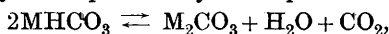


CLIII.—*The Dissociation Pressures of Alkali Bicarbonates. Part I. Sodium Hydrogen Carbonate.*

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It is the object of the present investigation to study the dissociation pressures of the various alkali bicarbonates in order to discover to what extent the relative stability of each is connected with the basigenic behaviour of its metal, and the position of the latter in the periodic system. The equilibria which must be investigated for this purpose may be expressed by the equation:



in which M indicates the atom of an alkali metal. This equation represents in its most general form a three-component equilibrium, but, as will be seen in the sequel, it is sufficient for the purpose we have in view to treat it as one derived from the two components MHCO_3 and M_2CO_3 , whereby we limit ourselves to the case in which water and carbon dioxide occur in equimolecular proportions in the gaseous phase.

Exact data connected with the subject are very scarce. In 1835 Rose (*Pogg. Ann.*, 1835, **34**, 158) proved that solutions of sodium and potassium hydrogen carbonates may decompose at the ordinary temperature, yielding the normal carbonate and carbon dioxide, and the same conclusion has been arrived at in different ways by several other experimenters (Magnus, *Pogg. Ann.*, 1837, **40**, 590; Marchand, *J. pr. Chem.*, 1845, **35**, 389; Treadwell and Reuter, *Zeitsch. anorg. Chem.*, 1898, **17**, 202).

Corresponding results for solid sodium hydrogen carbonate were obtained by Gautier in 1876, when temperatures above 35° were employed (*Ber.*, 1876, **9**, 1434). In connexion with his work on the solubilities of alkali bicarbonates, Dibbits, in 1874, determined approximately the partial pressure of carbon dioxide which was in equilibrium with saturated solutions of the respective salts at various temperatures (*J. pr. Chem.*, 1874, [ii], **10**, 440). Lescoeur, in 1892, attempted to measure the dissociation pressure of solid sodium hydrogen carbonate between 55° and 100°, but does not appear to have obtained a true equilibrium, since the recorded results are very much lower than ours (*Ann. Chim. Phys.*, 1893, [vi], **28**, 423). Lastly, McCoy, in 1903, carefully studied the equilibrium at 25° between a solution containing sodium carbonate and sodium hydrogen carbonate and a gaseous phase composed of air, carbon dioxide, and water vapour (*Amer. Chem. J.*, 1903, **29**, 437).

EXPERIMENTAL.

Method and Apparatus.—The experiments which we have carried out consist in determining the vapour pressures produced on heating a mixture of sodium hydrogen carbonate and anhydrous sodium carbonate. It is not a priori clear whether only the phases, anhydrous sodium carbonate, sodium hydrogen carbonate, and vapour, will be thus produced, or whether sodium carbonate monohydrate will also be formed, so that the four phases, anhydrous sodium carbonate, sodium carbonate monohydrate, sodium hydrogen carbonate, and vapour, corresponding with a three-component equilibrium, will be present.

If the former is the case, the partial pressure of the water vapour in the gaseous phase will be smaller than the vapour pressure of sodium carbonate monohydrate; and the combined pressures of carbon dioxide and water, which are equal, will be less than twice as great as the dissociation pressure of the monohydrate.

If the latter is the case the partial pressure of the water vapour will be equal to the vapour pressure of sodium carbonate monohydrate, and the partial pressure of the carbon dioxide greater than that of the water vapour, because some water will have been removed from the gaseous phase to form the monohydrate.

The total observed pressure due to carbon dioxide and water vapour will thus be more than twice as great as the vapour pressure of sodium carbonate monohydrate.

A comparison of the vapour pressure of sodium carbonate monohydrate with that of sodium hydrogen carbonate will therefore render a decision between the two alternatives possible; and actual measurements have proved that sodium carbonate monohydrate does not exist in the equilibrium mixture under the conditions of our experiments.

The method of working consisted in heating the mixture of sodium carbonate and sodium hydrogen carbonate in an evacuated flask contained in a thermostat. The vapour generated was accurately balanced against some air, the pressure of which was adjustable, a small gauge consisting of a U-tube containing mercury, which was sealed to the flask, and was also contained in the thermostat, serving as the zero instrument.* The pressure was then read on a manometer.

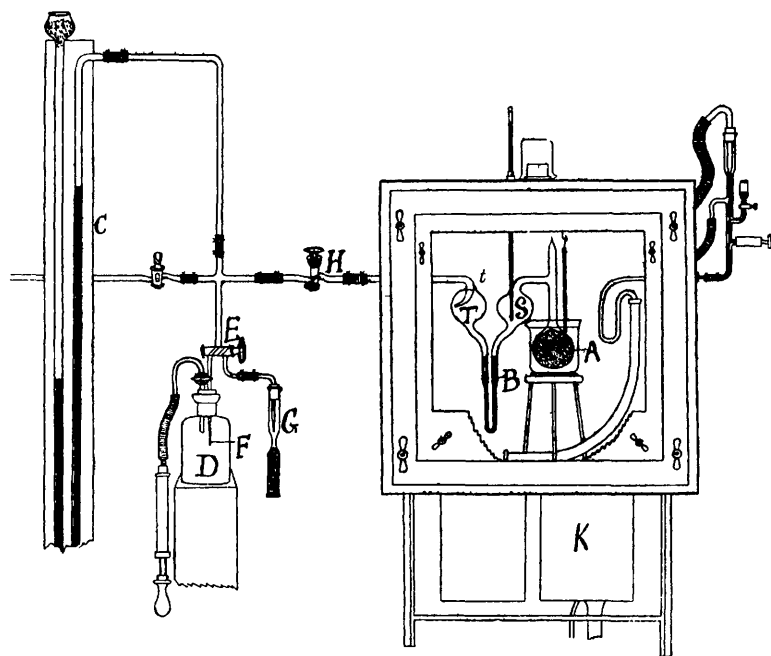
The apparatus was arranged so that it could be laid on its side

* Since these experiments were begun a very similar method for the measurement of vapour pressures has been described by Johnston (*Zeitsch. physikal. Chem.*, 1908, 62, 333).

without disconnecting during evacuation. Two special bulbs were provided for holding the mercury during this operation.

Fig. 1 shows the apparatus. *A* is the flask containing the reaction mixture, *B* the small mercury gauge, and *C* the manometer. *S* and *T* are the two bulbs just referred to. It will be seen that *T* is fitted with a trap *t*, which makes it possible to withdraw gas from the flask through the mercury without risk of allowing the latter to splash into the exit tubes of the apparatus. The bottle *D* can be either evacuated or fitted with compressed air, according as the

FIG. 1.



pressure to be read is smaller or greater than that of the atmosphere. According to the position of the three-way tap *E*, air can be cut off, or either allowed to enter or leave the apparatus very slowly through the capillaries *F* and *G*, thus permitting the levels of the mercury in the gauge *B* to be very accurately adjusted. The tap *H* was added for further convenience in manipulation.

The general construction of the air thermostat will be clear from the figure. As will be seen, it is double-walled, the products of combustion of the gas from the burner passing up the chimney *K* and between the two walls. Each jacket is provided with a remov-

able transparent front. The apparatus is made of sheet iron, and heavily coated with asbestos outside. Wide steel tubes passing through both jackets are fitted where openings are necessary. The regulator is of the Ostwald pattern, and is filled throughout with mercury. The tubes inside the thermostat are of steel, and are attached to those outside, which belong to a glass regulator of a commercial type, by means of a short, thick-walled rubber connexion.

All the steel joints are screwed, and made mercury-tight by means of oil and red lead. It was found that excellent constancy of temperature was obtained by immersing the flask of the tensimeter in a beaker containing slightly diluted sulphuric acid. Mechanical stirring of the air of the thermostat was tried, but discarded, as it did not improve the results. The temperature of the sulphuric acid was constant to 0.2° . It was read on a small, carefully calibrated Anschütz thermometer.

After the gauge had been charged with mercury and the flask with the reaction mixture, the latter was sealed off, and the necessary rubber connexion made. Thick-walled rubber tubing was employed, which was wired on and covered with shellac varnish; thus an air-tight joint was obtained. The tensimeter was then laid horizontally, so that the mercury ran into the bulbs; the apparatus could then be completely evacuated by employing first a water-pump, and then a Sprengel mercury-pump. After the tensimeter had been turned into the upright position, and the thermostat closed, the determination was begun.

Two principal difficulties were encountered in the course of the research. The first consists in obtaining a gaseous phase of equimolecular proportions of water-vapour and carbon dioxide. It is clear from the general laws of chemical equilibrium that if either molecular species were in excess, owing either to selective absorption of the other by the walls of the vessel, or to the presence of adsorbed water in the reaction-mixture or the apparatus, a too high result would be obtained for the decomposition pressure. The second difficulty was due to retardation in the establishment of equilibrium, and was doubtless the result of impermeable crusts formed on the reaction mixture.

We tried to meet the first difficulty by very carefully drying the apparatus before use, gently igniting the sodium carbonate, and leaving the sodium hydrogen carbonate in a desiccator over sulphuric acid for a considerable time before mixing it with the sodium carbonate. A transparent silica vessel was also tried. It was finally found necessary, however, to withdraw large quantities of gas evolved from the reaction mixture at high temperature, and

to continue the process of withdrawal until the readings obtained after two successive withdrawals were identical. The use of the silica vessel was abandoned in the later experiments.

The second difficulty gave a very great deal of trouble, and may very probably be the cause that the results here recorded have been hitherto unknown.

In order to obtain satisfactory readings, it was found necessary to take an amount of sodium hydrogen carbonate which was approximately five hundred-fold that theoretically required to evolve the necessary volume of gas at the highest pressure reached in the experiments. The excess of carbonate sufficient for the re-absorption of the gases on cooling was much smaller than this, an approximately fifty-fold value being sufficient. It is clear that retardation, owing to the formation of crusts, will cause the results to be too low when the temperature is being raised, and too high when it is being lowered. The results will be correct when the same value is obtained in both cases. It was thus found that only from 95° onwards could correct values be obtained on raising the temperature; and in the case of the lowest of these about ten days were necessary for the complete establishment of equilibrium.

On lowering the temperature constant readings were obtained much more rapidly. There is little doubt, moreover, that the numbers obtained in the latter case are substantially correct to about 85°, since they lie on the curve extrapolated from readings taken at higher temperatures.

The rate at which the reaction-mixture was heated was also found to have an effect, rapid heating tending to prevent retardation; the retardation was greatest after all trace of excess of water had been removed as described above.

Sodium Carbonate Monohydrate.

Table I gives the results obtained for the vapour pressure of sodium carbonate monohydrate. This salt was prepared by heating sodium carbonate decahydrate in a shallow dish on the water-bath until the mass had just become solid again after fusion. The product, after thorough mixing, contained 14.3 per cent. of water, instead of 14.45 according to theory.

A mixture of 40 grams of this salt with 4 grams of the anhydrous carbonate was employed in the experiment.

TABLE I.

<i>Temp. rising.</i>			<i>Temp. falling.</i>		
Temp.	Pressure mm. Hg.		Temp.	Pressure mm. Hg.	
	Observed.	Calculated.		Observed.	Calculated.
30.5°	7.9	8.7	92.7°	419.9	418.0
40.4	15.9	17.9	86.4	297.1	301.0
51.0	36.6	36.9	80.3	216.1	216.0
57.1	53.6	54.6	70.1	121.7	121.0
66.4	93.2	96.8	60.5	69.4	67.5
76.4	166.6	173.0	50.2	39.2	34.9
83.1	243.4	251.0	41.1	23.0	18.8
90.3	363.4	369.0	30.9	13.1	9.0
97.7	539.1	540.0	17.5	6.7	3.1

As is well known, the results of vapour-pressure experiments may be expressed with a considerable degree of accuracy by a formula of the type:

$$\log p = a - \frac{b}{T} \quad \dots \quad (1),$$

in which p is the vapour pressure, T the absolute temperature, and a and b are constants; b is connected with the heat of reaction q per gram-molecule of gas produced, by the formula:

$$q = \log_e 10 R b \quad \dots \quad (2),$$

in which the gas constant R equals 2 calories per gram-molecule per degree, and $\log_e 10 = 2.30$.

In the third column of table I values of p are calculated from equation (1) by making $a = 10.825$; $b = 3000.0$. It will be seen that the majority of the observed values agree closely with the calculated ones, the numbers obtained on raising the temperature being generally very slightly lower, and those found on lowering it, very slightly higher than the calculated values. The curve for sodium carbonate monohydrate is shown in Fig. 2.

Sodium Hydrogen Carbonate.

Table II contains a complete series of determinations of the decomposition pressure of sodium hydrogen carbonate.

A mixture of 50 grams of sodium hydrogen carbonate and 5 grams of sodium carbonate was taken, the constituents being dried separately in the manner described above, and then mixed. The same mixture was heated and cooled repeatedly for the purpose of obtaining the numbers given, as will be clear from the table.

The approximate quantities of gas withdrawn at various times and temperatures are shown. As will be readily understood, a knowledge of these quantities could be gained by a simple calculation, after withdrawing the gas into the bottle D (Fig. 1), of known

capacity (600 c.c.), and noting the pressure in the latter before and afterwards. It should be mentioned here that the fact that no air leaked in while gas was being withdrawn past the mercury has been proved repeatedly by cooling the apparatus to atmospheric temperature, and noticing that the pressure ultimately fell practically to zero.

The calculated values have been derived from equation (1) after making $a=11.8185$ and $b=3340$. It will be seen that at high temperatures the agreement is fairly close throughout, the experimental numbers obtained on lowering the temperature being usually slightly higher, and those found on raising it slightly lower than the calculated values. Those numbers which have obviously been considerably vitiated by "retardation" are enclosed in brackets.

Table III gives the results of some earlier experiments, which will be found in the main to confirm those of table II. The

TABLE II.

Series.	Temp.	Pressure in mm. of mercury.			Approx. vol. of gas withdrawn.
		Observed.		Calculated.	
		Rising.	Falling.		
(I.)	90.0°	—	—	—	38 c.c.
	92.4	467.5	—	476.0	—
	104.1	—	936.6	915.0	—
	97.1	—	633.5	625.5	—
	89.6	—	(426.5)	405.0	—
	43.7	—	(51.2)	19.0	—
(II.)	107.0	—	—	—	38 c.c.
	108.4	1153.5	—	1151.4	—
	101.9	—	821.9	811.3	—
	92.0	—	473.3	465.1	—
	75.2	—	(210.5)	168.3	—
	49.9	—	(70.6)	29.7	—
(III.)	105.0	—	—	—	56 c.c.
	114.4	1594.8	—	1574.0	—
	112.4	—	1413.5	1420.0	—
	107.8	—	1106.7	1116.0	—
	101.2	—	776.2	781.0	—
	93.3	—	507.3	502.0	—
	84.1	—	308.3	292.0	—
	41.5	—	(30.1)	16.0	—
(IV.)	88.2	(153.9)	—	499.0	—
	95.8	567.7	—	578.0	—
	95.8	—	—	—	49 c.c.
	95.8	563.4	—	578.0	—
	102.8	836.5	—	853.0	—
	101.4	—	790.8	790.0	—
	101.4	—	—	—	31 c.c.
	101.8	808.6	—	807.5	—
	106.4	1033.2	—	1035.4	—
	107.4	1102.1	—	1093.0	—
	106.6	—	1043.6	1046.7	—

TABLE III.

Series.	Temp.	Pressure in mm. of mercury.			Approx. vol. of gas withdrawn.
		Observed.		Calculated.	
		Rising.	Falling.		
(I.)	107.4°	1097.6	—	1092.2	—
	111.7	1391.7	—	1369.0	—
	111.7	—	—	—	Large unknown vol.
	115.1	1662.9	—	1631.0	
	111.9	—	1391.7	1383.0	—
	107.7	—	1111.9	1109.0	—
	102.6	—	847.1	843.0	—
	98.7	—	691.7	680.0	—
	92.1	—	485.6	468.0	—
	85.5	—	(350.7)	317.5	—
	7.5	—	(2.3)	0.8	—
(II.)	110.9	1422.1	—	1313.3	—
	110.9	—	—	—	271 c.c.
	114.3	1642.2	—	1565.7	—
	106.9	1118.6	—	1063.5	—
	106.9	—	—	—	51 c.c.
	107.6	1130.8	—	1103.8	—
	107.6	—	—	—	39 c.c.
	107.6	1098.0	—	1103.8	—
	107.6	—	—	—	35 c.c.
	107.3	—	1091.0	1086.0	—
	105.0	—	978.5	960.0	—
	111.7	1399.2	—	1369.0	—
	115.5	1646.9	—	1664.2	—
	111.2	—	1325.7	1333.5	—
	108.4	—	1155.9	1151.0	—
	104.3	—	937.4	925.0	—
	99.4	—	743.0	707.0	—
	93.6	—	(570.1)	510.0	—
	19.4	—	(11.2)	2.5	—

amounts of substance taken for the determinations were 40 and 4 grams of sodium hydrogen carbonate and sodium carbonate respectively in series (i), and 50 and 5 grams respectively in series (ii).

The dissociation pressure curve of sodium hydrogen carbonate is shown in Fig. 2, together with that of sodium carbonate monohydrate. The curves themselves correspond with the equations, the observed values being indicated in the following manner:

⊙ = temp. rising; × = temp. falling.

It can be shown readily that if the equations derived from our experiments hold for the vapour pressures of sodium carbonate monohydrate and sodium hydrogen carbonate respectively, then the values of the former will be more than half as great as those of the latter at all temperatures below 218°; and that there is thus no possibility of the four-phase equilibrium: anhydrous sodium carbonate, sodium carbonate monohydrate, sodium hydrogen

carbonate, vapour, having been produced in our experiments (see p 1360).

The vapour pressure corresponding with this four-phase equilibrium may now be calculated. Indicating this pressure at any temperature by p , the corresponding partial pressures of the water vapour and carbon dioxide by p' and p'' respectively, we have:

$$p = p' + p''.$$

The quantity p' is the same as the dissociation pressure of sodium carbonate monohydrate, and may be obtained from the equation we have given for the latter.

The values of p'' may be derived as follows:

If we indicate the dissociation pressure of sodium hydrogen carbonate as obtained by the equation derived for it above by p_1 , then the partial pressure of the water vapour and of the carbon dioxide may each be taken as $p_1/2$, and by applying the law of mass action we find:

$$p'' = \frac{\left(\frac{p_1}{2}\right)^2}{p'}.$$

In this way the values given in table IV have been arrived at. The corresponding numbers for the three-phase equilibrium at the same temperature, which are always a little lower, are given for comparison. The curve for the four-phase equilibrium is also shown in Fig. 2. An attempt was made to verify these numbers experimentally with a mixture of 20 grams of sodium hydrogen carbonate, 15 grams of sodium carbonate monohydrate, and 10 grams of anhydrous sodium carbonate; but the retardation in the pressure values was so great that the experiment was abandoned.

TABLE IV.

Pressure in mm. of Mercury.

Temp.	Four-phase equilibrium.			Three-phase equilibrium.
	H ₂ O.	CO ₂ .	Total.	
30°	8.4	1.2	9.6	6.2
50	34.4	6.5	40.9	30.0
70	119.9	30.2	150.1	120.4
90	364.0	117.8	481.8	414.3
100	605.4	220.8	826.2	731.1
110	981.8	399.0	1380.8	1252.6

Heats of Dissociation.—By applying equation 2, the heats of dissociation per gram-molecule of gas produced are calculated to be: for sodium carbonate monohydrate, 13,800 calories, and for sodium hydrogen carbonate, 15,360 calories.

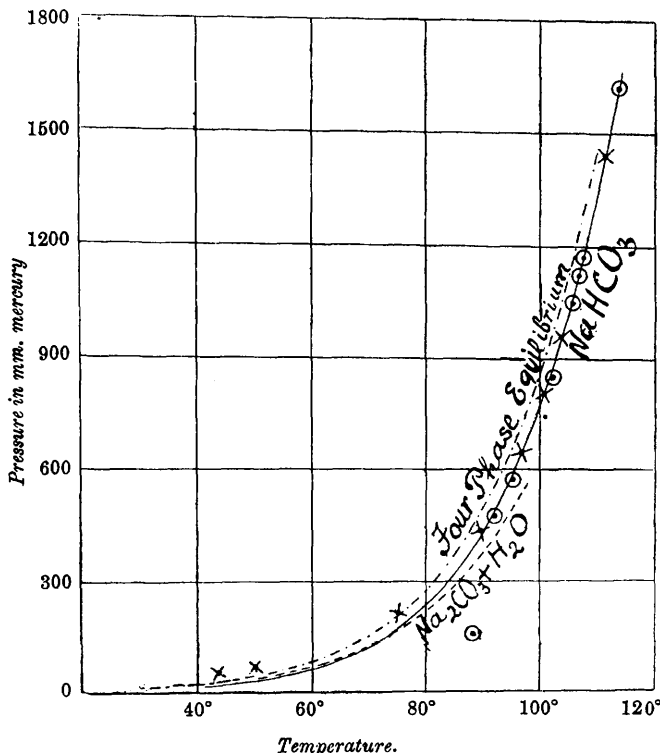
Therefore, employing Planck's notation, we have:

$$[\text{Na}_2\text{CO}_3, \text{H}_2\text{O}] = [\text{Na}_2\text{CO}_3] + \{\text{H}_2\text{O}\} - 13,800.$$

$$2[\text{NaHCO}_3] = [\text{Na}_2\text{CO}_3] + \{\text{H}_2\text{O}\} + \{\text{CO}_2\} - 30,700.$$

It is interesting to compare the last-named heat-toning with a value for the same reaction derived from direct thermochemical measurements. According to de Forcrand (*Compt. rend.*, 1909, 149, 719), the heats of formation from their elements of 1 gram-

FIG. 2.



molecule of sodium hydrogen carbonate and carbonate are respectively 228,380 and 271,970 calories. Taking the corresponding value for water (as steam at 100°) as 58,060 calories, and for carbon dioxide as 97,000 calories, we have, in Planck's notation:

$$[\text{NaHCO}_3] = -228,380, \quad [\text{Na}_2\text{CO}_3] = -271,970,$$

$$\{\text{H}_2\text{O}\} = -58,060, \quad \{\text{CO}_2\} = -97,000,$$

and substituting these values in the equation

$$2[\text{NaHCO}_3] = [\text{Na}_2\text{CO}_3] + \{\text{H}_2\text{O}\} + \{\text{CO}_2\} - x,$$

we find $x=29,700$ calories, instead of 30,700 calories, the figure derived from our experiments.

In view of the indirect nature of the method of comparison, this agreement must be considered quite satisfactory.

Summary.

The vapour pressure in mm. of mercury of sodium carbonate monohydrate can be represented with sufficient accuracy by the equation :

$$\log p = 10.825 - \frac{3000.0}{T},$$

that of sodium hydrogen carbonate by the equation :

$$\log p = 11.8185 - \frac{3340}{T}.$$

From the former equation the heat of dissociation of one gram-molecule of sodium carbonate monohydrate is calculated to be 13,800 calories; from the latter, that of two gram-molecules of sodium hydrogen carbonate to be 30,700 calories.

The pressure-values corresponding with the four-phase equilibrium, anhydrous sodium carbonate, sodium carbonate monohydrate, sodium hydrogen carbonate, vapour, have been calculated. They are somewhat higher than the vapour pressure of sodium hydrogen carbonate at all temperatures falling within the range of our experiments.

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