_E is better than that shown in Table 3 for the corresponding alloys. A comparison of D^* with D^*_E is made in Fig. 3 for demonstrating the significance of the excess volumes. In order to test the validity of the scaling law displayed in Fig. 3, we estimated the values of D_{12}, η_{12} and γ_{12}. The values of D_{12} estimated from Eq. (21) are summarized in Table 6. The values of η_{12} and γ_{12} are also evaluated using the values of σ_{12} and ξ given in Table 5 and of D_{12} in Table 6. It should be remembered that the interdiffusion coefficient D_{12} has the uncertainty of the order of 10 %. Unfortunately, no experimental values of D_{12} are available within the best knowledge of the present authors, so that it is difficult to give here about quantitative discussion in detail.

Table 5

Input data of the present calculation for 13 alloys ($c_1 = c_2 = 0.5$) with volume change on alloying. $\Omega = \Omega_0(1+\delta\Omega/\Omega_0)$, where $\Omega_0 = c_1\Omega_1 + c_2\Omega_2$ with c_1 and $c_2 = 0.5$. The values of $\delta\Omega/\Omega_0$ are taken from the table of Ref./9/. $\sigma_{12}(\mathrm{m}) = \sigma_{12}(\mathrm{au})\cdot a_B$, $\delta\Omega\,(\mathrm{m}^3) = \delta\Omega\,(\mathrm{au})\cdot a_B^3$, $\Omega_0(\mathrm{m}^3) = \Omega_0(\mathrm{au})\cdot a_B^3$ and $\Omega\,(\mathrm{m}^3) = \Omega\,(\mathrm{au})\cdot a_B^3$ where a_B is the Bohr radius ($a_B = 0.529177\times10^{-10}(\mathrm{m})$). The values of C_{AGW}, which are dependent on packing fraction ξ, are obtained by the chord approximation using molecular dynamics of Alder *et al.* /11, 20/.

Alloy	T (K)	$\delta\Omega$ (au)	Ω_0 (au)	$\delta\Omega/\Omega_0$	Ω (au)	ξ	σ_{12} (au)	C_{AGW}
AgAu	1350	0.00	129.45	0.000	129.45	0.4379	4.7660	0.990
BiCd	773	3.60	200.20	0.018	203.80	0.4061	5.4068	1.164
BiSn	608	-0.85	213.15	-0.004	212.30	0.4399	5.6289	0.978
CdSn	773	3.20	177.81	0.018	181.01	0.4158	5.2383	1.121
CdPb	773	1.53	191.60	0.008	193.13	0.4245	5.3900	1.069
CdTl	673	1.82	182.00	0.010	183.82	0.4365	5.3512	0.998
CdZn	800	0.83	137.60	0.006	138.43	0.4234	4.8195	1.076
InZn	700	0.75	150.25	0.005	151.00	0.4290	4.9828	1.043
PbSn	773	0.21	208.38	0.001	208.58	0.4227	5.5219	1.081
SnZn	700	2.29	152.50	0.015	154.79	0.4277	5.0189	1.051
BiPb	700	0.69	228.65	0.003	229.34	0.4249	5.7092	1.067
CdIn	723	1.22	174.65	0.007	175.87	0.4249	5.2260	1.067
PbZn	926	(1.71)	171.40	(0.010)	173.11	0.4026	5.1060	1.175

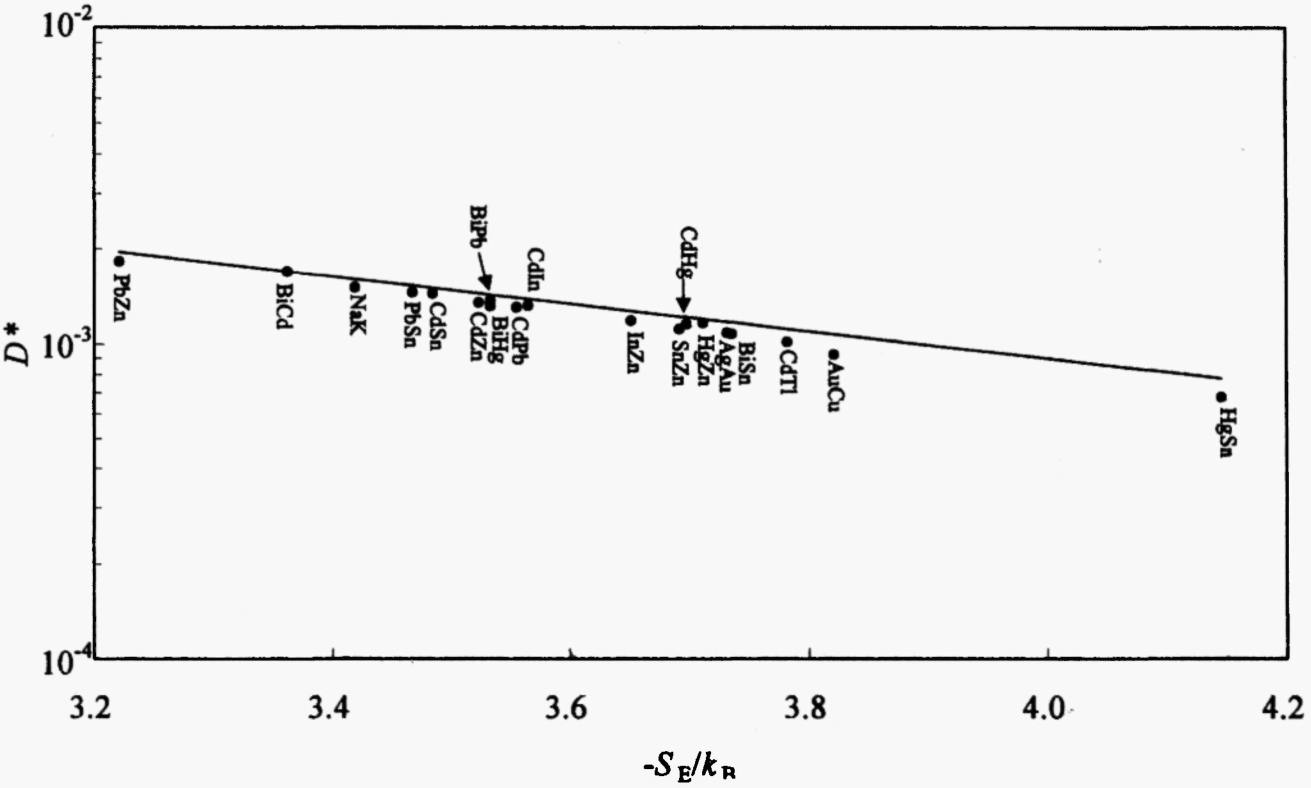

Fig. 1: The scaled diffusion coefficient D^* for simple alloys as a function of the excess entropy S_E (expressed in units of k_B). D^* is dimensionless diffusion coefficient defined by Eq. (8). The solid line denotes D^*_E obtained from Eq.(10).

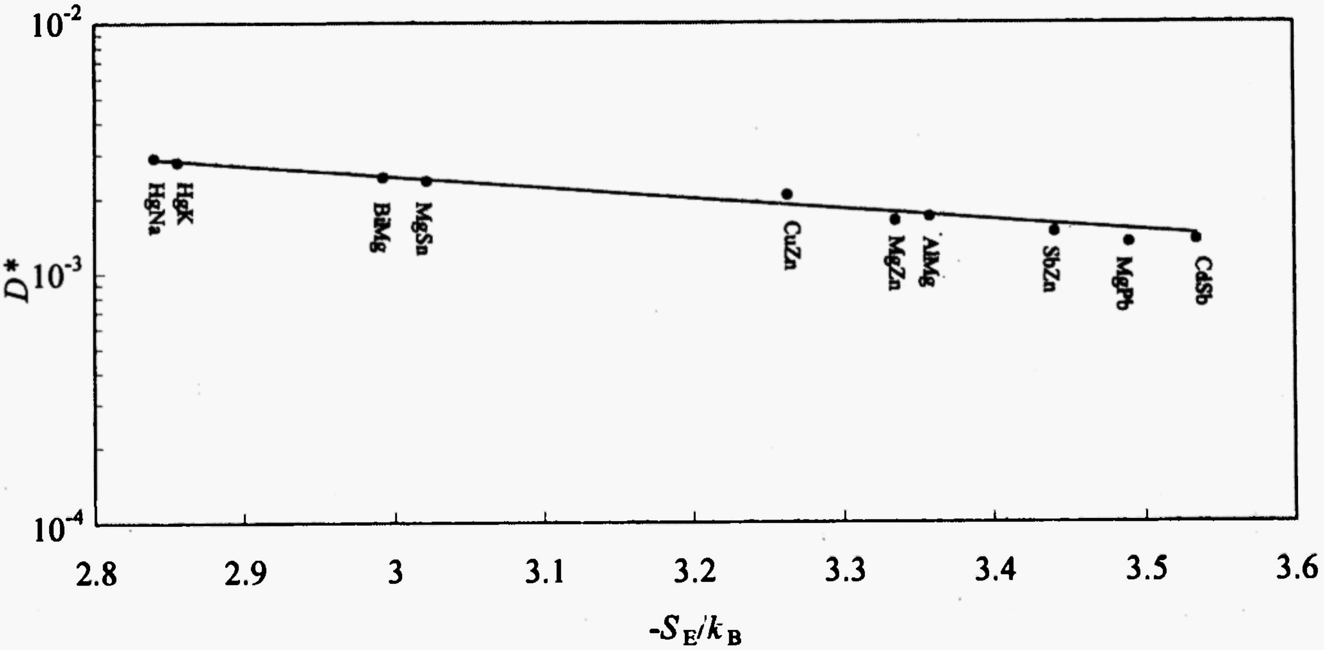

Fig. 2: The scaled diffusion coefficient D^* for compound-forming alloys as a function of the excess entropy S_E (expressed in units of k_B). D^* is dimensionless diffusion coefficient defined by Eq. (8). The solid line denotes D^*_E obtained from Eq.(10).

Table 6

D_{12}, η_{12} and γ_{12} of 13 alloys ($c_1 = c_2 = 0.5$) with volume change on alloying. The values of S_E and D^*_E are given in Table 3. The values of D_{12}, which has errors within about 10 %, η_{12} and γ_{12} are obtained from Eqs.(21), (24) and (27), respectively.

Alloy	T (K)	D^* (10^{-3})	D^*/D^*_E	D_{12} (10^{-9} m^{2}s^{-1})	η_{12} (mPas)	γ_{12} (Nm^{-1})
AgAu	1350	1.086	0.93	4.03	2.89 ~ 3.48	0.736 ~ 0.885
BiCd	773	1.855	1.09	4.85	1.17 ~ 1.42	0.221 ~ 0.267
BiSn	608	1.046	0.90	3.01	1.48 ~ 1.77	0.243 ~ 0.292
CdSn	773	1.610	1.07	4.81	1.23 ~ 1.48	0.273 ~ 0.327
CdPb	773	1.373	0.98	3.98	1.46 ~ 1.74	0.273 ~ 0.327
CdTl	673	1.086	0.97	3.17	1.63 ~ 1.96	0.287 ~ 0.345
CdZn	800	1.405	0.97	4.89	1.37 ~ 1.64	0.351 ~ 0.421
InZn	700	1.223	0.96	4.35	1.31 ~ 1.58	0.314 ~ 0.376
PbSn	773	1.464	0.96	4.14	1.36 ~ 1.63	0.253 ~ 0.303
SnZn	700	1.229	1.01	4.39	1.29 ~ 1.55	0.305 ~ 0.366
BiPb	700	1.400	0.98	3.38	1.47 ~ 1.76	0.229 ~ 0.274
CdIn	723	1.381	1.00	4.23	1.32 ~ 1.58	0.284~ 0.341
PbZn	926	1.914	0.98	6.25	1.15 ~ 1.38	0.258 ~ 0.308

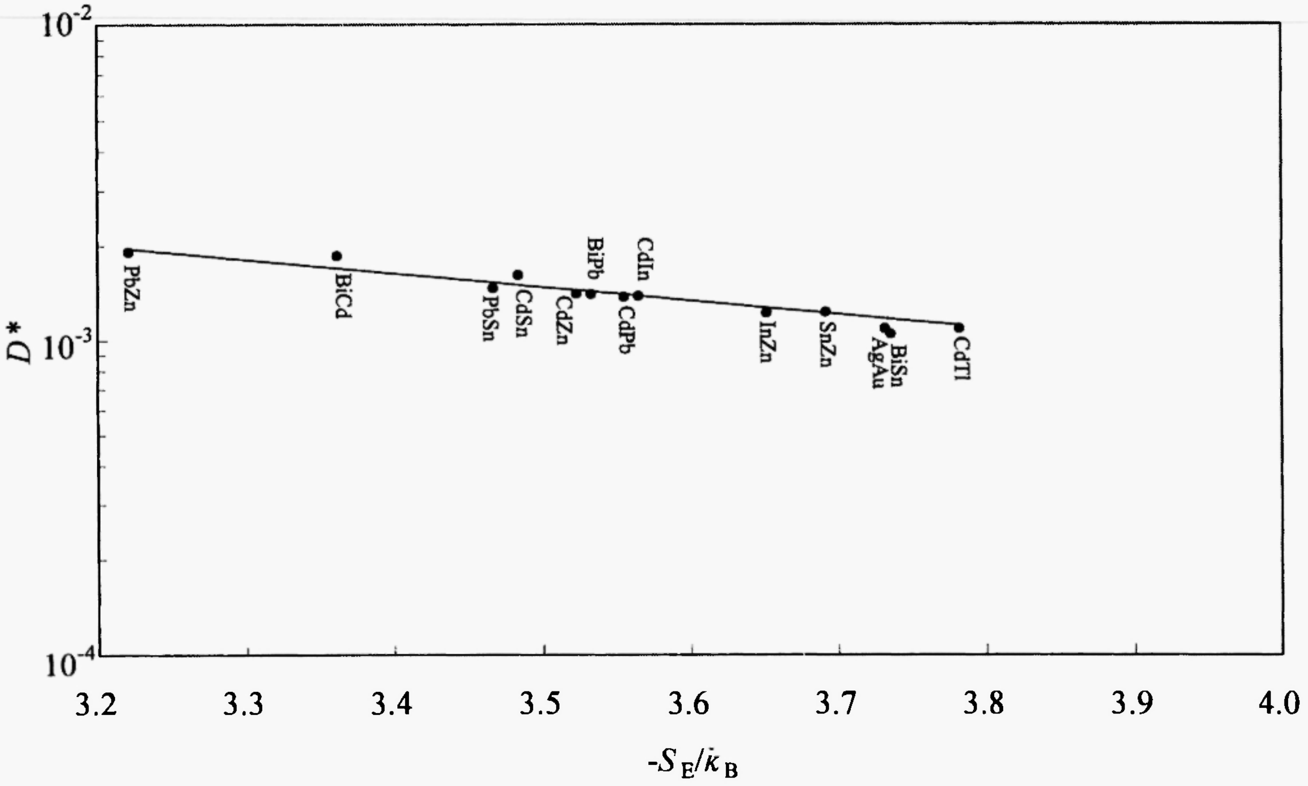

Fig. 3: The scaled diffusion coefficient D^* for 13 alloys with volume change on alloying as a function of the excess entropy S_E (expressed in units of k_B). D^* is dimensionless diffusion coefficient defined by Eq.(8). The solid line denotes D^*_E obtained from Eq.(10).

4. DISCUSSION

At first, we investigated 13 alloys with small volume change on alloying. Next, the Dzugutov scaling law /1, 2/ was examined when volume changes on alloying are significant. Let us take HgK and HgNa alloys for example, these two alloys have negative excess volumes as much as 20% as listed in Table 7. As also seen from the results of D^*/D^*_E in Table 8, the scaling law obviously does not hold for these two alloys.

The excess volume is considered to play a crucial role. The reason is that Eqs. (4a) and (4b) of the contact distribution functions in mixtures of additive hard-spheres cannot be used for liquids exhibiting chemical short-range order such as HgK and HgNa. For the compound- forming alloys with large excess volumes, the experimental data of g_{11}, g_{22}, and g_{12} must be used in formulae of Eqs. (3) and (7) (similar expressions for D_2 as well). In cases of alloys with chemical short-range order, σ_{11}, σ_{22} and σ_{12} can be interpreted as the position of the first maximum of g_{11}, g_{22}, and g_{12}, respectively. Therefore, it would be expected to predict D^* with sufficient reliability, when the experimental data of g_{11}, g_{22}, g_{12}, σ_{11}, σ_{22} and σ_{12} are used in Eqs. (3) and (7).

On the other hand, Eq.(21) is also not applicable to the system with chemical short-range order. According to Shimoji and Itami /20/, the following important relation for the interdiffusion coefficient D_{12} has been proposed by Darken /24/ in terms of the long wavelength limit of concentration fluctuations ,$S_{CC}(0)$:

$$D_{12} = (c_2 D_1 + c_1 D_2) c_1 c_2 / S_{cc}(0) . \qquad (28)$$

For the regular solution /14/, $S_{CC}(0)$ is given by

$$S_{cc}(0) = \frac{c_1 c_2}{1 - 2c_1 c_2 w / (k_B T)} , \qquad (29)$$

where w is the interchange energy, frequently estimated from the experimental heat of mixing data. Then, Eq.(28) takes the form

$$D_{12} = (c_2 D_1 + c_1 D_2)(1 - 2c_1 c_2 w / (k_B T)) . \qquad (30)$$

This equation indicates that the last factor is larger than unity for $w < 0$ (or the heat of mixing $\Delta H < 0$) and is smaller than unity for $w > 0$ (or$\Delta H > 0$). For an ideal solution, $w = 0$ and it is noteworthy that the Darken relation /24/ (Eq.(30)) becomes Eq. (21).

5. CONCLUSIONS

The concluding remarks drawn from the present work can be summarized.

1. The Dzugutov scaling law holds well for 29 binary alloys in the equiatomic composition ranges when volume changes on mixing are not taken into

Table 7

Input data of another calculation for HgK and HgNa with volume changes on alloying.

Alloy	T (K)	$\delta\Omega$ (au)	Ω_0 (au)	$\delta\Omega/\Omega_0$	Ω (au)	ξ	σ_{12} (au)	C_{AGW}
HgK	600	-93.53	374.10	-0.25	280.58	0.4797	6.3582	0.688
HgNa	648	-47.46	237.30	-0.20	189.84	0.4647	5.5231	0.824

Table 8

D^* and D^*_E of HgK and HgNa with volume changes on alloying.

Alloy	T (K)	D^* (10^{-3})	D^*_E (10^{-3})	D^*/D^*_E
HgK	600	0.498	2.818	0.18
HgNa	648	0.814	2.863	0.28

account. This was confirmed on the basis of a hard-sphere model.

2. The interdiffusion coefficient D_{12} was estimated for 13 alloys with volume changes less than 2%. It would be suggested that the values of D_{12} can be obtained within the uncertainty of the order of ±10%.
3. The viscosity coefficient, η_{12}, and the surface tension, γ_{12}, were also estimated using the modified Stokes-Einstein relation. The usefulness and validity of the Dzugutov scaling law are recognized as displayed in Fig. 3 and the predicted values of η_{12} and γ_{12} are considered to be reliable. Nevertheless, it should be mentioned that accurate experimental data of the structure and excess volume at the desired temperature are highly desirable for estimating the values of D_{12}, η_{12} and γ_{12} and therefore a definite conclusion for the formalism used in this work cannot be given from the present results alone.

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