Title	Heat of Fusion of Barium Fluoride by Cryoscopic Measurement
Author(s)	Iwamoto, Nobuya; Suito, Hideaki; Satoh, Ichiro
Citation	Transactions of JWRI. 1974, 3(1), p. 33-35
Version Type	VoR
URL	https://doi.org/10.18910/4157
rights	
Note	

Heat of Fusion of Barium Fluoride by Cryoscopic Measurement[†]

Nobuya IWAMOTO*, Hideaki SUITO** and Ichiro SATOH***

Abstract

The heat of fusion of barium fluoride has been obtained by means of cryoscopic measurement described previously.[1] It was found to be 4560±80 cal mol⁻¹ from the BaF₂ branch of the liquidus in the BaF₂-MgF₂ system.

1. Introduction

In the course of an investigation of alkaline-earth fluorides–alkaline-earth silicates system, a knowledge of the heat of fusion of the barium fluoride become necessary, since no calorimetrically measured values are available in the literature and the values drived from the phase diagram are widely scattered.[2), 3), 4)]

Okamoto and Nishioka[2)] determined the phase diagram of the BaF₂-MgF₂ system and the heat and entropy of fusion of barium fluoride were found to be 5100 cal mole⁻¹ and 3.2 e. u. from the BaF₂ branch of the liquidus. Petit and Cremieu[3)] reported the heat and entropy of fusion as 6800±100 cal mole⁻¹ and 4.35 e. u., respectively by cryoscopic measurement. Delbove[4)] summarized an extensive investigation of the formation of solid solutions in barium fruoride melts with various chlorides, fluoride, and alkaline-earth oxides as solutes. His reported heat and entropy of fusion were respectively; 5600 cal mole⁻¹ and 3.46 e. u. and he found that no solid solution of BaF₂ exists in the systems BaF₂-MgF₂ and BaF₂-NaF.

In the present work, the BaF₂ branch of the liquidus in the BaF₂-MgF₂ system has been determined by thermal analysis descrived previously.[1)] It was found that the heat of fusion from the BaF₂ branch of the liquidus in the BaF₂-NaF system included the experimental error due to the vaporization of NaF.

2. Experimental

The experimental apparatus and procedure were previously described in detail.[1)] Commercial barium fluoride (Kanto. Chem. G. R.) and commercial magnesium fluoride (Kanto. Chem. G. R.) were purified by mixing $NH_4F.HF$ and sorbed HF were driven off by heating further at 800 C under continuous argon flush until most of the excess $NH_4F.HF$ vaporied.

3. Results and Discussions

The activity a_s of the solvent at temperature T at which the pure solvent crystallized out of solution can be expressed as

$$\ln a_{s(T)} = \frac{-\Delta H_f^0}{R}\left(\frac{1}{T} - \frac{1}{T^0}\right) - \frac{\Delta C_p}{R}\left(\ln \frac{T^0}{T} - \frac{T^0 - T}{T}\right)$$

where ΔH_f^0 is the enthalpy of fusion of the solvent at melting point T^0 and ΔC_p is the difference in specific heat for liquid and solid.

Thus the measured freezing point depression of the solvent and the necessary calorimetric data enable the accurate calculation of activity of solvent at temperature T. If we neglect the ΔC_p term, eq. (1) can be reduced as

$$\frac{1}{T} = \frac{1}{T^0} - \frac{R}{\Delta H_f^0}\ln a_{s(T)}$$

Introducing $a_{s(T)} = N_s \gamma_s$ where N_s and γ_s are the mole fraction and activity coefficient of solvent.

We obtain

$$\frac{1}{T} = \frac{1}{T^0} - \frac{R}{\Delta H_f^0}(\ln N_s + \ln \gamma_s)$$

Plotting $\ln N_s$ as a function of $1/T$ should give a straight line in the region where deviation from an ideal solution are small, the heat of fusion being determined by the slope of the line. The experimental dataı

---

are given in **Table 1** and shown in **Fig. 1.**

Table 1.

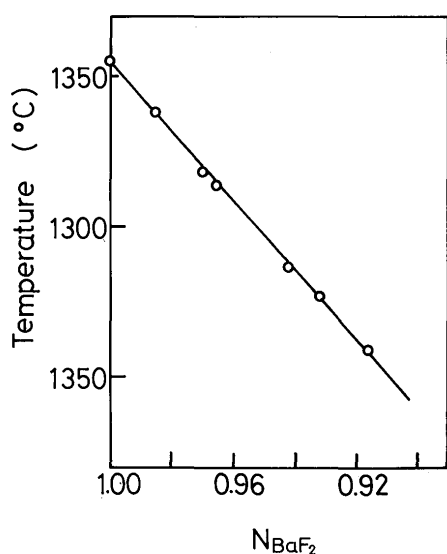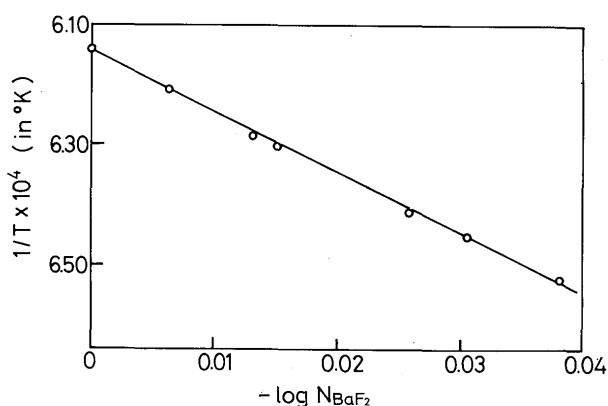| Mole Fraction of BaF_2	$-\log N_{BaF_2}$	T (°C)
1	0.	1355.0
0.9850	0.00656	1338.0
0.9701	0.01318	1318.2
0.9655	0.01525	1313.8
0.9421	0.02590	1286.7
0.9320	0.03058	1277.1
0.9161	0.03806	1259.0

Fig. 1. Freezing point diagram for BaF_2-MgF_2 system.

Fig. 2 shows $-\log N_{BaF_2}$ as a function of 1/T. From the slope in Fig. 2, the heat of fusion for BaF_2 was calculated by means of least-square method and found to be 4560 ± 80 cal mole^{-1}. The value of the heat of fusion may be compared with other values

Fig. 2. The relationship between mole fraction of barium fluoride ($-\log N_{BaF_2}$) and inverse temperature (1/T) for the system BaF_2-MgF_2.

from phase diagram measurements as given in **Table 2.** The heat and entropy of fusion determined in the present work are lower than other investigation's whereas the value of melting point in the present work is considerably higher than that found by other investigator.

Table 2.

ΔH_f^0 (cal mole^{-1})	ΔS_f^0 (e. u.)	T (°k)	Investigator
5100	3.21	1590	Okamoto and Nishioka[2]
6800 ± 100	4.35	1563	Petit and Cremieu[3]
5600	3.46	1619	Delbove[4]
4560 ± 80	2.80	1628	Present Study

The entropy of fusion calculated from the phase diagram in the present work may be compared with the entropy of fusion of alkaline-earth fluorides found calorimetrically by other investigators.[5,6,7,8] This is shown in **Fig. 3.** As shown in Fig. 3. the entropies of fusion in alkaline-earth halides trend to decrease with an increase in the size of the cation (excepting the Sr salts) and trend to increase with an increase in anion size (excepting $SrBr_2$ and $MgBr_2$). But they do not exhibit the simple regurarities in ΔS_f apparent in the alkali halides[9], since the alkaline-earth halides possess a variety of crystal structures.[10]
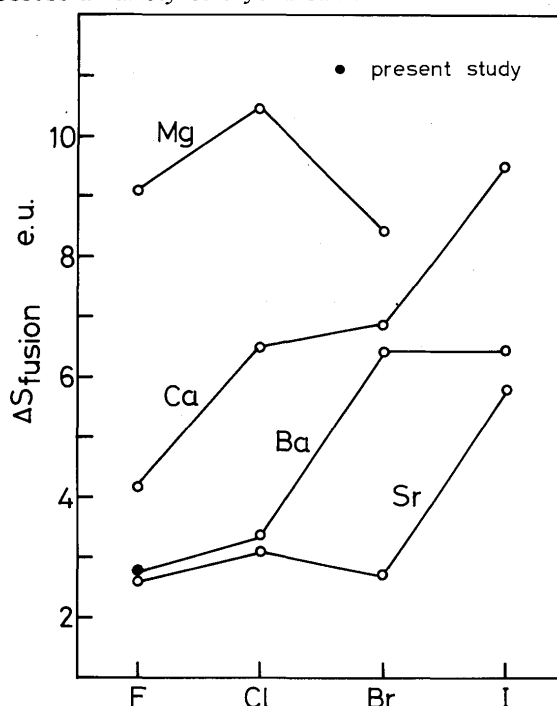

Fig. 3. Entropy of fusion of the alkaline-earth halides.

References

1) N. Iwamoto, H. Suito, S. Hamamatsu and I. Satoh : Transactions of JWRI. 2 (1973) 75.

2) M. Okamoto and U. Nishioka: Sci. Rep. Tohoku. Univ. (I) 24 (1935) 141.

3) G. Petit and A. Gremieu: Compt. Rend. Acad. Sci. 243 (1956) 360.

4) F. Delbove: Silicates indust. 7/8.(1967) 257.

5) A. S. Dworkin and M. A. Bredig: J. Phys. Chem. 67 (1963) 697.

6) G. E. Moore: J. Amer. Chem. Soc., 66 (1943) 1700.

7) B. F. Naylor: J. Amer. Chem. Soc. 67 (1945) 150.

8) G. J. Janz, F. J. Kelley and J. L. Pérano: Trans. Farad. Soc. 59 (1963) 2718.

9) A. S. Dworkin and M. A. Bredig: J. Amer. Chem. 64 (1960) 269.

10) Pascal (ed) Nouvelle Traite de Chimie Minerale vol iv (Masson et Cie, Paris, 1958).