106. *Lattice Energies of Some Alkali Selenides and Tellurides.*

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Term-by-term theoretical calculations of the lattice energies of alkali selenides and tellurides with the antifluorite structure are reported. The lattice energies, in kcal./mole (0° K), are: Li_2Se, 564·9; Na_2Se, 508·7; K_2Se, 461·8; Li_2Te, 528·8; Na_2Te, 477·3; K_2Te, 437·3. The results, in conjunction with experimental thermochemical data, yield a value for the two-stage electron affinity of atomic selenium, $E(\mathrm{Se} \longrightarrow \mathrm{Se}^{2-}) = -101$ kcal./mole (0° K).

The calculated lattice energies correspond to Karapet'yants's linear relationships. This has enabled an estimate to be made of the lattice energies of rubidium and cæsium monoselenides and monotellurides.

This paper reports calculations of the lattice energies of the monoselenides and monotellurides of lithium, sodium, and potassium. The results have been employed in conjunction with thermodynamic data to estimate the affinity of atomic selenium for two electrons, which cannot be found by direct experiment.

The theory underlying the calculations of the lattice energies is that of Born and Mayer,[1] and the method is similar to that used by Morris [2] for alkali monoxides and monosulphides.

Calculation of the Lattice Energies.—The lattice energy U_0 of an ionic crystal, namely, the energy required at 0° K to separate the constituent ions per mole to an infinite distance, can be expressed in the form:

$$U_0 = U_E - U_R + U_W - U_Z \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where U_E represents the Coulomb or electrostatic energy of attraction between the ions, U_R the repulsion energy, U_W the van der Waals energy, and U_Z the zero-point energy, which can all be evaluated. The application of this " term-by-term " procedure to calculation of the lattice energies of alkali monoselenides and monotellurides with the antifluorite structure is described below.

(a) *The Coulomb energy term.* This may be obtained from the equation:

$$U_E = e^2NA/r_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where e is the electronic charge ($4{\cdot}8024 \times 10^{-10}$ e.s.u.), N is the Avogadro number ($6{\cdot}023 \times 10^{23}$), and r_0 is the shortest equilibrium internuclear separation of oppositely charged ions in the stable crystal lattice. A is the Madelung constant referred to r_0 for the antifluorite (and fluorite) lattice [3] (5·03878).

Values of r_0 used in the present work have been obtained from the lattice constants a_0 compiled by Wyckoff [4]—for the antifluorite structure $r_0 = \sqrt{3}(a_0/4)$.

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[1] Born and Mayer, *Z. Physik*, 1932, **75**, 1.

[2] Morris, *Proc. Roy. Soc.*, 1957, *A*, **242**, 116; *Acta Cryst.*, 1958, **11**, 163; *J. Phys. Chem. Solids*, 1958, **5**, 264.

[3] Emersleben, *Z. Physik*, 1923, **24**, 73; *Z. phys. Chem. (Leipzig)*, 1955, *B*, **204**, 43; Benson and Van Zeggeran, *J. Chem. Phys.*, 1957, **26**, 1083; Sakamoto, *ibid.*, 1958, **28**, 164.

[4] Wyckoff, " Crystal Structures," Interscience Publ. Inc., New York, 1951.

(b) *The repulsion energy term.* This term may be represented by the expression:

$$U_{\mathrm{R}} = b\boldsymbol{N}\Big[nc_{+-}\exp\Big\{(r_+ + r_- - r_0)/\rho\Big\} + n'c_{++}\exp\Big\{(2r_+ - k_1r_0)/\rho\Big\} + \tfrac{1}{2}n''c_{--}\exp\Big\{(2r_- - k_2r_0)/\rho\Big\}\Big] \quad . \quad . \quad (3)$$

The symbols in this equation have the following significance: b = a repulsion constant obtainable from the condition $(\mathrm{d}U_0/\mathrm{d}r)_{r=r_0} = 0$; c_{+-}, c_{++}, c_{--} = factors introduced by Pauling [5] and given by the expression $c_{1,2} = (1 + z_1/\bar{n}_1 + z_2/\bar{n}_2)$, where z is the formal charge of an ion and $\bar{n}$ is the number of electrons in its outer shell; r_+, r_- = " basic radii " of cations and anions, respectively; n = co-ordination number of an anion; n', n'' = number of nearest like neighbours of a cation and an anion, respectively; ρ = a constant obtainable from compressibility data; k_1 = ratio of the shortest cation–cation distance to r_0; k_2 = ratio of the shortest anion–anion distance to r_0.

In the present calculations the constant ρ has been taken as having the value $\frac{1}{3} \times 10^{-8}$ cm. due to Huggins,[6] and corresponding basic radii due to Huggins [6] and to Huggins and Sakamoto [7] have been used.

(c) *The van der Waals energy term.* This dispersion energy term may be represented by the equation:

$$U_{\mathrm{W}} = \boldsymbol{N}\left\{\frac{C}{r_0^{\,6}} + \frac{D}{r_0^{\,8}}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where C and D are constants for a given crystalline compound, and refer to dipole–dipole and quadrupole–dipole attraction respectively. These constants may be evaluated from the equations:

$$C = S_6'd_{+-} + \tfrac{1}{2}S_6''d_{++} + \tfrac{1}{2}S_6'''d_{--} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$D = S_8'q_{+-} + \tfrac{1}{2}S_8''q_{++} + \tfrac{1}{2}S_8'''q_{--} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

$$d_{1,2} = \frac{3}{2}\alpha_1\alpha_2\frac{\varepsilon_1\varepsilon_2}{\varepsilon_1 + \varepsilon_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

$$q_{1,2} = \frac{9d_{1,2}}{4e^2}\left(\frac{\alpha_1\varepsilon_1}{p_1} + \frac{\alpha_2\varepsilon_2}{p_2}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where α refers to the polarisability of an ion, ε refers to an energy characteristic of the oscillators in the ion, and p refers to the " effective " number of outer electrons. S_6', S_6'', S_6''', S_8', S_8'', and S_8''' are sums of l^{-6} and l^{-8} over the unlike and the like points of the lattice, if l is the distance between the lattice points. The sums depend on the lattice type and on the choice of r, which is here taken as the distance between unlike neighbouring ions.

In the present work, polarisabilities and values of ε_- have been chosen by following a detailed consideration of data presented by Tessman, Kahn, and Shockley [8] and by Mayer.[9] As recommended by Mayer,[9] ε_+ has been taken as $0{\cdot}75I_2$ where I_2 is the ionisation potential of the gaseous cation. The values of the sums S_6', S_8', etc., are due to Morris [2] and have been computed from a Table of similar sums due to Jones and Ingham.[10] Values of p_- have been chosen by following a consideration of the results of Mayer [9] for Cl^- and I^-. It has been assumed that $p_+ = \bar{n}_+$.

The choice of values for some of these quantities employed in calculating the van der Waals energy is subject to uncertainty. However, owing to the use of an empirical repulsive potential, determined from the attractive potential and the constants of the crystal, the magnitude of error introduced into the computation of lattice energy by an error in the values of C and D is less than that introduced into the van der Waals energy.

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[5] Pauling, *Z. Krist.*, 1928, **67**, 377.
[6] Huggins, *J. Chem. Phys.*, 1937, **5**, 143.
[7] Huggins and Sakamoto, *J. Phys. Soc. Japan*, 1957, **12**, 241.
[8] Tessman, Kahn, and Shockley, *Phys. Rev.*, 1953, **92**, 890.
[9] Mayer, *J. Chem. Phys.*, 1933, **1**, 270.
[10] Jones and Ingham, *Proc. Roy. Soc.*, 1925, *A*, **107**, 636.

(d) *The zero-point energy term.* This term is given by the equation:

$$U_Z = \frac{27}{8} \boldsymbol{Nh}\nu_{\text{max.}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where $\boldsymbol{h}$ is Planck's constant ($6{\cdot}6242 \times 10^{-27}$ erg sec.) and $\nu_{\text{max.}}$ is the Debye maximum frequency.

Values of $\nu_{\text{max.}}$ have been derived for alkali selenides and tellurides from the relationship, due to Waddington,[11] between the absolute entropies at 298° K of crystals and $\nu_{\text{max.}}$. Where experimental entropy values have not been available, their magnitude has been estimated by Latimer's method.[12]

TABLE 1. *Lattice energies, U_0 (in kcal./mole at 0° K), of alkali monoselenides and monotellurides (all antifluorite types) calculated term-by-term.*

Compound Energy term	Li_2Se	Na_2Se	K_2Se	Li_2Te	Na_2Te	K_2Te
U_E	643·3	567·4	503·3	594·0	528·2	473·9
$-U_R$	−86·3	−75·5	−64·5	−73·2	−62·2	−55·8
U_W	9·1	17·4	23·4	9·2	11·8	19·5
$-U_Z$	−1·2	−0·6	−0·4	−1·2	−0·5	−0·3
U_0	564·9	508·7	461·8	528·8	477·3	437·3

Data employed for calculation of the terms

	Li_2Se	Na_2Se	K_2Se	Li_2Te	Na_2Te	K_2Te
r_0 (Å)	2·600	2·948	3·324	2·816	3·167	3·530
$10^{12}b$ (ergs/molecule)	1·547	1·864	1·995	1·204	1·455	1·605
n	8	8	8	8	8	8
n'	6	6	6	6	6	6
n''	12	12	12	12	12	12
k_1	1·154	1·154	1·154	1·154	1·154	1·154
k_2	1·633	1·633	1·633	1·633	1·633	1·633
r_+ (Å)	0·57	0·94	1·235	0·57	0·94	1·235
r_- (Å)	1·69	1·69	1·69	1·93	1·93	1·93
c_{+-}	1·25	0·875	0·875	1·25	0·875	0·875
c_{++}	2	1·25	1·25	2	1·25	1·25
c_{--}	0·5	0·5	0·5	0·5	0·5	0·5
$10^{60}C$ (erg cm.^{6})	160	626	1727	265·5	677	2117
$10^{76}D$ (erg cm.^{8})	242	1460	5090	428	1472	6264
$10^{24}\alpha_+$ (cm.^{3})	0·029	0·255	1·201	0·029	0·255	1·201
$10^{24}\alpha_-$ (cm.^{3})	6·0	10·9	11·3	8·7	11·7	14·7
$10^{12}\varepsilon_+$ (ergs/ion)	90·8	56·8	38·2	90·8	56·8	38·2
$10^{12}\varepsilon_-$ (ergs/ion)	13·0	9·6	9·5	10·8	9·3	8·3
p_+	2	8	8	2	8	8
p_-	3·6	3·6	3·6	4·0	4·0	4·0
S_6'	8·709	8·709	8·709	8·709	8·709	8·709
S_6''	1·524	1·524	1·524	1·524	1·524	1·524
S_6'''	0·762	0·762	0·762	0·762	0·762	0·762
S_8'	8·208	8·208	8·208	8·208	8·208	8·208
S_8''	0·506	0·506	0·506	0·506	0·506	0·506
S_8'''	0·253	0·253	0·253	0·253	0·253	0·253
$10^{60}d_{+-}$ (ergs cm.^{6})	3·0	34	155	3·7	36	181
$10^{60}d_{++}$ (ergs cm.^{6})	0·057	2·77	41·3	00·057	2·77	41·3
$10^{60}d_{--}$ (ergs cm.^{6})	351	856	910	613	955	1345
$10^{76}q_{+-}$ (ergs cm.^{8})	6·7	103	537	8·8	101	638
$10^{76}q_{++}$ (ergs cm.^{8})	0·015	0·98	46	0·015	0·98	46
$10^{76}q_{--}$ (ergs cm.^{8})	1483	4852	5293	2810	5068	8006
$10^{-12}\nu_{\text{max.}}$ (sec.$^{-1}$)	3·7	1·8	1·1	3·6	1·7	1·0
J (abs. joule/cal.)	4·1840	4·1840	4·1840	4·1840	4·1840	4·1840

(e) *Results.* The results of the term-by-term calculations are summarised in Table 1, together with data employed in the calculation of the different terms. Some doubts as to the correct value for ρ and in the estimation of U_W should not give rise to an uncertainty in the values of U_0 exceeding ± 5 kcal. mole.

[11] Waddington, *Adv. Inorg. Chem. Radiochem.*, 1959, **1**, 158.
[12] Latimer, *J. Amer. Chem. Soc.*, 1951, **73**, 1480.

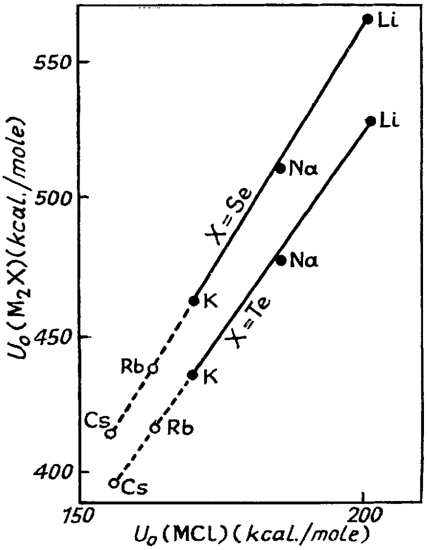
Discussion.—For the monoselenides, the consistency of the calculated lattice energies may be tested by using the values in conjunction with experimental thermochemical data to derive the two-stage electron affinity $E(\mathrm{Se} \longrightarrow \mathrm{Se}^{2-})$. This may be done by means of the Born–Haber cycle. Insufficient thermochemical results are available for a similar test of the consistency of the lattice energies of the monotellurides.

The values obtained for $E(\mathrm{Se} \longrightarrow \mathrm{Se}^{2-})$ and the relevant thermodynamic data from which they are calculated are shown in Table 2. The thermochemical data have been taken from the following sources. Values for the heats of formation of the cystalline selenides ΔH°_{298} have been taken from the National Bureau of Standards Circular.[13] The heat of atomisation, D, of selenium at 0° K has also been taken from this compilation. The heats of atomisation of the alkali metals, L_0 at 0° K, are the values adopted by Baughan,[14] while the ionisation potentials I of the elements at 0° K have been taken from Moore.[15]

TABLE 2. *The affinity (in kcal./mole) of atomic selenium for two electrons.*

	$-\Delta H^\circ_{298}$	D	$2L_0$	$2I$	$-U_0$	$E(\mathrm{Se} \longrightarrow \mathrm{Se}^{2-})$
Li_2Se	91·1	48·23	74	248·6	−564·9	−103·0
Na_2Se	63·0	48·23	52	237·0	−508·7	−108·7
K_2Se	79·3	48·23	43·2	200·0	−461·8	−91·4

Mean value $E(\mathrm{Se} \longrightarrow \mathrm{Se}^{2-}) = -101{\cdot}0 \pm 3{\cdot}8$ kcal./mole (0° K).



Karapet'yants type of plot of the lattice energies of alkali monoselenides and monotellurides, and the lattice energies of corresponding chlorides.

The $E(\mathrm{Se} \longrightarrow \mathrm{Se}^{2-})$ values refer to 0° K and are equal to the sum of the thermodynamic terms, corrected to 0° K where necessary. The small energy changes between the enthalpies of formation at 0° and 298·16° K have been estimated, and have been included in the calculation of the electron affinity, although they are not given explicitly in Table 2.

Although the probable error in the arithmetical mean for $E(\mathrm{Se} \longrightarrow \mathrm{Se}^{2-})$ is ±3·8 kcal. there is considerable uncertainty in some of the thermochemical data. The error is therefore multiplied by a factor of 3 to denote the reasonable limit of the arithmetical mean, and it is concluded that $E(\mathrm{Se} \longrightarrow \mathrm{Se}^{2-}) = -101{\cdot}0 \pm 11{\cdot}4$ kcal./mole or $-4{\cdot}38 \pm 0{\cdot}5$ ev (0° K). This result is in satisfactory agreement with values derived by Baughan [16] (−101 ± 3 kcal.)

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[13] Rossini, Wagman, Evans, Levine, and Jaffe, "Selected Values of Chemical Thermodynamic Properties," Nat. Bur. Standards, Circular no. 500, 1952.

[14] Baughan, *Trans. Faraday Soc.*, 1954, **50**, 322.

[15] Moore, "Atomic Energy Levels," Nat. Bur. Standards, Circular no. 467, 1949.

[16] Baughan, *Trans. Faraday Soc.*, 1959, **55**, 736.

and by Huggins and Sakamoto [7] (—116 ± 15 kcal.) from recent work on monoselenides of Periodic Group IIA.

Karapet'yants [17] has indicated various linear relationships between lattice energies. In the Figure the lattice energies calculated in the present work are plotted against the lattice energies of the corresponding alkali halides.[18] * Extrapolations permit estimation of the lattice energies of the monoselenides and monotellurides of rubidium and cæsium; the results, in kcal./mole (0° K), are:

	Rb_2Se	Rb_2Te	Cs_2Se	Cs_2Te
U_0	439	417	417	397

These lattice energies could not have been derived conveniently by direct term-by-term calculation, since the crystals have complicated structures.

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* In Morris's paper,[18] *I* should be 100·0 kcal./mole for potassium, and the Born–Haber cycle values for the lattice energies of potassium halides should be reduced by 2 kcal./mole.

[17] Karapet'yants, *Zhur. fiz. Khim.*, 1954, **28**, 1136.

[18] Morris, *Acta Cryst.*, 1956, **9**, 197.