

## 272. *The Chalcogenides of the Elements of the First Transition Series.*

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Kapustinskii's empirical equations have been used to calculate the lattice energies of the chalcogenides,  $M_2Ch$ ,  $MCh$ , and  $M_2Ch_3$ , of the metals from scandium to zinc. These have been used in Born-Haber calculations of the enthalpies of formation. Enthalpies of various disproportionation and reduction reactions of the chalcogenides have also been calculated, and the results are discussed.

Using the lattice energies of the neighbouring stable compounds in the Periodic Table and, for some compounds, figures calculated from the Born-Landé equation, Grimm and Herzfeld<sup>1</sup> calculated by the Born-Haber cycle the enthalpies of formation of a number of hypothetical compounds. However, the Born-Landé and certain other equations employed for the calculation of lattice energies depend on an exact knowledge of the crystal structures of the compounds. This restriction is not inherent in the equation devised by Kapustinskii:<sup>2</sup>

$$U = \frac{287 \cdot 2nZ_+Z_-}{r_+ + r_-} \left( 1 - \frac{0 \cdot 345}{r_+ + r_-} \right) \text{ kcal. mole}^{-1} \quad (\text{A})$$

where  $U$  is the lattice energy,  $n$  the total number of ions in the molecule, and  $Z_+$ ,  $Z_-$ , and  $r_+$ ,  $r_-$  the ionic charges and radii, respectively, of the species involved. Although this equation is subject to a number of criticisms<sup>3</sup> and gives lattice energies that are generally on the low side, it has led to the theoretical prediction and subsequent synthesis of a number of hitherto unknown compounds.<sup>4,5</sup>

A simpler equation proposed by Kapustinskii:<sup>2</sup>

$$U = 256 \cdot 1nZ_+Z_-/(r_+ + r_-) \text{ kcal. mole}^{-1} \quad (\text{B})$$

and giving somewhat higher lattice energies, has recently been invoked to provide lattice energies for the Born-Haber calculation of the enthalpies of formation of the solid mono-, di-, and tri-halides of the elements of the first transition series (scandium to zinc).<sup>6</sup> In view of the present considerable interest in the lubricating and electrical properties of the chalcogenides of these elements, this treatment has been extended to include the oxides, sulphides, selenides, and tellurides.

### CALCULATIONS AND RESULTS

Both equations (A) and (B) have been used to calculate lattice energies of the chalcogenides  $M_2Ch$ ,  $MCh$ , and  $M_2Ch_3$ , from scandium to zinc. The enthalpies of formation ( $\Delta H_f$ ) were then obtained from Born-Haber equations, with adjustments for ionisation potentials, electron affinity, and enthalpies of sublimation and dissociation appropriate to the type of compound.

The values of cation radii, sublimation enthalpies, and ionisation potentials listed by Barber, Linnett, and Taylor<sup>6</sup> were used. Other pertinent data are given in Table 1.

<sup>1</sup> Grimm and Herzfeld, *Z. Physik.*, 1923, **19**, 141.

<sup>2</sup> Kapustinskii, *Quart. Rev.*, 1956, **10**, 283.

<sup>3</sup> Waddington, *Adv. Inorg. Chem. Radiochem.*, 1959, **1**, 157.

<sup>4</sup> Yatsimirskii, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1948, 263.

<sup>5</sup> Kapustinskii and Vaver, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1951, 631.

<sup>6</sup> Barber, Linnett, and Taylor, *J.*, 1961, **3323**.

TABLE 1.

Data used in the calculation of lattice energies and enthalpies of formation.

	Oxygen	Sulphur	Selenium	Tellurium
Anion radius of $\text{Ch}^{2-}$ (Å) * .....	1.40	1.84	1.98	2.21
Dissociation enthalpy (kcal. g.-atom <sup>-1</sup> ) * ...	59	53	48	48
Electron affinity of $\text{Ch}^{2-}$ (kcal. g.-ion <sup>-1</sup> ) ...	-172 (ref. 2) -156 †	-100 (ref. 2) -79 †	-117 (ref. 2) -97 †	-64 ‡

\* Pauling, "The Nature of the Chemical Bond," 3rd edn., Oxford University Press, London, 1960.  
 † Pritchard, *Chem. Rev.*, 1953, **52**, 529. ‡ Calculated by Born-Haber cycle based on  $\Delta H_f$  for  $\text{Na}_2\text{Te}$  = -84 kcal. mole<sup>-1</sup> (ref. 7);  $U(\text{Na}_2\text{Te})$  = +486 kcal. mole<sup>-1</sup> [calculated from equation (B)]; ionisation potential of the sodium atom = +119 kcal. g.-atom<sup>-1</sup> (Nat. Bur. Stand. Circular No. 467, 1949); sublimation energy of sodium atom = +26 kcal. g.-atom<sup>-1</sup> (ref. 7); radius  $\text{Na}^+$  = 0.95 Å (ref. \*).

TABLE 2.

Enthalpies of formation ( $\Delta H_f$  in kcal. mole<sup>-1</sup>) of chalcogenides, based on lattice energies derived from equation (A).

	Electron affinity	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
$\text{M}_2\text{Ch}$											
Oxide .....	-172	+118	+148	+144	+73	+36	+120	+124	+102	+126	+86
						+51	+133	+149	+149		
	-156	+102	+132	+128	+57	+20	+104	+108	+86	+110	+70
						+35	+117	+133	+132		
Sulphide ...	-100	+117	+153	+153	+87	+54	+138	+142	+130	+131	+95
						+65	+148	+160	+157		
	-79	+96	+132	+132	+66	+33	+117	+121	+109	+110	+84
						+44	+126	+139	+136		
Selenide ...	-117	+151	+188	+189	+124	+92	+176	+170	+168	+166	+131
						+102	+184	+197	+192		
	-97	+131	+168	+169	+104	+72	+156	+150	+148	+146	+111
						+82	+164	+177	+172		
Telluride ...	-64	+129	+173	+170	+106	+76	+160	+164	+152	+151	+112
						+84	+167	+178	+173		
$\text{MCh}$											
Oxide .....	-172	-101	-99	-86	-67	-49	-14	-1	+13	+50	-8
		-47	-25	-25	-19					+78	
	-156	-117	-115	-102	-83	-65	-30	-17	-3	+34	-24
		-63	-41	-41	-35					+62	
Sulphide ...	-100	-58	-45	-29	-10	-4	+38	+52	+67	+103	+43
		-16	+11	+15	+26					+123	
	-79	-79	-66	-50	-31	-26	+17	+31	+46	+82	+22
		-37	-11	-6	+5					+102	
Selenide ...	-117	-12	+2	+18	+38	+41	+84	+99	+114	+150	+90
		+25	+53	+59	+71					+168	
	-97	-32	-18	-2	+18	+21	+64	+79	+94	+130	+70
		+5	+33	+39	+51					+148	
Telluride ...	-64	-21	0	+17	+38	+36	+80	+96	+112	+147	+86
		+15	+43	+53	+66					+163	
$\text{M}_2\text{CH}_2$											
Oxide .....	-172	-373	-283	-209	-158	-90	-150	-16	+100	+280	+282
								+26	+186	+416	+418
	-156	-421	-331	-257	-206	-138	-198	-64	+52	+232	+234
								-22	+138	+368	+360
Sulphide ...	-100	-145	-17	+68	+86	+202	+148	+294	+422	+578	+580
								+324	+484	+679	+681
	-79	-208	-80	+5	+23	+139	+85	+231	+359	+515	+517
								+261	+421	+616	+618
Selenide ...	-117	+13	+152	+238	+327	+375	+324	+473	+602	+754	+756
								+502	+660	+846	+848
	-97	-47	+92	+178	+267	+315	+264	+413	+542	+694	+696
								+442	+600	+786	+788
Telluride ...	-64	+33	+185	+275	+367	+417	+369	+520	+651	+799	+801
								+545	+705	+878	+880

Calculations were made for the different values of electron affinity of the di-negative chalcogenide ion quoted.

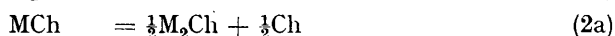
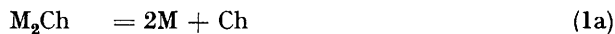
The calculated enthalpies of formation for the different chalcogenides, based on lattice energies derived from equations (A) and (B), respectively, are summarised in Tables 2 and 3. Appropriate enthalpies of formation were then used to determine the enthalpy

TABLE 3.

Enthalpies of formation ( $\Delta H_f$  in kcal. mole<sup>-1</sup>) of chalcogenides, based on lattice energies derived from equation (B).

	Electron affinity	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
<b>M<sub>2</sub>Ch</b>											
Oxide .....	-172	+95	+120	+111	+35	-6	+78	+82	+70	+98	+53
						+13	+94	+114	+117		
	-156	+79	+104	+95	+19	-22	+62	+66	+54	+82	+37
						-3	+78	+98	+101		
Sulphide ...	-100	+111	+144	+142	+73	+37	+121	+125	+113	+122	+84
						+51	+133	+148	+146		
	-79	+90	+123	+121	+52	+16	+100	+104	+92	+101	+63
						+30	+112	+127	+125		
Selenide ...	-117	+148	+182	+182	+114	+80	+164	+168	+156	+160	+124
						+92	+174	+188	+186		
	-97	+128	+162	+162	+94	+60	+144	+148	+136	+140	+104
						+72	+154	+168	+166		
Telluride ...	-64	+130	+167	+169	+103	+71	+155	+159	+147	+145	+111
						+81	+164	+176	+172		
<b>MCh</b>											
Oxide .....	-172	-150	-161	-149	-134	-100	-68	-60	-49	-9	-64
		-81	-64	-71	-70					+37	
	-156	-166	-177	-165	-150	-116	-84	-74	-65	-25	-80
		-97	-80	-87	-86					+21	
Sulphide ...	-100	-76	-70	-55	-37	-24	+16	+21	+42	+72	+21
		-27	-3	-27	+7					+104	
	-79	-97	-91	-76	-58	-45	-5	0	+21	+51	-1
		-48	-24	-48	-15					+83	
Selenide ...	-117	-25	-15	0	+23	+28	+69	+82	+97	+133	+73
		+19	+45	+49	+58					+155	
	-97	-45	-35	-20	+3	+8	+49	+62	+77	+113	+53
		-1	+25	+29	+38					+135	
Telluride ...	-64	-22	-8	-8	+28	+31	+74	+89	+104	+140	+79
		+14	+43	+50	+61					+158	
<b>M<sub>2</sub>Ch<sub>3</sub></b>											
Oxide .....	-172	-528	-518	-457	-386	-357	-427	-309	-210	+3	+5
								-251	-91	+186	+188
	-156	-576	-566	-505	-434	-405	-475	-357	-258	-45	-43
								-299	-139	+138	+140
Sulphide ...	-100	-216	-111	-34	-20	+90	+32	+169	+289	+462	+464
								+208	+368	+586	+588
	-79	-279	-173	-97	-83	+27	-31	+106	+225	+399	+401
								+145	+305	+523	+525
Selenide ...	-117	-35	+84	+165	+251	+295	+239	+382	+504	+669	+671
								+417	+575	+778	+780
	-97	-95	+24	+105	+191	+235	+179	+322	+444	+609	+611
								+357	+515	+718	+720
Telluride ...	-64	+16	+152	+239	+328	+376	+324	+470	+600	+754	+756
								+500	+660	+848	+850

changes (Table 4) for the following disproportionation reactions, the free chalcogen being shown as Ch to represent the standard state, *e.g.*,  $\frac{1}{2}\text{O}_2$  for oxygen,  $\text{S}_{\text{rh}}$  for sulphur:



Enthalpy changes (Table 4) for the following reductions were based on  $\Delta H_f$  for  $H_2O(g)$ ,  $H_2S(g)$ ,  $H_2Se(g)$ , and  $H_2Te(g)$ , as  $-58$ ,  $-5$ ,  $+21$ , and  $+37$  kcal. mole $^{-1}$ , respectively.<sup>7</sup>

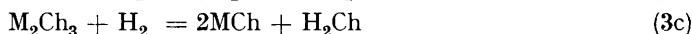
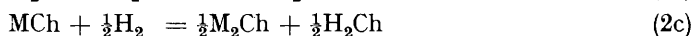
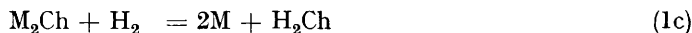


TABLE 4.

Enthalpy changes (kcal. mole $^{-1}$ ) of disproportionation and reduction reactions.  
(Mean of values calculated from data given in Tables 2 and 3, and  $\Delta H_f$  of  $H_2Ch$ .)

	Disproportionations					Reductions		
	$\Delta H_{1a}$	$\Delta H_{1b}$	$\Delta H_{2a}$	$\Delta H_{2b}$	$\Delta H_{3a}$	$\Delta H_{1c}$	$\Delta H_{2c}$	$\Delta H_{3c}$
<i>Oxides</i>								
Sc.....	-99	-201	+152	-56	+266	-156	+123	+199
Ti.....	-129	-221	+158	-47	+234	-184	+129	+176
V.....	-120	-210	+153	-26	+176	-178	+122	+108
Cr.....	-46	-127	+104	-18	+137	-104	+75	+76
Mn.....	-16	-99	+91	0	+41	-74	+62	+50
Fe.....	-86	-147	+98	-25	+108	-156	+69	+157
Co.....	-109	-148	+93	-16	+85	-167	+64	+30
Ni.....	-101	-141	+78	+17	-24	-159	+48	-82
Cu.....	-104	-73	+22	+35	-163	-162	-8	-193
Zn.....	-62	-116	+75	+55	-225	-120	+23	-345
<i>Sulphides</i>								
Sc.....	-103	-158	+106	-16	+102	-108	+105	+98
Ti.....	-138	-175	+107	+8	-26	-143	+102	-52
V.....	-137	-172	+102	+38	-53	-142	+101	-59
Cr.....	-70	-124	+47	+15	-30	-73	+47	-35
Mn.....	-41	-68	+46	+63	-164	-46	+44	-169
Fe.....	-124	-106	+46	+3	-26	-129	+44	-31
Co.....	-138	-108	+41	+46	-165	-126	+39	-170
Ni.....	-132	-82	+19	+76	-281	-131	+17	-276
Cu.....	-118	-26	-32	+92	-369	-121	-34	-370
Zn.....	-79	-58	-18	+160	-504	-84	+16	-509
<i>Selenides</i>								
Sc.....	-137	-148	+78	-6	+28	-119	+89	+44
Ti.....	-175	-164	+76	+18	-66	-155	+87	-45
V.....	-176	-154	+69	+36	-129	-155	+78	-108
Cr.....	-109	-72	+17	+49	-187	-88	+28	-163
Mn.....	-80	-57	+16	+77	-256	-61	+27	-233
Fe.....	-165	-98	+16	+18	-119	-144	+27	-98
Co.....	-171	-90	+5	+58	-253	-150	+16	-232
Ni.....	-163	-70	-13	+90	-364	-145	-2	-318
Cu.....	-153	-12	-68	+102	-449	-131	-57	-428
Zn.....	-117	-46	-7	+173	-591	-97	-2	-570
<i>Tellurides</i>								
Sc.....	-130	-133	+69	+12	-32	-93	+88	+6
Ti.....	-170	-151	+66	+33	-105	-133	+85	-93
V.....	-170	-143	+58	+58	-201	-133	+77	-164
Cr.....	-105	-57	+4	+67	-251	-68	+23	-264
Mn.....	-78	-45	+6	+99	-329	-41	+25	-293
Fe.....	-162	-85	+4	+39	-193	-125	+23	-156
Co.....	-169	-78	-8	+77	-324	-132	+6	-287
Ni.....	-161	-53	-28	+110	-490	-124	-8	-453
Cu.....	-148	+4	-78	+121	-519	-111	-59	-479
Zn.....	-112	-29	-27	+191	-657	-75	-8	-620

## DISCUSSION

The free-energy change is the fundamental property in predicting the ability of a reaction to proceed, but, for reactions involving condensed states only, the enthalpy change can give an indication of its probable course. Such predictions may be made for reactions

(1b) and (2b) and, when Ch = S, Se, or Te, also for reactions (1a), (2a), and (3a). Reactions (1c), (2c), and (3c), since they do not involve a change in volume, simulate condensed reactions, and predictions for these may also be made from enthalpy changes. The remaining reactions discussed involve an increase in volume due to gas formation, with a consequent increase in entropy which enhances the enthalpy change, giving a more negative free-energy change, thus increasing the probability of the reaction in the direction written.

Comparison of the calculated enthalpies of formation (Tables 2 and 3) with experimental values<sup>7</sup> discloses greater deviations than those previously noted for the halides.<sup>6</sup> This is to be inferred from the lower electronegativities of the chalcogens compared with those of the halogens. The electronegativity of oxygen is, however, exceeded only by that of fluorine, which accords with the largely ionic character of the oxides of the first transition series, as confirmed by the reasonable agreement between calculated and experimental enthalpies of formation for many of the metal oxides. Thus the simpler of the Kapustinskii equations, (B), gives lattice energies leading to enthalpies of formation (in parentheses) for the metal(II) oxides which compare with the following experimental values: MnO, -92 (-100 to -116); FeO, -64 (for Fe<sub>0.95</sub>O) (-68 to -84); CoO, -55 (-60 to -74); NiO, -58 (-49 to -64); ZnO, -83, (-64 to -80). The greater discrepancy for copper(II) oxide, -37 (-25 to +37) is probably due to the binding being more covalent, leading to greater stability. For the metal(III) oxides, however, the enthalpies calculated from lattice energies given by equation (B) are much higher than experimental values, but closer agreement is given by the enthalpies of formation derived from lattice energies obtained from equation (A), for example: Ti<sub>2</sub>O<sub>3</sub>, -367 (-283 to -331); V<sub>2</sub>O<sub>3</sub>, -290 (-209 to -257); Cr<sub>2</sub>O<sub>3</sub>, -270 (-158 to -206); Mn<sub>2</sub>O<sub>3</sub>, -232 (-90 to -138); Fe<sub>2</sub>O<sub>3</sub>, -197 (-150 to -198). Wider deviations can be expected for these oxides because the calculated enthalpies of formation represent the difference of two numbers which are considerably greater than 3000.

As the polarisability of the anion increases in the series, O<sup>2-</sup>, S<sup>2-</sup>, Se<sup>2-</sup>, Te<sup>2-</sup>, the enthalpy of formation of the various series of chalcogenides can be expected to become increasingly more negative than suggested by calculation (Tables 2 and 3). This is confirmed by the following comparisons, the values derived from equation (B) lattice energies being in parentheses: FeO, -64 (for Fe<sub>0.95</sub>O) (-68 to -84); FeS, -22 (+16 to -5); FeSe, -14, (+69 to +49). The comparison for the more ionic manganese(II) sulphide, -48 (-24 to -45), is much closer.

Since this discussion is largely concerned with interconversions of the chalcogenides between different oxidation states of the metal constituent, there will be some cancellation of the above errors, leading, as will be shown, to good correspondence between prediction and fact for the known compounds, and hence permitting the prediction of the possible existence or possible synthesis of certain hitherto unknown compounds.

The negative enthalpy changes in Table 4 indicate that the chalcogenides will disproportionate or will be reduced by hydrogen, the positive values indicating stability. Thus the consistent negative values for  $\Delta H_{1a}$  and  $\Delta H_{1b}$ , except  $\Delta H_{1b}$  for Cu<sub>2</sub>Te, permit the prediction that the chalcogenides M<sub>2</sub>Ch are unstable. In agreement with this prediction, compounds M<sub>2</sub>Ch are unknown, except for Cu<sub>2</sub>Ch where the oxide, sulphide, selenide, and telluride are known. These copper chalcogenides do, however, possess pronounced covalent character.

The positive values of  $\Delta H_{2a}$  for the oxides indicate stability of metal(II) oxides against spontaneous reduction to the metal(I) state, but for the sulphides, selenides, and tellurides  $\Delta H_{2a}$  becomes increasingly more negative in character. Thus copper(II) and zinc(II) sulphides, selenides, and tellurides, nickel(II) selenide and telluride, and cobalt(II) telluride should be unstable against reduction to the lower chalcogenide. In contradiction of this,

<sup>7</sup> Latimer, "Oxidation Potentials," 2nd edn., Prentice-Hall, Englewood Cliffs, 1959.

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for example, copper(II) sulphide is stable with respect to copper(I) sulphide at ordinary temperatures.<sup>8</sup> On the other hand, in passing from the oxides to the tellurides,  $\Delta H_{2b}$ , becomes increasingly more positive in nature, indicating increasing stability of MCh with respect to  $M_2Ch_3$ . Among the sulphides, selenides, and tellurides it is only for scandium(II) sulphide and selenide that  $\Delta H_{2b}$  is negative, whilst for the oxides its value is negative except for nickel(II), copper(II), and zinc(II). Since the sign deviations of  $\Delta H_{2a}$  and  $\Delta H_{2b}$  from those conferring stability are not of great magnitude, these trends support a general prediction that all the metal(II) chalcogenides should be capable of existence. Indeed, all are known except for scandium(II) sulphide and selenide, and the calculations therefore suggest that it might be worthwhile investigating the possibility of preparing these as well as scandium(II) oxide whose existence is doubtful. Many of the known compounds tend to be deficient in metal or chalcogen.

The positive values of  $\Delta H_{3a}$  for the oxides, except for nickel, copper, and zinc, conforms with the known existence of the metal(III) oxides. Nickel(III) oxide has been reported in the literature, but zinc(III) and copper(III) oxides are not known. For the sulphides, selenides, and tellurides, all the  $\Delta H_{3a}$  values are negative except for scandium(III) sulphide and selenide, both of which have been prepared. Contrary to prediction in this instance, titanium(III), vanadium(III), and chromium(III) sulphides, selenides, and tellurides are known except for vanadium(III) selenide and chromium(III) telluride. Scandium(III) telluride is also known. Such discrepancies are to be expected in view of the increasing ionic charge on the metal, coupled with the increasing polarisability of the anion. These confer properties more related to alloys and many of the metal(III) sulphides have a tendency to phase formations which are characteristic of alloy systems. These alloy properties are even more pronounced in the selenides and tellurides.<sup>9</sup>

From the trends discussed above copper(I) polonide and all the metal(II) polonides should be capable of existence, although it might be anticipated that the metal(II) compounds from chromium to zinc would show a tendency to exhibit some instability against disproportionation to the lower polonide.

Regarding interaction by hydrogen, all the metal(I) chalcogenides would, if they existed, be unstable and suffer reduction. Indeed,  $\Delta G^\circ - T$  diagrams<sup>8</sup> illustrate that copper(I) oxide but not copper(I) sulphide is reduced by hydrogen.

The metal(II) oxides, except the copper compound, are predicted to be stable against reduction by hydrogen. However, Ellingham diagrams<sup>8</sup> illustrate the instability of nickel(II) oxide under these conditions. Similar trends are apparent for the sulphides, selenides, and tellurides; the nickel, zinc, and, especially, copper compounds become increasingly prone to reduction.

The metal(III) oxides, except for the nickel(III), copper(III), and zinc(III) compounds, are resistant towards reduction by hydrogen, whilst the remaining metal(III) chalcogenides, except for the scandium compounds, should be very amenable to reduction by hydrogen, and if they existed, especially the cobalt to zinc compounds.

Here again, as for the halides,<sup>6</sup> the calculations of enthalpies using lattice energies derived from the empirical Kapustinskii equations account reasonably for the occurrence of the various compounds. The low stabilities of the manganese(III) chalcogenides in relation to the chromium(III) and iron(III) compounds are also very apparent. Finally, the high lattice energies of the metal(III) oxides favour the existence of many of them, whilst the lower lattice energies of the other metal(III) chalcogenides, coupled with the high ionisation potentials of the metals, seldom result in these being obtainable.

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[Received, April 4th, 1963.]

<sup>8</sup> Ives, "Principles of the Extraction of Metals," Royal Institute of Chemistry, London, 1960.

<sup>9</sup> Wells, "Structural Inorganic Chemistry," 3rd edn., Oxford University Press, London, 1962.