

substances may be transferred from one side to the other, (1) metallic thallium, (2) thallic chloride, (3) water, (4) sugar. Let us assume that the sugar does not combine with the ions and is not carried by the current. Of the three remaining processes the first two are capable of doing no work, for the activity of the thallium, and of the thallic chloride is the same on both sides. The activity of the water, however, is about 2 per cent. lower in the sugar solution. Since the transfer of water is the only process which is accompanied by a change of free energy, the electromotive force of the cell will be a direct measure of the amount of water transferred. The general equation will obviously be

$$E = \frac{n'RT}{F} \ln \frac{\xi'_1}{\xi'_2},$$

when  $\xi'_1$  and  $\xi'_2$  are the activities of the water on the two sides and  $n'$  is the number of mols of water carried with one Faraday.

The successful application of this simple method of determining the relative hydration of the ions depends solely upon finding a suitable non-electrolyte which itself is not carried with the current. An experimental investigation of the method has already been begun in this laboratory.

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(CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 32).

## THE FREE ENERGY CHANGES ATTENDING THE FORMATION OF CERTAIN CARBONATES AND HYDROXIDES.

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In recent years much attention has been directed to the measurement and calculation of the free energy changes attending chemical reactions. For the most part the equilibria studied for the purpose of determining the changes in free energy have been cases of homogeneous gaseous reactions, such as those studied by Haber and Nernst; in addition, certain heterogeneous equilibria have been investigated; for example, the decomposition of silver oxide by G. N. Lewis,<sup>1</sup> while calculations of free energy from electromotive force data have been made by M. de K. Thompson.<sup>2</sup>

It is the purpose of this article to present the results of such calculations from existing data in the cases of the hydroxides and carbonates of lithium, sodium, and alkaline-earth elements.

Unfortunately the various authors do not all define "free energy" in the same way. In the present calculations the increase in free energy,  $\Delta F$ , is defined by the following equation:

<sup>1</sup> THIS JOURNAL, 28, 158 (1906).

<sup>2</sup> *Ibid.*, 28, 731 (1906).

$$\Delta F = -W(\max.) + \Delta(\Sigma pv), \quad (I)$$

in which  $W(\max.)$  stands for the maximum work producible by the change in state, and  $\Delta(\Sigma pv)$  is the change in the sum of the  $pv$  terms for each part of the system. If the reaction occurs at constant pressure, which is nearly always the case, this quantity  $\Delta(\Sigma pv)$  represents the work done by the system against this pressure. In that case, therefore  $-\Delta F$  represents that part of the maximum work which is available for other purposes.

In the case of a chemical reaction  $A + B = C + D$  the free energy change can be shown to be expressed by the equation

$$\Delta F = RT \left( \ln \frac{p_C p_D}{p_A p_B} - \ln \frac{p'_C p'_D}{p'_A p'_B} \right) \quad (II)$$

where  $p_C$  and  $p_D$  represent the final pressures of C and D,  $p_A$  and  $p_B$  the initial pressures of A and B and  $p'_A$ ,  $p'_B$ ,  $p'_C$  and  $p'_D$  the pressures of the four substances when in equilibrium with each other.

It can be also shown by application of the Second Law of Thermodynamics that the increase of free energy accompanying the reaction is given by the following expression:<sup>2</sup>

$$\Delta F = \Delta H_o - \Delta C_p T \ln T - \frac{1}{2} \alpha T^2 - \frac{1}{6} \beta T^3 + RT \ln \frac{p_C p_D}{p_A p_B} + IT. \quad (III)$$

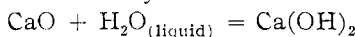
In this expression I is an integration constant, which has often been called the thermodynamically undetermined constant; the other quantities are defined by the following equations:

$$\Delta C_p = \Delta C_{p_o} + \alpha T + \beta T^2 \quad (IV)$$

$$\Delta H = \Delta H_o + \Delta C_{p_o} T + \frac{1}{2} \alpha T^2 + \frac{1}{3} \beta T^3 \quad (V)$$

in which  $\Delta H$  is the increase in total energy produced by the reaction taking place at constant pressure [that is,  $\Delta H$  is the amount of heat *absorbed* as ordinarily measured calorimetrically];  $\Delta C_p$  is the increase thereby produced in the heat capacity of the system, and  $\alpha$  and  $\beta$  are empirical temperature coefficients.<sup>3</sup>

Consider now the dissociation of calcium hydroxide into calcium oxide and water vapor. The mean value of the determinations by Thomsen and Berthelot of the heat evolved by the reaction



is 15,320 cal. In order to obtain  $\Delta H$  for the reaction  $\text{Ca(OH)}_2 = \text{CaO} + \text{H}_2\text{O}$  (vapor) it is necessary to add to this value 10,550 cal., the mean

<sup>1</sup> If  $n$  mols. of A, B, etc., enter into the reaction, then the corresponding  $p$  must be raised to the  $n$ th power, just as in an ordinary mass-action-law equation.

<sup>2</sup> A full discussion of the development of this equation will be given by Prof. G. N. Lewis in a forthcoming publication. See also Haber "Thermodynamics of Technical Gas-Reactions" translated by Lamb, pp. 26, *i. c.*, et seq.

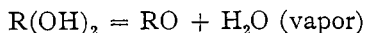
<sup>3</sup> It is only in rare cases that our knowledge of the heat capacities is accurate enough to enable us to determine the coefficient  $\beta$ ; indeed, it is usually impossible to determine  $\alpha$  with any great degree of accuracy.

value<sup>1</sup> of the molecular heat of vaporization of water;  $\Delta H$  for the latter reaction then becomes 25,870 cal. Now the heat capacity of water vapor at the mean temperature of the experiments, say  $T = 740$ , derived from the measurements of Holborn and Henning<sup>2</sup> is 8.66; and according to the Kopp-Neumann rule, the difference between the heat capacities of  $\text{Ca(OH)}_2$  and  $\text{CaO}$  (for neither of which experimental data are available) is equal to the molecular heat capacity of solid water, which is about 8.6. Therefore

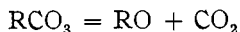
$$\Delta C_p = C_{p(\text{H}_2\text{O vap.})} - (C_{p\text{Ca(OH)}} - C_{p\text{CaO}}) = 8.66 - 8.6$$

so that  $\Delta C_p$  may be taken as zero, since the Kopp-Neumann rule is only approximately true; moreover, the uncertainty in the value of  $\Delta H$  renders futile the application of such a small correction.<sup>3</sup> The same reasoning applies also to the other hydroxides and the carbonates, as the uncertainty in the value of  $\Delta H$  is always greater than the amount of this correction.

Thus for the reactions studied in this paper, namely,



and



in which one mol  $\text{H}_2\text{O}$  (vapor) or  $\text{CO}_2$  appears for each mol of oxide, equations II and III reduce to the following simple expressions:

$$\Delta F = RT \ln p - RT \ln p' \quad (\text{VIa})$$

and

$$\Delta F = \Delta H + RT \ln p + IT \quad (\text{VIb})$$

When the system is in equilibrium at any one temperature  $T$ , the actual pressure  $p$  of the gas is equal to the dissociation pressure  $p'$  and  $\Delta F$  becomes zero; when  $\Delta H$  and  $p$  (which then represents the dissociation pressure) are known,  $I$  can be calculated.  $\Delta F$  can then be evaluated

<sup>1</sup> This value is derived from the following data: the means of the values of this quantity given in Landolt-Börnstein for the temperatures  $0^\circ$  and  $100^\circ \text{C.}$  are 10720 and 9670 respectively; whence by assuming that the variation with the temperature is linear, the value at  $18^\circ$  is 10540 cal. This agrees very closely with the value obtained from the recent determinations of A. W. Smith, *Phys. Rev.*, **25**, 145 (1907), which is 10,570 cal. at  $18^\circ$ .

<sup>2</sup> *Ann. Physik* [4], **23**, 809 (1907).

<sup>3</sup> In any case, if this correction amounted to two units, it would exert but a small influence on the calculated value of  $\Delta F$ , so long as the temperature range is not too great; it would cause, however, a large difference in the numerical value of the integration constant. Thus for the reaction  $\text{Ba(OH)}_2 = \text{BaO} + \text{H}_2\text{O}$ , the approximate value of  $\Delta C_p$  for the mean temperature is 10, but the value of the term  $\Delta C_p T \ln T$ , changes only from 6.84 ( $T = 943$ ) to 7.13 ( $T = 1271$ ); the inclusion of this term alters  $\Delta F$  by about 800 cal., an accuracy much greater than that attained in the experimental determination of  $\Delta H$  for this reaction. It goes without saying that the terms containing  $\alpha$  and  $\beta$ , which represent the change of  $\Delta C_p$  with the temperature, are negligible.

at any temperature for the case where the states of the system are those conventionally adopted as the standard—namely, where its initial and final pressure is one atmosphere—for the term  $RT \ln p$  then vanishes. From the value of  $\Delta F$  at any temperature, so obtained, the equilibrium pressure  $p'$  at that temperature can then be calculated by the relation  $\Delta F = RT \ln p/p' = -RT \ln p$ . In what follows are given the results of such calculations applied to the hydroxides and carbonates of lithium, sodium and the alkaline earth elements.

### The Experimental Data.

The thermochemical data required are contained in Table I. These are taken from Landolt-Börnstein,<sup>1</sup> with the exception of those for the series of carbonates, which has been quite recently investigated by de Forcrand.<sup>2</sup> In general the mean value has been chosen, except for the heat of formation of barium hydroxide, for which the values as determined by Thomsen and de Forcrand differ by more than 4000 cal; in this case, calculations have been made with both values. For the hydroxides, the values in the column "heat absorbed" are for the reaction  $R(OH)_2 = RO + H_2O$  (liquid); those in the last column are for the reaction  $R(OH)_2 = RO + H_2O$  (vapor).

TABLE I.

Reaction.	Heat absorbed.	Observer.	Value adopted.	$\Delta H$ .
$Mg(OH)_2 = MgO + H_2O$ .....	$\left\{ \begin{array}{l} 5400 \\ 5000 \end{array} \right.$	$\left\{ \begin{array}{l} \text{Berthelot} \\ \text{Marignac} \end{array} \right.$	5400	15950
$Ca(OH)_2 = CaO + H_2O$ .....	$\left\{ \begin{array}{l} 15540 \\ 15100 \end{array} \right.$	$\left\{ \begin{array}{l} \text{Thomsen} \\ \text{Berthelot} \end{array} \right.$	15320	25870
$2Li(OH) = Li_2O + H_2O$ .....	$\left\{ \begin{array}{l} 14400 \\ 13000 \end{array} \right.$	$\left\{ \begin{array}{l} \text{Berthelot} \\ \text{Beketoff} \end{array} \right.$	13700	24250
$Sr(OH)_2 = SrO + H_2O$ .....	$\left\{ \begin{array}{l} 17700 \\ 17100 \end{array} \right.$	$\left\{ \begin{array}{l} \text{Thomsen} \\ \text{Berthelot} \end{array} \right.$	17400	27950
$Ba(OH)_2 = BaO + H_2O$ .....	$\left\{ \begin{array}{l} 22260 \\ 17800 \end{array} \right.$	$\left\{ \begin{array}{l} \text{Thomsen} \\ \text{de Forcrand} \end{array} \right.$	...	32810 28350
$2NaOH = Na_2O + H_2O$ .....	$\left\{ \begin{array}{l} 35600 \\ 35440 \end{array} \right.$	$\left\{ \begin{array}{l} \text{Thomsen} \\ \text{Beketoff} \end{array} \right.$	35530	46080
$MgCO_3 = MgO + CO_2$ .....	28900	de Forcrand	...	28900
$CaCO_3 = CaO + CO_2$ .....	$\left\{ \begin{array}{l} 42520 \\ 43300 \end{array} \right.$	$\left\{ \begin{array}{l} \text{Thomsen} \\ \text{de Forcrand} \end{array} \right.$	...	42900
$Li_2CO_3 = Li_2O + CO_2$ .....	54230	de Forcrand	...	54230
$SrCO_3 = SrO + CO_2$ .....	$\left\{ \begin{array}{l} 55770 \\ 57300 \end{array} \right.$	$\left\{ \begin{array}{l} \text{Thomsen} \\ \text{de Forcrand} \end{array} \right.$	...	56500
$BaCO_3 = BaO + CO_2$ .....	$\left\{ \begin{array}{l} 62220 \\ 63440 \end{array} \right.$	$\left\{ \begin{array}{l} \text{Thomsen} \\ \text{de Forcrand} \end{array} \right.$	...	62800
$Na_2CO_3 = Na_2O + CO_2$ .....	76880	de Forcrand	...	76880

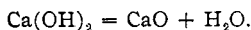
<sup>1</sup> Third edition, pp. 433-44; 460.

<sup>2</sup> *Compt. rend.*, **146**, 512 (1908).

The data on the dissociation pressures and the calculated values of the constant  $I$  are given in Tables II-IV. The pressures for all the hydroxides and for the carbonates of lithium and sodium are taken from a recent paper by the author;<sup>1</sup> the calculations have been made from every alternate value in the table interpolated from the experimental results. The data for calcium carbonate are from the recent work of Zavrieff,<sup>2</sup> and are probably considerably more accurate than the older measurements of Le Chatelier;<sup>3</sup> those for barium carbonate are by Finkelstein;<sup>4</sup> and the single values for strontium and magnesium carbonates are taken from a paper by Brill.<sup>5</sup> The value for magnesium carbonate is very doubtful, as Brill states that only the first tenth of the carbon dioxide is given off at 230° C., and that the carbonate is not completely transformed into oxide until a temperature of 560° is attained.

All pressures are expressed in atmospheres. The value of  $R$  has been taken as 1.987, so that  $R \ln p = 4.576 \log p$ ;  $\Delta F_{25}$  and  $p_{25}$  stand for the values of the increase in free energy in calories and of the dissociation pressure at 25°. For calcium hydroxide, the calculations are given in full. For the other substances only the corresponding values of  $p$ ,  $T, \frac{\Delta H}{T}$  and  $I$  are given. All the values of  $\Delta F_{25}$  and  $p_{25}$  are brought together in Table V. The dissociation points<sup>6</sup> of the various substances are also given.

TABLE II.



$t$ .	$T$ .	$p$ .	$25870/T$ .	$-4.576 \log p$ .	$-I$ .
389	662	0.0229	39.15	7.50	31.65
428	701	0.0724	36.95	5.22	31.73
468	741	0.196	34.95	3.24	31.71
507	780	0.467	33.20	1.51	31.69
547	820	1.00	31.58	0	31.58

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Mean — 31.67

Hence  $\Delta F_{25} = \Delta H + IT = 25870 - (31.67 \times 298) = 16430$  cal.

Moreover, since  $-RT \ln p_{25} = \Delta F_{25}$ , therefore  $\log p_{25} = -\frac{16430}{298 \times 4.576} = -12.05$ ,

whence  $p_{25} = 9 \times 10^{-13}$  atmospheres.

<sup>1</sup> *Z. physik. Chem.*, **62**, 330 (1908).

<sup>2</sup> *Compt. rend.*, **145**, 428 (1907).

<sup>3</sup> *Ibid.*, **102**, 1243 (1886).

<sup>4</sup> *Ber.*, **39**, 1586 (1906).

<sup>5</sup> *Z. anorg. Chem.*, **45**, 275 (1905).

<sup>6</sup> In analogy with boiling point, etc., I have used the term *dissociation point* to represent that temperature at which the dissociation pressure is equal to one atmosphere.

TABLE III.

<i>p.</i>	$\text{Sr}(\text{OH})_2 = \text{SrO} + \text{H}_2\text{O}.$			$2\text{LiOH} = \text{Li}_2\text{O} + \text{H}_2\text{O}.$		
	T.	27950/T.	—I.	T.	24250/T.	—I.
0.0229	761	36.7	29.2	867	27.88	20.38
0.0724	834	33.5	28.3	935	25.90	20.68
0.196	907	30.8	27.6	1013	24.00	20.76
0.467	979	28.5	27.0	1099	22.00	20.49
1.00	1051	26.6	26.6	1197	20.20	20.20

Mean — 27.7

Mean — 20.5

<i>p.</i>	T.	$\text{Ba}(\text{OH})_2 = \text{BaO} + \text{H}_2\text{O}.$			
		32810/T.	—I.	28350/T.	—I.
0.0229	943	34.8	27.3	30.05	22.55
0.0724	1022	32.0	26.8	27.70	22.48
0.196	1102	29.7	26.5	25.75	22.51
0.467	1183	27.7	26.2	24.00	22.49
1.00	1271	25.8	25.8	22.30	22.30

Mean — 26.5

Mean — 22.46

<i>p.</i>	$\text{Mg}(\text{OH})_2 = \text{MgO} + \text{H}_2\text{O}.$		
	T.	1590/T.	—I.
0.0229	317	50.3	42.8
0.0724	336	47.5	42.3
0.0196	359	44.5	41.2
0.0467	391	40.8	39.3

Mean — 41.4

TABLE IV.  
 $\text{CaCO}_3 = \text{CaO} + \text{CO}_2.$ 

<i>p.</i>	T.	42900/T.	—I.
0.088	998	43.0	38.2
0.303	1088	39.4	37.0
0.450	1113	38.5	36.9
0.658	1143	37.5	36.8
0.824	1165	36.8	36.4
0.993	1183	36.2	36.2
1.345	1199	35.8	36.4

Mean — 36.6

<i>p.</i>	$\text{Li}_2\text{CO}_3 = \text{Li}_2\text{O} + \text{CO}_2.$			$\text{BaCO}_3 = \text{BaO} + \text{CO}_2.$		
	T.	54230/T.	—I.	T.	62800/T.	—I.
0.00658	1013	53.5	43.5	1301	48.2	38.2
0.0132	1053	51.5	42.9	1343	46.8	38.2
0.0263	1113	48.7	41.5	1383	45.4	38.2
0.0658	1203	45.2	39.8	1437	43.7	38.3
0.132	1283	42.3	38.3	1483	42.3	38.3
1.00	..	..	..	1623	38.6	38.6

Mean — 41

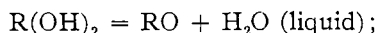
Mean — 38.3

Reaction.	$p$ .	T.	$\Delta H/T$ .	-I.
$\text{SrCO}_3 = \text{SrO} + \text{CO}_2$ .....	1.0	1430	39.6	39.6
$\text{MgCO}_3 = \text{MgO} + \text{CO}_2$ .....	1.0	500(?)	57.8	57.8
$\text{Na}_2\text{CO}_3 = \text{Na}_2\text{O} + \text{CO}_2$ .....	0.0066	1213	63.4	53.4

TABLE V.

Metallic element.	$\Delta F_{25}$ for the reaction		$p_{25}$ in atmospheres for		Dissociation points in degrees C	
	Hydroxide $\rightarrow$ oxide.	Carbonate $\rightarrow$ oxide.	Hydroxides.	Carbonates.	Hydroxides.	Carbonates.
Mg.....	3600	11700	$2.3 \times 10^{-3}$	$2.6 \times 10^{-9}$	160°(approx.)	230°(?)
Ca.....	16430	41450	$9.0 \times 10^{-13}$	$4.0 \times 10^{-31}$	547°	910°
Li.....	18100	42000	$5.4 \times 10^{-14}$	$1.6 \times 10^{-31}$	924°	ca 1160°
Sr.....	19700	44900	$3.6 \times 10^{-15}$	$1.2 \times 10^{-33}$	778°	1155°
Ba.....	$\left\{ \begin{array}{l} 25000 \\ 21720 \end{array} \right\}$	51400	$\left\{ \begin{array}{l} 4.8 \times 10^{-19} \\ 1.2 \times 10^{-16} \end{array} \right\}$	$2 \times 10^{-38}$	998°	1350°
Na.....	.....	61000	.....	$2 \times 10^{-45}$	...	ca 1350°

In the case of the hydroxides the above values of  $\Delta F_{25}$  are for the reaction  $\text{R(OH)}_2 = \text{RO} + \text{H}_2\text{O}$  (vapor); since, however, the vapor pressure of water at 25° is 0.031 atmosphere,  $\Delta F_{25}$  for the change  $\text{H}_2\text{O}$  (vapor)  $\rightarrow$   $\text{H}_2\text{O}$  (liquid) is -2056 cal., and it is only necessary to add this quantity to the value given in Table V in order to obtain  $\Delta F_{25}$  for the reactions



that is, the values of  $\Delta F_{25}$  for this reaction are 2036 calories *smaller* than the values given in Table V.

In Table V the hydroxides and carbonates are arranged in the order of increasing stability, for the magnitude of the free energy change gives a direct measure of the stability. This order of stability of both the hydroxides and the carbonates is the same, and is to be expected from the regularities of the periodic classification; for this same sequence is observed if we consider the solubilities of the compounds in water, their specific gravities, melting-points, or other physico-chemical properties. Further, the stability of the lowest members of a series—magnesium or lithium—is very much less than that of the others; the difference between successive members is at first great, but diminishes always as the series is ascended, as has been observed when any other property—or in fact the whole chemical behavior—is considered. It is of interest to note that the ratio which  $\Delta F_{25}$  for the carbonate bears to  $\Delta F_{25}$  for the corresponding hydroxide, is approximately constant: thus for Ca, Li, Sr, and Ba (using the lower value) the ratios are respectively 2.52, 2.32, 2.28, 2.36. This makes it probable that the lower value is more correct than the higher value, which is based on the heat of formation given by Thomsen. It seems probable also that the heat of formation of  $\text{Sr(OH)}_2$  is too high, as a lower value would give more concordant values of I, as well as a higher value of the above ratio. It is to be borne in mind, however, that the constancy of this ratio has no direct theoretical

significance, but is only accidental at this temperature; moreover, since in general  $\Delta F$  is not proportional to the absolute temperature, such constancy can only be found—if at all—in the neighborhood of one particular temperature, and then probably only for compounds which are very much alike, such as the substances under consideration. The values in Table V for the magnesium compounds are doubtful; no calculations were made for the free energy of NaOH, as the uncertainty in the pressure determinations is too great.

At the dissociation-point, equation VIb reduces to

$$\Delta H + IT = 0, \text{ or } T = \Delta H / -I. \quad (\text{VII})$$

Now Le Chatelier and de Forcrand proposed the rule that  $T = \Delta H / 30$ ; but since the observed values could be reproduced by means of Formula VII, with the values of  $-I$  ranging from 20 to 40, it is clear that the latter rule can give approximately correct results only for those substances for which the value of  $-I$  is near 30; this rule therefore gives correct results only in exceptional cases, and is to be classed in the same category as Trouton's rule.

Nernst<sup>1</sup> has derived for heterogeneous equilibria, such as we are here considering, the following approximate equation:

$$\log p = - \frac{\Delta H}{4.576 T} + 1.75 \log T + C.$$

$C$  is a constant, which for hydroxides and carbonates, has, according to Nernst, the values 3.7 and 3.2 respectively. Now for values of  $T$  ranging from 700 to 1300, the value of the term  $1.75 \log T$  varies only from 4.97 to 5.45; therefore, for the hydroxides and carbonates studied, all of which dissociate within the above temperature limits, the value of the expression  $1.75 \log T + C$  differs but little from 8.6. Hence, Nernst's formula, as applied to the substances under consideration, reduces to

$$\log p = - \frac{\Delta H}{4.576 T} + 8.6.$$

Now at equilibrium, when  $\Delta F = 0$ , equation VIb is

$$\Delta H + RT \ln p + IT = 0,$$

which may be written

$$\log p = - \frac{\Delta H}{4.576 T} - I,$$

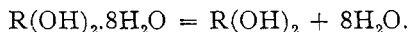
which is identical with Nernst's equation if  $-I$  is approximately 8.6. But we have seen that the value of  $-I$  ranges from 20 to 40, and that on

<sup>1</sup> *Nachr. Ges. Wiss. Göttingen*, 1906, 1. See also Johnston, *loc. cit.*, p. 349 and Brill, *Z. physik. Chem.*, **57**, 735 (1907), who has used this formula to calculate the dissociation points of certain carbonates, and in the examples chosen, has obtained fairly good concordance with the observed values. Certain other carbonates, however, which had also been investigated, do not show such good agreement between the observed and calculated values.



using these values, concordant results have been obtained, whence it is clear that correct results for the dissociation of hydroxides or carbonates can be obtained with Nernst's formula only if the numerical value of the integration constant does not differ much from 8 or 9, and this is probably so only in exceptional cases.

For the hydrated hydroxides of barium and strontium the only directly determined thermochemical data are for the reactions



Since, however, it is doubtful if any of the pressure measurements<sup>1</sup> correspond to this reaction, calculations of the free energy in which use is made of these values of  $\Delta H$  are of little value. Still, for each series, values of  $\Delta H$  and  $I$  deduced from two of the pressure measurements by solving the two simultaneous equations gave very concordant values of  $I$  when applied to the rest of the series of measurements. These results however have not been included, because the values of  $\Delta H$  derived in this manner refer always to the heat of reaction in vaporizing one mol of water, wherefore they cannot be compared with experimental thermochemical data until we know definitely which pair of hydrates is present in each particular case.

### Summary.

It is shown that the increase of free energy attending the reactions: hydroxide  $\rightleftharpoons$  oxide +  $H_2O$  (vapor) and carbonate  $\rightleftharpoons$  oxide +  $CO_2$ , may be expressed by the simple equation

$$\Delta F = \Delta H + RT \ln p + IT.$$

Calculations from existing pressure data for the hydroxides and carbonates of magnesium, calcium, lithium, strontium and barium give, in general, very concordant values of  $I$ , the thermodynamically undetermined constant, as is shown by Tables II-IV. In those cases in which  $I$  is inconstant, it is probable that the necessary thermochemical data are not yet known with sufficient accuracy. The increase in free energy at  $25^\circ$  attending the formation of these substances and their dissociation pressures at  $25^\circ$  have been calculated. The results are brought together in Table V; they show that, when these hydroxides or carbonates are arranged in the order of increasing stability, the series is: magnesium, calcium, lithium, strontium, barium, sodium. This order is in agreement with the known behavior of the compounds of those elements.

Further it is shown that the approximation formula of Nernst for heterogeneous equilibria cannot in general lead to correct results, and that it is to be classed with the empirical rule of Le Chatelier and de Forcrand.

Boston, June 29, 1908.

<sup>1</sup> Johnston, *loc. cit.*, p. 34.