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# **<sup>1</sup>An Equation for the Vapor Pressure of Liquid Metals and Calculation of Their Enthalpies of Evaporation**

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**Abstract**

An equation for the vapor pressure of liquid metals was derived by combining the formula based on a harmonic oscillator model of the theory of liquids with the modified Lindemann's equation proposed previously by one of the authors. The equation is expressed in terms of the enthalpy of evaporation and the surface tension as follows:

$$p = 3.0 \times 10^{12} \sigma^{3/2} T^{-1/2} \exp(-\Delta H_v / NkT)$$

where  $p$  is the vapor pressure,  $\sigma$  the surface tension,  $\Delta H_v$  the enthalpy of evaporation,  $T$  the absolute temperature,  $N$  Avogadro's number and  $k$  Boltzmann's constant.

The values of  $\Delta H_v$  for various liquid metals are calculated from this equation using the experimental data of surface tension. The calculated values of the enthalpy of evaporation of liquid metals at their melting points,  $\Delta H_{v,m}$ , and at their boiling points,  $\Delta H_{v,b}$ , agree well with experimental data within  $\pm 5$  per cent for  $\Delta H_{v,m}$  and  $\pm 20$  per cent for  $\Delta H_{v,b}$ , respectively. The values of  $\Delta H_{v,b}$  are predicted for some liquid metals for which experimental data are lacking.

**Key Words**

enthalpy of evaporation, liquid metals, lattice theory of liquid, model theory, harmonic oscillator model, modified Lindemann's equation

**1. Introduction**

A knowledge of evaporation processes of liquid metals is of great importance not only from the viewpoint of physical chemistry relating to the phase transition and the atomic interaction in a condensed liquid phase, but also from the viewpoint of industrial technologies concerning the PVD and CVD processes and the purification processes. Therefore, indispensable physical quantities in discussing the evaporation processes, i.e.,

the values of the vapor pressure and the enthalpy of evaporation, have been measured extensively over the past century for various pure liquid metals. The experimental data for liquid metals have been summarized in some textbooks /1,2/. Theoretical treatment of evaporation has mainly been made from the viewpoint of thermodynamics. On the other hand, some empirical and semi-empirical equations, for example, relationships between  $\Delta H_v$  and  $\sigma$  /3-5/ and between  $\Delta H_v$  and the boiling point /6/, have been proposed for liquid metals. Recently, theoretical evaluations of  $\Delta H_v$  and  $p$  for liquid metals from the microscopic point of view and using a thermodynamic perturbation theory have been performed by Minchin et al. /7/ and Waseda et al. /8,9/. The vaporization processes should be studied from various microscopic points of view for a clear understanding of the evaporation processes.

According to the harmonic oscillator model in a lattice theory of liquids, the vapor pressure is expressed in terms of the enthalpy of evaporation and the effective frequency of molecular vibration /10/. Previously, one of the authors proposed a modified Lindemann's equation based on a model theory /11,12/, which gives a simple expression for the effective frequency as a function of the surface tension of liquids. Since  $p$  is one atmospheric pressure at the boiling point, we can easily calculate the  $\Delta H_v$  value of a liquid metal, provided the value of the surface tension is given.

In this study, an equation for the vapor pressure of liquid metals has been proposed by combining the formula based on the harmonic oscillator model of liquids with the modified Lindemann's equation. Subsequently, the enthalpies of evaporation,  $\Delta H_v$ , of liquid metals are estimated using the equation, and the estimated values of  $\Delta H_v$  are compared with experimental data. The values of  $\Delta H_v$  are also predicted for some liquid metals for which no experimental data to the authors' knowledge have been reported.

## 2. Calculation of the Enthalpy of Evaporation

### A. Expression for the enthalpy of evaporation using the harmonic oscillator model based on a lattice theory

In the harmonic oscillator model based on a lattice theory of a liquid, it is assumed that the liquid has a quasi-crystalline structure, and that each molecule of the liquid vibrates about a lattice point, i.e., a position of minimum potential energy, as an isotropic three-dimensional harmonic oscillator with the effective frequency,  $\nu$ . According to this model, one can describe the partition function and the chemical potential of the liquid. When the liquid is in equilibrium with its vapor at temperature,  $T$ , the vapor pressure,  $p$ , is given by [10]

$$p = \frac{(2\pi m)^{3/2} \nu^3}{(kT)^{1/2}} \exp\left(-\frac{\Delta H_v}{NkT}\right) \quad (1)$$

where  $m$  is the molecular mass. To evaluate the value of  $\Delta H_v$  from Eq. 1, an appropriate and ingenious determination of  $\nu$  is the most important.

### B. Evaluation of the Effective Frequency, $\nu$

There have been several approaches to evaluate the effective frequency of the characteristic frequency of liquid metals. In the 1940s, Harashima [13] evaluated  $\nu$  for liquid metals from the shapes of the first peaks of the radial distribution functions obtained by X-ray diffraction. Recently, Sinha et al. [14] determined the values of  $\nu$  for liquid metals so as to reproduce the experimental results of the first peaks in the structural factors modified by the Debye-Waller factor. Yokoyama and Arai [15] calculated the values of  $\nu$  from the equation for the angular frequency of the independent phonon using the Percus-Yevick phonon model. Although these evaluations require X-ray diffraction data and somewhat tedious calculations, the effective frequencies of liquid metals can be evaluated in these ways.

On the other hand, the modified Lindemann equation for pure liquid metal proposed by one of the

authors [11,12] is expressed in the following simple form:

$$\nu = 6.8 \times 10^{11} \left(\frac{\sigma}{M}\right)^{1/2} \quad (2)$$

where  $M$  is the molecular weight ( $M=Nm$ ). It should be noted that Eq. 2 would be applied to liquids in temperatures ranging from their melting points to their boiling points and that the microscopic physical quantity,  $\nu$ , is replaced by macroscopic quantities, i.e.,  $\sigma$  and  $M$ . By using Eq. 2, we can easily evaluate  $\nu$  for pure liquid metals, provided their values of  $\sigma$  are given.

By combining Eqs. 1 and 2, we obtain the following equation for the vapor pressure of liquid metals:

$$p = 3.0 \times 10^{12} \frac{\sigma^{3/2}}{T^{1/2}} \exp\left(-\frac{\Delta H_v}{NkT}\right) \quad (3)$$

Eq. 3 can easily be applied to various pure liquids since it does not explicitly contain the molecular weight. Since  $p$  is one atmospheric pressure, i.e.,  $1.013 \times 10^5$  Pa, at the boiling point, only the value of the surface tension is required for calculating the value of the enthalpy of evaporation of a liquid at its boiling point,  $\Delta H_{v,b}$ .

## 3. Results and Discussion

### A. The enthalpies of evaporation of liquid metals at their melting points

The enthalpies of evaporation of liquid metals at their melting points,  $\Delta H_{v,m}$ , have been calculated using the experimental data of the surface tension,  $\sigma_m$ , [11] and the vapor pressure,  $p_m$  [1]. The subscript  $m$  refers to the melting point. The data used for calculating  $\Delta H_{v,m}$  are given in Table 1.

Fig. 1 shows the comparison between the calculated and the experimental data of  $\Delta H_{v,m}$ . Experi-

Table 1

The experimental data used for calculating the enthalpies of evaporation of liquid metals

Element	$T_m/K$	$T_b/K$	$\sigma_m/mNm^{-1}$	$\sigma_b/mNm^{-1}$	$\log p_m/Pa$
Li	454	1597	398	238	-7.74
Be	1560	2745	1390	1046	0.65
Na	371	1155	191	113	-4.99
Mg	922	1363	559	408	2.63
Al	933	2793	914	263	-6.08
Si	1685	3553	865	622	-1.34
K	336	1043	115	58	-3.94
Ca	1112	1757	361	297	2.35
Ti	1943	3563	1650	1231	-0.19
Cr	2130	2945	1700	1450	—
Mn	1517	2305	1090	932	2.19
Fe	1809	3133	1872	1223	0.36
Ni	1726	3183	1778	1224	-0.41
Cu	1356	2833	1303	963	-1.37
Zn	693	1180	782	699	1.34
Ga	303	2693	718	479	-35.76
Ge	1246	3107	621	128	-4.03
Rb	311	961	85	46	—
Sr	1041	1654	303	242	2.20
Mo	2893	4873	2250	1659	—
Pd	1825	3213	1500	1195	0.61
Ag	1234	2473	966	731	-0.47
Cd	594	1040	570	454	1.13
In	430	2346	556	384	-18.54
Sn	505	2878	560	346	-20.33
Sb	904	1860	367	319	1.30
Te	723	1261	180	148	—
Cs	303	831	70	38	-3.60
Ba	1002	1973	227	199	0.19
La	1193	3732	720	—	-7.05
Nd*	1289	3343	689	505	—
Gd*	1585	3543	810	497	—
Hf	2503	4873	1630	1141	-0.41
Ta*	3288	5723	2150	1535	-0.09
W	3683	5828	2500	1869	—
Os*	3303	5303	2500	1845	—
Ir	2716	4703	2250	1634	—
Pt	2042	4373	1800	1404	-1.68
Au	1336	3133	1169	720	-3.08
Hg	234	630	498	419	—
Tl	577	1746	464	370	-5.38
Pb	600	2023	458	273	-6.32
Bi	544	1837	378	288	-8.07
U	1405	4408	1550	1130	—
Pu	913	3693	550	272	—

\* The values of  $\Delta H_{v,b}$  were predicted in this study.

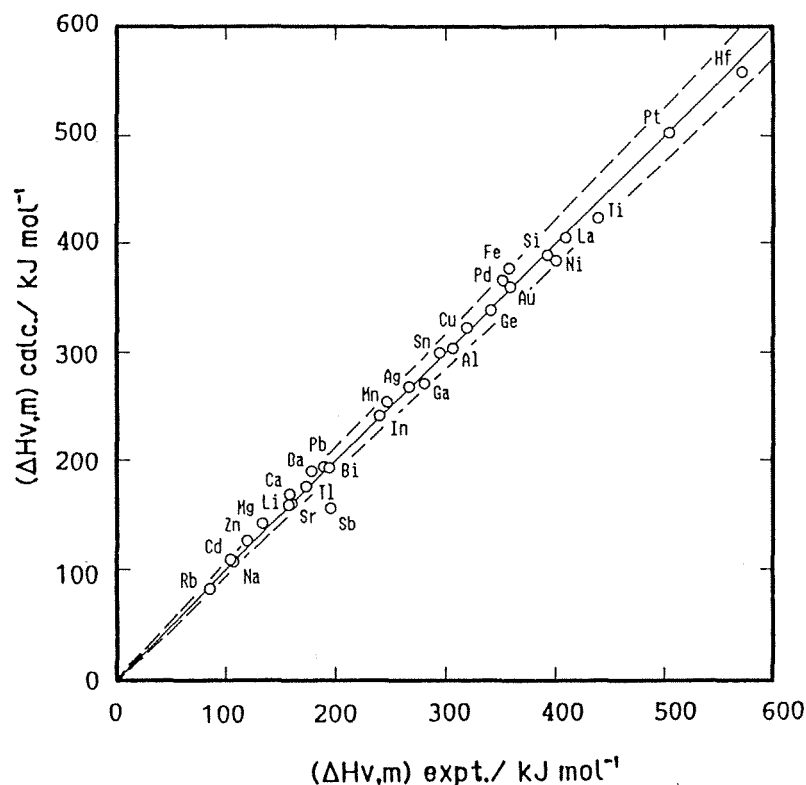


Fig. 1: Comparison of the calculated enthalpies of evaporation for liquid metals at their melting points,  $(\Delta H_{v,m})_{\text{calc.}}$ , with the experimental data,  $(\Delta H_{v,m})_{\text{expt.}}$ . The broken lines represent the  $\pm 5$  per cent error band.

mental data for  $\Delta H_{v,m}$  were taken from Kubaschewski and Alcock /1/. As is obvious in Fig. 1, the calculated values agree well with the experimental data within the  $\pm 5$  per cent error band. The agreement between calculation and experiment for these metals is surprisingly good. In contrast, the values of  $\Delta H_{v,m}$  calculated from Skapski's equation<sup>1</sup> are compared with the experimental

data in Fig. 2. As can be seen in Fig. 2, the calculated values for some liquid metals are outside the  $\pm 20$  per cent error band.

#### B. The Enthalpies of Evaporation of Liquid Metals at their Boiling Points

As mentioned in Section 2B, the enthalpies of evaporation of the liquid metals at their boiling points,  $\Delta H_{v,b}$ , can easily be evaluated from Eq. 3 using only the experimental data of the surface tension,  $\sigma_b$ , /12/ extrapolated to the boiling points,  $T_b$ , where the subscript b refers to the boiling point. Their values are listed in Table 1.

In Fig. 3, the calculated values of  $\Delta H_{v,b}$  are com-

<sup>1</sup> Skapski's equation /3,12/ can be expressed in the form

$$\Delta H_{v,m} = 5.5 \times 10^8 \sigma V_m^{2/3}$$

where  $V_m$  is the molar volume. The constant of proportionality was determined so as to best fit the experimental data given in Kubaschewski and Alcock /1/ and Iida and Guthrie /12/.

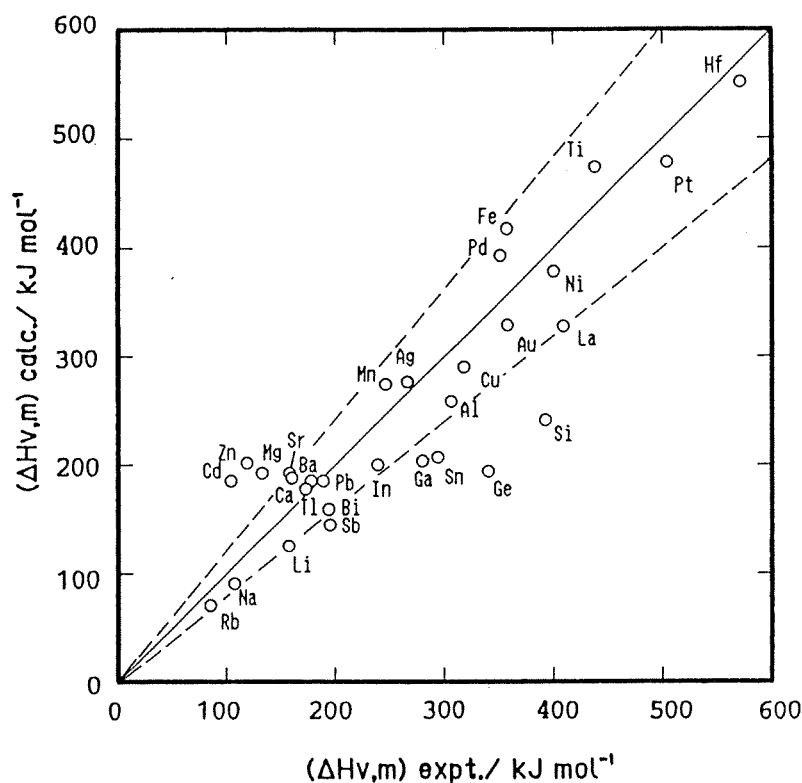


Fig. 2: Comparison of the calculated enthalpies of evaporation for liquid metals at their melting points by using Skapski's rule,  $(\Delta H_{v,m})_{\text{calc.}}$ , with the experimental data,  $(\Delta H_{v,m})_{\text{expt.}}$ . The broken lines represent the  $\pm 20$  per cent error band.

pared with experimental data. As can be seen in Fig. 3, the calculated values agree well with experimental data within the  $\pm 20$  per cent error band. In Fig. 4, the  $\Delta H_{v,b}$  values calculated from Trouton's rule ( $\Delta H_{v,b} = 91.2T_b$  in SI units) are compared with experimental data. Fig. 4 shows that the metals with larger values of  $\Delta H_{v,b}$  are apt to have larger discrepancies between the experimental and the calculated values. It is noteworthy that the calculation of the entropy of evaporation using the thermodynamic perturbation theory based on the hard sphere model by Waseda et al. [8,9] requires information on some parameters, such as packing fraction, although agreement between the calculated and experimental values is similar to the present one.

Eq. 3 provides good results for  $\Delta H_v$  values of

liquid metals and can be used for predicting them. To the authors' knowledge, there are no experimental data on  $\Delta H_{v,b}$  for liquid metals such as Nd, Gd, Ta, Os. The predicted values are listed in Table 2. Incidentally, extrapolated values for the surface tension,  $\sigma_b$ , are also given in Table 1.

#### 4. Conclusions

An equation for the vapor pressure of liquid metals is proposed based on model theories of liquids. The equation is expressed in the form:

$$p = 3.0 \times 10^{12} \sigma^{3/2} T^{-1/2} \exp(-\Delta H_v/NkT)$$

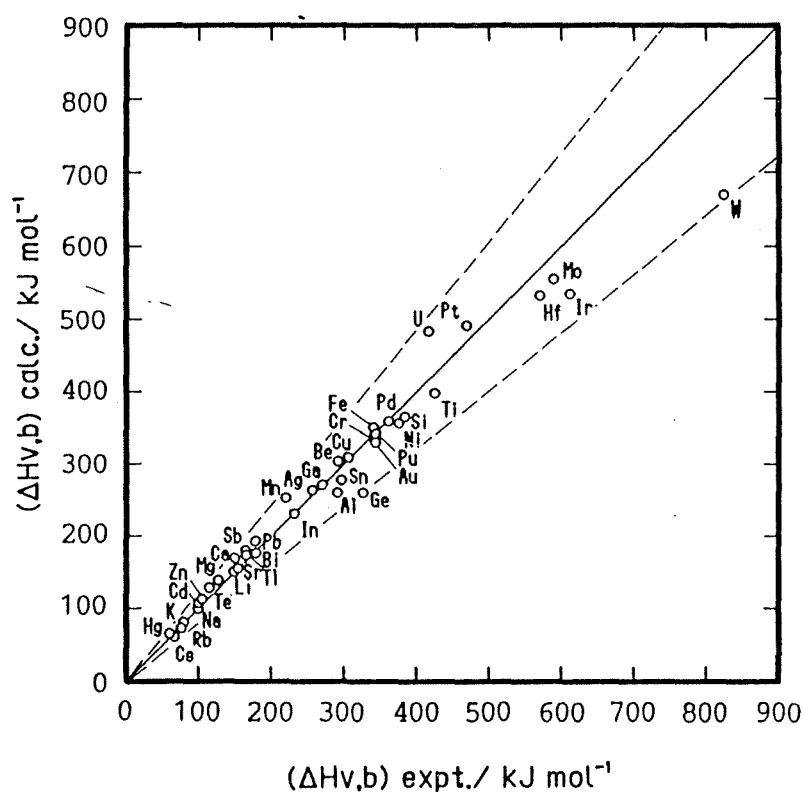


Fig. 3: Comparison of the calculated enthalpies of evaporation for liquid metals at their boiling points,  $(\Delta H_{v,b})_{\text{calc.}}$  with the experimental data,  $(\Delta H_{v,b})_{\text{expt.}}$ . The broken lines represent the  $\pm 20$  per cent error band.

Table 2

The predicted values of the enthalpies of evaporation for several liquid metals at their boiling points.

Metals	Nd	Gd	Ta	Os
$\Delta H_{v,b}/\text{kJmol}^{-1}$	337	356	643	610

The enthalpies of evaporation of liquid metals both at their melting points,  $\Delta H_{v,m}$ , and at their boiling points,  $\Delta H_{v,b}$ , were calculated from this equation using the experimental data of the surface tension,  $\sigma$ . The calculated values of  $\Delta H_v$  agreed with the experimental data

within the  $\pm 5$  per cent error band for  $\Delta H_{v,m}$  and  $\pm 20$  per cent error band for  $\Delta H_{v,b}$ , respectively.

The values of  $\Delta H_{v,b}$  were predicted for some liquid metals for which experimental data are lacking.



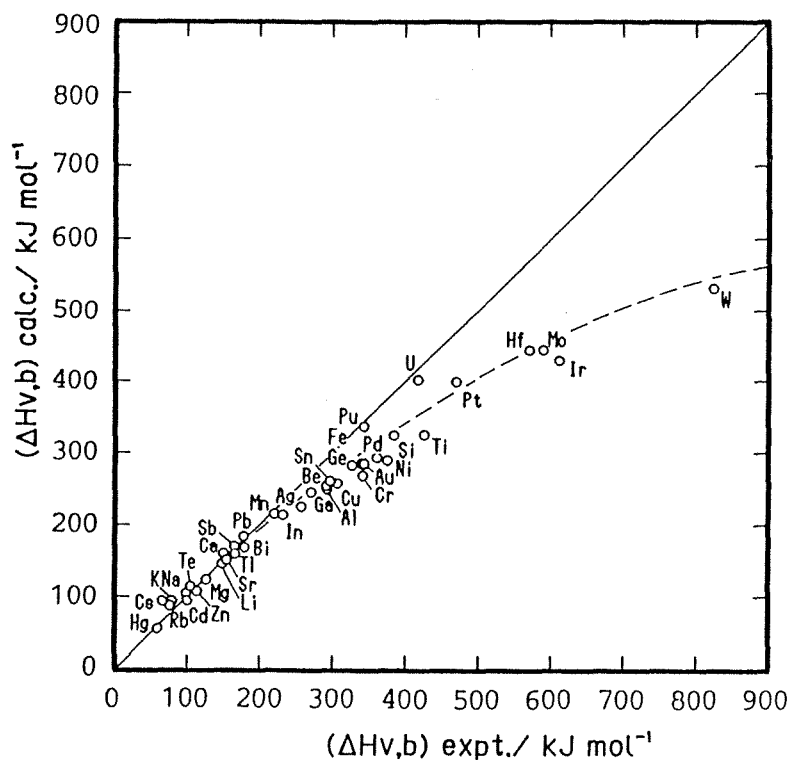


Fig. 4: Comparison of the calculated enthalpies of evaporation for liquid metals at their melting points by using Trouton's rule,  $(\Delta H_{v,b})_{\text{calc.}}$ , with the experimental data,  $(\Delta H_{v,b})_{\text{expt.}}$ . The broken curve represents a tendency to vary with the plots of  $\Delta H_{v,b}$ .

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