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# The Lattice Energies of some Alkali Sulphides and the Affinity of Sulphur for two Electrons

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The lattice energies of the alkali monosulphides $Na_2S$, $K_2S$ and $Rb_2S$ have been derived by theoretical calculation. The lattice energies in kcal./mole at 0° K. are computed to be, for $Na_2S$ 524·4, for $K_2S$ 472·9, and for $Rb_2S$ 461·4. These values, in conjunction with known thermodynamic data, have been used to derive the affinity of atomic sulphur for two electrons: $E(\mathrm{S} \rightarrow \mathrm{S}^{2-}) = -94{\cdot}5 \pm 2{\cdot}7$ kcal. or $-4{\cdot}10 \pm 0{\cdot}1$ e.V. (0° K.).

## 1. Introduction

This paper reports calculations of the lattice energies of the monosulphides of sodium, potassium and rubidium; these are thought to be the sulphides in which the chemical bonding corresponds most closely to the ideal ionic type. The calculations are based on the theory of Born & Mayer (1932).

The lattice energies have been employed in conjunction with thermodynamic data to derive the affinity of sulphur for two electrons $E(\mathrm{S} \rightarrow \mathrm{S}^{2-})$. The value obtained from a comparison of the three sulphides is $E(\mathrm{S} \rightarrow \mathrm{S}^{2-}) = -94{\cdot}5 \pm 2{\cdot}7$ kcal. (0° K.). (This may be converted to the affinity at 298° K. by the addition of about 2 kcal.)

This value is in reasonable agreement with that adopted by Huggins & Sakamoto (1957), $-99 \pm 15$ kcal. (0° K.), which has been based on calculations of the lattice energies of alkaline earth sulphides. A higher result, $-80$ kcal. (298° K.),* has been quoted by Pritchard (1953) in his review on electron affinities, and Kapustinskii (1956) has derived the value $E(\mathrm{S} \rightarrow \mathrm{S}^{2}) = -100 \pm 2$ kcal. (298° K.).

## 2. The calculation of lattice energies

The method of calculation employed in the present work is similar to that used by Morris (1957) for alkali monoxides.

The lattice energy per mole at 0° K. of an ionic crystal may be expressed in the following form (Born & Mayer, 1932; Huggins, 1937):

$$U_0 = U_E - U_R + U_W - U_Z\,, \tag{1}$$

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. By evaluating the terms $U_E$, $U_R$, $U_W$, and $U_Z$, the lattice energy of the crystal may be determined.

In the case of alkali monosulphides the terms may be assumed to be represented by the following equations:

$$U_E = e^2NA/r_0\,, \tag{2}$$

$$\begin{aligned} U_R = bN[&nc_{+-} \exp\{(r_+ + r_- - r_0)/\varrho\} \\ &+ n'c_{++} \exp\{(2r_+ - k_1r_0)/\varrho\} + \tfrac{1}{2}n''c_{--} \\ &\times \exp\{(2r_- - k_2r_0)/\varrho\}]\,, \end{aligned} \tag{3}$$

$$U_W = N(C/r_0^6 + D/r_0^8)\,, \tag{4}$$

$$U_Z = \tfrac{27}{8}Nh\nu_{\mathrm{max.}}\,. \tag{5}$$

The symbols in these equations have the following significance:

$N$ = Avogadro's number = $6{\cdot}02283 \times 10^{23}$;
$e$ = electron charge = $4{\cdot}8024 \times 10^{-10}$ e.s.u.;
$A$ = Madelung constant, referred to $r_0$, for the antifluorite (and fluorite) lattice;
$r_0$ = shortest equilibrium $M$–S distance: for alkali monosulphides with the antifluorite lattice $r_0 = \frac{1}{4}\sqrt{3}\,.\,a_0$, where $a_0$ is the lattice constant;
$b$ = a repulsion constant obtainable from the condition $(dU_0/dr)_{r=r_0} = 0$;
$n$ = the number of nearest unlike neighbours of a sulphide ion;
$n'$, $n''$ = the number of nearest like neighbours of an alkali metal ion and a sulphide ion, respectively;
$r_+$ = 'basic radius' for an alkali metal ion;
$r_-$ = 'basis radius' for a sulphide ion;
$c_{+-}$, $c_{++}$, $c_{--}$ = factors introduced by Pauling (1928) for the dependence of the repulsion of two ions on their charges and the number of electrons in their outermost shells;
$\varrho$ = a constant obtainable from compressibility data (Born & Mayer, 1932);
$k_1$ = ratio of the shortest $M$–$M$ distance to $r_0$;
$k_2$ = ratio of the shortest S–S distance to $r_0$;
$C$, $D$ = van der Waals constants, calculated as described below;

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* If the value for the heat of atomization of sulphur taken by Pritchard had been used in the present work, the result $E(\mathrm{S} \rightarrow \mathrm{S}^{2}) = -82{\cdot}8$ kcal. (0° K.) would have been obtained.

$h$ = Planck's constant = $6{\cdot}6242\times10^{-27}$ erg sec.;
$\nu_{\text{max.}}$ = characteristic Debye frequency for the solid sulphide.

The experimental lattice constants employed in the present work are those listed by Wyckoff (1951). The constant $\varrho$ has been taken as having the value $\frac{1}{3}\times10^{-8}$ cm. due to Huggins (1937). The 'basic radii' of the cations have been taken from Huggins (1937), while the value for the sulphide ion is from Huggins & Sakamoto (1957).

The van der Waals constants $C$ and $D$ refer to dipole–dipole and quadrupole–dipole attraction, respectively. They may be evaluated using the following equations:

$$C = S_6'd_{+-}+\tfrac{1}{2}S_6''d_{++}+\tfrac{1}{2}S_6'''d_{--}\,, \tag{6}$$

$$D = S_8'q_{+-}+\tfrac{1}{2}S_8''q_{++}+\tfrac{1}{2}S_8'''q_{--}\,, \tag{7}$$

$$d_{1,2} = \tfrac{3}{2}\alpha_1\alpha_2\frac{\varepsilon_1\varepsilon_2}{\varepsilon_1+\varepsilon_2}\,,\quad q_{1,2} = \frac{9d_{1,2}}{4e^2}\left(\frac{\alpha_1\varepsilon_1}{p_1}+\frac{\alpha_2\varepsilon_2}{p_2}\right), \tag{8}$$

where $\alpha$ refers to the polarizability of an ion, $\varepsilon$ refers to an energy characteristic of the oscillators in the ion, and $p$ refers to the effective number of outermost electrons.

In the present calculations the values of the $S$ constants for the antifluorite lattice are from Morris (1957). The values of $\alpha_+$ are those of Pauling (1927) and the values of $\alpha_-$ have been chosen from an examination of the data of Fajans & Joos (1924) and Tessman, Kahn & Shockley (1953). Following Mayer (1933), $\varepsilon_+$ has been given the value $0{\cdot}75I_2$, where $I_2$ is the ionization potential of the particular gaseous ion. The values of $\varepsilon_-$ have been obtained from the approximation equation

$$\varepsilon = (h^2e^2p/4\pi^2m\alpha)^{\frac{1}{2}} \tag{9}$$

due to Herzfeld & Wolf (1925); in utilizing this equation the electron number $p$ of the sulphide ion has been assumed to have the same value 3·2 as that computed by Mayer (1933) for the chloride ion.

The choice of values of 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.

### *Results*

The results of the term-by-term calculations are listed in Table 1 (line 41), together with requisite data employed in their derivation.

Table 1. *Calculation of the lattice energies of alkali sulphides*

| | $Na_2S$ | $K_2S$ | $Rb_2S$ |
|---|---|---|---|
| 1. Crystal type | Antifluorite | Antifluorite | Antifluorite |
| 2. $r_0$ (Å) | 2·825 | 3·200 | 3·31 |
| 3. $10^{-23}\,N$ | 6·023 | 6·023 | 6·023 |
| 4. $10^{10}\,e$ (e.s.u.) | 4·802 | 4·802 | 4·802 |
| 5. $A$ | 5·039 | 5·039 | 5·039 |
| 6. $10^{12}\,b$ (ergs/mol) | 1·295 | 1·368 | 1·217 |
| 7. $n$ | 8 | 8 | 8 |
| 8. $n'$ | 6 | 6 | 6 |
| 9. $n''$ | 12 | 12 | 12 |
| 10. $k_1$ | 1·154 | 1·154 | 1·154 |
| 11. $k_2$ | 1·633 | 1·633 | 1·633 |
| 12. $r_+$ (Å) | 0·940 | 1·235 | 1·370 |
| 13. $r_-$ (Å) | 1·69 | 1·69 | 1·69 |
| 14. $c_{+-}$ | 0·875 | 0·875 | 0·875 |
| 15. $c_{++}$ | 1·25 | 1·25 | 1·25 |
| 16. $c_{--}$ | 0·5 | 0·5 | 0·5 |
| 17. $10^8\,\varrho$ (cm.) | 0·3333 | 0·3333 | 0·3333 |
| 18. $10^{60}\,C$ (erg cm.$^6$) | 288 | 920 | 1432 |
| 19. $10^{76}\,D$ (erg cm.$^8$) | 577 | 2710 | 4691 |
| 20. $10^{24}\,\alpha_+$ (cm.$^3$) | 0·179 | 0·83 | 1·40 |
| 21. $10^{24}\,\alpha_-$ (cm.$^3$) | 6·4 | 7·9 | 8·2 |
| 22. $10^{12}\,\varepsilon_+$ (ergs/ion) | 56·8 | 38·2 | 33·1 |
| 23. $10^{12}\,\varepsilon_-$ (ergs/ion) | 11·9 | 10·7 | 10·5 |
| 24. $S_6'$ | 8·709 | 8·709 | 8·709 |
| 25. $S_6''$ | 1·524 | 1·524 | 1·524 |
| 26. $S_6'''$ | 0·762 | 0·762 | 0·762 |
| 27. $S_8'$ | 8·208 | 8·208 | 8·208 |
| 28. $S_8''$ | 0·506 | 0·506 | 0·506 |
| 29. $S_8'''$ | 0·253 | 0·253 | 0·253 |
| 30. $10^{60}\,d_{+-}$ (ergs cm.$^6$) | 16·9 | 82 | 137 |
| 31. $10^{60}\,d_{++}$ (ergs cm.$^6$) | 1·37 | 19·7 | 48·7 |
| 32. $10^{60}\,d_{--}$ (ergs cm.$^6$) | 366 | 501 | 529 |
| 33. $10^{76}\,q_{+-}$ (ergs cm.$^8$) | 44 | 289 | 525 |
| 34. $10^{76}\,q_{++}$ (ergs cm.$^8$) | 0·9 | 38 | 117 |
| 35. $10^{76}\,q_{--}$ (ergs cm.$^8$) | 1700 | 2583 | 2778 |
| 36. $10^{-12}\,\nu_{\text{max.}}$ (S$^{-1}$) | 4·9 | 4·3 | 3·6 |
| 37. $U_E$ (kcal./mole) | 592·1 | 522·8 | 505·4 |
| 38. $-U_R$ (kcal./mole) | −76·3 | −64·4 | −63·2 |
| 39. $U_W$ (kcal./mole) | 10·2 | 15·9 | 20·4 |
| 40. $-U_Z$ (kcal./mole) | −1·6 | −1·4 | −1·2 |
| 41. $U_0$ (kcal./mole) | 524·4 | 472·9 | 461·4 |

## 3. The affinity of atomic sulphur for two electrons

The values of the lattice energies may be used to calculate the affinity of sulphur for two electrons, using the Born–Haber cycle.

The values obtained for the electron affinity $E(S\rightarrow S^{2-})$ and the relevant thermodynamic data from which they are calculated, are shown in Table 2. Values for the heats of formation $\Delta H$ of $Na_2S$ and $Rb_2S$ at 298·16° K. have been taken from Rossini *et al.* (1952); the corresponding figure for $K_2S$ has been

Table 2. *The affinity of sulphur for two electrons*
(Values in kcal./mole)

| | $-\Delta H$ | $D$ | $2L_0$ | $2I$ | $-U_0$ | $E(S\rightarrow S^{2-})$ |
|---|---|---|---|---|---|---|
| $Na_2S$ | 89·2 | 53·25 | 52 | 237·0 | −524·4 | −96·0 |
| $K_2S$ | 87·9 | 53·25 | 43·2 | 200·0 | −472·9 | −91·8 |
| $Rb_2S$ | 83·2 | 53·25 | 40·2 | 192·5 | −461·4 | −95·7 |

Mean value $E(S\rightarrow S^{2-}) = -94{\cdot}5\pm0{\cdot}9$ kcal. (0° K.).

taken from Brewer, Bromley, Gilles & Lofgren (1950). The heat of atomization $D$ of sulphur at 298·16° K. is the value listed by Rossini *et al.* (1952), and the heats of atomization of the metals $L_0$ at 0° K. are the quantities adopted by Baughan (1954). The ionization potentials $I$ of the elements at 0° K. have been taken from Moore (1949).

The $E(S \rightarrow S^{2-})$ 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 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 the table.

The good agreement between the values for the double electron affinity of sulphur obtained from the three sulphides supports the thesis that the forces operative in the crystals are those described above, which underlie the equation for lattice energy.

It appears that the probable error in the arithmetical mean for $E(S \rightarrow S^{2-})$ given in Table 2 as $\pm 0{\cdot}9$ kcal., may be outweighed by unknown systematic errors. This error is therefore multiplied by a factor of 3 to denote the reasonable limit of the arithmetical mean. It is concluded that

$$E(S \rightarrow S^{2-}) = -94{\cdot}5 \pm 2{\cdot}7 \text{ kcal. or } -4{\cdot}10 \pm 0{\cdot}1 \text{ e.V. } (0^\circ \text{ K.}).$$

## References

Baughan, E. C. (1954). *Trans. Faraday Soc.* **50**, 322.
Born, M. & Mayer, J. E. (1932). *Z. Phys.* **75**, 1.
Brewer, L., Bromley, L. A., Gilles, P. W. & Lofgren, N. F. (1950). *Chemistry and Metallurgy of Miscellaneous Materials, Thermodynamics.* National Nuclear Energy Series, div. IV, 19B, p. 40.
Fajans, K. & Joos, G. (1924). *Z. Phys.* **23**, 1.
Herzfeld, K. F. & Wolf, K. L. (1925). *Ann. Phys. Lpz.* **78**, 195.
Huggins, M. L. (1937). *J. Chem. Phys.* **5**, 143.
Huggins, M. L. & Sakamoto, Y. (1957). *J. Phys. Soc. Japan*, **12**, 241.
Kapustinskii, A. F. (1956). *Quart. Rev. Chem. Soc. Lond.* **10**, 283.
Mayer, J. E. (1933). *J. Chem. Phys.* **1**, 270.
Moore, C. E. (1949). *Atomic Energy Levels.* National Bureau of Standards, Circular No. 467.
Morris, D. F. C. (1957). *Proc. Roy. Soc.* A. **242**, 116.
Pauling, L. (1927). *Proc. Roy. Soc.* A, **114**, 181.
Pauling, L. (1928). *Z. Kristallogr.* **67**, 377.
Pritchard, H. O. (1953). *Chem. Rev.* **52**, 529.
Rossini, F. D., Wagman, D. D., Evans, W. H., Levine, S. & Jaffe, I. (1952). *Selected Values of Chemical Thermodynamic Properties.* National Bureau of Standards, Circular No. 500.
Tessman, J. R., Kahn, A. H. & Shockley, W. (1953). *Phys. Rev.* **92**, 890.
Wyckoff, R. W. G. (1951). *Crystal Structures.* New York: Interscience Publishers.

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# Contributions of One- and Two-Phonon Scattering to Temperature Diffuse Scattering

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Borie has recently given a procedure for obtaining the atomic scattering factor and the Debye–Waller factor independently from a set of X-ray measurements taken at one temperature. In analyzing the temperature diffuse scattering, use was made of Warren's formula derived for the case that the Debye–Waller factor is much less than unity and based on single-phonon scattering. Borie has extended Warren's formula into a region where the Debye–Waller factor is of the order of unity and where two-phonon processes are as important as one-phonon contributions. It is here shown why the Warren formula is a better approximation than the usual single-phonon temperature diffuse scattering term. A formula for two-phonon temperature diffuse scattering in powders is derived and compared with experiment. The importance of two-phonon scattering effects is also clearly demonstrated using Borie's temperature diffuse scattering data taken on copper powders.

## Introduction

Borie (1956) has recently published a procedure for obtaining the atomic scattering factor $f_0$ and the Debye–Waller factor $2M$ independently from a set of measurements made at one temperature. The method makes use of the fact that the temperature diffuse scattering (TDS) and the intensity of a Bragg peak depend differently on $f_0$ and $2M$. Thus, the experimental data when combined with appropriate theoretical relationships yield two independent equations for $f_0$ and $2M$. These equations may, in turn, be solved for the appropriate values of $f_0$ and $2M$ at the given temperature. In applying this technique to copper powder, Borie made use of Warren's TDS