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Correlations for calculating the surface tension and enthalpies of sublimation of alkali halides

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ABSTRACT

The capability of a new model on predicting the surface tension of molten alkali halides is described. A relationship, with a simple form of calculation, exists between the surface tension (γ) at the melting point, molar volume (V), inter-nuclear distance (D) and the enthalpy of sublimation (E_s). The basic idea results from the assumption that all the parameters are constants that are usually easy to acquire. Moreover, two previous models (Furth and Schytil equations) were also checked and applied for calculating surface tension of molten salts. The three formulas have been examined for 20 salts and showed remarkable agreement between calculated and experimental data with a difference of less than 10% for most of the salts studied. The heats of sublimation of alkali halides were, theoretically, calculated and compared to literature values.

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1. Introduction

High temperature melts such as molten salts are substances which are solids at room temperature and liquids at high temperature. Molten alkali halides are of great importance in industry and have a scientifically interesting behavior. The surface tension of high temperature melts are not well established [1]. Considerable efforts have been made to the experimental measurement of the surface tension of molten salts, but the available data is limited due to experimental difficulties, such as strong chemical activity and therefore are corrosive to materials of container and sensors. Information on the surface tension of molten salts is needed for high temperature fuel cells, thermal-energy storage units, fusion reactors and production of new materials in microgravity conditions. Although there are reported models on the prediction of the surface tension of pure molten alkali halides [2–13], it is still necessary to develop simple models or empirical relations capable to calculate such a thermo-physical property. Therefore, precise surface tension data for molten salts and establishment of theoretical models are always required. This paper describes the capability of three relations for predicting the surface tension of alkali halides. The accuracy of these approaches lie in the accuracy of the constants. A correlation for calculating the enthalpy of sublimation of alkali halides is also investigated. Now that the magnitude of the required parameters seems to be generally accepted, it seems worthwhile to calculate the surface tension and the enthalpies of sublimation of the molten alkali halides up-to-date theoretical and experimental data. The values of the surface tension and the relevant physical data from which they are calculated are shown in Table 1.

2. Theory and discussion

The development of scientific research leads to fast increase of experimental data. In order to make proper use of their information, a careful comparison with theoretical calculations must be done.

2.1. Relation I

According to Furth [11], the surface tension (γ) of melts is given as follows:

$$\gamma = 0.51\left(\frac{kT_m}{D^2}\right) \quad (1)$$

where γ is the surface tension (mJ m^{-2}), T_m is the melting point temperature (K), k is the Boltzmann constant (1.38×10^{-23} J K^{-1}) and D (m) is the inter-nuclear distance between ions in an ionic structure (the bond length) which is equal to the sum of the radii of the ions (Table 1). After checking this equation against molten salts, it was found to be invalid, and therefore, it was corrected by introducing the fraction of broken bonds at the surface instead of

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Table 1
Calculated and reported surface tension and enthalpies of sublimation values of alkali halides, and parameters needed for calculations (the reported surface tension values were taken from Refs. [8,15–31]).

Salt	E_s (kJ mol^{-1}) Cal/rep	T_m (K)	ρ ($\times 10^3$ kg m^{-3})	Molar mass ($\times 10^{-3}$ kg mol^{-1})	D ($\times 10^{-10}$ m)	γ (Cal) (mJ m^{-2}) Eq. (2)	γ (Cal) (mJ m^{-2}) Eq. (3)	γ (Cal) (mJ m^{-2}) Eq. (5)	γ (Rep) (mJ m^{-2})
LiF	237/277	1118	2.635	25.9	2.01	233	256	273	252, 236, 217, 221, 232
LiCl	187/212	878	2.068	42.4	2.49	120	123	124	138, 131, 128, 127
LiBr	175/205	825	3.464	86.8	2.64	100	105	104	110, 123, 109
LiI	158/204	742	4.076	133.8	2.88	75	76	86	91, 94, 99, 95
NaF	269/281	1266	2.558	42	2.31	200	195	190	201, 187, 186, 185, 184
NaCl	229/230	1074	2.165	58	2.79	117	126	114	114, 111, 106, 138, 116
NaBr	217/222	1020	3.210	102.9	2.94	100	106	98	106, 99, 95, 93, 100, 103
NaI	199/200	934	3.670	149.9	3.18	78	83	75	88, 87, 82, 80, 86, 83
KF	240/241	1131	2.480	58	2.66	135	145	132	141, 146, 144, 143, 127, 132, 138
KCl	222/221	1043	1.984	74.5	3.14	89	97	89	91, 98, 99, 101, 97, 100
KBr	214/217	1007	2.750	119	3.29	78	86	80	82, 89, 90, 88
KI	202/205	954	3.123	166	3.53	65	71	66	79, 77, 81, 78
RbF	227/229	1068	3.557	104.4	3.81	114	117	106	130, 127, 126, 125
RbCl	210/197	991	2.800	120.9	3.29	77	84	72	99, 98, 95, 91, 87
RbBr	205/176	966	3.350	165.3	3.44	69	75	58	91, 87, 84, 86
RbI	196/193	920	3.110	212.3	3.68	57	57	50	81, 76, 71, 77, 80
CsF	202/205	955	4.115	151.9	3.00	90	91	80	107, 106, 104
CsCl	195/196	918	3.990	168.3	3.48	64	79	78	91, 92, 85, 89
CsBr	193/195	909	4.440	212.8	3.63	58	73	71	83, 77, 82
CsI	190/194	894	4.510	259.8	3.87	50	63	63	75, 72, 69, 73

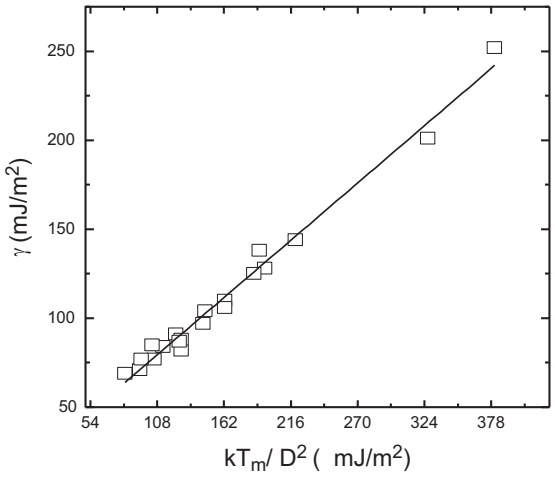

Fig. 1. Correlation of reported surface tension versus KT_m/D^2 for alkali halides.

the numerical value 0.51. Thus, Eq. (1) becomes

$$\gamma = (1-f)\left(\frac{kT_m}{D^2}\right) = 0.613\left(\frac{kT_m}{D^2}\right) \quad (2)$$

In molten salts, the fraction of broken bonds (f) is equal to 0.387. The ratio of coordination number of the surface to the bulk in liquid state (ξ) are given by $\xi = 1-f = 0.613$ [14]. f is a Dimensionless independent temperature constant parameter (a positive fractional number) and it expresses the fraction of broken bonds. The uncertainty of the parameter f, which is a direct factor in the calculated surface tension, is $\pm 4\%$. The f value is determined without calculating the values of bulk and surface coordination numbers, and may be considered as a semi-empirical fitting parameter. The origin and the source of the given numerical f value, which plays a vital role, is obtained by an extensive study of the surface tension of all the molten alkali halide salts. Fig. 1 shows how the surface tension for alkali halides depends on kT_m/D^2. The tangent of the line is $(1-f)$ which was found to be 0.613. It is of interest to see the D^2 (correlation coefficient). This value indicated $f = 0.387$ with three digits of accuracy.

Eq. (2) has been checked against all the molten alkali halides, and the calculated values were found in fair agreement with the reported data (Table 1) [8,15–31]. This simple empirical relation that links the surface tension and the internuclear distance of alkali halide salts is expected to be very useful for calculating the surface tension of molten alkali halides at the melting point in a straightforward fashion and may be applied to molten alkaline earth halides. The good agreement between the calculated and reported values provides strong evidence of its reliability. Also, the agreement tends to confirm the validity of inter-nuclear distance values for the alkali halides which have been employed in the calculations described above.

2.2. Relation II

Schytil equation [13] for calculating surface tension (J m^{-2}) of liquid metals is given by

$$\gamma = C_s\left(\frac{T_m}{V^{2/3}}\right) \quad (3)$$

where V is the molar volume (cm^3 mol^{-1}) and C_s is Schytil coefficient which is equal to 4.1×10^{-7} J mol$^{2/3}$ K^{-1} [31]. Similar relation is also observed for molten alkali halides and other salts [32,33] with $C_s = 0.93$ [34]. However, applying Schytil equation to molten alkali halides with $Cs = 1.05 \times 10^{-7}$ J mol$^{2/3}$ K^{-1} results in surface tension values that are in accord with the reported data (Table 1). Note that $V = M/\rho$, where ρ is the density (kg m^{-3}) and M is molar mass (kg mol^{-1}). Fig. 2 shows how $V^{2/3}$ depends on D^2. A straight line is obtained with high correlation and with a slope of 1.05. This straight line indicates that there is a strong connection of Eqs. (2) and (3).

2.3. Relation III

A new empirical formula is proposed for calculating the surface tension of pure molten alkali metal halides at the melting point. The surface tension is proportional to sublimation energy (E_s), and thus, the simplest way to estimate surface tension value of bulk is correlate the surface tension with enthalpy of sublimation,

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