## THE THERMODYNAMICS OF STRONTIUM

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Research on the thermodynamics of strontium and its compounds is The standard electrode potential has been only far from exhaustive. approximately evaluated,<sup>1</sup> the entropy of the ion has been calculated from unpublished data,<sup>2</sup> while the calculations of the heats of reaction <sup>3</sup> are in the majority of cases based on quite old determinations. There is disagreement between calorimetric data and calculations from the equilibria Taking all this into consideration, we thought that it would constants. not be undesirable to undertake an investigation aimed at filling in the above-mentioned gaps in the chemistry of strontium.

### The Heat of Formation of Strontium Carbonate.

It has already been shown by one of us 4 that the thermodynamic study of carbonates is a convenient means for obtaining a thermodynamic characteristic of the corresponding cation. At practically the same time critical studies were published by Rossini and Bichowsky 8 and by Kelly and Anderson<sup>5</sup> containing noticeably differing values for the heat of formation of SrCO<sub>a</sub> from the elements, namely, 290,400 and 279,200 cal., respectively. On the basis of high-temperature equilibria, data obtained by Jones and Becker, 6 and Tamaru and Siomi, 7 Chipman 8 proposed the value of 53,600 cal., for the heat of dissociation of the carbonate to the oxides, whereas the value recommended in the International Critical Tables is 56,150 cal. To elucidate this question we first of all carried out a measurement of  $\Delta H_{298}$  for SrCO<sub>3</sub>. As elsewhere,<sup>4</sup> we considered that the best procedure is a determination of the heat of solution of a previously prepared pure crystalline carbonate in dilute hydrochloric acid.

The isothermal calorimeter we employed enabled us to carry out measurements at a standard temperature of  $25^{\circ}$  C. The copper calorimeter chamber was immersed in a large water bath, the temperature of which was constant to  $\pm 0.02^{\circ}$  C. In the middle of this chamber was placed a pyrex beaker provided with a tightly fitting lid through which passed a glass stirrer, a heating spiral, a Beckmann thermometer, a tube for a cooling mixture, and a tube with a thin-walled bulb at its end. Into the latter was placed a weighed quantity of SrCO<sub>3</sub>, and into the beaker the hydrochloric acid, sufficiently concentrated to dissolve the carbonate completely but without sputtering. The experiment was started by breaking the bulb on the bottom of the beaker, and was completed (main period) The temperature was read with an accuracy approaching in 10 minutes. 0.001° C. with the aid of a cathetometer mounted at a distance of 1.5 m. As in Bäckstrom's experiments,<sup>9</sup> we employed 0.5 molal c.p. HCl previously saturated with CO<sub>2</sub> at 25° C. To determine the water equivalent of the

<sup>1</sup> Latimer, The Oxidation States of the Elements, 1938.

<sup>2</sup> Latimer, Pitzer and Smith, J. Am. Chem. Soc., 1938, 60, 1829.

<sup>a</sup> Rossini and Bichowsky, *Thermochemistry*, 1936.
<sup>4</sup> Kapustinsky, *Acta Physicochimica*, U.R.S.S., 1941, 14, 503.
<sup>5</sup> Kelley and Anderson, Bull. 384, U.S. Bureau of Mines, 1935.
<sup>6</sup> Jones and Becker, J. Chem. Soc., 1927, 2669; Becker, J. Steel Inst. (London), 1930, 121, 337. <sup>7</sup> Tamaru and Siomi, Z. physik. Chem., A, 1932, 159, 227.

- <sup>8</sup> Chipman, Trans. Faraday Soc., 1933, 29, 1266.
- <sup>9</sup> Bäckstrom, J. Am. Chem. Soc., 1925, 47, 2432.

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system we employed a thin glass spiral filled with mercury and immersed in the reaction mixture through which a current was passed to obtain the same temperature rise as in the heat of dilution experiment. Thus, just as in Rossini's 10 investigations, the quantity of heat liberated during the reaction was directly compared with the quantity of electrical energy necessary to produce the temperature rise, so that the thermometer (which had a certificate of the Institute of Metrology and Standards) was employed rather as a zero point instrument than a basic measuring device. The electrical energy was measured with the aid of a Rapps potentiometer, standard resistances and a Weston cell (all of which had certificates), a mirror galvanometer, and a stop-watch checked in the Engelhardt Observatory.<sup>11</sup> The necessary corrections were introduced as described elsewhere.<sup>4, 11</sup> Furthermore, a correction amounting to 12 cal. per g. of SrCO<sub>3</sub> due to the heat of vaporisation of water into the bubbles of the liberated CO<sub>2</sub> was specially determined and introduced. The precision in measuring the heat of solution was 1-2 %, and in determining the heat capacities, 0.1-0.2 %.

TABLE I.-THE HEAT OF SOLUTION OF STCO3 IN 0.5 MOLAL HCI AT 25° C. AND I ATM.

	Weight of SrCO <sub>2</sub> (g.).	Amount of HCl (g.).	Water Equivalent of System.	Temperature Rise,	Heat of Solution.		
Exp. No.					per gram of SrCO <sub>3</sub> (cal.).	per gram mol. of SrCO <sub>3</sub> (cal.).	
1 2 3 4 5	7·7820 6·9510 6·7043 6·3426 6·4031	385.73 387.33 387.53 386.64 386.75	424.76 399.25 429.85 429.23 425.10	0.1990 0.1923 0.1734 0.1698 0.1706 Mean	10.911 11.045 11.118 11.492 11.326 : 11.178	1610·8 1630·6 1641·4 1697·0 1672·0 1650·4	

In preliminary experiments we established, in agreement with Townley and Whitney,12 that the purest and at the same time crystalline SrCO<sub>3</sub> is obtained by precipitation upon the addition of SrCl, to a boiling 5 % solution of  $(NH_{a})_{2}CO_{3}$ . The salt used in the experiments (Kahlbaum) was recrystallised twice. The precipitate was washed with hot water and dried at  $250^{\circ}$  C. for 12 hours to constant weight. Tests for Ca and Ba were negative. Sr was determined as SrSO<sub>4</sub>. The SrCO<sub>3</sub> content in the finely crystalline product we obtained was 98.6-99.0 %. The rest was hygroscopic water, which could not be driven off without decomposing the salt. The determinations carried out with this reagent gave the data compiled in Table I.

The small correction due to the heat of evaporation of water into the CO<sub>2</sub> bubbles amounts to 84.5 cal. per g. mol. of strontianite according to our measurements. Taking this into account we get :

$$\Delta H_{298} = -1735$$
 cal.

On interpolating <sup>3</sup> the heat of dilution of SrCl<sub>2</sub> from o·1 molal to 1 molal (60 cal.), we find :

$$\begin{aligned} \text{SrCO}_{3}(\text{s}) + \text{HCl} (0.5 \text{ molal}) &= \text{SrCl}_{2}(1 \text{ molal}) + \text{CO}_{2}(\text{g}) + \text{H}_{2}\text{O}(1) \end{aligned} (1) \\ \Delta H_{298} &= -1675 \text{ cal.} \end{aligned}$$

- <sup>10</sup> Rossini, Proc. Nat. Ac. Sciences, 1930, 16, no. 11, 694. <sup>11</sup> Kapustinsky and Klokman, Bull. Acad. Sc. U.R.S.S., 1934, 4, 259.
- <sup>12</sup> Townley and Whitney, J. Am. Chem. Soc., 1937, 59, 631.

The most precise values of the heat of formation of CO<sub>2</sub> and H<sub>2</sub>O were given by Rossini,<sup>13</sup> while the heat of formation of HCl and SrCl<sub>2</sub> for the concentrations that we employed are given by Rossini and Bichowsky.<sup>3</sup> From the data of our experiments it is possible to find the heat of formation of SrCO<sub>3</sub> from the elements :

	Reaction.	$\Delta H_{298}$ (in c	al.).
1.	$H_2O(l) + CO_2(g) + SrCl_2(1 \text{ molal}) = SrCO_3(s) + 2HCl(0.5 \text{ molal})$	1675.0	
2.	$H_2(g) + I/2O_2(g) = H_2O(l)$	- 68318.1	
3.	$C_{(gr)} + O_{2}(g) = CO_{2}(g)$	- 94029.8	
4.	$2\mathrm{HCl}_{(0.5 \mathrm{molal})} = \mathrm{H}_{2}(g) + \mathrm{Cl}_{2}(g)$	- 78764.0	
5.	$\operatorname{Sr}_{(8)} + \operatorname{Cl}_2(g) + \operatorname{aq.} = \operatorname{SrCl}_2(1 \operatorname{molal})$	-208978.0	
	$Sr_{(s)} + C_{(gr)} + \frac{3}{2}O_{2}(g) = SrCO_{3}(s)$	-290886.9	(2)

The above data together with  $\Delta H$  for SrO and CO<sub>2</sub> lead to the heat of reaction :

 $\operatorname{SrO}_{(8)} + \operatorname{CO}_{2}(g) = \operatorname{SrCO}_{3}(s)$  $\Delta H_{298} = -56057$  cal. (3)

Roth, Berendt and Wirths 14 pointed out the great deviations in the  $\Delta H$  of this reaction as determined by different authors. Berthelot's <sup>15</sup> and Thomsen's 16 determinations differ by more than 2000 cal. Kelly and Anderson <sup>5</sup> and also Chipman <sup>8</sup> made use of approximate computations. Their estimates' differ from each other as well as from the value recommended by Rossini and Bichowsky<sup>8</sup> and still more from de Forcrand's determinations.<sup>17</sup> The extreme values are 53,200 reported by Berthelot, and 57,300 reported by de Forcrand. Recently Roth 18 proposed a value of 55,000; however, this value, too, is doubtful, by his own opinion.

We attribute the differences mentioned to the non-crystallinity of the SrCO<sub>a</sub> employed by previous investigators and the indefiniteness of corrections for the heat capacity of the system, *i.e.* to the shortcomings done away with in the present investigation. This gives us confidence in recommending our value of the heat of formation.

The same applies to the heat of formation of the strontium ion from the metal in an aqueous solution at 25° C. and 1 atm. which, according to our data, is equal to :

> $\Delta H_{298} = -130,214$  cal.  $Sr_{(8)} + 2H^+ = Sr^{++} + H_2(g)$ (4)

### The Entropy of the Strontium Ion and the Electrode Potential of Metallic Strontium.

Latimer, Pitzer and Smith,<sup>2</sup> on the basis of a private communication from Zimmerman, calculate the entropy of the Sr ion (-7.3). How reliable it is is hard to say since Zimmerman has not published his work and nothing has been published on this subject by other authors.

In calculating the entropy of the Sr ion we draw upon our data quoted Equation (4) cannot be used since the entropy of metallic Sr above. is not known. If we are to use (2), on the other hand, it is necessary to introduce into the calculation the free energy of solution of  $SrCO_3$  in water, obtained from the solubility of SrCO<sub>3</sub>, a quantity likewise not known with sufficient accuracy.

Thus values of  $1.35 \times 10^{-4}$  and  $0.73 \times 10^{-4}$  were obtained by Kohlrausch and Rose <sup>19</sup> and Holleman,<sup>20</sup> respectively, by electrical

<sup>13</sup> Rossini, Chem. Rev., 1940, 24, 21. <sup>14</sup> Roth, Berendt and Wirths, Z. Electrochem., 1941, 47, 185.

<sup>15</sup> Berthelot, Thermochimie, Paris, 1897.
 <sup>16</sup> Thomsen, Thermochemische Untersuch., vol. 3, Leipzig, 1883.

<sup>17</sup> De Forcrand, Compt. Rend., 1908, 146, 512.

- <sup>16</sup> Roth, J. pract. Chem., 1941, 158, 117.
   <sup>19</sup> Kohlrausch and Rose, Z. physik. Chem., 1893, 12, 24.
- <sup>20</sup> Holleman, *ibid.*, 1893, **12**, 125.

conductivity measurements of aqueous SrCO<sub>3</sub> solutions, while chemical analytical determinations made by McCoy and Smith<sup>21</sup> and Townley and Whitney <sup>12</sup> gave 0.396 × 10<sup>-4</sup> and 0.553 × 10<sup>-4</sup>, respectively. We wish to point out that the work of the latter authors was later criticised by Hogga and Johnston.<sup>22</sup> The disagreement existing here corresponds to the differences in estimating the entropy of the strontium ion equal to 6 E.V. which is altogether inadmissible. Inasmuch as it is hard to tell which of the above values should be given preference, we undertook the determination of the solubility of SrCO<sub>3</sub> in water at 25° C. as well.

The titration method is insufficiently reliable to determine such small concentrations. As is known, a more exact method is electrical conductivity, but this has one shortcoming, namely, that it is difficult to circumvent the influence of impurities and the absorption of CO<sub>2</sub> from the air, which could have occurred in the experiments of Kohlrausch, Rose and Holleman. Taking this into account we constructed a simple apparatus that made it possible to measure the electrical conductivity in vacuum. A finely crystalline sample of SrCO<sub>2</sub> dried at 150° C. was placed on the bottom of a hermetically covered vessel with platinum electrodes which was connected with a set-up for distilling water in vacuo. Twice distilled and freshly boiled water was distilled directly into the experimental vessel under a pressure of 12-15 mm. Hg. The SrCO<sub>3</sub> was first shaken thoroughly with small portions of this water, which was then poured off from the precipitate, thus removing easily soluble impurities. Only after this procedure had been repeated four times in vacuo, was a quantity of water necessary for carrying out the electrical conductivity measurements distilled into the vessel, after which the latter was disconnected from the set-up and shaken in a constant temperature bath at  $25^{\circ}$  C. until equilibrium was established. The performance of all the operations in vacuo was a guarantee against the solution of any CO<sub>2</sub>. After the precipitate remaining undissolved had settled, the electrical conductivity was measured by the usual Kohlrausch method, the electrical conductivity of pure water being determined under exactly the same conditions. The capacity of the vessel was determined with a KCl solution.

The mean value from the seven determinations is equal to

$$0.52 \times 10^4 \text{ mol./l.} (\pm 0.02 \times 10^{-4})$$

From these data we obtain the solubility product of SrCO<sub>3</sub>:

$$L_{p^{25}} = (Sr^{++})(CO_{3}^{-}) = (0.52 \times 10^{-4})^{2} = 2.71 \times 10^{-9}$$
 (5)

and the free energy of solution :

Further making use of the data we have obtained, and the values for the free energies of formation of water, carbon dioxide and the carbonate ion taken from the above-mentioned papers by Kelly and Anderson and by Rossini, it is easy to calculate the free energy of solution of strontium carbonate in acid :

Reaction.	$\Delta F_{298}$ in cal.
1. $SrCO_{3}(s) + aq. = Sr^{++}aq. + CO_{3}^{}aq.$	11,688
2. $CO_3^{}aq. = C_{(gr)} + 3/2O_2(g) + aq.$	126,160
3. $C(gr) + O_2(g) = CO_2(g)$	-94,239
4. $H_2(g) + I/2O_2(g) = H_2O(l)$	-56,720
$SrCO_{3}(s) + 2H^{+} = Sr^{++} + CO_{2}(g) + H_{2}O(l)$	-13,111

Thus, the entropy change in the latter reaction is :

$$\Delta S = \frac{\Delta H - \Delta F}{T} = \frac{-1.675 + 13.111}{298} = 33.36 \text{ E.U.}$$

<sup>21</sup> McCoy and Smith, J. Am. Chem. Soc., 1911, 33, 468.
 <sup>22</sup> Hogga and Johnston, *ibid.*, 1939, 61, 2154.

Giaque, in collaboration with Egan,<sup>23</sup> Stout <sup>24</sup> and Archibald,<sup>25</sup> found on the basis of spectroscopic and thermal measurements the values 16.764 and 51.11 E.U. for the entropy of water and carbon dioxide respectively, while Anderson <sup>26</sup> obtained the value  $S_{228} = 23.21$  E.U. for the entropy of SrCO<sub>a</sub>. Since the entropy of a hydrogen ion is taken as zero in accordance with Latimer,27 we obtain :

$$S_{sr^{++}} = 38\cdot 36 - 16\cdot 764 - 51\cdot 11 + 23\cdot 21 = -6\cdot 29 \text{ E.U.},$$
 (7)

or, having regard to the limits of accuracy, -6.3 E.U.

The entropy of metallic strontium has not as yet been measured and therefore a thermodynamic calculation of the electrode potential of Sr is insufficiently reliable. Making use of an empirical equation proposed by Latimer,<sup>28</sup> we calculated the entropy of metallic strontium from the corresponding value for calcium :

$$S_{\rm sr} = 12.2 \, {\rm E.U.}$$

Since  $\Delta H_{298}$  for reaction (4) is known, and since according to Kelley <sup>29</sup> the entropy of hydrogen is equal to  $31.22 \pm 0.01$ , we may find the bound energy

$$T\Delta S = 298 \left( S_{sr^+} + S_{H_2} - S_{sr} - 2S_{H^+} \right) = -3,801.5$$

and the free energy

$$\Delta F = \Delta H - T\Delta S = -130,214 - 3,801.5 = -134,015.5,$$

whence the electrode potential of the metal becomes :

$$E^{0} = \frac{\Delta F}{n \times f} = \frac{-134,015\cdot 5}{2 \times 23,066} = -2.9 \text{ volts},$$
(8)

consistent with Latimer's approximate estimate 1 but not with the calculated value obtained by Kelley and Anderson 5 based on McCov and Smith's work.<sup>21</sup> The value of the electrode potential cited above seems to us more likely since it is in agreement with electrical conductivity measurements of SrCO<sub>3</sub> solutions.

In our previous paper 4 we established that a linear dependence exists between the entropy of an aqueous ion and its charge divided by its radius (crystallochemical

radius). The value for the entropy of the strontium ion obtained here obeys this rule.

### The Heat Capacity of the Strontium Ion.

In the calorimeter described above we also made measurements of the heat capacity of SrCl<sub>2</sub>-solutions, aimed at establishing the hitherto unknown value of the apparent



FIG. 1.—The dependence of the apparent heat capacity of SrCl<sub>2</sub> in aqueous solution at  $25^{\circ}$  C. upon the square root of the molality.

- 23 Giaque and Egan, J. Chem. Physics, 1937, 5, 53
- 24 Giaque and Stout, J. Am. Chem. Soc., 1936, 58, 1144.
- <sup>25</sup> Giaque and Archibald, *ibid.*, 1937, **59**, 561. <sup>26</sup> Anderson. *ibid.*, 1931, **56**, 340. <sup>27</sup> Latimer, Chem. Rev., 1936, 18, 348. <sup>26</sup> Anderson, *ibid.*, 1931, 56, 340.
   <sup>27</sup> Latimer, C
   <sup>28</sup> Latimer, J. Am. Chem. Soc., 1921, 43, 818.
   <sup>29</sup> Kelley, Bull. 434, U.S. Bureau of Mines, 1941.

heat capacity of the strontium ion. The substances employed were a twice crystallised C.P. Kahlbaum SrCl, reagent and water purified as



FIG. 2.-The dependence of the apparent heat capacity of bivalent aqueous ions upon the inverse of the ionic radius.

already described. The electrical energy expended on heating up the solution was measured potentiometrically as described elsewhere.<sup>11</sup> For the concentration range 4.5-14 % we obtained the data given in Table II. As can be seen in Fig. 1, the values of the partial molal heat capacity calculated from them are a linear function of the square root of the molality, in complete accordance with the theory of electrolytes. Extrapolating to infinite dilution and assuming as Bates,<sup>30</sup> that the apparent heat capacity of

hydrogen is zero and chlorine -30 (see Pitzer 31), we get for the apparent heat capacity of the strontium ion

$$\overline{C}_{\mathbf{p}^0} = -10.2.$$

This value, just as the values for other ions, agrees satisfactorily with the linear dependence upon the inverse of the ionic radius that was earlier derived theoretically by Kapustinsky on the basis of Bernal and Fowler's <sup>33</sup> concepts of the structure of water (see Fig. 2).

### The Dissociation Pressure and the Free Energy of Formation of Strontium Carbonate.

Chipman,<sup>8</sup> not being in possession of data on the heat capacities of SrO and SrCO<sub>2</sub>, deduced an equation for the free energy of dissociation of SrCO<sub>3</sub>, proceeding from the heat capacities of CaO and CaCO<sub>3</sub> and measurements of the dissociation of SrCO<sub>3</sub> made by Jones and Backer <sup>6</sup> and Tamaru and Siomi.<sup>7</sup> The value for the heat of reaction he calculated with the aid of his equation (53.6 cal.) differs from the one we found (56.1 cal.) by nearly 5 %. This spurred us on to attempt to introduce greater precision into the determination of the free energy of dissociation. At our suggestion V. Anosov and N. Voskresenskaya working in our laboratory carried out several measurements of the heat capacities of SrO and SrCO<sub>a</sub> from 90° C. to 180° C. and from 90° C. to 500° Ĉ. respectively. The data obtained may be expressed by the following equations :

SrO 
$$C_{p} = 10.49 + 0.0032.T$$
 . . . (9)

SrCO<sub>3</sub> 
$$C_{p} = 1725 + 0.01386 \cdot T$$
 . (10)

These heat capacities differ but little from those of the corresponding calcium compounds investigated by Gronow and Schwiete.<sup>34</sup> In accordance with Kelley and Anderson,<sup>5</sup> we took the heat capacity of CO<sub>2</sub> equal to

CO<sub>2</sub> 
$$C_{\rm p} = 10.34 + 2.74 \times 10^{-3} T - 1.955 \times 10^{5}$$
.  $T^{2}$ 

which gives for reaction (3)

$$\Delta C_{\rm p} = -3.58 + 0.00792 \times T + 195,500 \times T^{-2}.$$

30 Bates, J. Am. Chem. Soc., 1939, 61, 522.

- <sup>31</sup> Pitzer, *ibid.*, 1937, **59**, 2365. <sup>32</sup> Kapustinsky, Acta Physicochimica U.R.S.S., 1942, **17**, 152. <sup>33</sup> Bernal and Fowler, Trans. Faraday Soc., 1933, **29**, 1049.
- 34 Gronow and Schwiete, Z. anorg. Chem., 1933, 216, 185.

Substituting into the heat content equation :

 $\Delta H = \Delta H_0 - 3.58 \times T + 0.00396 \times T^2 - 195,500 \times T^{-1} .$ (11) our value  $\Delta H_{200} = -56,057.1$ , calculating  $\Delta H_0 = -54,686.1$ , introducing (11) into the thermodynamic equation (12)

$$\frac{\Delta F}{T} = -\int_0^T \frac{\Delta H}{T^2} \qquad . \qquad . \qquad . \qquad (12)$$

TABLE I	I.—Тне	SPECIE	TIC AND	APPARE	NT HEA	т Сара	CITIES OF	
Aqueous	Solutio	NS OF	STRONT	IUM CHL	ORIDE I	N CAL.	AT 25° C.	

Exp.	Concentration.		Specific Heat	Molal Heat	√ <del></del>	Apparent Heat
No.	Molal.	Per cent.	Capacity.	Capacity.	• m.	Capacity ( <b>@).</b>
1 2 3	1.0340	14.08	0.8271 0.8246 0.8259	961•26	1.012	-35.32
		mea	.n : 0·8259			
4 5 6	0.7720	10.94	0.8574 0.8608 0.8644	966•60	o•88o	-40·27
		mea	n : 0·8609			
7 8 9	0.6946	9.93	0.8710 0.8757 0.8735	969•64	0.833	40.26
		mea	n : 0.8734			
10 11 12	0.6029	8.57	0.8865 0.8871 0.8837	971.63	o·778	-43.51
		mea	n: 0·8864			
13 14 15	0.2013	7.36	0·8998 0·9016 0·9024	972.95	0.708	-49.29
		mea	n: 0.9013			
16 17 18	0.3015	4.22	0.9398 0.9359 0.9365	982.10	0.249	-52.16
		Inca	ш. 0 <sup>-</sup> 9374			

and integrating it, we arrive at an equation for the free energy containing the integration constant *I*. The latter may be easily evaluated with the experimental data of Jones and Becker • and Tamaru and Siomi.<sup>7</sup> In view of the fact that the data of these investigators are close, we followed Chipman • in using mean values for computations. Since the heat capacity of SrO and SrCO<sub>3</sub> was investigated only up to 773° K., we chose for the computation decomposition pressures corresponding to a temperature range not too far removed from this temperature, namely, 923° K.-I, 173° K. (six points). Upon calculating the free energy  $\Delta F = -RT \ln I/P_{003}$ for each measurement of the decomposition pressure, introducing its value

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into the integral formula (12) and obtaining the value of I for each temperature (which was found to be equal to  $17 \cdot 1 \pm 0.4$ ), we get from (3) the following equation of the free energy of formation of SrCO<sub>3</sub>:

$$\Delta F = -54,686 \cdot 0 = 3 \cdot 58 \times T \times \ln T - 0 \cdot 00396 \times T^2 - 97,750 \times T^{-1} + 17 \cdot 1 \times T \quad (13)$$
whence:  $\Delta F_{298} = -44,185 \cdot 0$  cal.

As an indirect check of the value obtained we may employ the low temperature heat capacity data for SrO and SrCO<sub>3</sub> obtained by Anderson,<sup>27</sup> as well as by Giaque and Egan <sup>24</sup> for carbon dioxide, who gave an estimation of the so-called absolute entropies :

SrO 
$$S_{298} = 13.0$$
 e.u. SrCO<sub>3</sub>  $S_{298} = 23.21$  e.u. CO<sub>2</sub>  $S_{298} = 51.11$  e.u.  
Since we found the value  $\Delta H_{298} = -56.057$  cal. by a direct calorimetric determination, it is not difficult to determine with the aid of these entropies the free energy of dissociation, found to be equal to

$$\Delta F_{298} = \Delta H_{298} - 298 \times \Delta S = -43,862 \text{ cal.}$$
(14)

which conforms with the value we proposed above with an accuracy of 0.7 %, *i.e.*, within experimental error. This permits us to regard as sufficiently reliable both the equation for the free energy of dissociation of strontianite and the standard free energy of its formation; moreover, the disagreement previously existing between calorimetric and high temperature equilibria data may now be regarded as removed.

#### Summary.

1. Measurements of heats of solution of strontium carbonate in hydrochloric acid were carried out which make it possible to determine the heats of reaction :

 $\begin{array}{l} \mathrm{SrO}\,_{(8)}\,+\,\mathrm{CO}_{2}\,_{(g)}\,=\,\mathrm{SrCO}_{3}\,_{(8)}\quad\Delta H_{298}\,=\,-\,290,887\,\,\mathrm{cal.}\\ \mathrm{Sr}\,_{(8)}\,+\,\mathrm{C}\,_{(\mathrm{gr})}\,+\,3/2\mathrm{O}_{2}\,_{(g)}\,=\,\mathrm{SrCO}_{8}\,_{(8)}\quad\Delta H_{298}\,=\,-\,56,057\,\,\mathrm{cal.}\\ \mathrm{Sr}\,_{(8)}\,+\,2\mathrm{H}^{+}\,=\,\mathrm{Sr}^{++}\,+\,\mathrm{H}_{2}\,_{(g)}\quad\Delta H_{298}\,=\,-\,130,214\,\,\mathrm{cal.} \end{array}$ 

and the entropy of the aqueous strontium ion.

$$S_{298} = -6.3 \text{ e.u.}$$

2. The solubility of strontium carbonate in water at  $25^{\circ}$  C. ( $0.52 \times 10^{-4}$  mol/l.) determined by the electrical conductivity method, and the heat capacities of aqueous solutions of strontium chloride at the same temperature in the concentration range 4.5 %-I4 %, were determined. On the basis of the data obtained there were computed : the free energy of solution of strontianite in water  $\Delta F = 11,688$  cal., the solubility product  $L_p = 2.71 \times 10^{-9}$ ; the electrode potential of strontium :

$$Sr_{(s)} = Sr^{++} + 2\theta$$
  $E_0 = -2.9$  volts

(which is in agreement with the former theoretical value given by Latimer). The linear dependence of the apparent heat capacity of a salt upon the square root of the molality is corroborated and the apparent molal heat capacity of the strontium ion calculated  $\overline{C}_{p^0} = -10.2$ . It is shown that the heat capacities of bivalent cations, strontium in their number, are inversely proportional to the ionic radii (a dependence previously established by Kapustinsky on theoretical grounds).

3. With the aid of heat of reaction, heat capacity and decomposition pressure data for the reagents, an equation is derived for the free energy of dissociation of strontianite at high temperatures :

 $\Delta F = -54,686 \cdot 0 + 3 \cdot 58 \times T \ln T - 0 \cdot 00396 \times T^2 - 97,750 \times 10^{-1} + 17 \cdot 1 \times T,$ and the standard free energy of the reaction, computed :

$$SrO_{(8)} + CO_{2}(g) = SrCO_{3}(s)$$
  $\Delta F_{298} = -44,185$  cal.

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which is in agreement with an accuracy of up to 0.7 % with the measurements of the absolute entropies of the reagents made by Anderson. The disagreement between the calorimetric and high temperature equilibria data may be considered as removed.

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