# **555.** *Lattice Energies and Crystal-field Stabilization Energies of Transition-type Metal Compounds.*

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Lattice energies and crystal-field stabilization energies are presented for some oxides and halides of the first and second transition series of metals. It is shown that a further stabilization is present in the metal lattice which masks the effect of the crystal field upon the experimental enthalpies of formation of these compounds.

THE lattice energy $U$ of a crystalline compound is, in a sense, an artificial quantity, since it relates to the formation of the compound from its ions in the state of an ideal-gas mixture. A more practical quantity for the comparison of stabilities of a series of compounds having a common anion is the enthalpy of formation, $\Delta H_f$, as generally defined.

From spectroscopic studies [1] of compounds which involve the *d*-electrons of cations, it is observed that the co-ordination of ions or molecules (" ligands ") round the cation results in a splitting of the *d*-electron energy levels, to an extent dependent upon the number of such electrons and upon the nature of the ligand. The change in energy resulting from this splitting is zero where the number of *d*-electrons is 0, 5, or 10. It is generally assumed that a monotonic variation in $U$ with atomic number of the cation shown by such a series (for example, the halides or oxides of $Ca^{2+}$, $Mn^{2+}$, and $Zn^{2+}$) takes into account all effects of increasing atomic number other than those due to *d*-orbital splitting.[2, 3, 4] Deviations of other lattice energies within the series from this smooth curve, in the cases where the number of *d*-electrons is 1—4 or 6—9, are found to be in the negative direction, and are taken as a first approximation to the crystal-field stabilization energy, *i.e.*, the extra stability of the crystal lattice with respect to its formation from the gaseous ions.

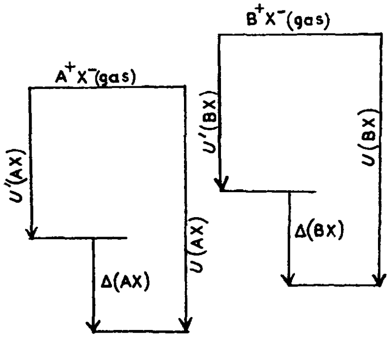

FIG. 1. Energy levels relating to the crystalline compounds AX and BX.

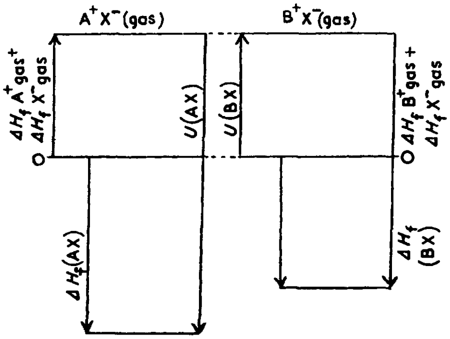

FIG. 2. Interrelation of $U$ ($\Delta H_f$ $A^+$ gas + $\Delta H_f$ $X^-$ gas) and $\Delta_f H$ for the crystalline compounds AX and BX.

Whilst agreeing in principle with this interpretation, we show in the present paper that this stabilization is not, in general, represented in the enthalpies of formation of these compounds, which are more practical characteristics than their lattice energies; this is because the crystal-field effect is to a large extent outweighed by a similar effect within the metal lattice.

If we consider two crystalline compounds having a common anion, say, AX and BX, we can represent their energy levels as in Fig. 1. Δ(AX) and Δ(BX) represent the respective

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[1] Dunn, " Modern Co-ordination Chemistry," ed. Lewis and Wilkins, Interscience Publ. Inc., New York, 1960.

[2] Penney, *Trans. Faraday Soc.*, 1940, **35**, 627.

[3] Hush and Pryce, *J. Chem. Phys.*, 1958, **28**, 244.

[4] Orgel, " An Introduction to Transition Metal Chemistry," Methuen, London, 1960.

crystal-field stabilization energies as defined above; $U$(AX) and $U$(BX) are the " observed " lattice energies derived from a Born–Haber cycle, and $U'$(AX) and $U'$(BX) are the corresponding values read from the smooth curve. The question arises, will the progressive change in $U$ with atomic number of cation be demonstrated in $\Delta H_\mathrm{f}$, which is of importance in the preparation of a compound? From Fig. 2 it is clear that $\Delta H_\mathrm{f}$ will follow the changes in $U$ only if the gaseous ions $A^+$ and $B^+$ happen to be located on a common energy level with respect to the elements A and B in their standard states. Since both compounds contain the common anion $X^-$ the energy of the change X (standard state) ⟶ $X^-$ (gas) is common to both. If the gaseous cations are not on a common energy level, changes in $U$ are the sum of the changes in both $\Delta H_\mathrm{f}$ $A^+$ (gas) and $\Delta$(AX), so that they will not necessarily be apparent in $\Delta H_\mathrm{f}$(AX).

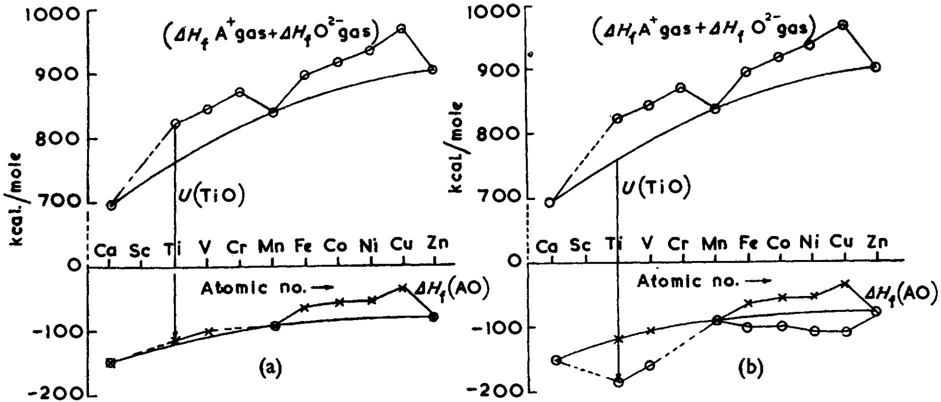

FIG. 3. (a) Variation with atomic number ($Z$) of ($\Delta H_\mathrm{f}$ $A^+$ gas + $\Delta H_\mathrm{f}$ $X^-$ gas) and $\Delta H_\mathrm{f}$ for the oxides of the first transition series of metals. (b) Similar but showing the evaluation of $\Delta$(AX).

The values of $\Delta H_\mathrm{f}$ and of ($\Delta H_\mathrm{f}$ $A^+$ gas + $\Delta H_\mathrm{f}$ $X^-$ gas) are plotted in Fig. 3(a) for the oxides of the first transition series of metals, as a function of atomic number $Z$. Thermochemical data were taken from recent sources: enthalpies of formation from Kubaschewski and Evans;[5] ionisation potentials from Finkelnburg and Humbach,[6] corrected for the electronic heat content of metal atoms and valency-state preparation energy by George and McClure[7] where the number of $d$-electrons is not equal to 0, 5, or 10: sublimation energies from Stull and Sinke;[8] electron affinities from Pritchard;[9] and dissociation enthalpies from Rossini *et al.*[10] Drawing smooth curves through the points representing $Ca^{2+}$, $Mn^{2+}$, and $Zn^{2+}$, and also CaO, MnO, and ZnO, shows that for this series $\Delta H_\mathrm{f}$ does not reflect the changes in lattice energy; nickel oxide, for example, with a lower lattice energy than manganous oxide, has a higher (less negative) enthalpy of formation, as shown in Table 1.

TABLE 1.

Lattice energies and enthalpies of formation of the oxides, fluorides, and iodides of Mn(II) and Ni(II) (kcal./mole).

| | NiO | MnO | $NiF_2$ | $MnF_2$ | $NiI_2$ | $MnI_2$ |
|---|---|---|---|---|---|---|
| $-\Delta H_\mathrm{f}$ ............................ | 57·5 | 92 | 158 | 190 | 23 | 58 |
| $-U$ ................................ | 993 | 928 | 724 | 657 | 619 | 558 |

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[5] Kubaschewski and Evans, " Metallurgical Thermochemistry," 3rd edn., Pergamon Press, London, 1958.

[6] Finkelnburg and Humbach, *Naturwiss.*, 1955, **42**, 35.

[7] George and McClure, " Progress in Inorganic Chemistry," ed. Cotton, Vol. I, Interscience Publ. Inc., New York, 1959.

[8] Stull and Sinke, " Advances in Chemistry," No. 18, Amer. Chem. Soc., 1956.

[9] Pritchard, *Chem. Rev.*, 1953, **52**, 529.

[10] Rossini, Wagman, Evans, Levine, and Jaffe, Nat. Bur. Stand. Circ. No. 500, 1952.

In Fig. 3(a) the zero energy-level is that of the elements in their standard states; consequently the crystal-field stabilization energies are the differences between the smooth curve drawn through $\Delta H_f$ of CaO, MnO, and ZnO, and the curve obtained by plotting the lattice energies downwards from the smooth curve drawn through ($\Delta H_f$ $A^+$ gas + $\Delta H_f$ $X^-$ gas) for the same three cations; this is illustrated in Fig. 3(b). The results are listed in Table 2, together with corresponding values for the fluorides and iodides of the same series. The values of $\Delta(AX)$ are numerically equal to those obtained by plotting the lattice energies from zero energy-level corresponding to that of the ideal ion-gas mixture,[3,4,7] this method of plotting seems to us to imply calculation of the lattice energies from an electrostatic model. In the present paper, lattice energies have been derived from a Born–Haber cycle, which implies the energy zero shown in Figs. 3(a) and 3(b).

TABLE 2.

Lattice energies and crystal-field stabilization energies of the oxides, fluorides, and iodides of the first transition series (kcal./mole).

| | Oxides | | Fluorides | | Iodides | |
|---|---|---|---|---|---|---|
| | $-U$ | $-\Delta(AX)$ | $-U$ | $-\Delta(AX)$ | $-U$ | $-\Delta(AX)$ |
| Ca | 848 | 0 | 617 | 0 | 487 | 0 |
| Ti | 948 | 67 | 653 | 28 | 548 | 35 |
| V | 947 | 50 | 656 | 21 | 569 | 42 |
| Cr | — | — | 684 | 38 | 587 | 43 |
| Mn | 930 | 0 | 659 | 0 | 560 | 0 |
| Fe | 958 | 15 | 694 | 23 | 588 | 14 |
| Co | 974 | 18 | 706 | 23 | 604 | 17 |
| Ni | 995 | 27 | 726 | 33 | 621 | 22 |
| Cu | 1005 | 28 | 727 | 26 | 633 | 26 |
| Zn | 984 | 0 | 708 | 0 | 614 | 0 |

The cations are doubly charged in all these compounds; no data are available for Sc(II).

We consider now the curve representing the experimental $\Delta H_f$ of the crystalline compounds. In most cases it lies above the smooth curve, suggesting reduced stability. The form of the experimental curve is due to variations in both crystal-field stabilization energy and $\Delta H_f$ $A^+$ (gas). The departure of the experimental values of $\Delta H_f$ $A^+$ (gas) from the smooth-curve values is in the opposite sense to that of the crystal-field stabilization energies, and is in most cases larger; it is the difference between these two variations which is reflected in the experimental $\Delta H_f$ curve.

There seems to exist in the elemental metal an effect comparable with the crystal-field stabilization, which we shall call the " metal-lattice stabilization "; it leads to a double-humped curve for a plot of the quantity $\Delta H_f$ $A^+$ (gas) against atomic number of the metal. This might be expected from the similarity of environment of the metal cation in an ionic crystal and in the metal lattice; the term $\Delta H_f$ $A^+$ (gas) reveals the effect, since it represents the enthalpy of removal of the " ion-gas " $A^+$ from its surrounding field in the metal. It is noteworthy that " crystal-field " and " metal-lattice " stabilization occur only with metals having incomplete *d*-shells, and their compounds; no similar effect is found with the lanthanide and actinide series, in which lattice energies and the $\Delta H_f$ $A^+$ (gas) terms evolve steadily with increasing atomic number along a smooth curve.[11] Spectroscopic evidence shows that *f*-level-splitting is absent.[1]

We have considered also the second transition series of dichlorides, from Sr($4d^0$) to Cd($4d^{10}$). The thermodynamic data are less complete than in the previous series; nevertheless, similar trends in $U$ and in $\Delta H_f$ $A^+$ (gas) are observed, as shown in Fig. 4. The corresponding crystal-field stabilization energies are listed in Table 3.

We have calculated also the variation of the crystal-field stabilization energy with change of anion, for a series of crystalline compounds of nickel(II); the results are given

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[11] Ladd and Lee, *J. Inorg. Nuclear Chem.*, 1961, **23**, 199.

TABLE 3.

Crystal-field stabilization energies and lattice energies for the dichlorides of the second transition series (kcal./mole).

| | $-U$ | $-\Delta(AX)$ | | $-U$ | $-\Delta(AX)$ | | $-U$ | $-\Delta(AX)$ |
|---|---|---|---|---|---|---|---|---|
| $SrCl_2$ ......... | 505 | 0 | $MoCl_2$ ......... | 607 | 67 | $RhCl_2$ ......... | 638 | 68 |
| $ZrCl_2$ ......... | 631 | 112 | $TcCl_2$ ............ | (550) | 0 | $PdCl_2$ ......... | 663 | 86 |
| $NbCl_2$ ......... | (670) | (96) | $RuCl_2$ ......... | (585) | (40) | $CdCl_2$ ......... | 600 | 0 |

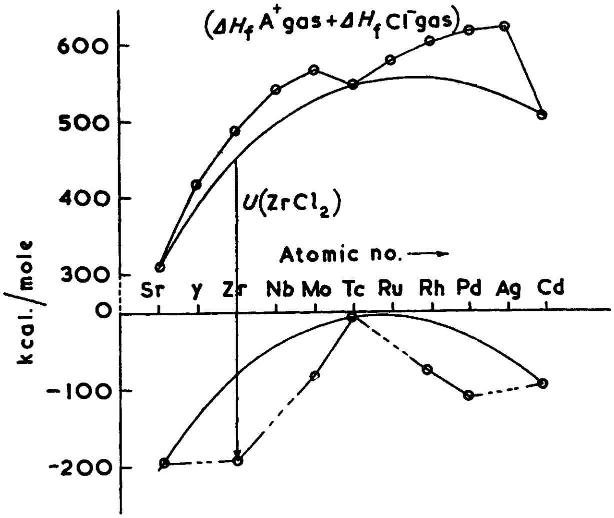

FIG. 4. Variation with atomic number of ($\Delta H_f$ $A^+$ gas + $\Delta H_f X^-$ gas) and $\Delta H_f$ for the dichlorides of the second transition series of metals.

in Table 4. The lattice energies from which Δ's were derived were calculated from a Born–Haber cycle; enthalpies of formation are from Rossini[10] and Kubaschewski and Evans.[5]

TABLE 4.

Crystal-field stabilization energies for compounds of $Ni^{2+}$ (kcal./mole).

| Anion | $O^{2-}$ | $S^{2-}$ | $Se^{2-}$ | $Te^{2-}$ | $F^-$ | $Cl^-$ | $Br^-$ | $I^-$ | $CN^-$ | $NO_3^-$ | $SO_4^{2-}$ | $OH^-$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $-\Delta(NiX)$... | 30 | 29 | 42 | 43 | 40 | 30 | 32 | 30 | 43 | 25 | 30·0 | 31·0 |
| $-\Delta H_f$ ...... | 57·5 | 22·2 | 10·0 | 9·0 | 158 | 73·0 | 51·8 | 23·0 | −27·1 | 102·2 | 212·5 | 128·6 |

There appears to be no parallel between the crystal-field stabilization energy and the stability of the crystal with respect to formation from its elements. The anions fall into three classes, with (for compounds of $Ni^{2+}$) the average crystal-field stabilizations:

| | |
|---|---|
| $CN^-$, $Se^{2-}$, $Te^{2-}$, $F^-$ .................................... | 40 kcal./mole |
| $O^{2-}$, $S^{2-}$, $Cl^-$, $Br^-$, $I^-$, $SO_4^{2-}$, $OH^-$ ............... | 30 ,, |
| $NO_3^-$ ..................................................... | 25 ,, |

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