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RELATIONS BETWEEN THE HEATS OF FORMATION OF THE ALKALI CHALCOGENIDES AND THE ELECTRONEGATIVITIES OF THE CHALCOGEN IONS (O, S, Se AND Te)

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ABSTRACT

The heats of formation of M_2X chalcogenides (M = Li, Na, K, Rb and Cs; X = O, S, Se and Te), $-\Delta H^{\ominus}_{298}$, may be expressed empirically in terms of the electronegativities χ_A of the chalcogen ions

$$-\Delta H^{\ominus}_{298}\frac{\left(-2e^2/r_A\right)}{\left(e^2/r_C\right)^2}=a\chi_A+b$$

where a and b are empirical constants and -2, e, r_C and r_A represent the valence of the anion, the electronic charge, the cation radius and the anion radius, respectively. The values of e^2/r_C and $-2e^2/r_A$ correspond to the electrostatic energy arising between the effective nuclear charge of the M^+ and/or X^{2-} ion and an electron at a distance from the nucleus equal to the ionic radius r_C and/or r_A.

Although its physical meaning is not clear, this empirical equation is useful in predicting the heat of formation. The heats of formation of Rb_2Te(solid) and K_2Te(solid) are estimated as −87 and −89 kcal (th) mol^{-1}, respectively.

INTRODUCTION

Pauling's electronegativity was introduced as an attribute of an atom in a covalent compound. Therefore, his equation $0.208\sqrt{\Delta} = |\chi_X - \chi_Y|$ does not satisfactorily describe the relation between $\sqrt{\Delta}$ and $|\chi_X - \chi_Y|$ in an ionic compound. Ohashi [1–4] has found that the ratio of the heat of formation to the potential energy ($P_E = ne^2/r$) is an effective scaling to correlate the heat of formation of the ionic compound with Pauling's electronegativity. This study examines the relation between the heats of formation of the alkali chalcogenides and the electronegativities of the chalcogen and alkali metal ions concerned.

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The electronegativities of the relevant alkali and chalcogen ions obtained using Pauling's method are listed in Table 1, along with the ionic radii in octahedral sites and the potential energy P_E. The P_E value corresponds to the electrostatic energy between the effective nuclear charge of the M^+ and/or X^{2-} ion and an electron at a distance from the nucleus equal to the ionic radius r. If r is given in Ångströms, P_E may be evaluated, using the expression $N_A ne^2/r = 332(n/r)$ kcal(th) mol^{-1}, where N_A, n, e and r represent Avogadro's number, the valence, the electronic charge and the ionic radius, respectively. The heats of formation of the compounds M_2X (M = alkali metal, X = chalcogen), $-\Delta H^{\ominus}_{298}$(solid), are listed in Table 2. Compared with the heats of formation of the alkali halides, these values have noticeable errors.

Figure 1 illustrates the relation between $-\Delta H^{\ominus}_{298}$(oxide) and χ_C. The heat of formation of an alkali oxide increases as the alkali metal becomes more electronegative, that is, as the $|\chi_{alkali} - \chi_{oxygen}|$ value decreases. Pauling's equation $0.208\sqrt{\Delta} = |\chi_X - \chi_Y|$ does not satisfactorily describe the relation between $\sqrt{\Delta}$ and $|\chi_X - \chi_Y|$ in an alkali oxide.

Figure 2 illustrates the relation between $-\Delta H$ $(= -\Delta H^{\ominus}_{298}(-2e^2/r_A)/(e^2/r_C)^2)$ and χ_C. Although the physical meaning is not clear, the ratio of the heat of formation to the potential energy P_E is an effective scaling to correlate the heat of formation of the alkali chalcogenide with Pauling's electronegativity. The scaled value $-\Delta H$ decreases as the alkali metal becomes more electronegative. However, the $-\Delta H$ values for the potassium chalcogenides deviate significantly from the trends shown in Fig. 2. These deviations suggest that the potassium ion is more electropositive than the

TABLE 1

Electronegativity χ [5], ionic radius r [6] and potential energy (ne^2/r) for alkali metal and chalcogen ions

Ion	χ	r (Å)	ne^2/r (kcal(th) mol^{-1}) [a]
Cs	0.7	1.67	198.8
Rb	0.75 [b]	1.52	218.4
K	0.8	1.38	240.6
Na	0.9	1.02	325.5
Li	1.0	0.76	436.8
O	3.5	1.40	−474.3
S	2.5	1.84	−360.9
Se	2.4	1.98	−335.4
Te	2.1	2.21	−300.5

[a] 1 cal(th) = 4.184 J.

[b] From ref. 1.

TABLE 2

Heat of formation $-\Delta H^{\ominus}_{298}(s)$ [7] and $-\Delta H$ values for the compounds studied

Compound	$-\Delta H^{\ominus}_{298}(s)$ (kcal(th) mol^{-1}) [a]	$-\Delta H$ [b]
Cs_2O	75.9	0.911
Cs_2S	81.1	0.741
Cs_2Se		
Cs_2Te	86.4 [c]	0.657
Rb_2O	78.9	0.785
Rb_2S	83.2	0.630
Rb_2Se		
Rb_2Te		
K_2O	86.8	0.711
K_2S	102.4	0.638
K_2Se	89.0	0.516
K_2Te		
Na_2O	99.2	0.444
Na_2S	89.5	0.305
Na_2Se	82.0	0.260
Na_2Te	82.0	0.233
Li_2O	142.6	0.355
Li_2S	106.7	0.202
Li_2Se	96.0	0.169
Li_2Te	85.0	0.134

[a] 1 cal(th) = 4.184 J.

[b] $-\Delta H = -\Delta H^{\ominus}_{298}(-2e^2/r_A)/(e^2/r_C)^2$.

[c] From ref. 8.

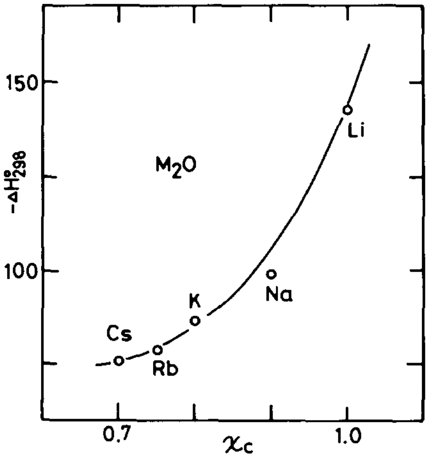

Fig. 1. Heats of formation $-\Delta H^{\ominus}_{298}$ (kcal/mol) of M_2O (M = Li, Na, K, Rb, Cs) plotted against the electronegativities χ_C of the M^+ ions.

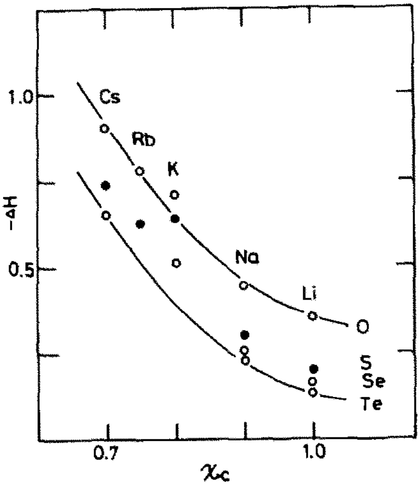

Fig. 2. Values of $-\Delta H$ for the chalcogenides M_2X (M = Li, Na, K, Rb, Cs) plotted against the electronegativities χ_C of the M^+ ions.

value of 0.8 given in Pauling's scale. This assumption results in the simple and uniform $-\Delta H$ vs. χ_C relations not only for alkali chalcogenides but also for alkali halides (e.g. fig. 2 in ref. 1).

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Figure 3 illustrates the relation between $-\Delta H$ and χ_A. Since the $-\Delta H$ value for K_2S is unusually large, the datum point was rejected. Solid lines

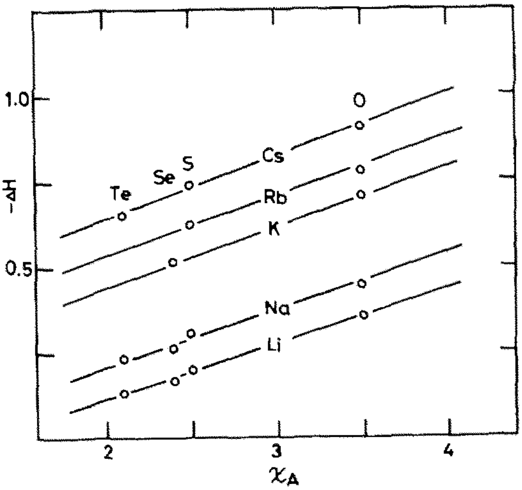

Fig. 3. Values of $-\Delta H$ for the chalcogenides M_2X plotted against the electronegativities χ_A of the X^{2-} ions.

connect the data points for $-\Delta H$. These lines are the result of a least-squares fit to the equation

$$-\Delta H^{\ominus}_{298}\frac{\left(-2e^2/r_A\right)}{\left(e^2/r_C\right)^2}=a\chi_A+b \qquad (1)$$

where a and b are empirical constants. The shape of eqn. (1) is the same as the shapes of the empirical equations for MX, MX_2, MX_3 and MX_4 halides [1–4]. From the correlations shown in Fig. 3, the $-\Delta H$ values of Rb_2Te and K_2Te are estimated as 5.5 and 4.6, and the heats of formation of Rb_2Te and K_2Te as -87 and -89 kcal(th) mol^{-1}, respectively, with noticeable error.

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