Thermal expansivity of NaCl and KCl at high temperatures

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Abstract:

A new mathematical equation for temperature dependence of thermal expansivity of Alkali halides (NaCl and KCl) has been developed for high temperatures. This relation is used to calculate thermal expansivity of NaCl and KCl for temperature range 350K to 750K along with available values of melting temperature. The results obtained are compared with available data. A good agreement between calculated and available data verifies the validity of obtained relation.

Keywords: Thermal expansivity, Alkali halides, Melting temperature, 2010 Mathematics, Subject Classification, 00A79.

1. Introduction

Thermal expansivity is a very useful parameter to measure the thermodynamic and dielectric properties of solids at high temperatures because it has been emphasized⁶ that most of the errors are found in the calculations of thermodynamic functions due to uncertainty of thermal expansivity. To overcome such type of difficulty a model for evaluating and predicting thermal expansivity in the region of high temperatures is developed. Several attempts²⁻⁵ have been made to investigate the temperature dependence of thermal expansivity considering its linear as well as non-linear dependence. We have used the thermodynamic data, compiled by Anderson¹, for four ionic solids viz. NaCl and KCl. The melting temperature of NaCl and KCl are nearly 800K, respectively.

In the present study, a new expression for thermal expansivity dependent on temperature has been developed using equation of state. This relation is used to calculate values of thermal expansivity at higher temperatures for NaCl and KCl. The results thus obtained are in good agreement with standard results.

2. Method of Analysis

The Anderson-Gruneisen parameter δ_T of material is given by following relation¹

$$\delta_T = -\frac{1}{\alpha K_T} \left(\frac{\partial K_T}{\partial T} \right) \dots\dots\dots (1)$$

Where K_T is isothermal bulk modulus. Let us assume that δ_T remains constant with change in temperature, at atmospheric pressure, then following equation is valid¹

$$\frac{K_T}{K_{T0}} = (V/V_0)^{-\delta_T} \dots\dots\dots (2)$$

Here subscript “0” refers to the value of concern parameter at zero or near to Debye temperature.

Singh et al¹¹. explained a relationship between α and K_T on the basis of experimental data¹ and calculated data for solids NaCl and KCl. for high temperatures.

The linear relationship between α and K_T is given by¹¹

$$\alpha + MK_T = C \dots\dots\dots (3)$$

Where M and C are constant which depends on material. Values of M and C are available elsewhere¹¹.

Using Eq. (3) along with Eq. (2), we obtain

$$(C - \alpha) (V/V_0)^{\delta_T} = \text{constant} \dots\dots\dots (4)$$

Differentiation of Eq. (4) with respect to temperature T we have

$$(V/V_0)^{\delta_T} \left[-\left(\frac{\partial \alpha}{\partial T}\right) \right] + (C - \alpha) \delta_T (V/V_0)^{\delta_T} \frac{1}{V} \frac{\partial V}{\partial T} = 0 \dots\dots\dots (5)$$

The mathematical expression for thermal expansivity is given by

$$\alpha = \frac{1}{V} \frac{\partial V}{\partial T} \dots\dots\dots (6)$$

Using Eq. (6) in Eq. (5) we get following expression

$$\frac{\partial \alpha}{\partial T} = m \alpha \left(1 - \frac{\alpha}{C} \right) \dots\dots\dots (7)$$

Here m is given by

$$m = C \delta_T \dots\dots\dots (8)$$

On integration of Eq. (7) for high temperature we get

$$\alpha = C \left[1 + \frac{(C - \alpha_0)}{\alpha_0} \exp(-C \delta_T (T - T_0)) \right]^{-1} \dots\dots\dots (9)$$

In the recent literature^{3,5,11} the equation of state has been used widely to study the properties of ionic solids at high pressure and temperatures. The inter atomic distance can be calculated using equation of state. Shanker et al¹⁴. used the method based on the Taylor series expansion of lattice potential energy and calculated the melting temperature of some solids. It has been found that the relation derived by researcher¹¹ is contained in the theory of equation of state and may be obtained in simplified way¹.

The equation of state for solids can be written as,

$$P = -\frac{dW}{dV} + P_{Th} \dots\dots\dots (10)$$

where P is pressure, W is potential energy, V is volume and P_{Th} is thermal pressure. By expanding W in the powers of volume using Taylor series expansion and considering the terms up to cubic in volume, Shanker et al¹⁴ obtained following relation.

$$\frac{V}{V_0} - 1 = \frac{1 - [1 - \frac{(2K'_0 + 1)}{K'_0} \Delta P_{Th}]^{1/2}}{K'_0 + 1} \dots\dots\dots (11)$$

and

$$\Delta P_{Th} = \alpha_0 K_0 (T - T_0) \dots\dots\dots (12)$$

Where α coefficient of thermal expansion, B is bulk modulus, B' is first derivative of bulk modulus and T is temperature. Here 0 refers to its initial value.

Eq. (11) can be written as

$$\frac{V}{V_0} - 1 = \frac{1 - [1 - 2\alpha_0 (K'_0 + 1) (T - T_0)]^{1/2}}{K'_0 + 1} \dots\dots\dots (13)$$

Eq. (13) can be used for calculation of inter atomic distances. Results obtained show the increasing behavior with temperature up to finite value of temperature and becomes imaginary, when the temperature further increased. This temperature will be called as melting temperature and calculated from following simple relation.

$$2\alpha_0 (K'_0 + 1) (T_m - T_0) = 1$$

or

$$\alpha_0 = \frac{1}{2 (K'_0 + 1) (T_m - T_0)} \dots\dots\dots (14)$$

Using Eq. (14) Eq. (9) can be written as

$$\alpha = C [2C (T_m - T_0) (K'_0 + 1) \exp - C\delta_T (T - T_0)]^{-1} \dots\dots\dots (15)$$

Results and Discussion

Eq. (15) is based on linear relationship between α and δ_T in high temperature and presents a relation for temperature dependence of thermal expansivity. To verify the suitability of new relation given by Eq. (15), we calculated thermal expansivity of NaCl and KCl in high temperature range.

The required input data are given in Table 1. The calculated values are compared with experimental data¹ in table 2. It has been observed that calculated values are close agreement with experimental data.

Table 1

Solids	δ_T	C (10^{-5} K^{-1}) Ref 1	T_m	K'_0
NaCl	5.56	27.0	1074	5.39
KCl	5.84	25.9	1049	5.47

Table 2

Comparison of calculated values of thermal expansivity of NaCl and KCl with available experimental data					
NaCl α (10^{-5} K^{-1})			KCl α (10^{-5} K^{-1})		
T (K)	Equation (15)	Experimental Ref 1	T (K)	Equation (15)	Experimental Ref 1
300	10.1	11.8	300	10.3	11.0
350	10.8	12.2	350	11.1	11.3
400	11.7	12.7	400	12.0	11.7
450	12.6	13.2	450	12.9	12.1
500	13.7	13.7	500	13.9	12.6
550	14.7	14.3	550	15.0	13.2
600	15.8	14.8	600	16.2	13.7
650	17.0	15.4	650	17.5	14.2
700	18.4	16.0	700	18.8	14.7
750	19.6	16.6	750	20.3	15.2

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