LV.—*Equilibrium Constants for the Decomposition of Ammonium Bicarbonate.*

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DURING a general investigation of the separation of ammonia from gases containing also carbon dioxide and water vapour, it became necessary to determine the conditions under which solid ammonium bicarbonate might be formed according to equation $NH_3 + CO_2 + H_2O \rightleftharpoons (NH_4)HCO_3$.

There appeared to be no accepted values for the equilibrium constant of this reaction, *viz.*,

$$K = p_{CO_2} \times p_{NH_3} \times p_{H_2O} \quad . \quad . \quad . \quad . \quad (1)$$

Berthelot and André (*Compt. rend.*, 1886, **103**, 665) found the pure dry salt to be abnormally stable, exerting a total pressure of not more than 1 mm., although on addition of a few drops of water at 18° the pressure rose rapidly to 60 mm., attaining 135 mm. with more water. Bonnier (*Ann. Chim.*, 1926, **5**, 37) measured the decomposition pressure at temperatures between 25·4° and 60°; at the lower temperature a period of 4—6 days was required for equilibrium to be established, and at temperatures above 33° the results were complicated by the condensation of water vapour upon the crystals.

It is thermodynamically necessary that a vapour in equilibrium with the saturated solution should be in equilibrium also with the solid, and the same equilibrium constant, K, must be satisfied whether, as in the hypothetical case of the pure dry salt, the partial pressures of the three components are equal, or, as in the more general case of the presence of the saturated solution, they are unequal. The extremely low vapour pressure found in the experiments of Berthelot and André was probably due to the slow rate of decomposition of the dry salt, which made it impossible to attain equilibrium. Results obtained on addition of a little liquid water showed that the decomposition could proceed more readily by way of the saturated solution. The method now used has been to determine the partial pressures of ammonia, carbon dioxide, and water in equilibrium with saturated solutions of ammonium bicarbonate, and so to calculate an equilibrium constant, which is also the constant for the dissociation of the solid. Further, since the saturated solution is always present, the partial pressure of water vapour is practically constant at constant temperature, and a simplified form of equilibrium constant becomes applicable, *viz.*,

$$K_1 = p_{CO_2} \times p_{NH_3} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

This form was particularly suited to the purposes of the present investigation, and experiments described below show that it is satisfied over a wide range of concentrations of carbon dioxide and ammonia. The partial pressure of water vapour was determined in a few experiments and enables a result to be obtained also for the more general constant, K.

The mean values of K and K_1 at 20° and 10° are :

	$K = p_{CO_2} \times p_{NH_3} \times p_{H_2O}$.	$K_1 = p_{CO_2} \times p_{NH_3}$.
At 20°	3000	180
„ 10°	253	29·5

The general equation for the constant K is given by

$$\log_{10}K = 33{\cdot}88 - 40{,}600/2{\cdot}303RT$$

The value of 40,600 cals. for the heat of formation of solid ammonium bicarbonate is in good agreement with that of 40,000 cals. from the International Critical Tables.

EXPERIMENTAL.

The apparatus consisted of a temperature-equalising coil, three saturators each of 100 c.c. capacity, and a spray trap, all immersed in a thermostatically controlled water-bath. Streams of carbon dioxide from a cylinder and of pure dry air, each measured by its own flow gauge, were mixed and passed through the coil, the train of saturators, and the spray trap to a T-piece tap. One limb of the tap was vented to air by way of a seal, and the other was connected, by way of a T-piece, to a pair of Drechsel bottles containing standard sulphuric acid, from which the gas would pass through a soda–lime tower to a 1/40th c. ft. gas meter. The T-piece provided a connexion to a constant-rate gas sampler having mercury as the confining liquid (Pexton and Hutchison, *J. Soc. Chem. Ind.*, 1929, **48**, 242T).

The method of operation was as follows. Each saturator was filled with 50 c.c. of a saturated solution of A.R. ammonium bicarbonate containing excess of the solid crystals. The carbon dioxide–air mixture of predetermined composition was passed at a uniform rate through the saturators, of which the outlet was vented to air. To carry out a test, the gas was passed into the analysis train, the gas sampler being started simultaneously.

Ammonia in the gas was absorbed in a known volume of $N/50$-sulphuric acid and the excess of acid remaining at the end of a test was freed from carbon dioxide and determined by addition of potassium iodide–iodate mixture, and titration of the liberated iodine with $N/50$-thiosulphate.

Carbon dioxide was determined in the sample by means of a laboratory-type Haldane apparatus. The sides of the sampling vessel were kept moist with 10% sulphuric acid to absorb ammonia.

The passage of gas of a given composition was continued until the carbon dioxide and ammonia in the issuing gas became constant, showing that the liquor was now in equilibrium with the gas. The rate of gas passage was usually 60—70 c.c. per minute. Confirmatory tests at different rates showed that equilibrium was being reached.

The partial pressure of water vapour was not normally determined, since it differed by only a small amount from that of pure water at the same temperature, as the following figures show :

	Vapour press. of pure water.	Partial press. of water in equilibrium with satd. $(NH_4)HCO_3$ soln.
20°	17·5 mm.	16·7 mm.
10°	9·2 „	8·6 „

The results of experiments at 20° and 10° are given in the tables.

Temperature, 20°.

Rate of gas passage, c.c./min.	p_{CO_2}, mm.	p_{NH_3}, mm.	K_1.	Mean.
66	89·5	1·98	177	187
66	94·5	2·08	196	
67	100	1·89	189	
104	160	1·12	179	175
78	172	1·065	183	
39	176	1·00	176	
78	175	0·97	170	
67	191	0·89	170	170
50	294	0·64	188	188

Mean $K_1 = 180$

$$K = p_{CO_2} \times p_{NH_3} \times p_{H_2O} = K_1 \times p_{H_2O} = 3000.$$

Temperature, 10°.

64	46·9	0·59	27·6	27·6
64	56·5	0·49	27·6	
40	81·1	0·365	29·6	30·9
40	78·5	0·345	27·1	
56	78·5	0·46	36·1	
105	101	0·31	31·3	30·4
150	99·4	0·30	29·8	
60	111	0·27	30·0	
80	159	0·185	29·4	29·4
45	242	0·12	29·0	29·1
60	265	0·11	29·2	

Mean $K_1 = 29·5$

$$K = p_{CO_2} \times p_{NH_3} \times p_{H_2O} = K_1 \times p_{H_2O} = 253.$$

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