4th International Conference on Molten Slags and Fluxes, 1992, Sendai, ISIJ

ESTIMATION OF THE ENTHALPY OF EVAPORATION OF MOLTEN SALTS AND FLUXES BASED ON A HARMONIC OSCILLATOR MODEL

Takamichi Iida, Yoshifumi Kita and Zen-ichiro Morita

Department of Materials Science and Processing,
Faculty of Engineering, Osaka University, Japan

Synopsis:

The enthalpies of evaporation of molten salts have been estimated using the equation proposed recently by the authors. The equation based on a harmonic oscillator model of a liquid is expressed in terms of some known physical quantities, as

$$p = 4.2\times 10^{13}\sigma^{3/2}T^{-1/2}\exp(-\Delta H_v/NkT) \qquad (\text{ in SI units})$$

where, p is the vapor pressure, σ the surface tension, ΔH_v the enthalpy of evaporation, T the absolute temperature, N Avogadro's number, and k Boltzmann's constant.

The equation reproduces well experimental data for the enthalpies of evaporation of molten salts and fluxes.

The enthalpies of evaporation have been predicted for several molten salts, for which experimental data are lacking.

Keywords: enthalpy of evaporation, molten salts, lattice theory of liquid, model theory, harmonic oscillator model, modified Lindemann's equation, prediction of enthalpy of evaporation

1. Introduction

The enthalpy of evaporation, as well as the vapor pressure, of various materials, is an indispensable thermodynamic quantity both from the standpoint of physical chemistry relating to the phase transition and the atomic interaction in a condensed liquid phase, and from the standpoint of industrial technologies concerning metallurgical and chemical processes. Therefore, the values of the vapor pressure and the enthalpy of evaporation have been measured extensively for these several decades for various single molten salts and pure liquid metals. The measured data for single molten salts have been summarized in some textbooks[1] and handbooks[2]. Theoretical treatment of evaporation has been mainly carried out from the viewpoint of thermodynamics. For liquid metals, some empirical equations and semi-empirical equations have been proposed, representing relationships between ΔH_v and the surface tension σ [3-5], and between ΔH_v and the boiling point T_b[6]. However, theoretical evaluations of ΔH_v and p for single molten salts from the microscopic point of view have not yet been performed, to the authors' knowledge. The evaporation processes should be studied on various microscopic scales, for a clear understanding of the processes.

According to a harmonic oscillator model in a lattice theory of liquids, the vapor pressure of a liquid p is expressed in terms of the enthalpy of evaporation ΔH_v and the effective frequency ν of molecular vibration[7]. On the other hand, previously, one of the authors proposed a modified Lindemann's equation based on a model theory[8,9], which provides the effective frequency as a function of the surface tension of a liquid. Recently, on combining the equation for the vapor pressure of liquid based on the harmonic oscillator model with the modified Lindemann's equation, the authors have derived an equation for the vapor pressure as functions of some known physical quantities. Therefore, the enthalpy of evaporation for molten salts and fluxes can be calculated using measured surface tension.

In this study, the enthalpies of evaporation of molten salts have been estimated using the equation. An attempt is also made to estimate the temperature dependence of ΔH_v for some molten salts from their melting points to boiling points. The estimated values are compared with experimental data. In addition, The values of ΔH_v have been predicted for several molten salts for which no experimental data, to the authors' knowledge, have been reported.

2. Calculation of the enthalpy of evaporation

By combining the equation based on the harmonic oscillator model[7] which provides a relationship among p, ΔH_v and ν, and the modified Lindemann's equation[8,9] which provides a relationship between ν and σ, we derived the following equation for vapor pressure.

$$p = C\frac{\sigma^{3/2}}{T^{1/2}}\exp\left(-\frac{\Delta H_v}{NkT}\right) \qquad (1)$$

where C is a constant which is determined separately for liquid metals and molten salts. In this work, the value of 4.2×10^{13} (in SI units) for the constant C was determined for molten salts so as to best fit experimental values of ΔH_v. Equation (1) would be applied to the whole liquid range from the melting point to the boiling point. Equation (1) can easily be applied to various single molten salts and fluxes, since it does not contain explicitly the mass of the harmonic oscillator. Since p is one atmospheric pressure, i.e. 1.013×10^5 Pa, at the boiling point, only the value of σ is required to calculate the value of the enthalpy of evaporation of a molten salt at its boiling point $\Delta H_{v,b}$.

3. Results and discussion

3.1 The enthalpies of evaporation of molten salts at their boiling points

The enthalpies of evaporation of the molten salts at their boiling points $\Delta H_{v,b}$ can easily be evaluated from Eq.(1). In the evaluation, the extrapolated values were used for the surface tensions σ_b[2,10] at their boiling points T_b. Their values are listed in Table 1.

In Fig.1, the calculated values of $\Delta H_{v,b}$ are compared with those of experimental ones. As can be seen from Fig.1, the calculated values agree well with experimental ones within the ± 10 per cent error band. The agreement between calculation and experiment for these molten salts is surprisingly good. In Fig.2, the experimental values of $\Delta H_{v,b}$ for molten salts are plotted against their boiling points. It is seen from Fig.2 that Trouton's rule (for liquid metals, $\Delta H_{v,b} = 91.2T_b$ in SI units) is applicable to these molten salts with the slope of 100 $JK^{-1}mol^{-1}$ within the error band of ± 20 per cent.

3.2 The enthalpies of evaporation of molten salts at their melting points

The enthalpies of evaporation of molten salts at their melting points $\Delta H_{v,m}$ have been calculated using the experimental values of the surface tension σ_m[2,10] and the vapor pressure p_m[1] at their melting points T_m. The data used for the calculation of $\Delta H_{v,m}$ are given in Table 1.

Figure 3 shows the comparison between the calculated and the experimental values. The experimental data for $\Delta H_{v,m}$ are from Ref.[1]. As is obvious from Fig.3, the calculated values agree well with experimental ones within the ± 10 per cent error band. Also surprisingly good agreement is obtained between calculation and experiment for these molten salts. On the other hand, in Fig.4, the experimental values of $\Delta H_{v,m}$ for molten salts are plotted against their melting points. As can be seen from Fig.4, a well-known empirical linear relationship exists with the slope of 190 $JK^{-1}mol^{-1}$. However, molten $CaCl_2$ and $AgCl_2$ salts are outside the ±20 per cent error band from this relation.

An attempt has been made to estimate the temperature dependence of ΔH_v of some molten salts. In Fig.5, the calculated values from their melting points to boiling points are compared with the experimental data which are interpolated linearly. The calculated values of ΔH_v vary curvedly with temperature.

Equation (1) gives good results for ΔH_v values of molten salts, and can be used for predicting them. To the authors' knowledge, there are no experimental data on $\Delta H_{v,m}$ and

$\Delta H_{v,b}$ for molten salts such as AgBr at its melting point. The predicted values of $\Delta H_{v,m}$ and $\Delta H_{v,b}$ are listed in Table 2. Incidentally, the extrapolated values for the surface tension σ_b of molten salts are also given in Table 1.

Table 1 The experimental data used for calculating the enthalpies of evaporation for molten salts.

Salt	T_m/K	T_b/K	σ_m/mNm^{-1}	σ_b/mNm^{-1}	log p_m/Pa
LiF	1120	1954	250	160	0.427
NaF	1260	1983	186	127	1.528
KF	1131	1783	141	92	1.711
RbF	1048	1663	166	103	1.635
CsF	976	1483	106	71	2.060
LiCl	883	1655	136	83	0.396
NaCl	1074	1738	116	54	1.611
KCl	1043	1680	99	53	1.712
RbCl	988	1654	98	43	1.486
CsCl	919	1573	92	39	1.394
NaBr	1020	1666	100	60	1.615
KBr	1007	1656	89	43	1.677
RbBr	955	1625	101	62	1.288
CsBr	912	1573	83	43	1.213
NaI	933	1577	88	30	1.120
KI	954	1603	79	23	1.512
RbI	920	1577	81	36	1.158
CsI	899	1553	75	37	1.312
AgCl	728	1837	179	121	-3.383
*AgBr	707	1833	154	126	-4.639
MgF$_2$	1536	2605	228	180	1.052
CaF$_2$	1691	2783	298	206	0.936
SrF$_2$	1673	2753	282	190	1.004
BaF$_2$	1593	2655	235	139	1.296
**CaCl$_2$	1055	2273	152	88	-1.628
**SrCl$_2$	1148	2300	169	106	———
BaCl$_2$	1235	2103	166	97	———
CdCl$_2$	842	1234	112	84	2.382
SnCl$_2$	520	925	101	68	———
PbCl$_2$	774	1225	137	87	1.595
**CaBr$_2$	1015	1083	119	116	———
*BiCl$_3$	503	714	73	43	2.632
*BiBr$_3$	492	734	70	44	1.992

* $\Delta H_{v,m}$ values were predicted. ** $\Delta H_{v,b}$ values were predicted.

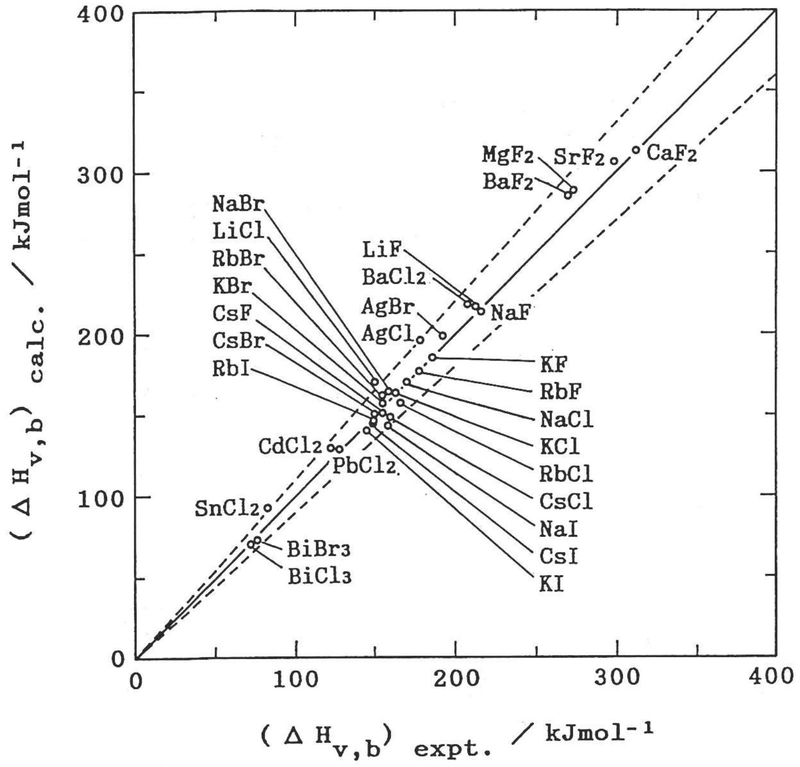

Fig.1. Comparison of the calculated enthalpies of evaporation for molten salts at their boiling points $(\Delta H_{v,b})_{calc}$ with the experimental data $(\Delta H_{v,b})_{expt}$. Dashed lines represent the ± 10 % error band.

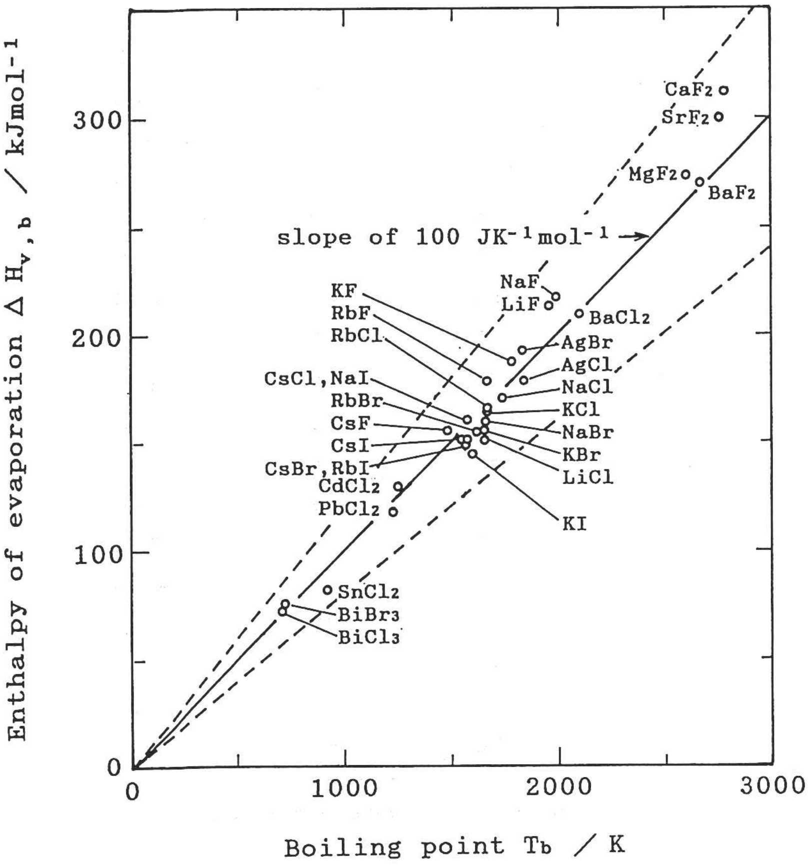

Fig.2. Relation between the enthalpies of evaporation for molten salts at their boiling points $\Delta H_{v,b}$ and their boiling temperatures T_b, representing Trouton's rule. Dashed lines represent the ± 20 error band.

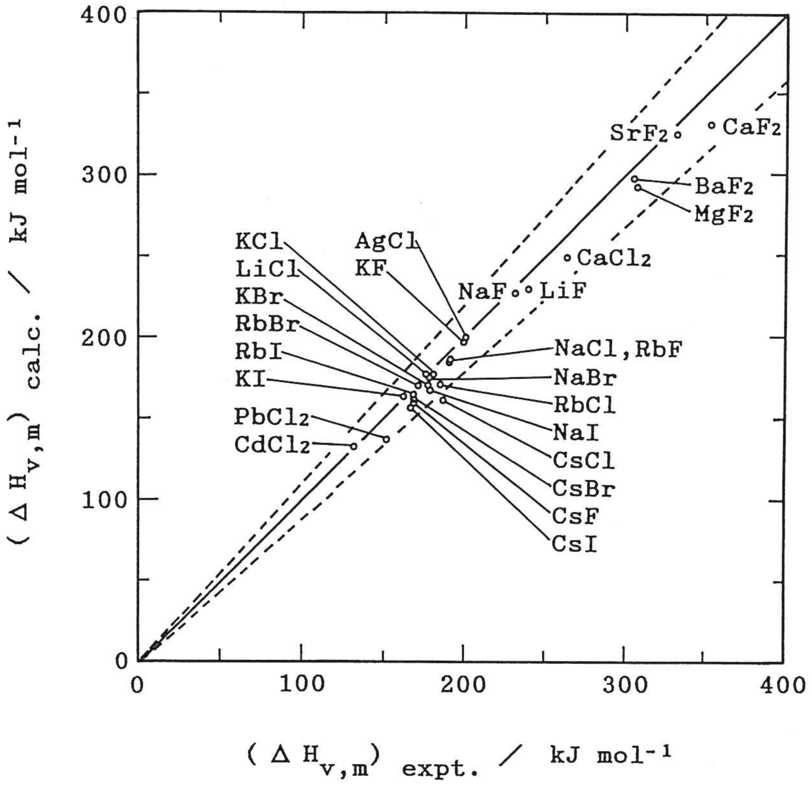

Fig.3.
Comparison of the calculated enthalpies of evaporation for molten salts at their melting points $(\Delta H_{v,m})_{calc}$ with the experimental data $(H_{v,m})_{expt}$. Dashed lines represent the ± 10 % error band.

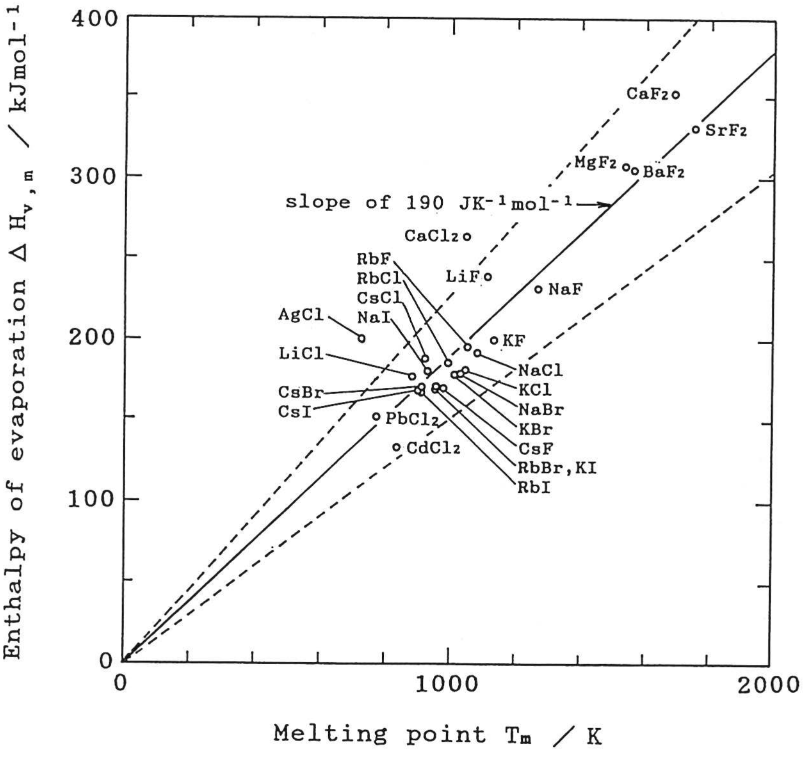

Fig.4.
Relation between the enthalpies of evaporation for molten salt at their melting points $\Delta H_{v,m}$ and their melting temperatures T_m. Dashed lines represent the ± 20 % error band.

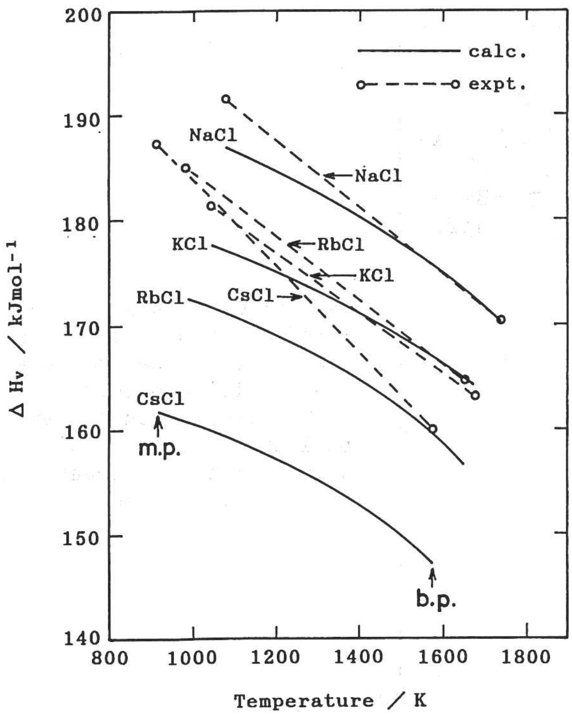

Fig.5. Temperature dependence of the enthalpies of evaporation ΔH_v for molten alkali chrolides.

Table 2. The predicted values of the enthalpy of evaporation for several molten salts at their melting points $\Delta H_{v,m}$ and at their boiling points $\Delta H_{v,b}$.

Molten salt	AgBr	$BiCl_3$	$BiBr_3$
Melting point/K	703	505	492
$\Delta H_{v,m}$/kJmol^{-1}	210	77	81

Molten salt	$CaCl_2$	$SrCl_2$	$CaBr_2$
Boiling point/K	2273	2300	1083
$\Delta H_{v,b}$/kJmol^{-1}	233	241	118

4. Conclusions

The enthalpies of evaporation of molten salts at their melting points and at their boiling points have been calculated using the equation proposed by the authors. The calculated values agreed well with the experimental data within the ± 10 per cent error band for both at their melting points $\Delta H_{v,m}$ and at their boiling points $\Delta H_{v,b}$.

The values of $\Delta H_{v,m}$ and $\Delta H_{v,b}$ were predicted for sevaral molten salts for which experimental data are lacking.

References:

1) For example, O.Kubaschewski and C.B.Alcock : Metallurgical Thermochemistry, Pergamon Press, (1979), P.258.
2) For example, G.J.Janz: Molten Salts Handbook, Academic Press New York, (1967)
3) A.S.Skapski : J.Chem.Phys., 16(1948), 389.
4) R.A.Oriani : J.Chem.Phys,, 18(1950), 575.
5) A.A.Grosse : J.Inorg.Nucl.Chem., 26(1964), 1349.
6) R.Stolevik : Acta Chem.Scand., 43(1989), 860.
7) For example, R.H.Fowler and E.A.Guggenheim : Statistical Thermodynamics, Cambridge Univ. Press, (1956), p.336.
8) T.Iida, K.Kasama, M.Misawa and Z.Morita : J.Jpn.Inst.Met., 38(1974), 177.
9) T.Iida and R.I.L.Guthrie : The Physical Properties of Liquid Metals, Clarendon Press·Oxford, (1988).
10) K.Ogino and S.Hara: Tetsu to Haganė, 64(1978), 523.