[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA]

Methods of Estimating the Entropies of Solid Compounds

BY WENDELL M. LATIMER

By taking into account the effects of mass, ionic size and ionic charge, tables have been prepared for the positive and negative constituents of solid inorganic compounds which enable one to make estimates of the entropies of such compounds.

In view of the labor required to determine entropies of solids from low temperature specific heat data and the very large number of solids, it is obvious that it will be quite some time before experimental values will be available for more than a small fraction of even the common solid compounds. However, for most compounds an estimate of the entropy, with an accuracy of one or two calories per degree, will permit a calculation of its free energy from the heat of formation with an accuracy comparable to that involved in the experimental determination of the heat. The purpose of this paper is the presentation of a method by which such estimates may be made.

The entropy of a solid compound is a function of the masses of the constituent atoms and the forces acting between these atoms: the greater the mass and the lower the force, the larger is the entropy. For compounds whose specific heat has reached the Dulong and Petit value of 6 cal. per gram atom, the mass is the principal factor, and in 1921 the author[1] gave an equation for the contribution of each element to the entropy of the compound.

$$S^0_{298} = {}^3/_2 R \ln \text{at. wt.} - 0.94 \qquad (1)$$

The dotted line in Fig. 1 is determined by this expression. For simple salts, such as the alkali halides, the entropy may be estimated with fair accuracy as the sum of the entropies of the constituent elements as given by this equation. However, the forces in solid salts are largely ionic attractions, and the effect of the ionic radii upon the force constants and the vibrational frequencies is appreciable: in general the entropy of a large ion is increased and the entropy of a small ion is decreased over the values given by equation (1). Since there is enough correlation between size and weight, the full line in Fig. 1 has been drawn to increase slightly the entropies of the heavier elements and decrease slightly the entropies of the lighter elements. The values taken from this curve are summarized in Table I and, by their use, the entropies of solid salts may be estimated with somewhat greater accuracy than by the values from equation (1).

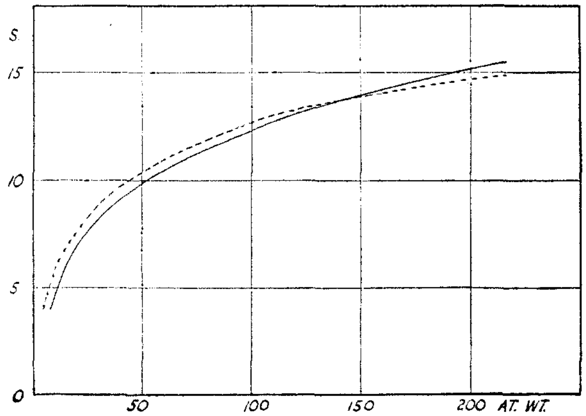

Fig. 1.—Entropies of the elements in solid compounds at 25° as a function of atomic weight: dotted line, Equation 1; full line curve used for Table I.

TABLE I

ENTROPIES OF THE ELEMENTS IN SOLID COMPOUNDS AT 298°K. VALUES IN CAL./DEG.

Ag	12.8	Dy	14.4	Mn	10.3	Se	(11.6)
Al	8.0	Er	14.5	Mo	12.3	Si	8.1
As	11.45	Eu	14.1	N	5.8	Sm	14.1
Au	15.3	F	(6.9)	Na	7.5	Sn	13.1
B	4.9	Fe	10.4	Nd	13.9	Sr	12.0
Ba	13.7	Ga	11.2	Ni	10.5	Ta	14.9
Be	4.3	Gd	14.3	Os	15.1	Tb	14.3
Bi	15.6	Ge	11.3	Pb	15.5	Te	(13.4)
Br	(11.7)	Hf	14.8	Pd	12.7	Th	15.9
C	5.2	Hg	15.4	Pr	13.8	Ti	9.8
Ca	9.3	Ho	14.5	Pt	15.2	Tl	15.4
Cb	12.2	I	(13.4)	Ra	15.8	Tm	14.6
Cd	12.9	In	13.0	Rb	11.9	U	16.0
Ce	13.8	Ir	15.2	Re	15.0	V	10.1
Cl	(8.8)	K	9.2	Rh	12.5	W	15.0
Co	10.6	La	13.8	Ru	12.5	Y	12.0
Cr	10.2	Li	3.5	S	(8.5)	Yb	14.7
Cs	13.6	Lu	14.8	Sb	13.2	Zn	10.9
Cu	10.8	Mg	7.6	Sc	9.7	Zr	12.1

In line with the argument just presented, it may be expected that the entropy of an ionic solid will also depend upon the magnitude of the ionic charges. To illustrate this effect, the apparent contribution of the chloride ion in combination with +1, +2 and +3 ions has been calculated (Table II) by subtracting from the experimental entropy of the salt, the entropy of the positive ion as given in Table I. The agreement of the calculated Cl values for each type of salt is remarkably good, and the average values 9.7, 8.1 and 6.9 for the positive ions M^+, M^{+2} and M^{+3} decrease with increasing positive charge as is to be expected.

The value for Cl from Table I is 8.8 and it may be seen from Table II that this is a fair approximation, but that much better agreement is obtained if the average values for the salt types MCl, MCl_2 and MCl_3 are employed. An examination of the data for a large number of negative ions shows that a similar charge effect exists in all cases.

It is proposed, then, to arbitrarily assign all the variation with charge to the negative ion and to prepare from the experimental entropies a table for the negative ions in which the value is modified by the charge on the positive ion. The entropy

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[1] W. M. Latimer, THIS JOURNAL, **43**, 818 (1921).

of any salt may then be estimated by combining the values in this summary for negative ions, Table V, with the values in Table I for the positive ions.

TABLE II

CONTRIBUTION OF Cl TO THE ENTROPY OF MCl, MCl_2 AND MCl_3 COMPOUNDS

Calculated by subtracting entropy of positive ion, Table I, from the entropy of the salt[2]

Salt	Entropy of salt	Entropy of Cl	Salt	Entropy of salt	Entropy of Cl	Salt	Entropy of salt	Entropy of Cl
NaCl	17.3	9.9	$PnCl_2$	32.6	8.5	$CrCl_3$	31.0	6.7
KCl	19.75	9.5	$ZnCl_2$	25.9	7.6	VCl_3	31.3	7.1
TlCl	24.8	9.3	$CdCl_2$	28.3	7.7			
AgCl	22.97	10.2	Hg_2Cl_2	46.8	8.0		Av.	6.9
			$NiCl_2$	25.6	7.8			
	Av.	9.7	$CoCl_2$	25.4	7.5			
			$FeCl_2$	28.6	9.0			
			$MnCl_2$	28.0	8.8			
			$CrCl_2$	27.4	8.7			
			VCl_2	23.2	6.6			
				Av.	8.1			

TABLE III

CONTRIBUTION OF SULFATE TO THE ENTROPY OF M_2SO_4, MSO_4 AND $M_2(SO_4)_3$ TYPE OF COMPOUNDS

Calculated by subtracting entropy of positive ion, Table I, from the entropy of the salt

Salt	Entropy of salt	Entropy of SO_4	Salt	Entropy of salt	Entropy of SO_4	Salt	Entropy of salt	Entropy of SO_4
Ag_2SO_4	47.8	22.2	$CuSO_4$	27.1	16.3	$Al_2(SO_4)_3$	57.2	13.7
K_2SO_4	42.0	22.6	$MnSO_4$	26.8	16.5			
Na_2SO_4	35.7	21.3	$BaSO_4$	31.6	17.8		Av.	13.7
			$CaSO_4$	25.6	16.3			
	Av.	22.0	$PbSO_4$	35.2	19.7			
			$ZnSO_4$	29.8	18.9			
			$CdSO_4$	32.8	19.9			
			$MgSO_4$	21.9	14.4			
			$FeSO_4$	25.7	15.3			
			Hg_2SO_4	48.0	17.2			
				Av.	17.2			

In addition to the simple negative ions, the summary includes values for the oxygen complex ions. As an example of the degree of consistency in the data employed, the calculations for sulfate are given in Table III. The average values for type salts are: M_2SO_4, 22.0; MSO_4, 17.2 and $M_2(SO_4)_3$, 13.7. The variations in the individual values are somewhat greater than those for the chlorides given in Table II, but the average deviation is only 1.3 cal./deg.

It is not possible to complete Table V from experimental data. For example, there are no data on fluorides of the types XF and XF_3. Where the trends appear fairly definite from similar compounds, estimates have been given (values in brackets). It will be noted that in some cases the values for the +4 ions are slightly larger than those for the +3 ions. There are sufficient data to establish this as a real effect, and it is doubtless due to the anion repulsion which exists with four large negative ions about a small positive ion. This repulsion tends to weaken the bond energies and increase the entropy.

The specific heats of oxides are considerably below the Dulong and Petit values, but consistent figures may be assigned for the contribution of the oxygen following the general scheme outlined above. The values given in the summary for oxygen in M_2O, MO and M_2O_3 are based upon data for thirty-five oxides and the average deviation is 0.6 cal. per deg. Values for oxygen in M_3O_4 and M_2O_5 have not been included in the summary, but the data are given in Table IV. Likewise values for carbide and nitride have not been included, since they have so many unusual valence types. Carbon in SiC and TiC has the values −4.2 and −4.1, respectively, and nitrogen in TiN and ZrN, the values −2.7 and −2.9.

TABLE IV

CONTRIBUTION OF OXYGEN TO THE ENTROPY OF M_3O_4 AND M_2O_5 TYPE OXIDES

Calculated by subtracting entropy of positive ion, Table I, from the entropy of the salt

Oxide	Entropy of oxide	Entropy of O	Oxide	Entropy of oxide	Entropy of O
Fe_3O_4	35.0	1.0	Ta_2O_5	34.2	0.9
Mn_3O_4	35.5	1.1	V_2O_5	31.3	2.1
Pb_3O_4	50.5	1.0	As_2O_5	25.0	0.4
	Av.	1.0		Av.	1.1

The entropies of hydrates may be estimated by assigning the value 9.4 cal. per deg. to the contribution of a mole of hydrated water. The following calculation for $BaCl_2 \cdot 2H_2O$ is given as an example

2Cl	16.2
$2H_2O$	18.8
Ba	13.7
Total	48.7 Exptl. 48.6

If the water is strongly bound to the positive ion, the increase in size of the ion will weaken the charge effect. Thus for $Cr(H_2O)_6Cl_3$ the value to be used for chloride should be taken one or two units higher than the +3 value of 6.7 given in the summary.

There is a paucity of reliable data on hydroxides, but the values given in the summary are probably correct to about an entropy unit, and in general better estimates are obtained by adding values for the metal ion and hydroxide than by considering the compound as the oxide plus water.

In complex salts, such as K_2PtCl_6, the best estimates result from using a value for the chloride corresponding to the average charge on the positive ions. For K_2PtCl_6, the average charge is +2, and one then calculates

2K	18.4
Pt	15.2
6Cl	48.6
Total	82.2 Exptl. 79.8

The oxygen complex cations offer considerable difficulty. In an ion such as UO_2^{++}, the oxygen entropy appears to be around 3. Since the complex cation is large, and especially if it is hydrated, the +1 value of the anion should be used. Thus, for $UO_2(NO_3)_26H_2O$

2O	6.0
U	16.0
$2NO_3$	43.4
$6H_2O$	56.4
Total	121.8 Exptl. 120.8

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[2] Experimental entropy values are taken from the summary by K. K. Kelly, Bureau of Mines, Bull. 477 (1948).

From the entropy of solid NH_4Cl, 23.6, and the value for Cl^-, 9.7, the value for NH_4^+ in solid salts is 13.9.

Table V includes all of the common negative ions, and the diversity of ion-types is such that estimates may be made on less common ions by comparison with the value for a similar ion given in the table.

TABLE V

SUMMARY OF ENTROPY CONTRIBUTION, IN CAL. PER DEGREE PER MOLE, OF NEGATIVE IONS IN SOLID COMPOUNDS AT 298°K.

Negative ion	Charge on positive ion +1	+2	+3	+4
F^-	(5.5)	4.7	(4.0)	5.0
Cl^-	9.7	8.1	6.9	8.1
Br^-	13.0	10.9	(9)	(10)
I^-	14.6	13.6	12.5	13.0
CN^-	7.2	(6)		
OH^-	(5.0)	4.5	3.0	
ClO^-	(14)	(10)	(8)	
ClO_2^-	19.2	(17)	(14)	
ClO_3^-	24.9	(20)		
ClO_4^-	26.0	(22)		
BrO_3^-	26.5	22.9	(19)	
IO_3^-	25.5	(22)		
$H_4IO_6^-$	33.9	(30)		
NO_2^-	17.8	(15)		
NO_3^-	21.7	17.7	(15)	(14)
VO_3^-	20.0	(18)		
MnO_4^-	31.8	(28)		
O^{--}	2.4	0.5	0.5	1.0
S^{--}	8.2	5.0	1.3	2.5
Se^{--}	(16)	11.4	(8)	
Te^{--}	(16.5)	12.1	(9)	
CO_3^{--}	15.2	11.4	(8)	
SO_3^{--}	(19)	14.9	(11)	
$C_2O_4^{--}$	(22)	17.7	(14)	
SO_4^{--}	22	17.2	13.7	(12)
CrO_4^{--}	26.2	(21)		
SiO_4^{----}	(19)	13.8	(9)	7.9
SiO_3^{--}	16.8	10.5	(7)	
PO_4^{---}	(24)	17.0	(12)	
HCO_3^-	17.4	(13)	(10)	
$H_2PO_4^-$	22.8	(18)		
$H_2AsO_4^-$	25.1	(21)		

BERKELEY, CALIF. RECEIVED OCTOBER 23, 1950

[CONTRIBUTION NO. 1455 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

A Reinvestigation of the Structures of Diborane and Ethane by Electron Diffraction[1,2]

BY KENNETH HEDBERG AND VERNER SCHOMAKER

The ethane-like model for diborane has been eliminated and the bridge model confirmed in an electron-diffraction reinvestigation of diborane and ethane which has led to the bond angle and bond distance values $\angle H_{bond}-B-H_{bond} = 121.5 \pm 7.5°$, B–B = 1.770 ± 0.013 Å., $B-H_{bond} = 1.187 \pm 0.030$ Å., and $B-H_{bridge} = 1.334 \pm 0.027$ Å. for diborane, and ∠C–C–H = 110.5 ± 3.5°, C–H = 1.114 ± 0.027 Å., and C–C = 1.536 ± 0.016 Å. for ethane. A reasonable combination of the values for ethane with the spectroscopic moments of inertia gives ∠C–C–H = 110.4°, C–H = 1.110 Å., and C–C = 1.535 Å., in excellent agreement with the purely electron-diffraction results and considerably more precise.

An early electron diffraction investigation of the structure of diborane by S. H. Bauer[3] led to the conclusion that the molecule had a configuration like that of the ethane molecule, in apparent agreement with certain other lines of physical evidence. More recently, the "bridge" or "protonated double bond" model of symmetry D_{2h}, illustrated in Fig. 1, has been strongly supported on the basis of reinterpretations of the older chemical and physical data[4] and by new evidence,[4,5] of which the spectroscopic results of Price[5] seem especially conclusive, and Bauer has evaluated its structural parameters (it had not been tested in his original investigation) by a partial reconsideration[6b,c] of the diffraction data. However, Bauer has maintained,[6] at least until the appearance of Price's results, that this model is in fact incompatible with the existence of a certain visible inner ring of the diffraction photographs and should accordingly be regarded as very probably incorrect or even eliminated from consideration.

In view of this situation the present independent reinvestigation of diborane with full consideration of both bridge and ethane-like models still seems to be in order. It was anticipated when this work was begun[7] that a choice between the two types of models by electron diffraction might be difficult or impossible because there would not necessarily be any differences between them in the magnitudes of the interatomic distances B–B, B–H, and B · · · H which make the principal contributions to the molecular scattering, while the corresponding numbers of distances (1:4,4:4 and 1:6:6) are different only by such rather small amounts as would probably not lead to a definite conclusion, at least not from visual interpretations of the diffraction pattern. It was to be hoped, however, that photographs could

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[1] This work was supported in part by the Office of Naval Research under Contract N6onr-24423.

[2] Presented before the Physical and Inorganic Chemistry Division of the American Chemical Society, 116th Meeting, Atlantic City, N. J., September, 1949.

[3] S. H. Bauer, THIS JOURNAL, **59**, 1096 (1937).

[4] See K. S. Pitzer, *ibid.*, **67**, 1126 (1945).

[5] W. C. Price, *J. Chem. Phys.*, **16**, 894 (1948); **15**, 614 (1947).

[6] (a) Private communication quoted by F. Stitt, *ibid.*, **9**, 785 (1941); (b) S. H. Bauer, *Chem. Revs.*, **31**, 46, 54 (1942); (c) private communication quoted by H. C. Longuet-Higgins and R. P. Bell, *J. Chem. Soc.*, 253 (1943); (d) S. H. Bauer, THIS JOURNAL, **70**, 119 (1948).

[7] Active reconsideration of the diborane problem was initiated in this laboratory in the summer of 1946 by Dr. Wm. Shand, Jr., just before his death. It was taken up again by the Authors in January, 1947, with the preparation of new photographs. Our conclusion as to type of model had already been reached on the basis of the photographs and some theoretical curves of Dr. Shand's before we learned of Price's results, but it had not been thoroughly checked.