215. *The System Potassium Carbonate–Ammonia–Water.*

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THE occurrence of two liquid coexistent phases is observed in few inorganic systems, being confined mainly to systems in which ammonia forms one component. Salting out of ammonia has been observed with the following inorganic salts: Potassium carbonate (Proctor, *Chem. News*, 1864, **9**, 25; Newth, J., 1900, **77**, 775; Pauly, *Ber.*, 1923, **56**, 1454); rubidium and cæsium carbonates (Pauly, *loc. cit.*); sodium silicate (Proctor, *loc. cit.*); tripotassium phosphate and potassium vanadate (Jänecke, *Z. physikal. Chem.*, 1927, **127**, 71); zinc sulphate (André, *Compt. rend.*, 1885, **100**, 241).

Only the tripotassium phosphate system has been studied quantitatively, Jänecke having determined the complete isothermal at 0°, the composition of the two layers in equilibrium with the solid salt at 15° and 25° and the vapour pressure of the monovariant system salt–two liquids–vapour from 0° to 30°. Recorded observations on the remainder of the above systems are in general only qualitative. In this and the following communication the results of an extended phase-rule study of two further systems of this type are recorded.

EXPERIMENTAL.

Solubility Determinations.—Merck's pure potassium carbonate was found to be free from impurities except water and a little bicarbonate. After recrystallisation from water and ignition, the bicarbonate content was reduced to 0·57%. Solutions were prepared in electrically controlled thermostats at 25·06° and 18·05° with a maximum variation of 0·05° and in a bath of pure ice. Stirring was effected either by mercury-sealed stirrers or by a stream of ammonia gas obtained from a cylinder and preheated to the experimental temperature by passing through a long coil immersed in the thermostat. The systems were stirred for at least 6 hours and usually for 12; preliminary experiments showed that such a time was adequate. After standing in the thermostat till the liquid layers were quite clear, the liquids were blown over through a glass-wool filter into a transfer bottle also contained in the thermostat. When the lower layer was to be investigated the tube leading to the transfer bottle was closed by a thin bulb which was broken by pressing against the bottom of the solubility bottle; in this way transference of any of the upper layer was avoided. An accurately calibrated pipette previously brought to the experimental temperature was then used to remove samples from the transfer bottle. Its contents were run out into a weighed bottle of water whose increase in weight gave the weight of a measured volume of the solution under investigation and thus its density. In order to avoid loss of ammonia, all transferences and fillings of pipettes were performed by pressure and not by suction. Systems whose ammonia pressure exceeded atmospheric were made up by passing ammonia into a stirring bottle with an exit tube dipping under mercury of suitable depth. Solid samples for " rest " determinations were removed by a perforated ladle. In systems containing no ammonia the solid was freed from adhering liquid by pressing on filter paper; otherwise it was transferred as rapidly as possible to a weighing bottle containing a weighed quantity of water. The solutions were analysed for total alkali and ammonia by standard methods.

The composition of the vapour phase over the systems investigated was not determined except for the 4-phase systems. The partial pressure of ammonia rises from zero in the purely aqueous systems to approximately the vapour pressure of ammonia at the point which represents the solubility of potassium carbonate in anhydrous ammonia. An approximate determination of this point at 18° was made by sealing a small quantity of carefully dehydrated carbonate in a strong-walled tube into which dry ammonia had been liquefied. On keeping the tube at 18° for some hours, no noticeable diminution in the amount of salt was observed, and when the tube was cooled in carbon dioxide and ether as rapidly as possible, opened, and the clear decanted liquid evaporated, only a small trace of solid remained, *viz.*, 0·16 g. in 100 g. of solution. This may be taken as an upper limit for the solubility of the salt in ammonia. In all experiments the vapour phase was brought to equilibrium by maintaining a supply of ammonia at a fixed pressure until the concentrations showed no further change. Systems whose ammonia pressure was less than atmospheric were, of course, subject to a certain air pressure in the solubility bottles but it may safely be assumed that the errors so produced are negligible.

The results at the three temperatures are given in the following tables. The data for the solid phase refer to the wet solid analysed for the purpose of identifying the hydrate of potassium carbonate by the " rest " method. The results given for the solubilities of the salt in water and for the four-phase points are in each case the mean of at least four closely concordant determinations.

The concentrations are in each case expressed in g. per 100 g. of solution. Densities are recorded at 0° and 18°, from which volume concentrations may be calculated.

Aqueous layer.			Ammoniacal layer.			Solid.		
d.	NH_3.	K_2CO_3.	*d.*	NH_3.	K_2CO_3.	NH_3.	K_2CO_3.	Phases.
				Temperature, 0°.				
1·539	—	50·69	—	—	—	—	75·23	Dihydrate, solution, vapour.
1·517	1·06	49·37	—	—	—	0·52	64·91	
1·507	1·57	48·84	—	—	—	0·65	65·79	
1·483	2·51	47·42	—	—	—	1·38	62·12	
1·475	2·52	47·13	0·901	32·07	2·72	—	—	Dihydrate, two solutions, vapour.
1·421	3·26	42·54	0·928	27·41	2·99	—	—	Two solutions, vapour.
1·371	3·70	39·44	0·946	24·59	3·73	—	—	
1·340	4·41	35·95	0·968	22·02	5·84	—	—	
1·240	6·91	28·92	1·038	16·17	12·44	—	—	
1·109	12·09	18·51	1·109	12·09	18·51	—	—	
	(Critical solution)							
—	—	—	—	42·9	2·3	24·1	34·7	Dihydrate, solution, vapour.
				Temperature, 18·05°.				
1·550	—	51·72	—	—	—	—	—	Dihydrate, solution, vapour.
—	—	—	—	61·95	2·10	—	—	
1·455	2·88	46·50	0·894	30·48	4·76	—	—	Dihydrate, two solutions, vapour.
1·407	2·75	43·60	0·917	27·24	5·98	—	—	Two solutions, vapour.
1·404	2·83	42·78	0·919	26·75	6·15	—	—	
1·406	3·05	43·50	—	—	—	—	—	
1·351	4·14	39·31	0·950	23·08	8·87	—	—	
1·104	12·74	21·05	1·104	12·74	21·05	—	—	
		(Critical solution)						
				Temperature, 25·06°.				
1·556	—	51·47	—	—	—	—	73·26	Dihydrate, solution, vapour.
—	0·550	50·91	—	—	—	0·372	58·95	
—	1·004	50·71	—	—	—	0·672	59·14	
—	1·286	50·30	—	—	—	0·975	58·66	
—	1·842	49·77	—	—	—	1·060	61·13	
—	2·885	48·79	—	—	—	1·974	55·90	
—	3·450	47·00	—	30·85	4·83	—	—	Dihydrate, two solutions, vapour.
—	4·79	40·69	—	25·81	7·48	—	—	Two solutions, vapour.
—	—	—	—	25·69	7·83	—	—	
—	6·04	36·36	—	21·98	10·85	—	—	
—	8·19	30·94	—	8·19	30·94	—	—	
		(Critical solution)						

The results at 0° are represented by Fig. 1. At the higher temperatures the results are very similar. The concentrations of the conjugate solutions saturated with solid alter little with temperature. The point representing the critical solution, however, moves further from the line of the saturated solutions as the temperature falls, so the area of separation into two liquid layers increases with fall of temperature.

Repeated attempts were made to find the upper critical temperature above which coexistence of two liquid layers with solid and vapour no longer occurs. For this purpose a strong-walled tube was charged with a two-layer system and a quantity of salt, sealed, and gradually heated in an oil-bath with frequent shaking. At

155°, the highest temperature reached, the two layers still persisted and appeared to have appreciably different densities since they still separated rapidly after shaking. We therefore conclude that the upper critical solution temperature is probably considerably above 155°.

The Stable Hydrate of Potassium Carbonate.—The only hydrate of potassium carbonate stable under ordinary conditions has been variously formulated as $K_2CO_3,2H_2O$ or $2K_2CO_3,3H_2O$, authorities being almost equally divided. As, however, the evidence put forward depends only on analysis of the very soluble salt imperfectly separated from its mother-liquor and dried by more or less intensive methods, the uncertainty is not unexpected. The opportunity of triangulation with a third substance which this investigation affords is sufficient to show that the stable hydrate is the dihydrate. The method of plotting employed in Fig. 1 is unsuited to show this, since the tie-lines between the saturated solutions and corresponding wet solids would be crowded towards the K_2CO_3–H_2O side of the triangle. The relevant figures have therefore been plotted again in

FIG. 1.

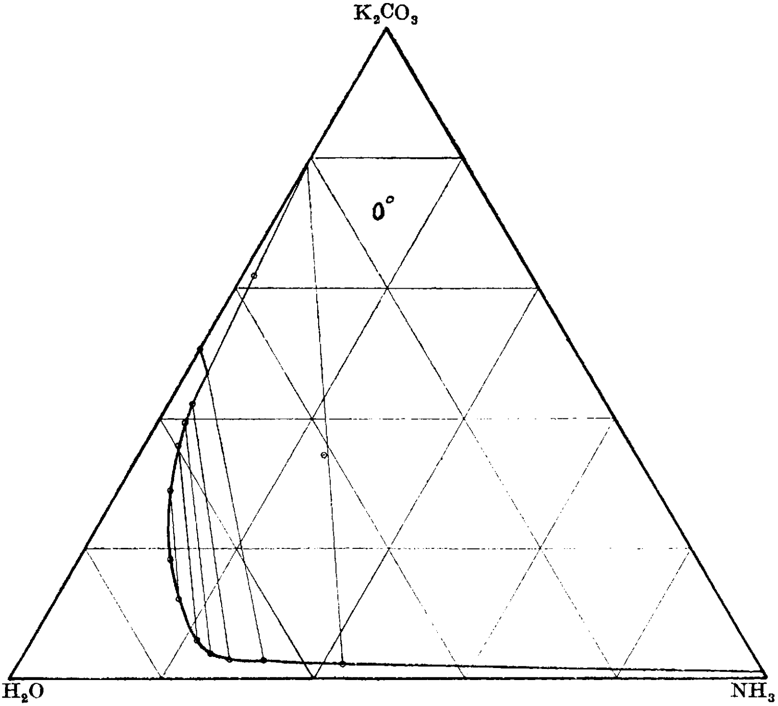
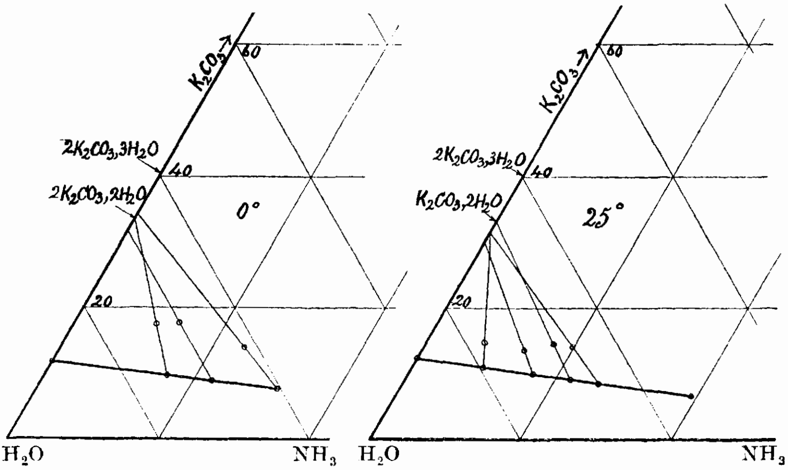


Fig. 2 as molecular percentages with the assumed molecular weights corresponding to the formulæ NH_3,$(K_2CO_3)_{10}$, and $(H_2O)_{10}$. This device spreads out the tie-lines and makes it clear that at both temperatures studied the salt is a dihydrate.

The Vapour Pressure of the Four-phase System.—It was observed in performing the solubility experiments that the system of two liquid phases in contact with the solid salt could be easily maintained at 0° and at 18°, but that at 25° the pressure inside the solubility bottle had to be raised above atmospheric to maintain the upper liquid layer as a stable phase. The system is univariant, so that a definite equilibrium pressure exists for each temperature. The observations referred to seemed to show that this equilibrium pressure exceeds one atmosphere at some temperature between 18° and 25°.

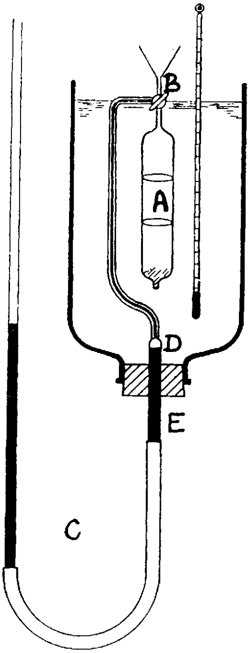
FIG. 2.

Molecular percentages (enlarged scale for NH_3*).*



The equilibrium pressure was measured over the range 0—30° by means of the apparatus shown in Fig. 3. The bulb *A* was first charged with dry salt and thoroughly evacuated through the tube *E*. The rubber connexion was then made, the manometer tube charged with mercury, and strong ammonia solution was introduced through the funnel *B*. Finally, any residual air was removed by lowering the open tube of mercury and manipulating the three-way tap in such a way as to boil off into the manometer space several fractions of ammonia which could then be discharged to atmosphere through the funnel. This procedure was frequently repeated between determinations. It was found that, with rising temperatures, equilibrium was only very slowly established, owing no doubt to the slow rate of solution of the solid. With falling temperatures, however, constancy was soon reached : each experiment was accordingly performed by first maintaining the system for a few hours at a temperature some degrees above the desired temperature which was thus always approached from above. Each of the results given below represents the mean of a number of concordant experiments.

FIG. 3.



Equilibrium Vapour Pressures.

Temp.	0·0°	9·5°	18·04°	24·95°	30·05°
Press. (cm. Hg)	31·23	47·03	63·38	82·55	99·88

The pressure of the system thus reaches 76 cm. at about 22·5°.

Summary.

1. The system potassium carbonate–ammonia–water has been investigated at three temperatures.

2. The system gives two liquid layers which when saturated with solid salt appear to persist to temperatures exceeding 155°.

3. Equilibrium pressures of the univariant system solid–two liquids–vapour have been measured from 0° to 30°.

4. The application of the "rest" method shows that the stable hydrate of potassium carbonate is the dihydrate.

[*Received, March* 30*th*, 1932.]