Surface Tension and Its Temperature Coefficient for Liquid Metals

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Temperature-dependent surface tension $\gamma_{lv}(T)$ and its temperature coefficient $\gamma'_{lv}(T)$ [$=d\gamma_{lv}(T)/dT$] for liquid metals are thermodynamically determined on the basis of an established model for surface energy of crystals. The model predictions correspond to the available experimental or theoretical results. It is found that for metallic liquids $\gamma_{lv}(T_m) \propto H_v/V_m^{2/3}$, $\gamma_{lv}(T) \propto T$, and $\gamma'_{lv}(T) \propto T$ over a certain temperature range (including $T < T_m$ and $T \geq T_m$), where H_v and V_m are the liquid−vapor transition enthalpy at boiling temperature T_b and the atomic volume at melting temperature T_m, respectively. Furthermore, $T_m\gamma'_{lv}(T_m)/\gamma_{lv}(T_m)$ almost remains constant, which gives a way to estimates of $\gamma'_{lv}(T_m)$ values when T_m and $\gamma_{lv}(T_m)$ are known.

Introduction

$\gamma_{lv}(T)$ is known to be one of the fundamental and important quantities in the theory and practice of materials processing (e.g., crystal growth, welding, and sintering), and $\gamma'_{lv}(T)$ governs the well-known Marangoni convection on the surface of melt. There are several characteristics of the liquid surface. First, the liquid surface usually takes an equilibrium configuration with the minimum energy due to the high mobility of liquid molecules.[1] Second, because the liquid fails with respect to elastic deformation resistance, $\gamma_{lv}(T)$ (surface tension) equals surface stress when surface adsorption is not taken into account, which is defined as the reversible work per unit area involved in forming a new surface of a substance plastically.[1] Although early methods of measurement of $\gamma_{lv}(T)$ are sufficiently precise, there is still uncertainty regarding its absolute values and particularly regarding the $\gamma'_{lv}(T)$ function mainly due to the effect of impurities, which strongly changes the measured results. Therefore, considerable efforts have recently been directed toward the experimental determinations of $\gamma_{lv}(T)$ and $\gamma'_{lv}(T)$ of metals, and progress has been achieved with the advent of levitation processing and oscillating drop techniques.[2−4] However, such an experiment often suffers from the ambiguities in the interpretation of the resulting frequency spectra,[2] and it is also unlikely that experimental measurements will ever encompass all possible temperature ranges of interest for all metals.

In contrast to the determination of the $\gamma_{lv}(T_m)$ value, the $\gamma'_{lv}(T_m)$ value is not well-known experimentally even for elemental metallic liquids.[5] A recent analysis of existing data shows that this quantity is known with accuracy better than 50% for only 19 metals while for 28 metals, the accuracy is worse, For 18 metals (mainly refractory metals), there are no experimental results.[5]

Computer simulations with Monte Carlo or molecular dynamics methods are also considered to be one of the reliable methods[6] with which γ_{lv} can be calculated either using the mechanical expression for the surface stress or from the viewpoint of the surface energy. Unfortunately, the former approach suffers from rather high fluctuation and statistical

uncertainty, while the latter introduces additional complexity into the performance. Thus, the demand of developing reliable prediction methods has never declined.

Semiempirical predictions based on the correlation between the surface and bulk thermodynamic properties are always possible.[7−11] Stephan first links γ_{lv} to the heat of evaporation H_v' at 0 K[7]

$$\gamma_{lv}(T_m) = c'H_v'/V_m^{2/3} \tag{1}$$

with c' being an unknown constant. Since there is no suitable theoretical determination of c', eq 1 seems to apply to only transition metals.[5,7] Although eq 1 has existed for more than 100 years, attempts to theoretically determine c' are rare.

On the other hand, $\gamma_{lv}(T)$ of pure substances may be evaluated from values of critical temperature T_c by the Eötvos or Guggenheim empirical equations[12]

$$\gamma_{lv}(T)V^{2/3} = A + BT; \quad T_c = -A/B \tag{2a}$$

or

$$\gamma_{lv}(T)/\gamma_{lv}(T_m) = (1 - T/T_c)^a \tag{2b}$$

where the exponent a is system-dependent, e.g., $^4/_5$ for strongly hydrogen bonded substances or $^{11}/_9$ for H_2, N_2, CO, etc.[12] However, an a value for liquid metals has not been determined to the best of our knowledge. Moreover, unlike those of organic fluids, T_c values of liquid metals are only available for alkali metals and mercury,[13] which severely restricts the use of eq 2a.

When $\gamma_{lv}(T_m)$ and $\gamma'_{lv}(T_m)$ values are known, under the assumption that $\gamma'_{lv}(T)$ is nearly a constant being equal to $\gamma'_{lv}(T_m)$, the $\gamma_{lv}(T)$ function is also calculated by[14]

$$\gamma_{lv}(T) = \gamma_{lv}(T_m) + \gamma'_{lv}(T_m)(T - T_m) \tag{3}$$

However, eq 3 has not been strictly examined. Thus, both $\gamma_{lv}(T)$ and $\gamma'_{lv}(T)$ functions need to be further considered.

Recently, through modification of the classic broken-bond rule, an improved formula for calculating the solid−vapor surface energy of elemental crystals (γ_{sv}) has been

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developed and is expressed as[15]

$$\gamma_{sv} = mE/(N_a A_S) \tag{4}$$

where $m = [(2 - k_1 - k_1^{1/2}) + \beta(2 - k_2 - k_2^{1/2})]/[2(1 + \beta)]$, where k is the ratio of the coordination number between surface atoms and the corresponding bulk atoms and subscripts 1 and 2 denote the nearest neighbor and next-nearest neighbor, respectively, and β denotes the total bond strength ratio between the next-nearest neighbor and the nearest neighbor. E is the cohesive energy at 0 K. A_S is the area of the two-dimensional unit cell of solid, and N_a is Avogadro's number. The predictions in terms of eq 3 for 52 elemental crystals agree with experimental and the first-principles calculations, although deviations are present for several divalent sp metals.[15] Because of the structural similarity of the liquid and solid at least near T_m, eq 4 for γ_{sv} should give suggestions for γ_{lv} modeling and analytical determination of the c' value in eq 1.

In this paper, the $\gamma_{lv}(T)$ and $\gamma'_{lv}(T)$ functions are quantitatively developed on the basis of eq 4. The model predictions for 48 elements correspond to the available experimental or theoretical results. In terms of these agreements, some characteristics of $\gamma_{lv}(T)$ and $\gamma'_{lv}(T)$ functions are further discussed.

Model

Approximately 60 years ago, noting that fusion has only small effects on the volume, cohesive forces, and specific heat of substance, Frenkel reached the conclusion that "the character of the heat motion in liquid bodies, at least near the crystallization point, remains fundamentally the same as in solid bodies, reducing mainly to small vibrations about certain equilibrium position".[16] The very slight change in volume on melting is also thought to imply that the atoms in a liquid are tightly bound to one another like those in a crystalline solid.[17] Thus, the structural and energetic differences between a solid and a liquid are very small in comparison with those between a solid and a gas or between a liquid and a gas. Consequently, eq 4 can be extended to determine γ_{lv} with several modifications. (i) Since $T \geq T_m$ for all the amounts that have been studied, which is much higher than 0 K, E at 0 K should be replaced by $H_v(T)$ and A_S should be substituted with $A_L(T)$, where the subscript L denotes liquid. (ii) The influence of the molar excess surface entropy $S(T)$ should contribute γ_{lv} due to the high temperature. (iii) The first coordination number of a liquid is usually determined by integrating the radial distribution function (RDF) up to the first minimum, while the distance of the second minimum of RDF is approximately twice that; the effect of the next nearest neighbors thus may be neglected in terms of the Lennard-Jones potential function, namely, $\beta \approx 0$. Thus, eq 4 can be rewritten for determining $\gamma_{lv}(T)$

$$\gamma_{lv}(T) = [m'H_v(T) - TS(T)]/[N_a A_L(T)] \tag{5}$$

where $m' = (2 - k_1 - k_1^{1/2})/2$.

Since metallic liquid is closely packed, the packing density of a random close packing ($\eta = 0.637$) can be employed for the liquid.[18] As discussed in ref 19, the volume change on melting $\Delta V/V$ is not solely determined by the difference in packing density η between two phases. The Goldschmidt premise for lattice contraction should also be considered.[19] Otherwise, when the η_L of 0.637 is compared with the η_{fcc} of 0.74, $\Delta V/V = \eta_{fcc}/\eta_L - 1 \approx 16\%$, which is larger than the experimentally observed value of 2-6%.[19] Note that the η_L of 0.637 is the maximum value that the single-component liquid can take, which leads to the fact that the specific volume

difference between a solid with bcc structure and the corresponding liquid is only 0.2% in terms of eq 2 of ref 19. Whether a metal can be undercooled depends on the energetic nucleation barrier. When the volume change upon crystallization is small, the corresponding nucleation barrier should be also small, which leads to a large degree of undercooling.[20] If this rule can also be applied to elementary substance, the local order in the metallic liquid is very similar to the bcc-type short-range order (SRO).[21] This is the case for liquid Zr.[22] Correspondingly, this consideration can also be applied on the surface structure of liquid metals with a similar (110) surface of bcc structure to ensure the minimum of the surface energy.[8] Thus, the expression of A_{bcc} is assumed to be applicable also to the liquid as a first-order approximation. As a result, $k_1 = {}^3/_4$ and $A_L = 8^{1/2}h^2/3$, with h being the atomic diameter. For any pure, isotropic, condensed material, $h = (6\eta V/\pi)^{1/3}$. V can be calculated from atomic weight M and $\rho(T)$ by the relation $V = M/[N_a\rho(T)]$. Thus, $A_L(T)$ can be determined as

$$A_L(T) = f\{M/[N_a\rho_L(T)]\}^{2/3} \tag{6}$$

where $f = (8^{1/2}/3)(6\eta/\pi)^{2/3}$. $\rho_L(T)$ is equal to $\rho_L(T_m) + (d\rho_L/dT)(T - T_m)$ with $d\rho_L/dT$ being the temperature coefficient of liquid density since $d\rho_L/dT \approx d\rho_L(T_m)/dT$ for liquid metals in the temperature range of T_m-2T_m. This range could be up to $3T_m$ for Rb and Cs and $4T_m$ for Li and K.[23]

It is known that $H_v(T)$ for most substances is zero at critical temperature T_c and reaches the maximum at triple point T_t, where T_t is very close to T_m for metals.[24] Recently, the empirical equation $H_v(T)/H_v(T_m) = (1 - t)^{it+j}$ has been proposed for liquids having a triple point where $t = (T - T_m)/(T_c - T_m)$, $i = 0.44$, and $j = -0.137$.[25] In terms of the known T_m, T_b, and T_c values for alkali metals (mercury is not involved in this work),[13] it is found that the temperature dependence of $H_v(T)$ between T_m and T_b is very small (<2%) and thus negligible. Moreover, it is reported that the $H_v(T_m)$ values of Cd, Cr, Mn, and Zn are 101, 344, 234, and 115 kJ/mol, respectively, while the corresponding $H_v(T_b)$ values are 100, 339, 226, and 119 kJ/mol, respectively.[13,24] Their differences are smaller than 3.5%. Thus, the relation $H_v(T_m \leq T \leq T_b) \approx H_v(T_m) \approx H_v$ does not lead to a large deviation and can be accepted as a first-order approximation.

In Skapski's model,[8] the main contribution to surface entropy S results from the change in oscillation frequency ν of atoms in the surface. Note that according to the Lindemann criterion,[26] the mean value of ν reaches a certain value at T_m, which leads to a constant S value at T_m. It is known that H_v determines the bond strength of liquid atoms, which further determines the size of ν. Since $H_v(T)$ varies little between T_m and T_b, the temperature dependence of $S(T)$ is thus negligible and the equation $S(T) \approx S(T_m) \approx S$ can also be assumed.

With these considerations and insertion of eq 6 into eq 5, $\gamma_{lv}(T)$ between T_m and T_b can be determined as

$$\gamma_{lv}(T) = \left(\frac{m'H_v - TS}{fN_a^{1/3}}\right)\left[\frac{\rho_L(T)}{M}\right]^{2/3} \tag{7a}$$

or

$$\frac{\gamma_{lv}(T)}{\gamma_{lv}(T_m)} = \left(1 + p - p\frac{T}{T_m}\right)\left(1 - q + q\frac{T}{T_m}\right)^{2/3} \tag{7b}$$

where $p = 1/[m'H_v/(T_mS) - 1]$ and $q = (d\rho_L/dT)[T_m/\rho_L(T_m)]$ and are constants for certain metals.

Temperature Coefficient of Liquid Metals

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TABLE 1: Comparison of γ_{lv} Values for Liquid Metals between $\gamma_{lv}(T_m)$ of eq 7a and Experimental Results for $\gamma_{lv}{}^e(T_m)$,[5,14,27] as Well as Comparison of γ'_{lv} between $\gamma'_{lv}(T_m)$ of eq 8 and Experimental or Estimated Results for $\gamma'_{lv}{}^3(T_m)$[5,14,27,28]

	$\gamma_{lv}(T_m)$ (mJ/m²)	$\gamma_{lv}{}^e(T_m)$ (mJ/m²)	$-\gamma'_{lv}(T_m)$ (mJ m⁻² K⁻¹)	$-\gamma'_{lv}{}^e(T_m)$ (mJ m⁻² K⁻¹)	H_v (kJ/mol)	T_m (K)	ρ_L (kg/m³)	$d\rho_L/dT$ (kg m⁻³ K⁻¹)
Cu[a]	1352	1355, 1310	0.21	0.19, 0.23	300	1358	8000	−0.801
Ag[a]	925	910, 925	0.18	0.17, 0.21	255	1234	9346	−0.907
Au[a]	1211	1138, 1145	0.18	0.19, 0.20	330	1338	17360	−1.500
Ni[a]	1810	1838, 1796	0.33	0.42, 0.35	378	1728	7905	−1.160
Pd	1467	1475, 1482	0.25	0.28, 0.28	380	1828	10490	−1.266
Pt[a]	1896	1746, 1860	0.31	0.29, 0.31	490	2045	19000	−2.900
Co[a]	1779	1830, 1881	0.30	0.37, 0.34	375	1768	7760	−0.988
Rh	2010	2000, 1970	0.26	0.30, 0.66	495	2237	10800	−0.896
Ir[a]	2241	2140, 2250	0.20	0.23, 0.25	560	2716	20000	−0.935
Fe[a]	1650	1830, 1855	0.26	0.23, 0.39	355	1811	7015	−0.883
Ru	2363	2180, 2250		0.31	580	2607	10900	
Os	2508	2500, 2500		0.23	630	3306	20100	
Mn	986	1152, 1100	0.21	0.20, 0.35	226	1519	5730	−0.700
Tc	2245	2350			550	2430	10300	
Re[a]	2755	2520, 2700	0.20	0.23	705	3459	18800	−0.800
Cr	1582	1628, 1642	0.19	0.20, 0.20	339	2180	6280	−0.300
Mo	2110	2250, 1915	0.21	0.20, 0.30	600	2896	9340	−0.743
W[a]	2676	2500, 2310	0.23	0.29, 0.21	800	3680	16200	−1.250
V[a]	1902	1855, 1900	0.23	0.19, 0.31	453	2175	5700	−0.531
Ti	1520	1525, 1500	0.27	0.26, 0.20	425	1941	4110	−0.702
Zr[a]	1669	1480, 1435	0.14	0.20, 0.17	580	2128	5800	−0.310
Hf[a]	1591	1630, 1490		0.21, 0.19	575	2506	11100	
Sc	895	939, 870		0.12, 0.12	318	1814	2846	
Y	899	872, 800		0.09, 0.09	380	1799	4243	
Ce	845	794, 740	0.09	0.07, 0.08	350	1068	6685	−0.227
Pr	782	743, 716	0.09	0.09, 0.08	330	1208	6611	−0.240
Nd	658	689, 687	0.10	0.09, 0.09	285	1297	6688	−0.528
Gd	690	664, 664		0.06, 0.06	305	1585	7140	
Th	1108	1006, 978		0.14	514	2028	10500	
U	1453	1550, 1552	0.15	0.14, 0.27	420	1405	17900	−1.031
Al[a]	1031	1070, 867	0.19	0.15, 0.16	283	933	2385	−0.280
Pb[a]	466	462, 457	0.12	0.11, 0.11	178	601	10678	−1.317
Tl[a]	439	461, 459	0.11	0.09, 0.11	165	577	11280	−1.430
Na[a]	215	200, 197	0.09	0.10, 0.09	98	371	927	−0.236
K[a]	110	112, 110	0.07	0.08, 0.07	79	337	827	−0.229
Rb	90	90, 85	0.06	0.07, 0.06	76	312	1437	−0.486
Cs[a]	73	69, 70	0.05	0.06, 0.05	69	302	1854	−0.638
Ca[a]	328	337, 366	0.09	0.11, 0.10	164	1115	1365	−0.221
Sr[a]	268	289, 286	0.08	0.08, 0.08	144	1050	2480	−0.262
Ba	231	226, 267	0.07	0.07, 0.07	150	1000	3321	−0.526
Mg	359	557, 583	0.14	0.15, 0.26	128	923	1590	−0.265
Zn	466	789, 815	0.18	0.25, 0.21	119	693	6575	−1.100
Cd	305	637, 642	0.13	0.20, 0.15	100	594	8020	−1.160
Ta[a]	2467	2180, 2010	0.22	0.25, 0.20	735	3290	15000	−1.147
Nb[a]	2335	2040, 1840	0.27	0.24, 0.18	690	2750	7830	−0.800
Li	465	404, 399	0.15	0.16, 0.15	137	454	525	−0.052
Be	1637	1350, 1320	0.24	0.29	297	1560	1690	−0.116
La	901	737, 728	0.09	0.11, 0.10	400	1193	5955	−0.237

[a] The accuracy on $\gamma'_{lv}{}^e(T_m)$ is better than 50%. $S = 5.30$ J mol⁻¹ K⁻¹,[11] $m' \approx 0.19$, H_v and T_m are cited from ref 13, while that of Hf is taken from ref 29 since it is unreasonable to assume that the H_v of 630 kJ/mol is larger than the E of 621 kJ/mol.[13,15] ρ_L and $d\rho_L/dT$ are taken from ref 28. Since the $d\rho_L/dT$ values of Rh, Ir, Re, Sr, Mo, Nb, Ta, W, V, and Zr are unavailable in ref 28, refs 23 and 30 are employed.

Derivative of eq 7a with respect to T leads to

$$-\gamma'_{lv}(T) = \frac{\gamma_{lv}(T)}{T}\left[\frac{1}{m'H_v/(TS) - 1} - \frac{2}{3}\frac{T}{\rho_L(T)}\frac{d\rho_L}{dT}\right] \quad (8)$$

Results and Discussion

A. Determination of $\gamma_{lv}(T_m)$ Values. Table 1 gives the comparison between the predicted $\gamma_{lv}(T_m)$ values for 48 liquid metals in terms of eq 7a and the corresponding available mean values of experimental $\gamma_{lv}{}^e(T_m)$ results.[5,14,27] These experimental data are mainly obtained by the maximum bubble pressure technique for low-melting-point oxidizable metals such as Na, the sessile drop technique for moderate-melting-point metals such as Cu, and the drop weight technique employed at the

extremity of a pendant wire with electron bombardment heating for refractory metals such as W.[14]

It is found that $\delta = |\gamma_{lv}(T_m) - \gamma_{lv}{}^e(T_m)|/\gamma_{lv}{}^e(T_m)$ for 40 elements (from Cu to Ba; see Table 1) and $\delta < 10\%$. Note that although a $\gamma_{lv}{}^e(T_m)$ of 867 mJ/m² was proposed for Al,[5] several measurements suggested that the most data for $\gamma_{lv}{}^e(T_m)$ of Al pertain to oxygen-saturated material and that for pure Al it could be ∼1070 mJ/m².[25,31] If this result is used, δ for Al will be only 3.6%. For divalent metals Mg, Zn, and Cd, the predictions are evidently smaller than $\gamma_{lv}{}^e(T_m)$. According to Miedema and Boom,[27] these three metals have an exceptionally stable free atomic configuration, which is close to that of rare gas. Thus, smaller $\gamma_{lv}(T_m)$ values in terms of eq 7a may be reasonable. Although δ values of Ta, Nb, Li, Be, and La range from 13 to 22%, the causes are unknown.
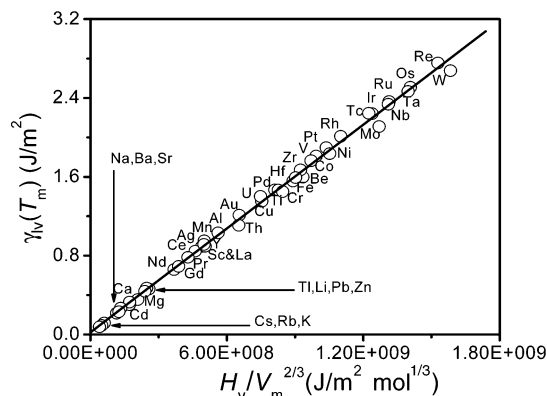
Figure 1. Plot of $\gamma_{lv}(T_m)$ vs $H_v/V_m^{2/3}$ for liquid metals in terms of eq 9 where the solid line is linearly regressed.

Figure 2. $-\gamma'_{lv}(T_m)$ as a function of $\gamma_{lv}(T_m)/T_m$ for (a) the fourth (▲), (b) the fifth (□), and (c) the sixth (▼) period A family metals where the solid lines are determined by eq 11.

The data given above imply that eq 7a is suitable not only for transition metals but also for all metals, although the deviations from transition metals are slightly larger than those for other metals.

$\gamma_{lv}(T_m)$ values of transition metals increase along an isoelectronic row, where a heavier element has a larger $\gamma_{lv}(T_m)$ value. This is because the d level of a heavier element is higher in energy and the corresponding d wave functions with stronger bonding are more extended. Two exceptions are Pd and Zr. For Pd, the fully filled d orbital drops the system energy in terms of Hund's rule, which means that its H_v value only approaches that of Ni. Since V_m and T_m values of Pd are obviously larger than those of Ni, $\gamma_{lv}(T_m)$ of Pd is thus smaller than that of Ni in terms of eq 7a. For Zr, the H_v and V_m values approach those of Hf while its T_m value is obviously smaller than that of Hf, and $\gamma_{lv}(T_m)$ of Zr is thus larger than that of Hf in terms of eq 7a. The reason for the larger H_v value of Zr is unclear.

$\gamma_{lv}(T_m)$ values of sp metals except that of Be are smaller than those of d metals because of the bond nature of s and p electrons, which are more mobile than the localized d electrons. Moreover, in contrast to the transition metals, $\gamma_{lv}(T_m)$ values of sp metals decrease along an isoelectronic row. This arises because the outmost ns electrons (the number of period $n = 2-6$) are progressively bound more loosely as they are screened from the nucleus by the increasing number of filled inner shells in the ionic core.

To find the similarity between eqs 1 and 7a, the prefactor c' in eq 1 can be determined by rearranging eq 7a at $T = T_m$, which is

$$\gamma_{lv}(T_m) = cH_v/V_m^{2/3} \qquad (9)$$

with

$$c = (m' - T_m S/H_v)/(fN_a^{1/3}) \qquad (10)$$

Equation 10 has determined the c' value in eq 1, although eq 9 differs slightly from eq 1 due to the difference between H_v and H_v', or $c = c'H_v'/H_v$.

Figure 1 gives a plot of $\gamma_{lv}(T_m)$ versus $H_v/V_m^{2/3}$ for considered liquid metals in terms of eq 9 with a linearly regressed slope c of 0.174×10^{-8} mol$^{1/3}$, where the correlation coefficient of the fit is 0.998. All elements can thus be estimated by the same c value, which implies that T_m/H_v is almost a constant (since the S value has been taken to be a constant according to Lindemann's criterion, $m' \approx 0.19$ and $f \approx 1.08$) in terms of eq 10, which also confirms the correctness of eq 9. It is known that $H_v \propto H_m^{11}$ and $T_m/H_m = 1/S_m$, where H_m and S_m are the melting
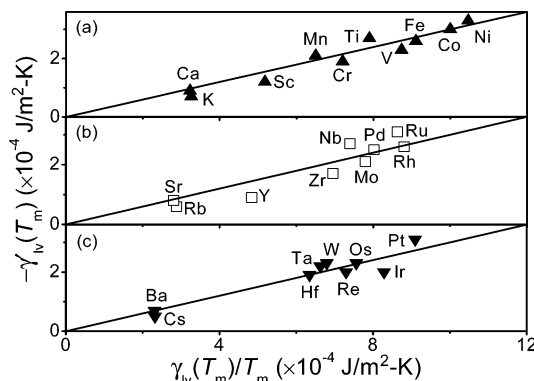
enthalpy and melting entropy, respectively. Since S_m is almost a constant for metallic elements, the c value as a constant is reasonable. In terms of the H_v' data listed in Table 1 of ref 27, it is found that H_v'/H_v is nearly a constant (≈ 1.09) for transition metals. Thus, $c = c'H_v'/H_v = 0.174 \times 10^{-8}$ mol$^{1/3}$, where $c' = 0.16 \times 10^{-8}$ mol$^{1/3}$ as determined.[5,11] In contrast to eq 1, which is considered to be suitable only for transition metals,[5,11,27] both transition and nontransition metals are involved in Figure 1. This improvement of eq 9 from eq 1 is only induced by the substitution of H_v' with $H_v(T_m)$. $H_v(T_m)$ describes the atom bonding of a stable liquid and can be exactly measured, while H_v' can be obtained only by extension of experimental results. In addition, the differences between 0 K and T_m for transition metals are larger than that for nontransition metals lead to a larger difference between $H_v(T_m)$ and H_v' for transition metals than for nontransition metals. This results in a smaller suitability range for eq 1 than for eq 9.

In terms of eq 7a, the introduction of S reduces the value of $\gamma_{lv}(T)$. At T_m, the decreasing extents range from 8 (for La and Ce) to 20% (for Mg and Sr).

B. Determination of $\gamma'_{lv}(T_m)$ Values. Table 1 also shows the comparison between $\gamma'_{lv}(T_m)$ values in terms of eq 8 and the available experimental or estimated results for $\gamma'^e_{lv}(T_m)$.[5,14,27,28] Good agreement is also found, which indicates that eq 8 provides a satisfactory description for $\gamma'_{lv}(T_m)$.

Equation 8 when $T = T_m$ can be written as

$$-\gamma'_{lv}(T_m) = (p - 2q/3)\gamma_{lv}(T_m)/T_m \qquad (11)$$

In terms of the expressions for c and p, $p = m'/(cfN_a^{1/3}) \approx 0.19$. If a mean value of -0.17 is assumed for $q = (d\rho_L/dT)[T_m/\rho_{L^-}(T_m)]$, slope $\varphi = p - 2q/3 \approx 0.30$.

The relations between $-\gamma'_{lv}(T_m)$ and $\gamma_{lv}(T_m)/T_m$ for the fourth, fifth, and sixth periods are plotted in Figure 2 in terms of eq 11 with the given slope φ being equal to 0.30, where $-\gamma'_{lv}(T_m)$ functions increase almost linearly with an increase in $\gamma_{lv}(T_m)/T_m$ for the A family metals in the same period, and the sequence is nearly the same as that in the periodic table of the elements, although some deviations appear. It is understandable since their outermost electric configurations of s+d electrons undergo nearly the same situation from the leftmost (IA metals) of one to the rightmost (VIIIA metals) of 10 in these periods. The exceptions are as follows. (i) In the fourth period (from K to Ni), the anomalies of Mn and Cr are present where their 3d orbital is half-filled. (ii) Similarly, the appearance of the full 4d orbital also results in the anomaly of Pd of the fifth period (from Rb to Pd). On the other hand, the occurrence of a half-full 4d orbital in Mo does not change the sequence; the half-
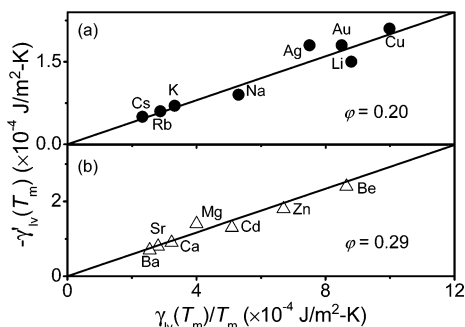
Temperature Coefficient of Liquid Metals

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Figure 3. $-\gamma'_{lv}(T_m)$ as a function of $\gamma_{lv}(T_m)/T_m$ for (a) IA and IB (●) as well as (b) IIA and IIB (△) metals.

full 5d orbital of Re in the sixth period (from Cs to Pt) also does not change it. These may be explained as follows. In terms of Hund's rule, the half and full fillings of an orbital usually lead to a decrease in the system energy and the effect of full filling is more effective. For example, the H_v values of Cr and Mn are evidently smaller than those of neighbor elements V and Fe as shown in Table 1. It is also applicable to Pd in comparison with Rh (Ag is not involved because Ag is a B family metal). While the increase in the electronic shell decreases the effect of electric configuration, the H_v value of Mo (Re) is thus between those of Nb (W) and Tc (Os). Since $\gamma_{lv}(T_m)$ is proportional to the total energetic level of the system H_v in terms of eq 8, the abnormity only happens in Cr, Mn, and Pd.

Note that Tc and the lanthanide elements are not involved in Figure 2 because the $\gamma'_{lv}(T_m)$ value of Tc is absent while those of the lanthanide elements are abnormally small possibly due to the effect of f electrons on the $\gamma'_{lv}(T_m)$ value. Since the s+d electrons of most lanthanide elements remain constant, their $\gamma'_{lv}(T_m)$ values hardly change as shown in Table 1, and the corresponding φ values thus approach zero. In other words, f electrons hardly work as valence electrons.

When elements with empty or fully filled electrons of the second outermost subshell are considered, only the outermost electron layer (*s* electron layer) is valence electrons, and two groups of elements exist, namely, cases in which $s = 1$ (IA and IB metals) and $s = 2$ (IIA and IIB metals). A linear correlation between $\gamma'_{lv}(T_m)$ and $\gamma_{lv}(T_m)/T_m$ as shown in Figure 3 still exists. When Figures 2 and 3 are compared, the φ value of metals in groups IIA and IIB where $s = 2$ is similar to eq 11. However, the φ value for metals in groups IA and IB where $s = 1$ is 30% smaller than that when period number n remains constant.

As shown in Figures 2 and 3, all elements with the subshell of $(n - 1)$d are located at the right of the figure while all elements with the subshell of $(n - 1)$p are found at the left of the figure. When the subshell is $(n - 1)$s, the elements are located in the middle or at the right of the figure. In addition, as n increases, $-\gamma'_{lv}(T_m)$ values decrease linearly. Thus, the electron orbital movements and valence electron contributions of subshells are different for different orbitals and different n values as the temperature increases. From a thermodynamic point of view, the difference in φ between Figure 3a and Figure 2 is induced by different p values in eq 11 since the corresponding H_v/T_m value is systematically larger than that of the transition metals.

Note that $\gamma_{lv}(T_m)$ values of 359, 466, and 305 mJ/m² for Mg, Zn, and Cd, respectively, based on eq 7a are employed in plotting Figures 1 and 3, and the existence of these linear correlations implies that these calculated values may be reasonable.
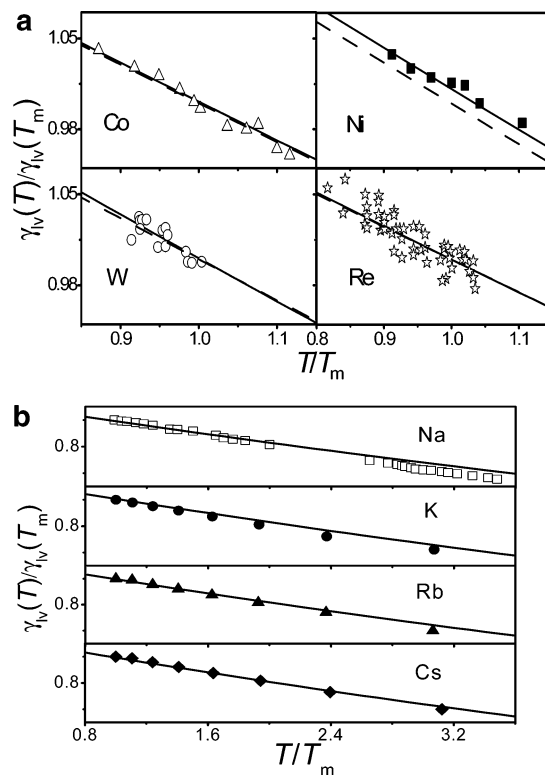

Figure 4. (a) Comparison of the $\gamma_{lv}(T)/\gamma_{lv}(T_m)$ function among the predictions of eq 7b (solid line) and eq 3 (the two-point segment) and available experimental data for transition metals Ni (■), Co (△), Re (☆), and W (○).[2,32–34] (b) Comparison of the $\gamma_{lv}(T)/\gamma_{lv}(T_m)$ function between the predictions of eq 7b (solid line) and available experimental results for nontransition alkali metals Na (□), K (●), Rb (▲), and Cs (◆).[35,36]

In terms of eq 8, the $\gamma'_{lv}(T_m)$ values are contributed by S and $d\rho_L/dT$, where the contribution of S to $\gamma'_{lv}(T_m)$ ranges from 36% (for metals such as Nb and Pt with larger γ_{lv} values) to 78% (for metals such as Cd, Li, and Sr with smaller γ_{lv} values). Neither S nor $d\rho_L/dT$ is thus negligible.

C. Estimation of $\gamma_{lv}(T)$ and $\gamma'_{lv}(T)$ Functions. Figure 4a shows the comparison of $\gamma_{lv}(T)/\gamma_{lv}(T_m)$ between the predictions of eqs 3 and 7b and the available experimental results for transition metals Ni, Co, Re, and W with good agreement.[2,32–34] The experimental data for liquid Ni, Co, Re, and W in the temperature ranges of 1573–1893, 1541–1943, 2800–3600, and 3360–3700 K, respectively, correspond to the undercooling of 155, 227, 659, and 320 K as well as the overheating of 165, 175, 141, and 20 K, respectively.[2,32–34] The plots in terms of eqs 3 and 7b are nearly identical for Co, Re, and W. Although it seems that the difference between eqs 3 and 7b is large for Ni, its actual value is only ~1%. The agreements shown in Figure 4a not only confirm the validity of eqs 3 and 7b but also indicate that the linear correlation between $\gamma_{lv}(T)$ and T exists at T near T_m (including cases in which $T < T_m$ and $T \geq T_m$); namely, eqs 3 and 7b can also be applied to supercooled liquid metals.

Figure 4b shows the comparisons of $\gamma_{lv}(T)/\gamma_{lv}(T_m)$ between the predictions of eq 7b and the available experimental results for nontransition metals Na, K, Rb, and Cs.[35,36] It is found that the differences between the predictions and the experimental data are smaller than 5% in cases where the experimental data encompass the largest temperature range (from T_m to $3.5T_m$) to the best of our knowledge. Here, the approximately linear relation between $\gamma_{lv}(T)$ and T is present again, which implies that eq 3 is a good approximation of eq 7b.

Substituting the expression $\rho_L(T) = \rho_L(T_m) + (d\rho_L/dT)(T - T_m)$ into eq 7a produces the relation $\gamma_{lv}(T) = [(m'H_v - TS)/fN_a^{1/3}]\{[1 + u(T - T_m)]/M/\rho_L(T_m)\}^{2/3}$, where $u = (d\rho_L/dT)/\rho_L(T_m)$. Since $(d\rho_L/dT)/\rho_L(T_m)$ is nearly a constant being equal to -10^{-4} K^{-1},[5,11] while $T - T_m$ values in Figure 4 are smaller than 800 K, $u(T - T_m)$ is smaller than 0.1. Considering the mathematical relation of $(1 + x)^{2/3} \approx 1 + 2x/3$ when x is sufficiently small (e.g., $x < 0.1$), eq 7a can be rewritten as $\gamma_{lv}(T) \approx (m'H_v - TS)[1 + 2u(T - T_m)/3]/(fN_a^{1/3}V_m^{2/3})$. Because $(m'H_v - TS)[1 + 2u(T - T_m)/3] = \nu + (T - T_m)\{-S + (2u\nu/3)[1 - S(T - T_m)/\nu]\}$ where $\nu = m'H_v - T_mS$, there is

$$\gamma_{lv}(T) \approx (\nu + (T - T_m)\{-S + (2u\nu/3)[1 - S(T - T_m)/\nu]\})/(fN_a^{1/3}V_m^{2/3}) \quad (12)$$

In terms of m', H_v, T_m, and S values listed in Table 1, $S(T - T_m)/\nu < 0.1$ for the most metals when $T - T_m < 800$ K and thus negligible as a first-order approximation. Thus, eq 12 can be simplified as $\gamma_{lv}(T) \approx [\nu + (-S + 2u\nu/3)(T - T_m)]/(fN_a^{1/3}V_m^{2/3})$. Since $\nu/(fN_a^{1/3}V_m^{2/3}) = \gamma_{lv}(T_m)$ and $(-S + 2u\nu/3)/(fN_a^{1/3}V_m^{2/3}) = \gamma'_{lv}(T_m)$, the agreement between eqs 3 and 7a shown in Figure 4a is not only understandable but also inevitable.

Since $\gamma_{lv}(T)$ is related to the bond strength of atoms and its derivative corresponds to the bond strength change or electron orbital change as the temperature varies, as long as the substance remains liquid and the temperature is below T_c, electron orbitals of liquids change linearly with temperature. Derivative of eq 12 with respect to T leads to

$$\gamma'_{lv}(T) \approx \gamma'_{lv}(T_m) + e(T - T_m) \quad (13)$$

where $e = -4uS/(3fN_a^{1/3}V_m^{2/3})$ being the temperature coefficient of $\gamma'_{lv}(T)$.

Equation 13 indicates that $\gamma'_{lv}(T)$ is positively proportional to T since $e > 0$ induced by $u < 0$. This tendency against T is in reverse to that of $\gamma_{lv}(T)$ because the energetic difference between a liquid and a gas drops as T increases. Although eq 13 ultimately gives a positive temperature dependence, it should be indicated that e has only a secondary effect and can be neglected by a first-order approximation. For instance, $e \approx 3.0 \times 10^{-5}$ and 1.6×10^{-5} mJ m^{-2} K^{-2} for Ni and V. Even when $T - T_m = 1000$ K, $\gamma'_{lv}(T)/\gamma'_{lv}(T_m)$ values of Ni and V are only 1.09 and 1.08, respectively, or the error range is smaller than 10%.

Note that the simulated results based on the Monte Carlo method in conjunction with the embedded-atom method show 20−60% underestimations for Al, Ni, Cu, Ag, and Au and 20% overestimation for Co when they are compared with the experimental data.[37−39] Thus, computer simulation methods for estimation of $\gamma_{lv}(T)$ values of metals need to be further improved, which indicates that the theoretical method described above is a powerful and even unique tool at present for determining the $\gamma_{lv}(T)$ function with good accuracy. Furthermore, we will try to model the surface tension of alloys on the basis of this method with the considerations of the interaction between the components.

Conclusion

In summary, the quantitatively thermodynamic expressions for $\gamma_{lv}(T_m)$, $\gamma'_{lv}(T)$, and $\gamma_{lv}(T)$ functions have been developed on the basis of eq 4. The model predictions for 48 liquid metals

correspond to the available experimental data. It is found that $\gamma_{lv}(T_m)$ is directly proportional to $H_v/V_m^{2/3}$ for both transition and nontransition metals, while both $\gamma_{lv}(T)$ and $\gamma'_{lv}(T)$ are linear functions of T and the relation $\gamma'_{lv}(T) \approx \gamma'_{lv}(T_m)$ is a good approximation. Moreover, in the n range of 4−6, $T_m\gamma'_{lv}(T_m)/\gamma_{lv}(T_m) \approx -0.30$, where the outermost layers of atoms are s+d electrons. When elements with empty or fully filled electrons of the second outmost subshell are considered, similar cases are found, although the corresponding constant varies a little.

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