

I. PHYSICS

Chemical Physics

VAPORIZATION OF ALKALI HALIDE CRYSTALS

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The equation for heat of vaporization of ionic crystals has been derived using Gaussian and Woodcock potential energy functions. These equations have been used to generate two sets of data for the heat of vaporization of alkali halides using the crystalline state data and the gaseous state data respectively. The calculated values are compared with those obtained from the thermochemical cycles.

Keywords: Enthalpy of Vaporization; Alkali Halide Crystals; Interaction Potential; Woodcock Potential

INTRODUCTION

VARIOUS empirical and semi-empirical interaction potential energy functions have been suggested to understand the binding of ionic crystals. If the binding between the atoms of a crystalline is known, it is possible to compute various properties of the crystals. The first property which was calculated by Born using the theory of ionic crystals (Born & Huang, 1954) is the lattice energy. While dealing with the energetics of the ionic crystals, the more realistic processes are vaporization, dissociation and atomization. A number of workers (Narayan & Ramaseshan, 1976; Sanderson, 1967, 1968; Sangster *et al.*, 1978*a, b*; and Thakur, 1974, 1975, 1977) have evaluated the atomization energy and dissociation energy of the ionic salts. In the present paper, we have evaluated the values of enthalpy of vaporization, $\Delta H_V^0(MX)$ (*c*), of alkali halides on the basis of Gaussian (Varshni & Shukla, 1961) and recently proposed Woodcock (1974) potentials and the results are compared with the cyclic data.

THEORETICAL

The potential energy of an ion pair interacting with each other and with the rest of lattice is given by

$$\phi(r) = - \frac{\alpha Z_1 Z_2 e^2}{r} + M\psi(r), \quad \dots(1)$$

where α is the Madelung constant, e is the electronic charge, M the coordination number of the lattice, $\psi(r)$ the repulsive potential, Z_1 and Z_2 are the charges on the

ions and r is the distance between them. The potential energy at interionic distance r of a single ion pair interacting with each other is

$$U(r) = - \frac{Z_1 Z_2 e^2}{r} + \psi(r) \quad \dots(2)$$

The energy required to change a crystal into the ion pairs having the interionic distance, r_0 , (the nearest neighbour distance in the crystalline state) is,

$$-\Delta E_1 = \phi(r_0) - U(r_0) \quad \dots(3)$$

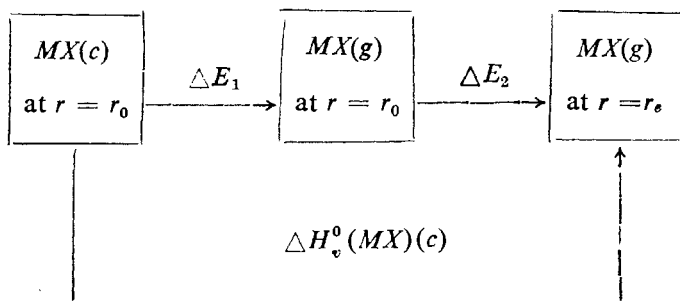
where $U(r_0)$ is the potential energy of an ion pair interacting only with each other. Energy required to change the interionic distance of the ion pair from r_0 to r_e is given by

$$\Delta E_2 = \int_{r_0}^{r_e} \left[\frac{dU(r)}{dr} \right] dr, \quad \dots(4)$$

where r_e is the equilibrium interionic distance of ion pair in gaseous molecule. Therefore the total enthalpy of vaporization of the crystal is

$$\Delta H_v^0 (MX) (c) = \Delta E_1 + \Delta E_2 \quad \dots(5)$$

The above process for the calculation of $\Delta H_v^0 (MX) (c)$ takes the following steps of transformation:



Now considering the Gaussian (Varshni & Shukla, 1961) potential energy function for $\psi(r)$,

$$\psi(r) = P \exp(-kr^2) \quad \dots(6)$$

and for Woodcock (1974) potential function for $\psi(r)$,

$$\psi(r) = AR^{-m} \exp[-B(R^n - 1)] \quad \dots(7)$$

We get from eqns. (1) to (5),

$$\begin{aligned} \Delta H_v^0 (MX) (c) = & \frac{Z_1 Z_2 e^2}{r_0} (\alpha - 1) - P(M-1) \exp(-kr_0^2) \\ & + Z_1 Z_2 e^2 (r_0^{-1} - r_e^{-1}) \\ & - P \left[\exp(-kr_0^2) - \exp(-kr_e^2) \right] \quad \dots(8) \end{aligned}$$

and

$$\begin{aligned} \Delta H_v^0(MX)(c) = & \frac{Z_1 Z_2 e^2}{r_0} (\alpha - 1) - A (M - 1) r_0^{-m} \exp \left[-B (r_0^n - 1) \right] \\ & + Z_1 Z_2 e^2 (r_0^{-1} - r_e^{-1}) - A \left\{ r_0^{-m} \exp \left[-B (r_0^n - 1) \right] \right. \\ & \left. - r_e^{-m} \exp \left[-B (r_e^n - 1) \right] \right\}, \end{aligned} \quad \dots(9)$$

where P , k , A and B are potential parameters and m and n were taken from Woodcock's paper (1974).

RESULTS AND DISCUSSION

For the calculation of enthalpy of vaporization from eqns. (8) and (9), we require the values P , k , A , and B . We have obtained two sets of values of these parameters according to the following criteria corresponding to the crystalline state and gaseous state respectively

$$\phi'(r_0) = 0 \quad \dots(10a)$$

$$\phi''(r_0) = \frac{9Cr_0}{\beta} \quad \dots(10b)$$

and

$$U'(r_e) = 0 \quad \dots(11a)$$

$$U''(r_e) = k_e \quad \dots(11b)$$

where C is the crystal structure parameter, β the compressibility and k_e is the force constant of the MX gaseous molecule. From these two sets of the values for P , k , A , and B , we generate two sets of the values of $\Delta H_v^0(MX)(c)$ with Gaussian

potential and two sets of the values of $\Delta H_v^0(MX)(c)$ with Woodcock potential for alkali halides as listed in Table I. The values of crystal parameter r_0 and β , and molecular constants r_e and k_e used in the calculation of P , k , A , and B according to eqns. (10a, b) and (11a, b) are taken from the literature (Pandey, 1970). In order to compare our results, we calculated the values of enthalpy of vaporization from thermochemical cycles. Considering the cycle on p . 538, the following equations for

$\Delta H_v^0(MX)(c)$ can be obtained :

$$\Delta H_v^0(MX)(c) = E_a - D_e \quad \dots(12)$$

$$\Delta H_v^0(MX)(c) = \Delta H_f^0(MX)(c) - \Delta H_f^0(MX)(g) \quad \dots(13)$$

and
$$\Delta H_v^0(MX)(c) = U_L - D_i \quad \dots(14)$$

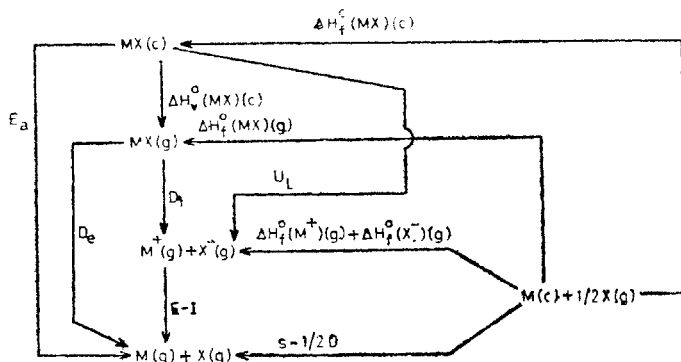


TABLE I

Enthalpy of vaporization $\Delta H_v^o(MX)(c)$ of alkali halides from different sources (in K. J. mol.⁻¹)

Alkali halides	$\Delta H_f^o(MX)(c)$ eqn. (8) ^a	$\Delta H_v^o(MX)(c)$ eqn. (8) ^b	$\Delta H_g^o(MX)(c)$ eqn. (9) ^a	$\Delta H_f^o(MX)(c)$ eqn. (9) ^b	$\Delta H_v^o(MX)(c)$ eqn. (12) ^c	$\Delta H_g^o(MX)(c)$ eqn. (13) ^c	$\Delta H_v^o(MX)(c)$ eqn. (14) ^d
LiF	239.8	366.9	296.4	235.9	275.3	—	280.9
LiCl	253.6	303.8	263.5	274.2	208.0	187.1	220.3
LiBr	243.6	284.9	251.7	240.1	203.7	178.8	208.4
LiI	228.2	262.4	236.6	224.9	202.0	204.2	189.1
NaF	262.9	309.7	312.0	365.2	308.7	267.8	285.1
NaCl	251.7	283.3	256.4	264.1	231.1	229.1	251.2
NaBr	241.7	269.3	247.7	213.8	215.0	208.0	221.9
NaI	227.0	247.6	234.7	209.5	205.9	200.5	202.7
KF	264.4	291.4	281.2	264.0	249.8	—	227.3
KCl	235.1	259.5	243.9	215.2	224.1	220.0	227.3
KBr	227.1	244.1	228.1	225.1	214.0	—	217.8
KI	215.8	222.6	209.0	—	202.7	—	206.5
RbF	257.5	286.2	229.6	248.4	195.1	—	231.1
RbCl	229.5	248.8	231.1	226.0	201.7	—	217.6
RbBr	219.9	238.3	219.1	202.7	200.0	—	210.2
RbI	210.9	217.2	209.7	193.9	195.6	—	201.4
CsF	257.1	259.9	252.5	239.9	155.6	—	194.6
CsCl	214.0	233.9	221.3	221.1	188.0	—	206.1
CsBr	208.6	225.4	213.7	187.3	190.2	—	198.9
CsI	197.9	206.2	201.4	180.6	195.0	—	195.0

a. Potential parameter obtained from the crystal data according to condition(10a, b).

b. Potential parameter obtained from the gaseous state data according to condition(11a, b).

c. Calculated from eqn. (12) using E_a of Sanderson (1967) and D_e of Gaydon(1953).

d. Calculated from eqn. (14) using the experimental values of U_L and D_e compiled by Woodcock (1974).

The values of $\Delta H_v^0(MX)(c)$ are calculated according to eqns. (12) to (14) and given in Table I. The values of various thermochemical data used for these calculations are taken from literature (Bernard & Busnot, 1978; Gaydon, 1953; Pandey, 1970; Sanderson, 1967; and Woodcock, 1974). We have presented the values of $\Delta H_v^0(MX)(c)$, according to eqn. (13), for only eight crystals, because we could not obtain the values of $\Delta H_f^0(MX)(c)$ for other crystals. The calculated values of $\Delta H_v^0(MX)(c)$ from eqn. (8) are listed in the second and third columns of Table I. The computed values of $\Delta H_v^0(MX)(c)$ from eqn. (9) are listed in column (4) and (5). From Table I, it can be seen that some values of $\Delta H_v^0(MX)(c)$ do not fit into the sequence. For example in the case of cesium halides, the values of $\Delta H_v^0(MX)(c)$ from eqn. (12) are in increasing order, whereas in most of the cases these values are in decreasing order. Therefore, no specific comments can be made about this. Further, the computed values of $\Delta H_v^0(MX)(c)$ from eqn. (13) show fairly good agreement for sodium halides in comparison to the other theoretical values. It is found that the calculated values of $\Delta H_v^0(MX)(c)$ from eqns. (8) and (9) agree fairly well with the various cyclic data. These data may be useful in correlating the crystalline state and gaseous state energetics of a salt. In addition, the results listed in Table I show that Woodcock potential gives better agreement than the Gaussian potential.

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