

If this difference is assumed to be due to the cause suggested the material studied by Cooke had the approximate composition, 99%  $\text{SbBr}_3$ , 1%  $\text{HBr}$ .

### Summary.

In an all-glass apparatus, 3 preparations of antimony were combined with bromine, the resulting product twice distilled under a pressure of 5 to 10 mm. while gaseous materials could yet be removed, then distilled a third time under less than one mm. pressure into a series of small bulbs which were sealed off from each other as individual samples. From the time the pure dry materials were placed in the apparatus till the bulbs were broken under tartaric acid solution, only inert gases came into contact with the preparation. The resulting product was analyzed for bromine in two ways; first, by finding the amount of silver equivalent to the sample in the usual way; second, by adding excess of silver nitrate, then filtering out and weighing the silver bromide. Precautions taken and corrections applied include all described within recent years in similar work. In eleven analyses a total of 46.76580 g. of antimony bromide required 41.86463 g. of silver and formed 72.88245 g. of silver bromide. The ratios are 1.117074 and 0.641611, from which the respective values for the atomic weight of antimony would be 121.799 and 121.755. If for the antimony bromide to silver bromide ratio samples C-IV, D-I and D-II are omitted since in these cases the fused silver bromide did not give a clear mass, the weights would be 35.69757 g. of antimony bromide to 55.63121 g. of silver bromide, corresponding to an atomic weight of 121.767. The ratios of silver to silver bromide are 0.574413 and 0.574427, according to whether the imperfect silver bromide determinations are included or omitted. Baxter's determinations of this ratio gave 0.57445. Averaging the volumetric results for the 11 samples with the gravimetric results for 8 samples, the most probable atomic weight for antimony (assuming  $A_g = 107.880$ ) becomes 121.773.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

## THE MASS EFFECT IN THE ENTROPY OF SOLIDS AND GASES.

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The Third Law of Thermodynamics, by means of which the entropy of a substance may be calculated from specific heats, has made possible the determination of free energy changes in chemical reactions from thermal data alone. However, the difficulties involved in the accurate measurements of specific heats at low temperatures are so great as to make highly desirable some method of calculating the entropy of a substance from other physical quantities. Many attempts in this direction have been made. A large number of these, including the determination

of Nernst's chemical constants, have been based wholly or in part, upon the quantum theory. Gratifying as have been the results from the specific heat formulas of Einstein, Nernst and Lindemann, and Debye, these formulas do not as yet offer a reliable method of estimating the entropy of solids.

The fact that mass is a factor of considerable importance in the entropy of a substance has long been recognized. By classical methods the equation for the entropy of a perfect monatomic gas has been developed as

$$S = \frac{5}{2} R \ln T - R \ln P + \text{constant.} \quad (1a)$$

If the constant of this equation is assumed to depend upon the mass law alone, it has been shown<sup>1</sup> by the quantum theory, by the principle of dimensions and by the principle of similitude that the equation takes the form

$$S = \frac{3}{2} R \ln m + \frac{5}{2} R \ln T - R \ln P + S_0 \quad (1b)$$

where  $S_0$  must now be a constant independent of the nature of the substance.

This equation, first developed by Sackur, has been verified as far as the existing data permit by both Nernst and Tolman. From a critical study of the data now at hand it seems possible to go further and state that the entropy of large classes of substances at a given temperature and pressure approaches a limiting value which is determined solely by the mass and by the number of degrees of freedom of the molecules composing the substance.

### Entropy of Solids.

It is obvious from consideration of specific heat data that at a given temperature the entropy of an atom in a solid depends both upon the mass of the atom and the constraint by which it is held. However, a postulate will be made, namely, that there is a limiting value of the constraint, below which the effect upon the entropy is negligible. Then since an atom in a solid has three degrees of freedom of motion, we will write for the entropy of each element

$$S_{298} = \frac{3}{2} R \ln \text{at. wt.} + S'_0 \quad (2)$$

where  $S'_0$  is the same for all elements in which the condition postulated in regard to the constraints is fulfilled. The data on the entropy of solids other than metals will be considered first, and a second postulate made, that the entropy of a compound is the sum of the entropies of the elements in the compound as given by Equation 2. The criterion by which we shall decide whether this condition is fulfilled is that the Kopp's

<sup>1</sup> Sackur, *Ann. Phys.*, **36**, 598 (1911); **40**, 67 (1913); Tetrode, *ibid.*, **33**, 434 (1912); Keesom, *Physik. Z.*, **15**, 217 (1914); Nernst, *Verh. deut. physik. Ges.*, **18**, 83 (1916); Ratnowsky, *ibid.*, **18**, 263 (1916); Lorentz, *Proc. Acad. Sci. Amsterdam*, **19**, 737 (1917); Tolman, *This Journal*, **42**, 1185 (1919).

law constant for the specific heat of the element in the compound shall have reached the Dulong and Petit value of approximately 6 per gram atom. In order to evaluate  $S_0$  the value of  $S_{298} = 19.70$  for potassium chloride, as calculated by Lewis and Gibson<sup>1</sup> from the data of Nernst and Lindemann will be used, since this is probably the most accurate of the specific heat data on the salts. Then from Equation 2 and the postulate that the entropy of a compound is the sum of the entropies of its elements.

$$19.70 = \frac{3}{2} R \ln 35.45 + \frac{3}{2} R \ln 39.1 + 2S_0.$$

The value for  $S_0$  thus calculated is  $-0.94$ . Using this value for  $S_0$  the  $S_{298}$  values for a number of elements in their compounds have been calculated and are given in Table I.

TABLE I.—ENTROPY OF ELEMENTS IN COMPOUNDS AT 298° K.

Na.....	8.41	Ag.....	13.02	Br.....	12.12
K.....	9.99	Hg.....	14.88	I.....	13.52
Si.....	9.06	Tl.....	14.93	C.....	6.51
Ti.....	10.62	Pb.....	14.97	S.....	9.43
Sn.....	13.40	Cl.....	9.71		

Although a great deal of the data is not of great accuracy there are some eighteen cases by which the postulates made in regard to the entropies of solid compounds may be tested. Lewis and Gibson<sup>2</sup> in their paper on the Third Law of Thermodynamics and the entropy of the elements summarized most of the existing specific heat data and calculated the value of  $S_{298}$  for KCl, KBr, NaCl, PbCl<sub>2</sub>, PbI<sub>2</sub>, HgCl, AgCl, AgI and TiCl. These values, together with their values for the entropies of the elements,<sup>3</sup> will be used in the following calculations.

*Potassium Chloride.*—The value  $S_{298} = 19.7$  has been used in evaluating the constant of Equation 2.

*Potassium Bromide.*— $S_{298} = 22.4$ , calculated from specific heat data, is probably accurate to 0.5 of an entropy unit. By Equation 2  $S_{298} = 9.99 + 12.12 = 22.11$ .

*Sodium Chloride.*—From specific heat data  $S_{298} = 17.44$ . Using the relationship  $\Delta F = \Delta H - T\Delta S$ , Lewis and Gibson calculate  $\Delta S = -18.7$  from measurements of e. m. f. and heats of formation of sodium chloride from its elements. Then using  $S_{298} = 25$  for chlorine and  $S_{298} = 12.2$  for sodium, we find for sodium chloride

$$S_{298} = -18.7 + 25 + 12.2 = 18.5$$

By Equation 2,  $S_{298} = 8.41 + 9.71 = 18.12$ .

*Lead Chloride.*— $S_{298} = 33.2$  from specific heat data.  $S_{298} = 35.2$  from e. m. f. and thermochemical data discussed by Lewis and Gibson, and  $S_{298} = 25$  for chlorine and  $S_{298} = 15.4$  for lead. By Equation 2  $S_{298} = 14.97 + 2(9.71) = 34.39$ .

*Lead Iodide.*— $S_{298} = 41.3$  from specific heat data. By Equation 2  $S_{298} = 14.97 + 2(13.52) = 42.01$ .

<sup>1</sup> Lewis and Gibson, *THIS JOURNAL*, **39**, 2554 (1917).

<sup>2</sup> Lewis and Gibson, *loc. cit.* All following references to Lewis and Gibson are to this paper.

<sup>3</sup> The value 25.0 has been used for chlorine in place of 25.7. The reasons for this change are discussed later.

*Mercurous Chloride.*— $S_{298} = 23.2$  from specific heat data. Lewis and Rupert<sup>1</sup> found  $\Delta F_{298} = -25,130$ , and the heat of formation obtained by Nernst<sup>2</sup> and by Varet<sup>3</sup> gives  $\Delta H_{298} = -31,300$ . Using the values  $S_{298} = 25$  for chlorine and  $S_{298} = 17.8$  for mercury,  $S_{298} = 22.3$  for mercurous chloride. By Equation 2  $S_{298} = 9.71 + 14.88 = 24.55$ .

*Silver Chloride.*— $S_{298} = 23.4$  from specific heat data. Lewis and Gibson give for the entropy of formation from its elements  $\Delta S_{298} = -10.1$ . There is, however, an uncertainty of several hundred calories in the value of  $\Delta H_{298}$ . Using  $S_{298} = 10.2$  for silver and  $S_{298} = 25$  for chlorine,  $S_{298} = 25.2$ . By Equation 2  $S_{298} = 13.02 + 9.71 = 22.73$ .

*Silver Iodide.*— $S_{298} = 26.8$  from specific heat data. By Equation 2  $S_{298} = 13.02 + 13.52 = 26.54$ .

*Thallium Chloride.*—From the data of Pollitzer, Lewis and Gibson have calculated  $S_{298} = 28.6$ . Lewis and von Ende<sup>4</sup> found from e. m. f. measurements  $\Delta F_{298} = -44,110$ . For  $\Delta H_{298}$  Thomsen gives  $-48,580$ . Using  $S_{298} = 25$  for chlorine and  $S_{298} = 14.6$  for thallium,  $S_{298} = 24.6$  for thallium chloride. This value is checked very closely by a recent investigation by Lewis and Gerke, as yet unpublished, in which the  $\Delta S$  of formation has been calculated directly from temperature coefficients of a cell. By Equation 2  $S_{298} = 14.93 + 9.71 = 24.64$ .

*Tetrachlorides of Carbon, Silicon, Titanium and Tin.*—The specific heats of these four compounds have been determined by the author from the temperature of liquid hydrogen to  $298^\circ \text{K.}$ , and the results of the investigation will be published shortly. It was the obvious effect of mass in the entropy of these compounds which led to the present theorem. Although they are all liquids at  $298^\circ \text{K.}$ , the difference in the entropy of the liquid and extrapolated solid is only a few tenths of an entropy unit, subtracting of course the entropy of fusion. The experimental values of  $S_{298}$  are, respectively, 42.53, 47.3, 49.36 and 53.5, and by Equation 2, 45.53, 47.90, 49.46 and 52.24. Carbon tetrachloride probably should not be included in these calculations since carbon has not reached the Dulong and Petit value. The deviation between experimental and calculated values is in the direction anticipated.

*Sodium Bromide, Sodium Iodide and Potassium Iodide.*—E. Koref<sup>5</sup> has determined the average specific heats between  $82$  and  $193^\circ \text{K.}$ , and  $197$  and  $273^\circ \text{K.}$ , for the halides of sodium and potassium. Although as a rule it is difficult to interpret average specific heats, the problem is simplified in this case by assuming that all these halides have the same general specific heat curve. Since the whole curves for potassium chloride, potassium bromide and sodium chloride are known, together with the corresponding average values of Koref, they have been used as a check in the following calculations. Again using the notation of Lewis and Gibson, we find for sodium bromide  $\log \theta = 1.735$ ,  $S_{v298} = 19.80$  and  $S_{298} = 20.08$ . For sodium iodide  $\log \theta = 1.65$ ,  $S_{v298} = 22.26$  and  $S_{298} = 22.54$ . For potassium iodide  $\log \theta = 1.61$ ,  $S_{v298} = 23.14$ ,  $S_{298} = 23.42$ . The corresponding calculated values are 20.53, 21.93 and 23.51.

*Iodine* is the only solid non-metallic element having  $C_v = 6$  for which any data are available. From the meager data of Nernst, Lewis and Gibson have calculated  $S_{298} = 31.4$ . In their calculation they have assumed the validity of the formula  $S = f(T/\theta)^n$ . Jones and Hartmann,<sup>6</sup> as a result of their work on the temperature coefficient of the iodine-silver iodide cell, find  $\Delta S_{298} = 4.5$  and  $3.7$ , for the reaction  $\text{Ag} + \text{I} = \text{AgI}$ . For

<sup>1</sup> Lewis and Rupert, *THIS JOURNAL*, 33, 299 (1911).

<sup>2</sup> Nernst, *Z. physik. Chem.*, 2, 23 (1888).

<sup>3</sup> Varet, *Ann. chim. phys.*, [7] 8, 102 (1896).

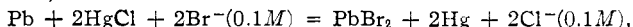
<sup>4</sup> Lewis and von Ende, *THIS JOURNAL*, 32, 732 (1910)

<sup>5</sup> E. Koref, *Ann. Physik.*, [4] 36, 49 (1911).

<sup>6</sup> Jones and Hartmann, *THIS JOURNAL*, 37, 767 (1915).

the same reaction U. Fischer<sup>1</sup> finds  $\Delta S_{298} = 2.419, 1.267$  and  $1.66$ . As an average of these values we will take  $2.7$ . Using  $S_{298} = 26.8$  for silver iodide and  $S_{298} = 10.2$  for silver, we find for iodine the value  $S_{298} = 13.9$ . By Equation 2  $S_{298} = 13.52$ . These calculated values for  $S_p$  assume that the value of  $S_p - S_p^0$  is the same for all substances as for potassium chloride. In some cases a correction should be made. For iodine whose  $C_p - C_v$  value is abnormally high this correction amounts to at least  $0.4$  of a unit. From the average atomic heats of bromine and chlorine, between the boiling points of hydrogen and nitrogen, Lewis and Gibson have calculated the entropies of chlorine and bromine at low temperatures assuming the same value for  $n$  that they used for iodine. Although a revision of the  $S_{298}$  values of these elements will not be attempted, it may be pointed out that the  $S_{298}$  value, as calculated from  $\Delta F$  and  $\Delta H$  measurements for a dozen or more chlorides, bromides and iodides, indicates that the entropy from specific-heat data is approximately  $2$  units too high per gram atom. This is the same difference that was found with the value of iodine as calculated by Equation 2.

*Lead Bromide.*—Although no specific-heat data are available the entropy of lead bromide may be calculated from data on  $\Delta F_{298}$ ,  $\Delta H_{298}$  and  $S_{298}$  of lead and bromine. For the reaction,



Lewis and Brighton<sup>2</sup> found  $E = 0.551$ . Making an estimated correction of  $0.002$  for the appreciable solubility of lead chloride in potassium chloride on the calomel side,  $E = 0.549$ . Hence  $\Delta F_{298} = -25,160$ . For the  $\Delta F_{298}$  of formation from the elements of mercuric chloride, and ions of bromine and chlorine we find, respectively,  $-25,130$ ,<sup>3</sup>  $-24,594$ ,<sup>4</sup> and  $-31,400$ ,<sup>5</sup> from which  $\Delta F_{298}$  of lead bromide =  $-61,808$ . The value of  $\Delta H_{298} = -64,456$  is given by Thomsen.<sup>6</sup> Then  $\Delta S_{298} = -8.9$  for the entropy of formation of lead bromide. Using  $S_{298} = 15.40$  for metallic lead,  $S_{298}$  for lead bromide =  $43.5$  or  $39.5$ , depending upon whether we use the value  $S_{298} = 18.5$  for bromine from specific heat data or the more probable value  $16.5$ . By Equation 2  $S_{298} = 14.97 + 2(12.12) = 39.21$ .

*Lead Sulfide.*—Although sulfur in many of its compounds has a Kopp's Law value considerably less than  $6$ , an average  $C_v$  per atom for lead sulfide, at  $298^\circ \text{K}$ ., of  $5.8$  was found by Eastman and Rodebush.<sup>7</sup> From their specific heat data extending down to  $65^\circ \text{K}$ ., we may calculate, using the method and notation of Lewis and Gibson,  $n = 0.8$ ,  $\log \theta = 1.675$ ,  $\log 298/\theta' = 0.64$ .  $S_{v298} = 22.4$  per mol, or  $S_{p298} = 22.8$ . It is not surprising that Equation 2 gives a slightly higher value.  $S_{298} = 14.97 + 9.43 = 24.40$ .

These 18 cases cover practically all the available data. Although the e. m. f. of several metals against dilute solutions of their ions are known, the free energies of dilution from saturated solutions of their salts to the dilute solutions are not known. Eucken and Schwerts<sup>8</sup> have determined the specific heats of calcium fluoride and iron disulfide, but unfortunately their  $C_v$ 's do not reach the Dulong and Petit value at  $298^\circ \text{K}$ . From Equation 2 it is obvious that the fact that the specific heats of boron, carbon, nitrogen, oxygen, fluorine, and sometimes sulfur are below the Dulong and Petit value must be due to other reasons than simply their small atomic weight. And of course their en-

<sup>1</sup> U. Fischer, *Z. anorg. Chem.*, **78**, 41 (1912).

<sup>2</sup> Lewis and Brighton, *THIS JOURNAL*, **39**, 1906 (1917).

<sup>3</sup> Lewis and Gibson, *loc. cit.*

<sup>4</sup> Lewis and Randall, *THIS JOURNAL*, **38**, 2348 (1916).

<sup>5</sup> Lewis and Rupert, *ibid.*, **33**, 299 (1911).

<sup>6</sup> Thomsen, *J. prakt. Chem.*, [2] **12**, 92 (1875).

<sup>7</sup> Eastman and Rodebush, *THIS JOURNAL*, **40**, 490 (1918).

<sup>8</sup> Eucken and Schwerts, *Berl. deut. physik. Ges.*, **15**, 578 (1913).

tries will continue to be below those corresponding to the other elements even at temperatures high enough that  $C_v$  has reached 6. While it certainly is true that compounds of all elements with low Kopp's Law constant have constraints greater than the postulated limiting value, the converse of the statement does not necessarily follow. Fortunately, however, the experimental evidence seems to justify the use of Kopp's Law as the criterion for the applicability of Equation 2 in calculating the entropy of the compounds. The entropies of the metals themselves deviate by several units from the values given by Equation 2. In the case of the more positive elements there is evidence<sup>1</sup> that the electrons have acquired considerable thermal energy. The experimental value for the entropy of metallic potassium is approximately twice that calculated. However, in the very hard metals, with the close packing of the atoms, the constraints must be very high, and again the entropies are low. For lead, which not only is not positive but quite soft as well, the experimental value 15.4 and the calculated value 14.99 agree very well. It is quite possible that for certain radicals such as sulfate, nitrate, organic acid, etc., a value for the entropy may be assigned which will remain constant in all of their compounds. From the specific heat data of Pollitzer<sup>2</sup> on mercurous sulfate the entropy of the sulfate radical should be  $52.5 - 2(14.88) = 22.74$ . It may also be pointed out that if the substance belongs to that group for which  $C_v$  is the same function of  $T/\theta$ , the whole specific heat curve down to absolute zero is determined by Equation 2.

The experimental and calculated data for the 18 cases considered are summarized in Table II.

TABLE II.—ENTROPY OF SOLIDS.

	$S_{298}$ from specific heats.	$S_{298}$ from $\Delta F$ , $\Delta H$ , and $S$ of elements.	$S_{298}$ calculated by Equation 2.
KCl.....	19.7	..	(19.7)
KBr.....	22.4	..	22.11
KI.....	23.42	..	23.51
NaCl.....	17.44	18.5	18.21
NaBr.....	20.08	..	20.53
NaI.....	22.54	..	21.93
PbCl <sub>2</sub> .....	33.2	35.2	34.39
PbI <sub>2</sub> .....	41.3	..	42.01
HgCl.....	23.2	22.3	24.59
AgCl.....	23.4	25.2	22.73
AgI.....	26.8	..	26.54
TiCl.....	28.6	24.6 (2 checks)	24.64
SiCl <sub>4</sub> .....	47.3	..	47.90
TiCl <sub>4</sub> .....	49.36	..	49.46
SnCl <sub>4</sub> .....	53.5	..	52.24
I.....	15.7	13.9	13.52 (13.92)
PbBr <sub>2</sub> .....	...	43.5 39.5	39.21
PbS.....	22.8	..	24.40

The average deviation of the experimental and calculated values is 0.7 entropy unit, which corresponds to an error of only 210 calories in  $\Delta F$  or  $\Delta H$ , and the maximum deviation is 1.8 units. This is certainly within the limits of the experimental errors. It should be noted that the agreement is best in those cases in which the experimental data seem the more reliable. As pointed out before, corrections in some cases of several

<sup>1</sup> Lewis, Eastman and Rodebush, *Proc. Nat. Acad. Sci.*, 4, 25 (1918).

<sup>2</sup> Pollitzer, *Z. Elektrochem.*, 19, 575 (1913).

tenths of a unit should be made in the calculated values for differences in  $S_p$  and  $S_v$ .

### Entropy of Gases.

Tolman<sup>1</sup> has reviewed in detail the evidence of the mass effect on the entropy of the monatomic gases. The agreement which he found was all that could be expected from the experimental data. In view of the results just obtained for the salts it seems worth while to attempt to apply the same methods to the diatomic gases. Then if the entropy of the gas is considered as due in part to the motion of the molecule as a whole and in part to the motion of the atoms<sup>2</sup> we may write<sup>3</sup> for the diatomic gas

$$S_{298} = \frac{3}{2}R \ln \text{mol. wt.} + R/2 \ln \text{at. wt.}_1 + R/2 \ln \text{at. wt.}_2 + S_0. \quad (3)$$

From careful study of specific heat data, Lewis and Gibson calculated  $S_{298}$  for the gases hydrogen, nitrogen, oxygen, carbon monoxide and chlorine. The values for bromine and iodine vapor may be obtained from measurements of vapor pressure of bromine and iodine and their heats of vaporization and sublimation, together with  $S_{298}$  for liquid bromine and solid iodine. In addition the entropies of hydrogen chloride, hydrogen bromide and hydrogen iodide are obtainable from their free energies and heats of formation and the entropies of their elements. The constant in Equation 3 has been determined from the average of the experimental results given below as  $S_0 = 30.22$ .

*Hydrogen.*—The value  $S_{298} = 31.8$  given by Lewis and Gibson is estimated as not being in error by more than 2 entropy units. By Equation 3  $S_{298} = 32.3$ .

*Nitrogen.*—From the data of Eucken  $S_{298} = 45.6$ . By Equation 3  $S_{298} = 45.42$ .

*Carbon Monoxide.*— $S_{298} = 45.55$ , which is also obtained from the work of Eucken. Calculated  $S_{298} = 45.50$ .

*Oxygen.*—The value calculated from Eucken's data is  $S_{298} = 48.2$ , with estimated error not greater than 2 units. By Equation 3  $S_{298} = 46.08$ . This value for oxygen reduces the discrepancy of 1.3 units found by Lewis and Gibson in the entropy of carbon monoxide to 0.3 of a unit. The data in this test of the Third Law of Thermodynamics they consider the most reliable of all their experimental data.

*Hydrogen Chloride.*—From the e. m. f. of the hydrogen and chlorine electrodes<sup>4</sup> the free energy of formation of hydrogen chloride from its

<sup>1</sup> Tolman, *loc. cit.*

<sup>2</sup> This is in accord with evidence being collected by G. N. Lewis that the additional energy of the diatomic gas is vibrational and not rotational as ordinarily assumed.

<sup>3</sup> The present paper will not attempt a strict theoretical justification, dimensionally or otherwise, for either Equation 2 or 3, but will be confined to consideration of the experimental data.

<sup>4</sup> Lewis and Rupert, *loc. cit.*

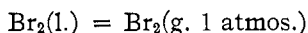
elements is  $\Delta F_{298} = -22,700$ . Both Thomsen and Berthelot give  $\Delta H_{298} = -22,000$ . Using  $S_{298} = 15.9$  for hydrogen and  $S_{298} = 25$  for chlorine,  $S_{298} = 43.25$  for hydrogen chloride. Calculated  $S_{298} = 44.49$ .

*Hydrogen Bromide.*—Lewis and Randall<sup>1</sup> give  $\Delta F_{298} = -12,592$  and  $\Delta H_{298} = -8265$ . From  $S_{298} = 15.9$  for hydrogen and  $S_{298} = 18.5$  for bromine,  $S_{298} = 48.9$  for hydrogen bromide. If the evidence considered before in regard to the entropy of bromine is accepted this becomes 46.9. Calculated  $S_{298} = 47.68$ .

*Hydrogen Iodide.*—Lewis and Randall<sup>2</sup> find  $\Delta F_{298} = 310$ . Thomsen gives  $\Delta H_{298} = 6000$  and Berthelot 6300. As an average we will use 6150. The value  $S_{298}$  becomes 51.20 or 49.20 depending upon the entropy of solid iodine. Calculated  $S_{298} = 49.49$ .

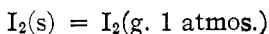
*Chlorine.*—From specific heat data  $S_{298} = 55.6$ . As a mean value calculated from the entropy of mercurous, silver, lead, thallium and sodium chlorides, Lewis and Gibson give 51.4. As thallium chloride from specific-heat data is certainly too high, the approximate value of 50 per mol. has been used throughout for chlorine. By Equation 3  $S_{298} = 50.04$ .

*Bromine.*—Ramsay and Young<sup>3</sup> give 213 mm. as the vapor pressure of liquid bromine at 300° K. For the heat of vaporization at that temperature we shall use the value calculated by Lewis and Randall,<sup>4</sup>  $\Delta H_{298} = 7570$ . The entropy change for the reaction



is  $\Delta S_{298} = 22.87$ , and  $S_{298}$  for bromine gas is 59.87 or 55.87, depending upon the value used for the entropy of liquid bromine. Calculated  $S_{298} = 54.10$ .

*Iodine.*—From the measurements of Baxter, Hickey and Holmes<sup>5</sup> the vapor pressure of solid iodine at 298° K. is 0.305 mm. and thus the entropy change in compressing the vapor to one atmosphere is  $\Delta S_{298} = -15.55$ , assuming of course the gas laws. For the heat of vaporization at 298° K., Baxter, Hickey and Holmes give 15,100, for which  $\Delta S_{298} = 50.7$ . The entropy for the reaction



is  $\Delta S_{298} = 35.15$ . Thus for iodine vapor  $S_{298} = 66.56$  or 62.56, depending upon the value taken for the entropy of solid iodine. By Equation 3  $S_{298} = 56.39$ . This discrepancy of 1800 cal. seems beyond the experimental error. However, the value for the heat of sublimation was calculated from measurements of vapor pressure over a range of 25° and may for that reason be quite erroneous.

<sup>1</sup> Lewis and Randall, *THIS JOURNAL*, 38, 2348 (1916).

<sup>2</sup> Lewis and Randall, *ibid.*, 36, 1259 (1914).

<sup>3</sup> Ramsay and Young, *J. Chem. Soc.*, 49, 453 (1886).

<sup>4</sup> Lewis and Randall, *THIS JOURNAL*, 28, 2348 (1916).

<sup>5</sup> Baxter, Hickey and Holmes, *THIS JOURNAL*, 29, 127 (1907).



The experimental and calculated values have been summarized in the following table.

TABLE III.—ENTROPY OF DIATOMIC GASES.

	$S_{298}$ (experimental).	$S_{298}$ (calculated).		$S_{298}$ (experimental).	$S_{298}$ (calculated).
H <sub>2</sub> .....	31.8	32.30	HBr.....	48.9 -46.9	47.68
N <sub>2</sub> .....	45.6	45.42	HI.....	51.20-49.20	49.49
CO.....	45.55	45.50	Cl <sub>2</sub> .....	55.6 -50.0	50.04
O <sub>2</sub> .....	48.2	46.08	Br <sub>2</sub> .....	59.87-55.87	54.10
HCl.....	43.25	44.49	I <sub>2</sub> .....	66.56?	56.39

### Summary.

The postulate is made that there is a certain limiting value of the constraints in a solid below which the effect of the constraints upon the entropy of the solid is constant. On this basis the entropy of solids in which this condition is fulfilled is the sum of the entropies of the elements in the solid. The entropy of the elements in such a solid is given by the equation

$$S_{298} = 3/2 R \ln \text{at. wt.} - 0.94.$$

The entropy of all compounds on which data are available, 18 in number, is found to agree with the equation within an average variation of 0.7 entropy unit. The one condition is that the Kopp's Law constant for the elements in the compound shall have reached approximately a value of 6.

The data on 10 diatomic gases are considered in connection with the equation

$$S_{298} = 3/2 R \ln \text{mol. wt.} + R/2 \ln \text{at. wt.}_1 + R/2 \ln \text{at. wt.}_2 + 30.22.$$

With the possible exception of iodine the agreement is within the limits of the experimental error.

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