650. *The Halides of the Transition Elements of the First Long Period.*

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The simple formula developed by Kapustinskii is used to calculate the lattice energies, and hence the heats of formation of the solid mono-, di-, and tri-halides of the elements from scandium to zinc in the Periodic Table. From these results the relative stabilities to be expected for the different valency states are determined and compared with experiment. It is found that the expected behaviour agrees well with observation, confirming the usefulness of Kapustinskii's formula.

Kapustinskii [1] has given formulæ for calculating the lattice energies of ionic crystals. In this paper, one of these is applied to the mono-, di-, and tri-halides of the elements from scandium to zinc. Some of these compounds are known and some are not, whilst others, *e.g.*, CuF, have been reported in the literature, only to have doubts thrown upon their method of preparation, etc. The existence, non-existence, and stability of the various halides are discussed in the light of the calculated results.

The lattice energies obtained are combined with other data to calculate, in particular, the heats of the following reactions:

$$\mathrm{MX} \longrightarrow \mathrm{M} + \tfrac{1}{2}\mathrm{X}_2 + \Delta H_{1a} \quad \ldots\ldots \quad (1a)$$

$$\mathrm{MX} \longrightarrow \tfrac{1}{2}\mathrm{MX}_2 + \tfrac{1}{2}\mathrm{M} + \Delta H_{1b} \quad \ldots\ldots \quad (1b)$$

$$\mathrm{MX}_2 \longrightarrow \mathrm{MX} + \tfrac{1}{2}\mathrm{X}_2 + \Delta H_{2a} \quad \ldots\ldots \quad (2a)$$

$$\mathrm{MX}_2 \longrightarrow \tfrac{2}{3}\mathrm{MX}_3 + \tfrac{1}{3}\mathrm{M} + \Delta H_{2b} \quad \ldots\ldots \quad (2b)$$

$$\mathrm{MX}_3 \longrightarrow \mathrm{MX}_2 + \tfrac{1}{2}\mathrm{X}_2 + \Delta H_{3a} \quad \ldots\ldots \quad (3a)$$

where M and X represent the metal and halogen atoms, respectively.

It is also possible to calculate the heats involved in the reactions:

$$\mathrm{M} + \mathrm{HX} \longrightarrow \mathrm{MX} + \tfrac{1}{2}\mathrm{H}_2 + \Delta H_{1c} \quad \ldots\ldots \quad (1c)$$

$$\mathrm{MX} + \mathrm{HX} \longrightarrow \mathrm{MX}_2 + \tfrac{1}{2}\mathrm{H}_2 + \Delta H_{2c} \quad \ldots\ldots \quad (2c)$$

$$\mathrm{MX}_2 + \mathrm{HX} \longrightarrow \mathrm{MX}_3 + \tfrac{1}{2}\mathrm{H}_2 + \Delta H_{3c} \quad \ldots\ldots \quad (3c)$$

If

$$\tfrac{1}{2}\mathrm{H}_2 + \tfrac{1}{2}\mathrm{X}_2 \longrightarrow \mathrm{HX} + \Delta H'$$

then

$$\Delta H_{1a} + \Delta H' + \Delta H_{1c} = 0$$

$$\Delta H_{2a} + \Delta H' + \Delta H_{2c} = 0$$

$$\Delta H_{3a} + \Delta H' + \Delta H_{3c} = 0$$

For X = F, Cl, Br, and I, $\Delta H' = -64, -22, -12$, and -1 kcal./mole.[2]

Reactions (2a) and (2b) relate to the conversion of MX_2 into the lower halide MX and the higher halide MX_3. The heats of these processes will be important factors in the stability of MX_2. Reactions (1a) and (1b) are the analogous pair of reactions for MX, while reaction (3a) represents the decomposition of MX_3. The heats involved in (1c), (2c), and (3c) are important in deciding which halide will be formed by the action of the hydrogen halide on the metal.

Calculations and Results

The formula used for calculating the lattice energies U_n was Kapustinskii's simplest one:

$$U_n = 256{\cdot}1 \sum nZ_+Z_-/(r_+ + r_-)$$

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[1] Kapustinskii, *Quart. Rev.*, 1956, **10**, 283.

[2] Cottrell, "The Strengths of Chemical Bonds," Butterworths, London, 1958.

where Z_+ and Z_- are the ionic charges, n is the number of ions in the " molecule," and r_+ and r_- are the ionic radii of the species involved, referred to a co-ordination number of 6. The empirical basis of this expression is discussed by Kapustinskii.[1] Values used for the ionic radii are listed in Table 1. For certain of the metal ions, some of which are unknown, *e.g.* Sc^{++}, calculations were made for the two extreme values of the radii; the extremes are shown in Table 1, where it will be seen that widely spaced limits were used. The ionisation potentials and latent heats of the metals examined are listed in Table 2. In addition to the above data the quantity $(E - \frac{1}{2}D)$ is required for each halogen, where E is the electron affinity, and D is the dissociation energy of the diatomic molecule. For F, Cl, Br, and I, $(E - \frac{1}{2}D)$ was taken to be 66·3, 63·6, 60·2, and 53·8 kcal./mole, respectively. It is worth noting that the range of this quantity for the different halogens is small.

The heats of formation of the different halides can now be calculated by using a Born–Haber cycle. This gives the general formula

$$U_n - \sum I_n + n(E - \tfrac{1}{2}D) - L + \Delta H_n = 0$$

where U_n is the lattice energy associated with the halide of the metal in the nth valency state; $\sum I_n$ is the sum of the first n ionisation potentials; E and D have the same meaning as above; L is the latent heat of vaporisation of the metal at room temperature; and ΔH_n is the heat of formation of the nth halide, so that

$$\Delta H_n = \sum I_n + L - n(E - \tfrac{1}{2}D) - U_n$$

These heats are listed in Table 3; the values in parentheses are those obtained for the extreme values of the ionic radii used. The heats of the reactions listed in the introduction can then be derived by the application of Hess's law to the data given in Table 3, the results being presented graphically in Figs. 1—12. There are three figures for each halogen, one relating to the stability of MX, one to MX_2, and one to MX_3. The heats of reactions (1c), (2c), and (3c), can be obtained arithmetically from these figures by making use of the values of $\Delta H'$ given in the Introduction. The data presented in Figs. 1 to 12, which constitute the main results of our calculations, will now be discussed.

TABLE 1. *Ionic radii of the metal ions. For* F^-, Cr^-, Br^-, *and* I^-, 1·36, 1·81, 1·95, *and* 2·16 Å *were used.**

	M^+	M^{2+}	M^{3+}
Sc	1·06	0·82—1·00	0·81
Ti	0·96	0·70—0·93	0·69
V	0·88	0·68—0·86	0·66
Cr	0·81	0·66—0·80	0·64
Mn	0·75—0·81	0·80	0·62
Fe	0·75—0·80	0·75	0·60
Co	0·75—0·85	0·72	0·57—0·60
Ni	0·75—0·90	0·70	0·54—0·60
Cu	0·96	0·72—0·80	0·60—0·70
Zn	0·88	0·74	0·60—0·70

* Pauling, " Nature of the Chemical Bond," Cornell Univ. Press, 1948.

TABLE 2. *The latent heats* (L) *and first, second, and third ionisation potentials* (I) *of the metals in kcal./g.-atom.**

	L	I_1	I_2	I_3		L	I_1	I_2	I_3
Sc	93	151	298	570	Fe	99	182	373	707
Ti	112	158	314	649	Co	102	181	393	773
V	122	155	328	685	Ni	101	176	419	833
Cr	94	156	380	714	Cu	81	178	468	849
Mn	68	171	361	777	Zn	31	217	414	915

* U.S. Bureau of Standards, Circulars 467, T. L. Cottrell, " Strengths of Chemical Bonds," Butterworths, 1958, for ionization potentials and latent heats, respectively.

Calculations of this type have been carried out by Grimm and Herzfeld [3] to demonstrate why salts such as sodium difluoride do not exist, but calculations were not made for the halides of the transition metals.

TABLE 3. *The calculated heats of formation of the halides (kcal./mole).*

	MF	MF_2	MF_3	MCl	MCl_2	MCl_3	MBr	MBr_2	MBr_3	MI	MI_2	MI_3
Sc	−34	[−244 −297]	−503	+2	[−133 −170]	−252	+14	[−100 −134]	−181	+31	[−52 −81]	−84
Ti	−28	[−220 −295]	−465	+20	[−104 −155]	−187	+33	[−70 −116]	−111	+52	[−21 −61]	−6
V	−18	[−220 −281]	−431	+23	[−88 −135]	−145	+36	[−62 −99]	−67	+54	[−12 −44]	+39
Cr	−52	[−214 −264]	−392	−9	[−86 −119]	−101	+4	[−49 −79]	−22	+24	[+3 −23]	+85
Mn	[−63 −70]	−244	−375	[−20 −25]	−116	−79	[−7 −11]	−79	+1	[+13 +9]	−27	+110
Fe	[−22 −28]	−208	−407	[+21 +17]	−73	−105	[+35 +31]	−35	−25	[+54 +51]	+18	+86
Co	[−15 −26]	−195	[−320 −343]	[+26 +19]	−59	[−18 −34]	[+44 +33]	−20	[+62 +49]	[+59 +53]	+34	[+174 +162]
Ni	[−16 −32]	−84	[−239 −288]	[+24 +13]	−44	[+63 +30]	[+37 +27]	−5	[+143 +115]	[+55 +47]	+51	[+254 +231]
Cu	−28	[−117 −144]	[−115 −192]	+10	[+11 −8]	[+161 +110]	+23	[+48 +31]	[+236 +190]	+41	[+100 +85]	[+341 +301]
Zn	−48	−203	[−114 −191]	−7	−68	[+162 +111]	+6	−29	[+237 +191]	+25	+24	[+342 +302]

DISCUSSION

The present calculations refer only to heats of reaction at room temperature. Thermodynamic stability is also dependent on entropy change, while the possibility of isolating and preserving a material is dependent on the energy of activation of processes that might lead to its changing to other compounds. As regards the former, the entropy factor is likely to be negligible for reactions (1b) and (2b) since only condensed substances are involved [1] but for reactions (1a), (2a), and (3a), the decomposition reactions will be favoured by the entropy factor, since *gaseous* halogens are evolved. These limitations to what has been done must be borne in mind when considering the deductions made from our results.

Before detailed consideration of how successful the present method is for understanding the stability of the various halides, the calculated heats of formation listed in Table 3 will be compared with experimental values.[4] It is found that the heats of formation of the dichlorides of the elements from titanium to cobalt are calculated satisfactorily: *e.g.* (observed results first, calculated figures in parentheses), $TiCl_2$ −121 (−104 to −155); VCl_2 −108 (−88 to −135); $CrCl_2$ −95 (−86 to −119); $MnCl_2$ −115 (−116); $FeCl_2$ −82 (−73); $CoCl_2$ −78 (−59). These results must be regarded as surprisingly good, bearing in mind that they are obtained as the difference between two large quantities, namely the energy expended on producing the ions, which is of the order of 600 kcal./mole, and the calculated lattice energy which is rather bigger than this. For $NiCl_2$ the comparison is: −76 (−44); for $CuCl_2$ −49 (−8 to +11); for $ZnCl_2$ −99 (−68). These discrepancies are about 30 kcal. for $NiCl_2$ and $ZnCl_2$ and about 50 for $CuCl_2$. They probably arise because more covalent bonding is involved in these than in the earlier dichlorides; it is known that in cupric chloride, where the discrepancy is the greatest, the binding is considerably covalent. This leads to an added stability. For the trichlorides the corresponding figures are: $ScCl_3$ −221 (−252); $TiCl_3$ −171 (−187); VCl_3 −137 (−145); $CrCl_3$ −135 (−101); $FeCl_3$ −97 (−105). Considering that these are obtained as the difference between two numbers both of which are greater than 1000 kcal., the agreement must be regarded as excellent.

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[3] Grimm and Herzfeld, *Z. Physik*, 1923, **19**, 141.

[4] U.S. Bureau of Standards, Circular 500, 1952, except that the data for the titanium chlorides were taken from Altman, Farber, and Mason, *J. Chem. Phys.*, 1956, **25**, 531, and those for the chromium iodides from Gregory and Burton, *J. Amer. Chem. Soc.*, 1953, **75**, 6054.

For the heats of formation of the dibromides (from solid metal and gaseous bromine) the following comparison can be made: $TiBr_2$ —102 (—70 to —116); $MnBr_2$ —98 (—79); $FeBr_2$ —67 (—35); $CoBr_2$ —62 (—20); $NiBr_2$ —61 (—5); $CuBr_2$ —40 (+31 to +48); $ZnBr_2$ —85 (—29). It will be seen that the discrepancies are greater than for the dichlorides, the dibromides being in fact more stable relative to the elements than is calculated. This is presumably because there is more covalent binding in the bromides than in the chlorides and again the discrepancy is greatest for the copper salt, which is to be expected. For the two tribromides the figures are: $ScBr_3$ —190 (—181); $TiBr_3$ —143 (—111). The agreement is surprisingly good (cf. $TiBr_2$). In agreement with the conclusion that the differences between calculated and observed heats of formation result from covalent character, it is found that the discrepancies are even greater for the di-iodides (from gaseous iodine also): TiI_2 —76 (—21 to —61); CrI_2 —52 (+3 to —23); MnI_2 —74 (—27); FeI_2 —45 (+18); CoI_2 —39 (+34); NiI_2 —36 (+51); CuI_2 —17 (+85 to +100); ZnI_2 —65 (+24). It does seem, therefore, that the later members of this di-iodide series are only stable to decomposition to the elements because of the covalent character of the binding in the crystals. For the tri-iodides only three heats of formation are known, and the comparison for these are: TiI_3 —103 (—6); CrI_3 —50 (+39). In both cases the discrepancy is large (about 90 kcal.), the tri-iodides being much more stable than calculated. This is presumably due again to the very high degree of covalent character arising from the high charge on the cation and large size of the anion. However, in calculating the stability relative to the di-iodides, differences are involved and consequently the discrepancy between theory and observation may be less than would be expected from the above figures. The differences between theory and experiment for the difluorides are in the reverse sense from those for the di-iodides, and this must be because there is less covalent binding in the fluorides than in the chlorides. The figures are: TiF_2 —198 (—220 to —295); CrF_2 —181 (—214 to —264); MnF_2 —189 (—244); CoF_2 —159 (—195); NiF_2 —159 (—184); CuF_2 —127 (—117 to —144); ZnF_2 —188 (—203). For the trifluorides the discrepancies are very much larger though it must be realised that for these the calculated lattice energies are of the order of 1500—2000 kcal. The three comparisons that can be made are: TiF_3 —315 (—465); CrF_3 —265 (—292); CoF_3 —187 (—320 to —343). It is clear therefore that the present calculations will give an exaggerated impression of the stability of the trifluorides.

Finally, the figures for the monohalides of copper are: CuCl —32 (+10); CuBr —29 (+23); CuI —23 (+41). The differences are 42, 52, and 64. The sequence is regular and the numbers suggest that some covalent bonding is involved. The corresponding discrepancies for the dihalides are greater. These results can be explained if the extent of covalency increases with the charge on the cation and the polarisability of the anion. These results are a natural consequence of the effects summarised in Fajans's rules. From the above it seems that the constant in Kapustinskii's empirical formula is such that the heats of formation of the chlorides are calculated quite accurately. The bromides and particularly the iodides tend to be more exothermic than the formula would suggest, while the fluorides tend to be less exothermic. Kapustinskii's formula, therefore, appears to be adjusted to allow for a certain amount of covalent bonding. However, in the results that follow, we shall be concerned more with the heats of interconversion of the halides of the different valency states so there will be some cancelling of the errors. These considerations suggest that it would be expected that the predictions for the chlorides are likely to be good. For the bromides the figures are likely to underestimate the stability of the halides and to favour slightly the lower halides, relative to the higher ones, more than is found in practice. The situation for the iodides will be similar but the effects are likely to be somewhat greater. For the fluorides the reverse will tend to be true, the stability of the higher fluorides (the trifluorides) being somewhat exaggerated. We shall see that these conclusions are, in fact, borne out though the correspondence between prediction and fact is, broadly speaking, astoundingly good.

It is interesting to compare the results obtained here with those of the detailed calculations by Waddington [5] on copper monofluoride. By using Pauling's value for the ionic radius, and assuming first a sodium chloride structure, he calculated the lattice energy to be 209 kcal./mole, whilst on a zinc blende model it becomes equal to 232 kcal./mole. Our value is 221 kcal./mole. Waddington also derives a value for the heat of formation of copper monofluoride and finds it in the first case (sodium chloride structure) to be —14 kcal./mole, and in the second case —36 kcal./mole. Our lattice energy gives it a value of —28 kcal./mole. The results, as can be seen, are in quite good agreement, allowance being made for the value of $(E - \frac{1}{2}D)$ for the fluorine molecule which he uses, namely 64·8 as opposed to 66·3 kcal./mole, the value we used.

The results summarised in Figs. 1—12 will now be discussed in the light of these considerations. Initially, their qualitative features are compared with observation in Tables 4 to 7, without making any allowance for departures from the calculated results. These Tables show that the conclusions derived from the calculations agree well, in broad terms, with the experimental results.

Fig. 1 shows that all the monofluorides are expected to be unstable as regards conversion into the difluoride and the element. In practice no monofluorides are known, though it is possible that CuF exists in admixture with CuF_2.[6] Fig. 1 shows that CuF is expected to be the least unstable. The graphs in Fig. 2 show that the difluorides should be stable to decomposition, though copper difluoride least so. It is not surprising, therefore, that this fluoride is the only one that shows some tendency to lose fluorine at high temperatures. This is probably a consequence of the entropy change involved in the decomposition. It is predicted that the difluorides of scandium, titanium, and vanadium should be unstable relative to $MF_3 + M$. This is in satisfactory agreement with experiment, though the position regarding vanadium difluoride in Fig. 2 is doubtful. The difluorides of chromium, manganese, and iron are obtained by the action of hydrogen fluoride on the metal, fluorine giving the trifluorides. It is perhaps surprising, from Fig. 2, that FeF_2 is not less stable. The action of fluorine on cobalt gives a mixture of di- and tri-fluoride. From the Figure, the difluoride would be expected to be just unstable relative to the trifluoride plus cobalt, but not enough to make its preparation impossible. The difluorides of nickel, copper, and zinc should be stable, and are in fact known. Fig. 2 shows that decomposition to the monofluoride is most likely to occur in the case of copper difluoride; this is a consequence of the high second ionisation potential of copper (cf. Table 2).

All the trifluorides of the elements from scandium to cobalt are known. This can be understood from Fig. 3. However this graph would suggest that nickel fluoride might also be obtainable. The figures given earlier show that the present calculations exaggerate the stability of the trifluorides and this may be the reason why nickel trifluoride has not been prepared. From Fig. 3 the existence of copper trifluoride would also be possible but in this case the error in the results for the trifluorides almost certainly means that this conclusion is unsound. The fact that zinc trifluoride is unknown can be understood from Fig. 3, this being a consequence of the high third ionisation potential of zinc.

It would be expected from Fig. 4 that all the monochlorides would be unstable relative to the dichlorides. In fact only copper monochloride is known, and that this is more readily obtained than copper monofluoride can be understood from a comparison of Figs. 1 and 4 (see earlier discussion of experimental data). This difference between CuF and CuCl is a consequence of the greater decrease in the lattice energy between copper difluoride and monofluoride than between copper dichloride and monochloride. None of the dichlorides is expected to be unstable to decomposition and, from Fig. 5, all but scandium dichloride should be stable to conversion into MCl_3 and M. In agreement with this, all the dichlorides except that of scandium are known. As pointed out above, cupric chloride has a partially

[5] Waddington, *Trans. Faraday Soc.*, 1959, **55**, 1531.

[6] Ebert and Woitinek, *Z. anorg. Chem.*, 1933, **210**, 269; Wartenberg, *ibid.*, 1939, **241**, 318.

covalent structure, rather than a purely ionic one. This must mean that the covalent structure is more stable than the ionic one, and since the latter should be stable relative to other valency states, the covalent structure is likely to be even more so. The results in Fig. 5 would suggest that scandium dichloride though probably unstable, should be obtainable.

The trichlorides of Sc, Ti, and V should, according to Fig. 6, be known, and they are. Chromium trichloride is on the borderline, but it is not surprising that it is known.

TABLE 4. *Comparison of the calculated behaviour of the fluorides, as shown in Figs. 1—3, and the observed behaviour.*

Element	MF		MF_2		MF_3	
	Exptl.	Theory	Exptl.	Theory	Exptl.	Theory
Sc	Unknown	Unstable to $MF_2 + M$	Unknown	Just unstable to $MF_3 + M$	Known	Stable to decomp.
Ti	Unknown	,,	Unknown	,,	Known	,,
V	Unknown	,,	Unknown	Might be just stable to $MF_3 + M$	Known	,,
Cr	Unknown	,,	Known (HF + Cr at red heat)	,,	Known	,,
Mn	Unknown		Known (from Mn + HF; $MnF_2 + \frac{1}{2}F_2 \longrightarrow MnF_3$)	Just unstable to $MF_3 + M$	Known (heat $\longrightarrow MnF_2 + \frac{1}{2}F_2$)	,,
Fe	Unknown	,,	Known (from Fe + HF or red. of FeF_3)	More unstable to $MF_3 + M$	Known ($Fe + F_2$)	,,
Co	Unknown		Known ($Co + F_2 \longrightarrow CoF_2 + CoF_3$)	Just unstable to $MF_3 + M$	Known (heat $\longrightarrow CoF_2 + \frac{1}{2}F_2$)	,,
Ni	Unknown	,,	Known (very stable)	Stable to $MF_3 + M$	Unknown	,,
Cu	Doubtful	,, (but least so)	Known (at 950° $\longrightarrow$ mixt. of $CuF + CuF_2$)	,,	Unknown	,,
Zn	Unknown	,,	Known	,,	Unknown	Unstable to decomp.

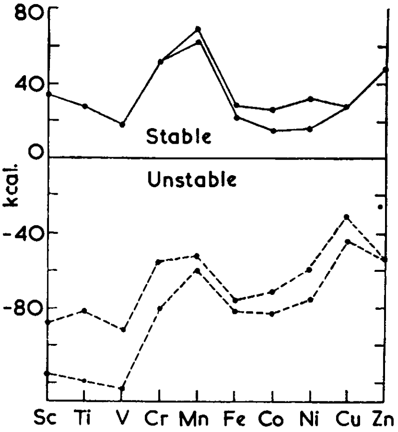
TABLE 5. *Comparison of the calculated behaviour of the chlorides, as shown in Figs. 4—6, and the observed behaviour.*

Element	MCl		MCl_2		MCl_3	
	Exptl.	Theory	Exptl.	Theory	Exptl.	Theory
Sc	Unknown	Unstable to $MCl_2 + M$	Unknown	Border line stable to $M + MCl_3$	Known	Stable to decomp.
Ti	Unknown	,,	Known ($TiCl_3 + H_2$)	,,	Known	,,
V	Unknown		Known ($H_2 + VCl_4$ at red heat)	Stable to both	Known (HCl + V at 350°)	,,
Cr	Unknown		Known (Cr + HCl at high temps.)	,,	Known ($Cr + Cl_2$ at high temps.)	Borderline stable to decomp.
Mn	Unknown	,,	Known (HCl on Mn)		Probably known, very unstable	Unstable to decomp.
Fe	Unknown		Known (HCl on Fe)	,,	Known ($Fe + Cl_2$)	Stable to decomp.
Co	Unknown	,,	Known ($Co + Cl_2$)	,,	Doubtful	Unstable to decomp.
Ni	Unknown	,,	Known ($Ni + Cl_2$)	,,	Unknown	,,
Cu	Known	Only just unstable to $Cu + CuCl_2$	Known (covalent structure)	Just stable to decomp.	Unknown	,,
Zn	Unknown	Unstable to $ZnCl_2 + Zn$	Known	Stable to both	Unknown	,,

Manganese trichloride probably exists, but is very unstable, which can also be understood from Fig. 6. The trichloride of iron is known and is stable, as would be expected from the Fig. Cobalt trichloride would be expected to be like manganese trichloride, and its existence is in fact doubtful. The trichlorides of Ni, Cu, and Zn are unknown, as would be expected from Fig. 6.

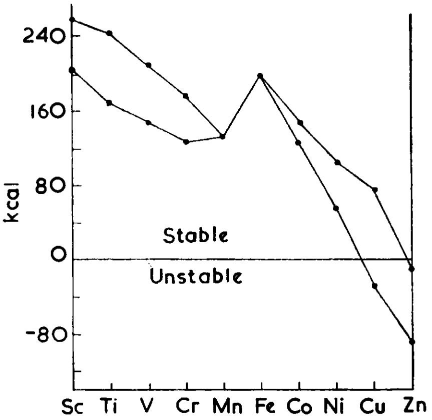
The lower stability, in general, of the trichlorides compared with the trifluorides is a consequence of their lower lattice energies. As a result of this, for several of the elements,

FIG. 1. *The heats of reactions involving the decomposition of the compounds* MF. (*In this and the following Figs., two points are plotted for each substance where there is uncertainty regarding ionic radii. The points correspond to the extremes.*)



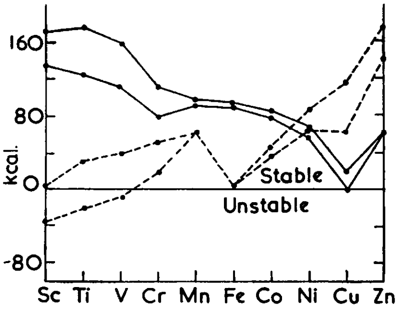
●——● ΔH_{1a} for $MF \longrightarrow M + \frac{1}{2}F_2$.
● – – – ● ΔH_{1b} for $MF \longrightarrow \frac{1}{2}MF_2 + \frac{1}{2}M$.

FIG. 3. *The heat of decomposition of* MF_3 *to* MF_2 *and* F_2.



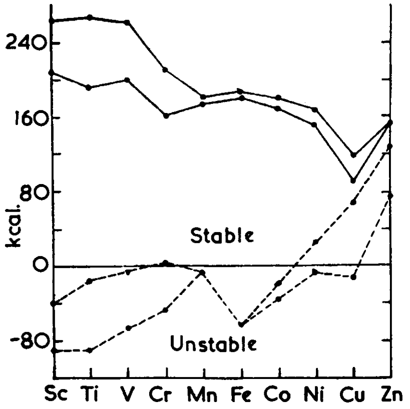
ΔH_{3a} for $MF_3 \longrightarrow MF_2 + \frac{1}{2}F_2$.

FIG. 5. *The heats of reactions involving the decomposition of the compounds* MCl_2.



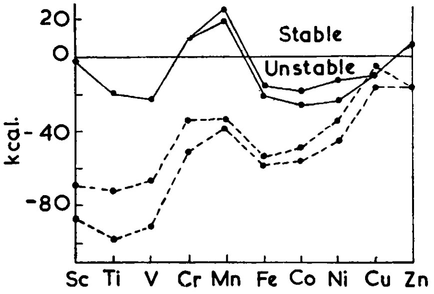
●——● ΔH_{2a} for $MCl_2 \longrightarrow MCl + \frac{1}{2}Cl_2$.
● – – – ● ΔH_{2b} for $MCl_2 \longrightarrow \frac{2}{3}MCl_3 + \frac{1}{3}M$.

FIG. 2. *The heats of reactions involving the decomposition of the compounds* MF_2.



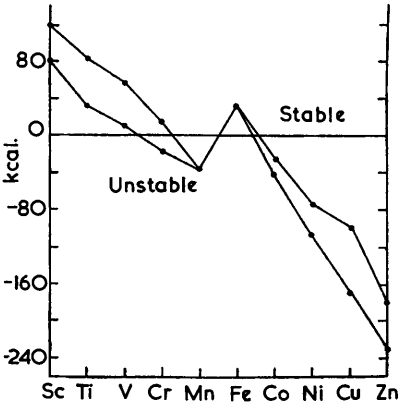
●——● ΔH_{2a} for $MF_2 \longrightarrow MF + \frac{1}{2}F_2$.
● – – – ● ΔH_{2b} for $MF_2 \longrightarrow \frac{2}{3}MF_3 + \frac{1}{3}M$.

FIG. 4. *The heats of reactions involving the decomposition of the compounds* MCl.



●——● ΔH_{1a} for $MCl \longrightarrow M + \frac{1}{2}Cl_2$.
● – – – ● ΔH_{1b} for $MCl \longrightarrow \frac{1}{2}MCl_2 + \frac{1}{2}M$.

FIG. 6. *The heat of decomposition of* MCl_3 *to* MCl_2 *and* Cl_2.



ΔH_{3a} for $MCl_3 \longrightarrow MCl_2 + \frac{1}{2}Cl_2$.

the increase in lattice energy between the dichloride and the trichloride is not sufficient to outweigh, in magnitude, the third ionisation potentials of the metals. This is only possible for Sc, Ti, V, Cr, and Fe, which have lower third ionisation potentials than Mn, Co, Ni, Cu, and Zn. The trichlorides of Ni, Cu, and Zn are unknown; these are the three metals with the highest third ionisation potentials.

TABLE 6. *Comparison of the calculated behaviour of the bromides, as shown in Figs. 7—9, and the observed behaviour.*

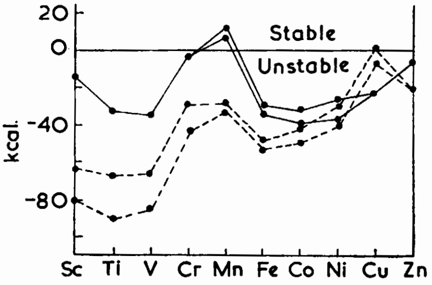
Element	MBr		MBr_2		MBr_3	
	Exptl.	Theory	Exptl.	Theory	Exptl.	Theory
Sc	Unknown	Unstable to M + MBr_2	Unknown	Borderline stable to Sc + $ScBr_3$	Known	Stable to decomp.
Ti	Unknown	,,	Known	Just stable to Ti + $TiBr_3$	Known	Borderline stable to decomp.
V	Unknown	,,	Known (VBr_3 + H_2)	Stable to both	Known (V + Br_2)	,,
Cr	Unknown	,,	Known	,,	Known	Unstable to decomp.
Mn	Unknown	,,	Known	,,	Unknown	,,
Fe	Unknown	Unstable to both	Known (Br_2 on Fe)	,,	Known, decomp. easily	Just unstable to decomp.
Co	Unknown	,,	Known	,,	Unknown	Unstable to decomp.
Ni	Unknown	,,	Known	,,	Unknown	,,
Cu	Known	Unstable to decomp.; borderline to Cu + $CuBr_2$	Known (covalent struct.)	Just unstable to decomp.	Unknown	,,
Zn	Unknown	Just unstable to both	Known	Stable to both	Unknown	,,

TABLE 7. *Comparison of the calculated behaviour of the iodides, as shown in Figs. 10—12, and the observed behaviour.*

Element	MI		MI_2		MI_3	
	Exptl.	Theory	Exptl.	Theory	Exptl.	Theory
Sc	Unknown	Unstable to decomp. and to M + MI_2	Unknown	Stable to decomp., just stable to ScI_3 + Sc	Known	Just stable to decomp.
Ti	Unknown	,,	Known (at 480° Ti + TiI_4)	Stable to both	Known (at 200° $\longrightarrow$ TiI_2)	Unstable to decomp.
V	Unknown	,,	Known (by heating VI_3)	,,	Known (I_2 + V at 150°; at 280° $\longrightarrow$ $VI_2 + I_2$)	,,
Cr	Unknown	,,	Known (stable to high temps.)	,,	Hydrates known, anhyd. CrI_3 said to be imposs. to make	,,
Mn	Unknown	,,	Known (hydrates lose I_2 at 80°)	,,	Unknown	,,
Fe	Unknown	,,	Known (I_2 + Fe)	Stable to FeI_3 + Fe, and to decomp. to FeI + I_2 (but just unstable to Fe + I_2)	Unknown	,,
Co	Unknown	,,	Known (HI + Co; at 540°, decomp.)	,,	Unknown	,,
Ni	Unknown	,,	Known (Ni + I_2)	Borderline stable to decomp. to NiI + I_2	Unknown	,,
Cu	Known	Unstable to decomp. but just stable to Cu + CuI_2	Very unstable ($\longrightarrow$ CuI + I_2)	Unstable to decomp.	Unknown	,,
Zn	Unknown	Unstable to both	Known	Borderline stable to decomp. to ZnI + I_2	Unknown	,,

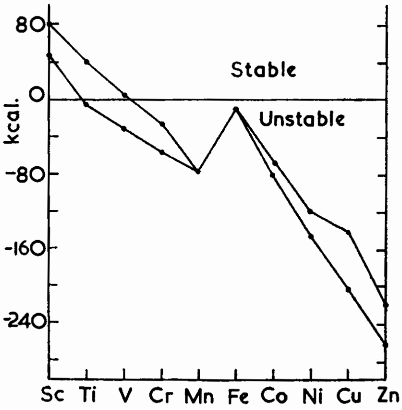
The non-existence of almost all the monobromides is in agreement with Fig. 7. The existence of copper monobromide would, from the Fig., be a little surprising, as it is predicted to be slightly unstable to decomposition, but, as we have seen above, its existence can be understood, because of the increased covalency of the binding in the crystal. The situation with the dibromide (Fig. 8) is very similar to that of the dichlorides (Fig. 5), and the experimental situation is also very similar. The stability of copper dibromide can also be understood in terms of covalency in the binding (see Figs. given earlier).

FIG. 7. *The heats of reactions involving the decomposition of the compounds MBr.*



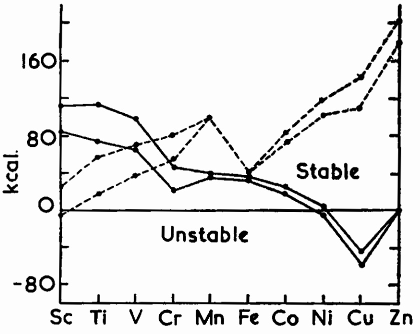
●——● ΔH_{1a} for $MBr \longrightarrow M + \frac{1}{2}Br_2$. ●- - -● ΔH_{1b} for $MBr \longrightarrow \frac{1}{2}MBr_2 + \frac{1}{2}M$.

FIG. 9. *The heat of decomposition of* MBr_3 *to* MBr_2 *and* Br_2.



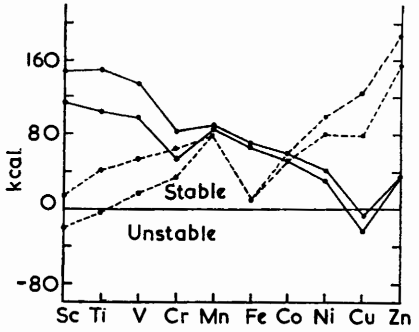
ΔH_{3a} for $MBr_3 \longrightarrow MBr_2 + \frac{1}{2}Br_2$.

FIG. 11. *The heats of reactions involving the decomposition of the compounds* MI_2.



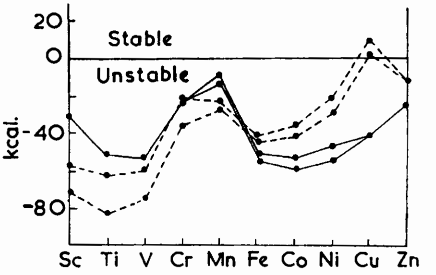
●——● ΔH_{2a} for $MI_2 \longrightarrow MI + \frac{1}{2}I_2$. ●- - -● ΔH_{2b} for $MI_2 \longrightarrow \frac{2}{3}MI_3 + \frac{1}{3}M$.

FIG. 8. *The heats of reactions involving the decomposition of the compounds* MBr_2.



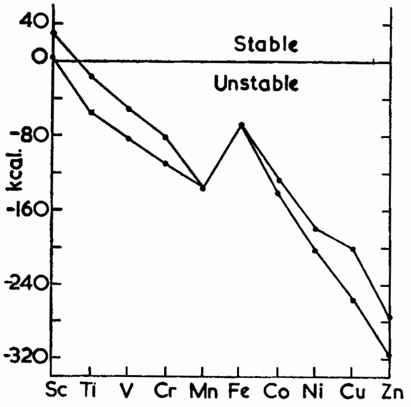
●——● ΔH_{2a} for $MBr_2 \longrightarrow MBr + \frac{1}{2}Br_2$. ●- - -● ΔH_{2b} *for* $MBr_2 \longrightarrow \frac{2}{3}MBr_3 + \frac{1}{3}M$.

FIG. 10. *The heats of reactions involving the decomposition of the compounds* MI.



●——● ΔH_{1a} for $MI \longrightarrow M + \frac{1}{2}I_2$. ●- - -● ΔH_{1b} for $MI \longrightarrow \frac{1}{2}MI_2 + \frac{1}{2}M$.

FIG. 12. *The heat of decomposition of* MI_3 *to* MI_2 *and* I_2.



ΔH_{3a} for $MI_3 \longrightarrow MI_2 + \frac{1}{2}I_2$.

Of the tribromides, those of Sc, Ti, V, Cr, and Fe are known, the others are not. This is quite consistent with the results presented in Fig. 9 (see also Table 3), and it is interesting that the calculations predict that manganese tribromide is likely to be non-existent (cf. $MnCl_3$). In those compounds consisting of a largish anion and a highly charged cation, there will be some covalent character in the binding, so that this is likely to contribute to the existence of the tribromides of chromium and iron. The latter is said to decompose easily, as would be expected from Fig. 9. The tribromides can be discussed in the same terms as the trichlorides.

Fig. 10 shows that all the monoiodides would be expected to be unstable to dissociation, and that all except copper monoiodide would be unstable relative to MI_2 and M. In fact only copper monoiodide is known. Undoubtedly, the additional stability of the CuI lattice (zinc blende) is achieved by the adoption of some covalent character in the binding, which will enhance its stability relative to decomposition.

Of the di-iodides, Fig. 11 suggests that all except copper di-iodide should be stable. In fact all are known except scandium di-iodide (copper di-iodide is very unstable), so that the calculated behaviour agrees fairly well with observations. The stability of the di-iodides of Fe, Co, Ni, and Zn, despite the fact that the calculations suggest that they should be unstable to decomposition to the metal and iodine, must be due to some covalent character in the bonding in their crystals. FeI_2 and CoI_2 have the CdI_2 layer structure, and NiI_2 the $CdCl_2$ structure, which undoubtedly are covalent in character.

Of the tri-iodides, all except that of scandium would be expected to be unstable. However, in addition to ScI_3, TiI_3 and VI_3 are known, although both decompose easily in the range 200—300°. This can be understood from Fig. 12, particularly if it is supposed that the iodides are not purely ionic, because it would be expected that there would be more covalent character in the tri-iodides than in the di-iodides (Fajans's rules), so that the relative stabilities of the tri-iodides would be increased (see above). The absence of the tri-iodides of the later members is to be expected.

It is clear that these quite simple calculations do account for the occurrence of these halides rather satisfactorily. Take the trihalides as an example; it is shown clearly how the greater lattice energy of the fluorides favours the existence of the trifluorides. On the other hand, the low lattice energies of the tri-iodides result in very few of these being obtainable, and most of those that are have low stability. The chlorides and bromides are intermediate, and calculations bring out clearly the low stabilities of $MnCl_3$ and $MnBr_3$ relative to $CrCl_3$ and $CrBr_3$, and $FeCl_3$ and $FeBr_3$. This is a consequence of the high third ionisation potential of manganese, the reason for this being that in Mn^{2+}, the *d*-shell is half-filled, and hence stable. There are many other effects that can be explained in similar terms, by examining the lattice energies, ionisation potentials, etc.

General Conclusions.—Kapustinskii's very simple formula provides a most useful means of estimating and comparing the stabilities of a number of solid inorganic halides. However, comparison of the calculated heats of formation with observed values shows that for structures in which there may be more covalent binding than in the chlorides (*e.g.*, the bromides and iodides), the lattice energy is underestimated by Kapustinskii's formula. For the fluorides this situation appears to be reversed, the formula exaggerating the lattice energies. When stabilities are considered some allowance must be made for these effects though, because differences are involved, the discrepancies in the heats of reaction may not be as great as those in the lattice energies.

The calculations suggest that it might be worthwhile to investigate the possibility of preparing such compounds as scandium dibromide and di-iodide and perhaps nickel trifluoride.

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