Vapour Pressure of Liquid Metals and Alloys

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The Gibbs-Bogoliubov formalism in conjunction with the pseudopotential theory is applied to the calculation of the vapour pressure of eight liquid metals from Groups I to IV of the periodic table and of alloys (Na-K). The calculated vapour pressure of the elements and their temperature dependencies, the partial pressures, activities and boiling points of the alloys are all found to be in reasonable agreement with measured data.

1. Introduction

The thermodynamics of liquid metals and alloys from a viewpoint of microscopic theory has made significant progress in the last few years. The success of the thermodynamical perturbation theory in conjunction with the Gibbs-Bogoliubov technique (Jones [1]) has motivated several applications to liquid metals and alloys (Hasegawa and Watabe [2], Umar et al. [3] and Hafner [4]). Recently, Minchin et al. [5] have calculated the vapour pressure of liquid sodium using this approach. This prompts us to report our extensive calculations on the vapour pressure of liquid metals and partial vapour pressure of liquid alloys, based on a method which is similar in principle but differs in the evaluation of input data.

2. Basic Equations and Method of Calculation

The condition of equilibrium between a liquid metal and its vapour is:

$$\mu_l = \mu_g \,, \tag{1}$$

where μ_l and μ_g are the chemical potentials of liquid and gas state.

If the hard sphere model is used as a reference system in the perturbation theory of liquid metals, then the chemical potential of a liquid metal is given by:

$$\mu_l = \mu_l^{hs} + \frac{\partial \{F_{ps} + NI\}}{\partial N} \tag{2}$$

where F_{ps} denotes the total free energy composed of electrons and ions in liquid metals, N and I are the number of ions and the ionization energy, respectively.

An expression for the total energy E_{tot} in liquid metals and alloys based on the pseudopotential theory has been discussed previously (for example, Hartmann [6]) and is not repeated here. The basic equations which are necessary for discussion are:

$$E_{tot} = E_{elec} + E_H + E_{es} + E_{bs} + E_{cc} + \tfrac{3}{2} kT \,, \tag{3}$$

$$E_{elec} = \frac{2.21}{r_s^2} Z - \frac{0.916}{r_s} Z - (0.115 - 0.031 \ln r_s) Z \,, \tag{4}$$

$$E_H = \lim_{q \to 0} \left(w^{bp} + \frac{8\pi}{q^2} Z \right) \frac{Z}{\Omega} \,, \tag{5}$$

$$E_{eff} = E_{es} + E_{cc} + \left[E_{bs} - \frac{1}{2} \sum_{q \neq 0} \frac{q^2}{8\pi} |w^{bp}|^2 \left(\frac{1}{\varepsilon(q)} - 1 \right) \right] \tag{6}$$

$$= \frac{1}{2} \sum \Phi_{eff}(q) [a(q) - 1] = \frac{1}{2\Omega} \int_0^\infty \Phi_{eff}(r)\, g(r)\, 4\pi r^2 \, dr \,, \tag{7}$$

where w^{bp} is the bare pseudopotential, Φ_{eff} means the effective interionic potential, and $g(r)$ and $a(q)$ are the pair distribution function and the structure factor, respectively. The other symbols have the usual meaning, and have been described previously (Waseda et al. [7]).

There have been several treatments for evaluating the pseudopotentials of bare ions in metals. The empty core potentials with the core radius of r_c (Ashcroft [8]) were used in this work. Equation (2) is valid for the systems in which the hard

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sphere model is a good reference one. This fact requires that the hard sphere structure factors are used to fit the experimental ones and then to determine the parameter of r_c in the bare pseudopotential by the zero pressure condition, $\partial E_{tot}/\partial \Omega = 0$ (see for example, Minchin et al. [5]). It is also desirable to take into account the contribution of core-core repulsion potential between ions, except for lighter elements. In this work, we used the repulsive core part of the effective interionic potential which was estimated from the experimental pair distribution function (Waseda and Tamaki [9]) by using the Johnson and March scheme. The reliability of the pair potential estimated by this scheme has been discussed in the literature (Gaskell [10], Kumaravadivel et al. [11], Ailawadi et al. [12], De Angeles and March [13]). It appears acceptable to use the repulsive part of the pair potential as a first approximation since the results for Na, K and Al are in good agreement with those of Wallace [14] who determined the core-core repulsion potential by fitting the experimental phonon spectrum.

The experimental structure factors for the elements investigated in this work are well expressed by the hard sphere model (Waseda [15]). Experimental structure factors are therefore used in the calculation, although the condition of the Gibbs-Bogoliubov inequality is slightly obscure. The use of experimental structure factors is consistent with the application of core-core repulsion potential derived semi-empirically. This is also supported by the close correspondence of the values for the parameter r_c determined in this work (Table 1) and those reported using the hard sphere model (Hartmann [6], Hasegawa and Watabe [2]).

3. Calculated Results and Discussion

3.1. *Vapour Pressure*

The entropy of electrons in simple liquid metals is negligibly small (Umar et al. [4]) and therefore F_{ps} can be approximated by the total energy E_{tot}. A diagram for the energy states of a liquid metal and its gas phase is shown as Fig. 1 in which the origin of energy level corresponds to isolated ions and valence electrons. From this figure, it is easy to understand that the chemical potential of the liquid metal is given by Equation (2).

Table 1. Comparison of calculated vapour pressure with experimental data.

	Temp. (°C)	Density (g/cm³)	r_c (a.u.)	$-S_{CS}/k_B$	$\left(\frac{\partial F_{PS}}{\partial N}+I\right)/k_BT$	$\ln n\,k_BT$ (atm.)	$\ln p$ (atm.)	p (atm.)		$-\left(\frac{\partial F_{PS}}{\partial N}+I\right)$ (kcal · mol⁻¹)	Heat of Vaporization (kcal · mol⁻¹)	
								calc.	exp.*	calc.	exp.*	exp.**
Li	190	0.504	1.37	4.13	− 39.89	7.94	− 27.82	8.27×10^{-13}	3.84×10^{-13}	36.7	35.16	32.48
Na	100	0.928	1.73	4.13	− 33.33	7.11	− 22.08	2.57×10^{-10}	1.47×10^{-10}	24.7	—	24.12
K	65	0.826	2.32	4.13	− 29.63	6.38	− 19.12	4.98×10^{-9}	1.46×10^{-9}	19.9	18.38	18.9
Rb	40	1.471	2.49	3.59	− 29.91	6.09	− 20.23	1.64×10^{-9}	1.66×10^{-9}	18.6	—	18.1
Cs	30	1.837	2.68	3.59	− 28.57	5.84	− 19.14	4.86×10^{-9}	3.05×10^{-9}	17.2	16.20	16.3
Mg	680	1.545	1.40	4.13	− 17.90	8.51	− 5.26	5.20×10^{-3}	7.38×10^{-3}	33.9	—	32.52
Al	670	2.327	1.18	3.94	− 38.32	8.82	− 25.56	7.97×10^{-12}	5.94×10^{-12}	71.8	69.5	67.9
Pb	340	10.66	1.27	4.13	− 35.80	7.86	− 23.80	4.59×10^{-11}	1.21×10^{-11}	43.6	42.53	42.4

* R. E. Honing and D. A. Kramer [18]. — ** C. J. Smithells [25].

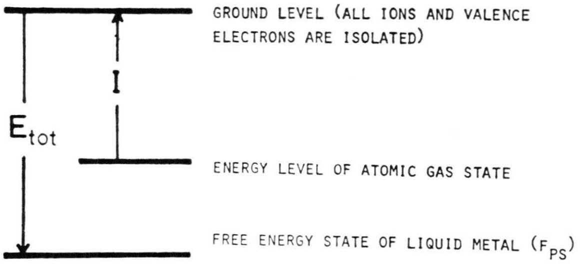

Fig. 1. Diagram of energy state. E_{tot}: total energy in the liquid state, I: ionization energy of atoms.

The chemical potential of gas atoms which is in thermal equilibrium with the liquid metal is simply given by:

$$\frac{\mu_{\mathrm{g}}}{k_{\mathrm{B}} T} = \ln\left[\frac{p}{k_{\mathrm{B}} T}\left(\frac{2\pi\hbar^2}{m\, k_{\mathrm{B}} T}\right)^{3/2}\right]. \tag{8}$$

The hard sphere term in the chemical potential of liquid metal is written as follows:

$$\frac{\mu^{\mathrm{hs}}}{k_{\mathrm{B}} T} = \ln\left[n\left(\frac{2\pi\hbar^2}{m\, k_{\mathrm{B}} T}\right)^{3/2}\right] - \frac{S(\eta)}{k_{\mathrm{B}}} \tag{9}$$

where the packing fraction η is given by $\eta = \pi n \sigma^3/6$, n being the number density and σ the hard sphere diameter. With respect to the quantity of $S(\eta)$, an empirical but a better expression for the entropy of the hard sphere system is the result of averaging the two Percus-Yevick pressures (Silbert et al. [16]), as given by the Carnahan-Starling equation:

$$\frac{S_{\mathrm{CS}}(\eta)}{k_{\mathrm{B}}} = 3 - \frac{2}{(1-\eta)} - \frac{1}{(1-\eta)^2}. \tag{10}$$

At thermodynamic equilibrium, the following relation is obtained.

$$\ln p = \ln n\, k_{\mathrm{B}} T - \frac{S_{\mathrm{CS}}(\eta)}{k_{\mathrm{B}}} + \frac{1}{k_{\mathrm{B}} T}\left\{\left(\frac{\partial F_{\mathrm{ps}}}{\partial N}\right) + I\right\}. \tag{11}$$

This expression is essentially equivalent to those obtained by Minchin et al. [5] and Reiss et al. [17].

The details of the calculation of vapour pressures of eight metals at their melting points based on Eq. (11) are summarized in Table 1, together with the experimental data (Honig and Kramer [18]). The calculated vapour pressures are in reasonable agreement with experimental inforamtion. As seen in Fig. 1, the binding energy in metals is approximately expressed by the latent heat of vaporization. Consequently, the term $-(\partial F/\partial N + I)$ corresponds to the latent heat of vaporization. This inference is supported by the close agreement between values for the quantities given in Table 1. The temperature dependence of the vapour pressure, calculated using Eq. (11), is compared with experimental information for Na and K in Figure 2.

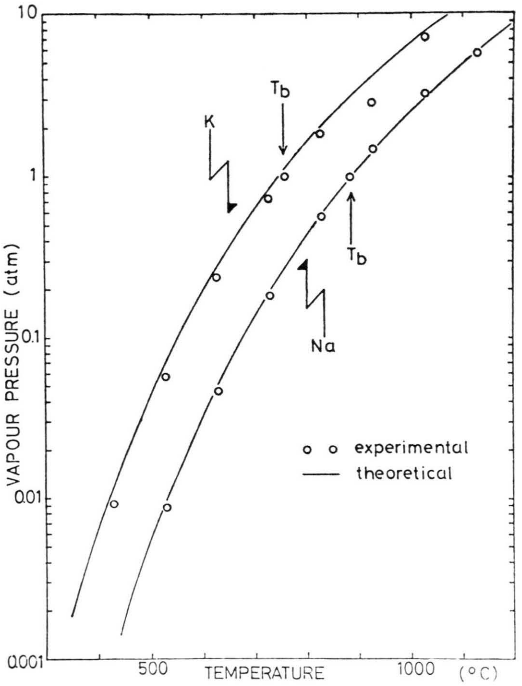

Fig. 2. Temperature dependence of the saturation vapour pressure for sodium and potassium. Tb: boiling point.

3.2. Entropy of Vaporization

Using the relation of Eq. (11), the entropy of vaporization at the boiling point (where $p = 1$ atm) is given by:

$$-\frac{1}{T_{\mathrm{b}}}\left\{\left(\frac{\partial F_{\mathrm{ps}}}{\partial N}\right)_{T_{\mathrm{b}}} + I\right\} = k_{\mathrm{B}}\left[\ln n_{\mathrm{b}}\, k_{\mathrm{B}} T_{\mathrm{b}} - \left\{3 - \frac{2}{(1-\eta_{\mathrm{b}})} - \frac{1}{(1-\eta_{\mathrm{b}})^2}\right\}\right], \tag{12}$$

where T_{b}, n_{b} and η_{b} are the boiling temperature, the number density, and packing fraction, respectively, of the liquid metal at the boiling point.

If there is no significant change in the electronic structure of liquid metals from their melting point

Table 2. Comparison of calculated entropy of vaporization with experimental data.

	α ($\times 10^{-4}$ deg^{-1})	η_m	η_b	$-(S_{CS}/k_B)_{T_b}$	$\ln n_b k_B T_b$	Entropy of vaporization (cal · deg^{-1} mol^{-1})	
						calc.	exp.*
Li	1.80	0.46	0.38	2.83	8.87	23.3	20.26
Na	2.75	0.46	0.38	2.83	8.10	21.7	20.27
K	2.90	0.46	0.38	2.83	7.29	20.1	18.60
Rb	3.38	0.43	0.35	2.44	6.92	18.6	18.79
Cs	3.95	0.43	0.35	2.44	6.64	18.0	20.32
Mg	1.90	0.46	0.42	3.42	8.83	24.3	23.56
Al	1.16	0.45	0.37	2.70	9.71	24.7	25.11
Pb	1.17	0.46	0.39	2.97	9.04	23.9	21.01

m: melting point; b: boiling point; * C. J. Smithells (1962) [25].

to the boiling point, the hard sphere model might not be less applicable with the increase in temperature. The change in the packing fraction with temperature can be estimated from thermal expansion coefficient α_V:

$$\eta(T) = \frac{\eta_m}{\{1 + \alpha_V(T - T_m)\}} \tag{13}$$

where the suffix *m* denotes the melting point.

Using the observed values for η_m (Waseda [15]) and α_V (Willson [19]), the entropies of vaporization at the boiling point are obtained, as shown in Table 2. The agreement between theory and experiments is satisfactory. It should be noted that the Trouton's rule suggests an average value of about 20 cal.deg.$^{-1}$ mol^{-1} for entropy of vaporization for metals.

3.3. Partial Vapour Pressures Over Alloys

The equilibrium partial vapour pressures over liquid binary alloys is given by:

$$p_A = p_A^0 \, a_A\,, \tag{14}$$

where p_A^0 is the vapour pressure of component A in its pure state and a_A is the activity of component A in liquid alloys.

A calculation of activities in liquid alloys based on the electron theory of metals has already been attempted by the present authors (Waseda et al. [7]). The essential features are summarized below: The activity a_A in a binary A-B alloy is given by:

$$a_A = \exp\left[\frac{\mu_A - \mu_A^0}{k_B T}\right], \tag{15}$$

where μ_A and μ_A^0 are the chemical potentials of element A in the alloy and in the pure standard state.

μ_A is given by the following expression:

$$\mu_A = \left(\frac{\partial G}{\partial N_A}\right)_{T,\,N_B} = \mu_A^{hs} + \left(\frac{\partial F_{ps}}{\partial N_A}\right)_{T,\,N_B}, \tag{16}$$

where $N_A + N_B = N$.

As mentioned before, F_{ps} can be approximated by the total energy. The derivation of the total energy of liquid metals and alloys based on the pseudopotential method is well described in the

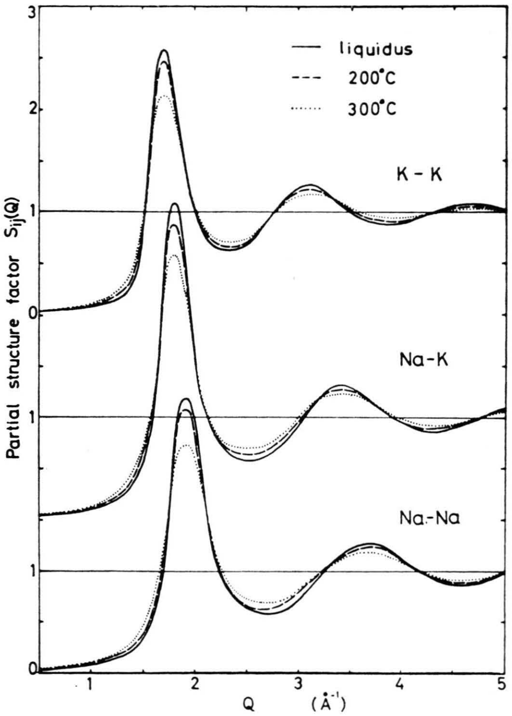

Fig. 3. Partial structure factors obtained experimentally for liquid Na-K alloys.

literature (Heine and Weaire [20], Stroud and Ashcroft [21], Harrison [22], Hafner [3]). In the case of liquid alloys, the parameters required to determine the total energy are the bare pseudopotentials of the elements, the dielectric function and the partial structure factors. The partial differentiation $(\partial F_{\mathrm{ps}}/\partial N_{\mathrm{A}})$ can be easily obtained from the plot of F_{ps} versus N_{A} (Waseda et al. [7]).

Following the method described in our previous work (Waseda et al. [7]), the activity of liquid Na-K alloys at 110 °C was estimated. However, in this calculation, we used the partial structure factors of Fig. 3 obtained experimentally. A more detailed information on the partial structure factors will be published elsewhere. Other parameters were almost identical to the previous ones. Namely, we used the empty core potentials which are fitted to satisfy the equilibrium condition in the pure state, and the Habbard-Sham dielectric function. As shown in Fig. 4, the estimated activity curve reasonably reproduces the observed one (Cafasso et al. [23]).

The partial vapour pressures estimated from the calculated activities using Eq. (14) are shown in Table 3. There is fair agreement between the calculated and experimental values.

The total pressure P over a binary alloy is given by the following relation:

$$P = p_{\mathrm{A}}^{0} a_{\mathrm{A}} + p_{\mathrm{B}}^{0} a_{\mathrm{B}} . \tag{17}$$

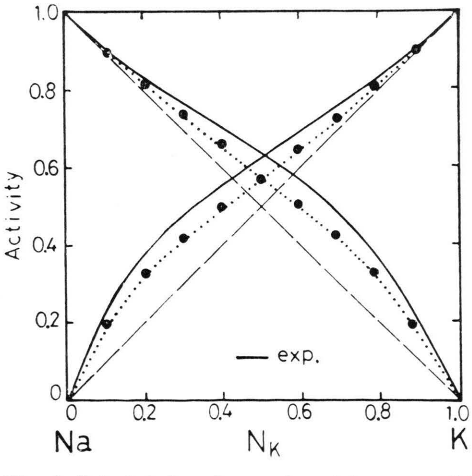

Fig. 4. Calculated and experimental curves of the activity of liquid Na-K alloys at 110 °C. Solid dotts: present calculation; dotted line: previous calculation with the hard sphere model (Waseda et al., 1977).

Table 3. Comparison of calculated partial vapour pressure of liquid Na-K alloys with experimental data.

Atomic fraction of Na	p_{Na} ($\times 10^{-9}$ atm.) calc.	p_{Na} ($\times 10^{-9}$ atm.) exp. *	p_{K} ($\times 10^{-9}$ atm.) calc.	p_{K} ($\times 10^{-9}$ atm.) exp. *
0.0	0.00	0.00	4.98	1.46
0.1	0.04_4	0.03_1	4.50	1.32
0.2	0.08_1	0.05_4	4.02	1.21
0.3	0.11	0.07_1	3.62	1.10
0.4	0.13	0.08_5	3.22	1.01
0.5	0.15	0.09_5	2.87	0.91
0.6	0.17	0.11	2.53	0.81
0.7	0.19	0.11	2.07	0.70
0.8	0.21	0.12	1.60	0.55
0.9	0.23	0.13	0.95	0.33
1.0	0.26	0.15	0.00	0.00

* F. A. Cafasso, V. M. Khanna and H. Feder (1967) [23].

Table 4. Comparison of calculated boiling point of liquid Na-K alloys with experimental data.

K (at.%)	Tb (°C) calc.	Tb (°C) exp. *
0	865	892
32	802	825
68	775	784
100	733	760

* C. B. Jackson (1955) [24].

Consequently, we could estimate the boiling point of a binary alloy from Equation (17). The boiling point of a binary alloy corresponds to the temperature which satisfies the condition of $P = 1$ atm. The estimated values are in good agreement with experimental data (Jackson [24]) as shown in Table 4.

As stressed in the work of Michin et al. [5], the present theory is adequate only for the systems in which the hard sphere reference is applicable and at pressures below one atmosphere. However, the results obtained in this extensive work suggest that the first order variational method of Gibbs-Bogoliubov is one way to discuss the vapour pressure of liquid metals and alloys in the pressure range amenable to experimental investigation.

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