incorrect strength of solvent alcohol. If the directions are properly followed, no free perchloric acid is left, and so there is no danger in heating the alcoholic solutions.

Summary

1. The method of Smith and Shead[1] has been extended to include the determination of small quantities of potassium in the presence of large amounts of sodium.

2. The salts of sodium and potassium, in the modified procedure, are converted to the neutral anhydrous perchlorates, dissolved in 95% alcohol, and treated with a moderate excess of chloroplatinic acid. The precipitate of potassium chloroplatinate can be weighed as such, or converted to platinum and the potassium calculated from this.

3. The method involves the direct precipitation of potassium (one operation) and no previous concentration to isolate the potassium for subsequent purification is required.

4. The method involves the use of but 0.20 g. of chloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$) per determination. The demand for, and cost of recovery of, platinum is therefore a small factor.

5. In analyses of samples of sodium chloride containing no more than 0.15% of potassium chloride, results obtained by the method should not be in error by more than 0.01%.

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The Systems (a) Ammonium *d*-Tartrate–Lithium *d*-Tartrate–Water, and (b) Ammonium Lithium *d*-Tartrate–Ammonium Lithium *l*-Tartrate–Water

BY ALAN NEWTON CAMPBELL AND LOUIS SLOTIN

Pasteur's first method of resolution of optically active substances has so far only been found applicable to a relatively few cases, the reason being that most inactive forms at room temperature are true racemates and not conglomerates. A study of the mixed solubilities will always tell whether or not the transition point lies in an attainable region. Such studies have been carried out by van't Hoff and by Findlay. So far as is known to the present authors, the only racemic salts whose transition points are known are sodium ammonium racemate,[1] sodium potassium racemate,[2] and rubidium racemate.[3]

It was thought therefore that it would be of interest to investigate the effect on the transition temperature of the substitution of lithium for so-

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(1) Van't Hoff and van Deventer, *Z. physik. Chem.*, **1**, 165 (1887).

(2) Van't Hoff, *ibid.*, **17**, 505.

(3) Van't Hoff and Muller, *Ber.*, **31**, 2206 (1898).

dium in sodium ammonium racemate. Such a study as this should. for completeness, comprise five systems, namely

NH_4 *d*-tartrate–Li *d*-tartrate–H_2O (1)
NH_4 *d*-tartrate–NH_4 *l*-tartrate–H_2O (2)
Li *d*-tartrate–Li *l*-tartrate–H_2O (3)
NH_4 *r*-tartrate–Li *r*-tartrate–H_2O (4)
NH_4Li *d*-tartrate–NH_4Li *l*-tartrate–H_2O (5)

Only with this complete knowledge can one be certain that system 5, on which interest centers, is really a three-component system. Only systems 1 and 5 were investigated by us, but it will be seen from an examination of the isotherms that we were justified in assuming that none of the components of system 5 broke into single constituents at the temperature of investigation.

Experimental

All the salts used in this investigation had previously been prepared. The information attainable in the literature is summarized in the table.

Salt	Prepared by	Formula assigned	Solubility in H_2O
NH_4 *d*-tartrate	Scacchi[a]	$(NH_4)_2C_4H_4O_6$	Unknown
Li *d*-tartrate	Dulk[b]	......	Readily soluble
NH_4Li *d*-tartrate	Scacchi[a]	$Li(NH_4)C_4H_4O_6 \cdot 0.5$ or $1H_2O$	14.186 g. per 100 g. soln. at 20°
NH_4Li *r*-tartrate	Scacchi[c]	$Li(NH_4)C_4H_4O_6 \cdot 0.5$ or $1H_2O$	13.104 g. per 100 g. soln. at 20°

[a] *Atti accad. Sci. Fis. Mat. (Napoli)*, **3**, No. 5 (1866); **6**, No. 25 (1867); No. 29, pp. 29, 33 and 38.

[b] *Ann. chim. phys.*, [3] **5**, 370.

[c] Scacchi, *Atti accad. Sci. Fis. Mat. (Napoli)*, No. 5, 3 (1866), and No. 25, 29 (1867).

Ammonium *d*-tartrate was prepared by the complete neutralization of Mallinckrodt C. P. tartaric acid with ammonia. The evaporation must be conducted in the presence of excess ammonia to prevent formation of the acid salt. The salt was recrystallized twice from water. A solution of the final preparation was neutral to litmus and had $[\alpha]^{30}_{D}$ +34.320°. Landolt[4] gives $[\alpha]^{20}_{D}$ 34.260°. NH_4 found by the distillation method, 19.58%; formula requires 19.59%.

Lithium *d*-tartrate was prepared by neutralizing C. P. tartaric acid with C. P. lithium carbonate until the solution was just alkaline to phenolphthalein. The crystallized salt was purified twice by recrystallization from water. It had $[\alpha]^{30}_{D}$ 35.87°. Landolt[4] gives $[\alpha]^{20}_{D}$ 35.84°. The lithium content was determined by ignition and conversion of the residual carbonate to sulfate.[5] Li found, 9.36%; formula requires 9.38%. This method of analysis was checked, since it was the method used throughout the solubility work, by precipitation of silver tartrate. In this way, for example, the following figures were obtained: weight of lithium tartrate, 1.3423 g.; weight of lithium tartrate calculated from weight of silver, 1.3425 g. Hence the above method is satisfactory for determining lithium.

Ammonium lithium *d*-tartrate was prepared by evaporation of an equimolar solution of ammonium and lithium tartrates and was purified by recrystallization from water.

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(4) Landolt, *Ber.*, **6**, 1676.

(5) Scott, "Standard Methods of Chemical Analysis," p. 414.

The purity of the salt was checked by analyzing weighed amounts and calculating from the formula the corresponding weight of double salt; thus, for example, (a) weight double salt, 3.421 g.; weight double salt from NH_4 determination, 3.4213 g.; (b) weight double salt, 1.6731 g.; weight double salt from Li determination, 1.6735 g.

For the inactive double salt, racemic acid was prepared by a method given elsewhere.[6] From this the double salt was prepared in the same way as the active double salt. The analytical figures were: (a) weight double salt, 1.6431 g.; weight double salt calculated from NH_4 determination, 1.6436 g.; (b) weight double salt, 2.0033 g.; weight double salt calculated from Li determination, 2.0029 g. The formula of the anhydrous double salt is therefore $(NH_4)_2C_4H_4O_6 \cdot Li_2C_4H_4O_6$.

All solubilities at temperatures higher than room temperature were determined by analyzing solutions obtained by stirring for a minimum of ten hours in contact with the appropriate solid phase, in an electrically heated and controlled thermostat. For this thermostat the temperature variations did not exceed 0.01°. At 0° the temperature was maintained constant by the use of ice and here the temperature variations amounted to 0.1°. For temperatures between 0° and room temperature, the arrangement of Walton and Judd[7] was adopted. It was found advantageous to couple this arrangement with an electrical heating unit, so that the bath was alternately heated by the heater or cooled by an entering stream of water. All thermometers were compared with a standard thermometer.

For accurate solubility work, especially where the wet solid phase is being analyzed, it is indispensable that filtration should be carried out actually in the thermostat. Accordingly, the following filtration apparatus, a modification of the previous one,[8] was used. Its construction is shown in the diagram.

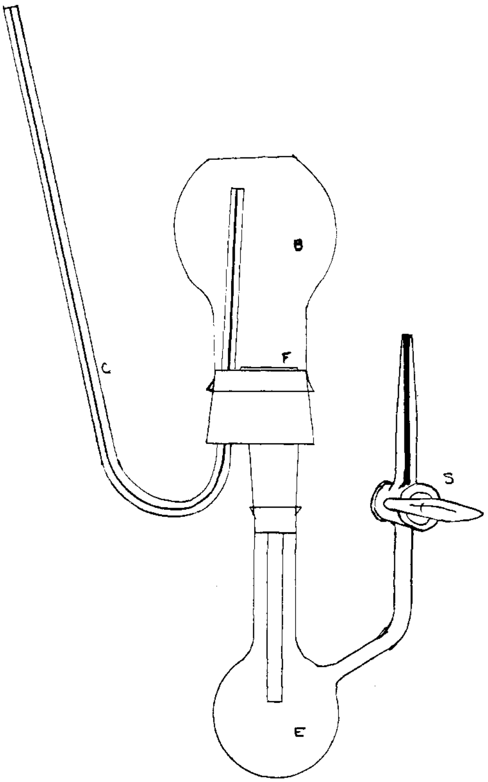

Fig. 1.

B is the bottle in which the saturated solution is prepared, F a sintered glass filter, C a capillary tube communicating with the atmosphere to equalize the pressure, E the receiver; the side-arm is for the purpose of applying suction. To operate the apparatus, the stirring apparatus is removed from the solubility bottle and the filtration apparatus and receiver inserted in its place. The whole unit is then inverted in the thermostat and the flask E slightly evacuated with a water pump. The stopcock S is then closed. The difference in pressure in the two flasks is sufficient to cause a rapid filtration of the saturated solution, the solid phase remaining on the surface of the stopper. The

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(6) Campbell, Slotin and Johnston, THIS JOURNAL, **55**, 2604 (1933).

(7) Walton and Judd, *J. Phys. Chem.*, **18**, 717 (1914).

(8) Campbell, *J. Chem. Soc.*, 181 (1930).

amount of evaporation from the solution during the evacuation of the lower flask is negligible, since the greater part of the liquid is in the upper part of the apparatus, and the evacuation is only carried on for a few seconds before the stopcock is closed. This method has the further advantage that no volumetric apparatus is required, both solutions and solid phase being weighed.

Solutions and solid phase were analyzed for ammonia by the distillation method, and for lithium by the method previously described. The polarimetric method was found to be insufficiently accurate for system 1, probably because of the high concentration of active material. Its use was unavoidable in system 5, where both active and inactive double salts were present, and here it seems to have been fairly accurate, possibly because no interaction is possible between the active and inactive material.

These results are expressed graphically on rectangular coördinates in Fig. 2.

TABLE I

SOLUBILITIES OF LI *d*-TARTRATE AND NH_4 *d*-TARTRATE IN THE PRESENCE OF EACH OTHER

Temperature, 0°

Solubility, g./100 g. H_2O		Liquid phase		Composition of wet residue	
$(NH_4)_2T$	Li_2T	%$(NH_4)_2T$	% Li_2T	%$(NH_4)_2T$	% Li_2T
0.0	42.106	0.0	29.62	...	...
2.510	36.857	1.80	26.44	0.67	61.61
3.473	32.561	2.55	23.93	0.92	64.40
6.013	30.160	4.42	22.15	13.44	54.80
8.022	22.125	6.20	17.00	39.51	38.05
14.491	14.092	11.27	10.95	35.22	30.03
23.081	8.846	19.00	6.21	44.76	36.89
36.610	7.011	25.49	4.88	40.85	27.50
43.916	0.0	30.51	0.0	...	...
44.251	1.973	30.26	1.35	78.00	0.25
45.125	3.952	30.27	2.65	72.21	0.95
45.930	6.026	30.28	3.96	65.21	12.31

Temperature, 30°

Solubility, g./100 g. H_2O		Liquid phase		Solid phase	
$(NH_4)_2T$	Li_2T	%$(NH_4)_2T$	% Li_2T	%$(NH_4)_2T$	% Li_2T
0.0	26.661	0.0	21.05	...	...
3.076	27.143	2.36	20.84	0.20	70.93
7.703	29.181	5.63	21.32	2.34	77.88
8.337	30.001	6.37	21.62	3.17	66.20
9.350	30.661	6.68	21.90	1.05	79.71
12.764	28.561	9.03	20.21	33.49	35.32
11.980	32.731	8.28	22.62	11.56	63.47
14.672	26.071	10.43	18.53	37.29	36.40
16.744	22.603	12.02	16.22	40.31	37.20
24.662	14.732	17.70	10.57	39.16	33.50
29.651	11.603	20.99	8.22	42.31	34.15
39.671	8.182	26.83	5.53	46.24	35.17
63.600	6.916	37.29	4.06	45.60	26.73
63.813	0.0	38.95	0.0	...	...
66.205	6.771	38.30	3.92	76.20	12.82
66.310	5.326	38.64	3.11	79.60	1.13
66.871	2.102	38.73	1.12	84.47	0.98

TABLE I (*Concluded*)

Temperature, 60°

Solubility, g./100 g. H_2O		Liquid phase		Solid phase	
$(NH_4)_2T$	Li_2T	% $(NH_4)_2T$	% Li_2T	% $(NH_4)_2T$	% Li_2T
0.0	29.522	0.0	22.80	...	...
5.110	14.211	31.33	8.54	46.51	35.52
5.807	30.051	4.27	22.12	1.56	73.00
11.003	31.452	7.72	22.08	2.10	76.94
16.349	34.242	10.86	22.74	3.02	78.97
19.510	35.912	12.55	23.11	4.31	74.44
23.121	37.981	14.35	23.58	19.03	63.00
24.431	27.609	16.07	18.16	40.16	37.41
33.521	20.001	21.84	13.03	44.21	38.01
41.083	16.151	26.13	10.28	47.82	40.42
55.823	13.781	32.92	8.13	45.85	33.10
63.011	13.103	35.78	7.44	48.30	35.98
87.171	0.0	46.56	0.0	...	...
90.247	3.631	46.55	1.89	78.73	0.82
92.943	10.510	45.68	5.17	50.79	36.74
92.832	6.650	46.51	3.33	83.10	1.13
98.392	10.244	47.16	4.91	69.08	13.12

From these diagrams it appears that the transition temperature below which the active double salt cannot exist lies below room temperature. An anomaly is caused, however, by the lithium tartrate curve changing direction, an anomaly due to lithium tartrate changing its hydration, and this renders the interpretation of the curve by mere inspection difficult.

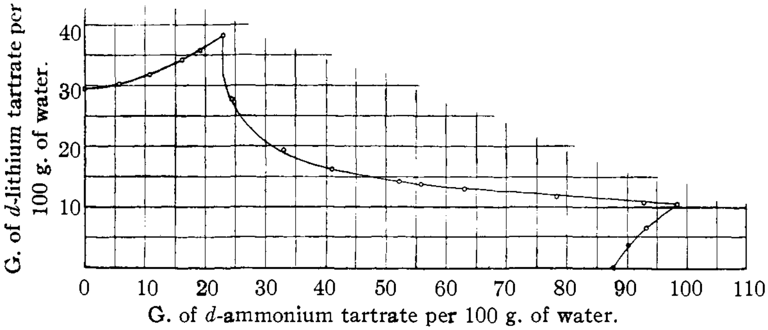

Fig. 2.—60°.

The complete triangular diagrams are given in Fig. 3.

The triangular diagram shows that the double salt has the formula $Li_2C_4H_4O_6 \cdot (NH_4)_2C_4H_4O_6$, and that it is anhydrous at all temperatures studied, although Schlossberg[9] gives to the doubled molecule 1 or $2H_2O$. The 0° triangular diagram shows that the solid phase along the lithium tartrate branch is $Li_2C_4H_4O_6 \cdot 2H_2O$, while at the higher temperatures this

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[9] Schlossberg, *Ber.*, **33**, 1084 (1900).

salt is anhydrous. The numerical value of the solubility also indicates this, lithium tartrate being more soluble at 0° than it is at 30 and 60°.

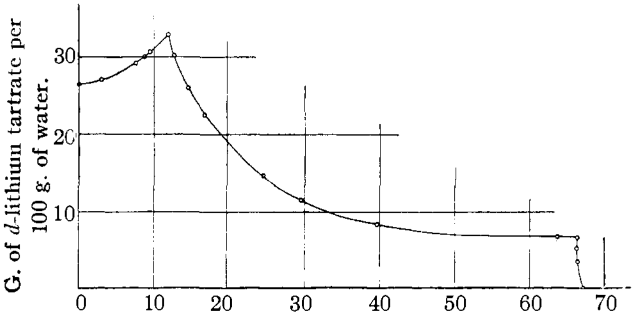

Fig. 3.—30°.

No reference to the hydration of lithium tartrate could be found in the literature, and it became advisable to determine the transition temperature of lithium tartrate dihydrate to anhydrous lithium tartrate. The dilatometric method and the solubility method were employed. By the former method the transition temperature resulted as 21.52°. The solubility figures are given in Table II.

TABLE II

SOLUBILITY OF LI *d*-TARTRATE IN WATER

Temp., °C....	60.0	45.0	30.0	25.0	20.0	10.55	8.0	0.0
Lithium tartrate per 100 g. of water, g.	29.522	27.510	26.663	26.711	27.052	31.495	33.451	42.106

When these figures are plotted against temperature, a marked point of inflection occurs at a temperature of 21.81°. Averaging the two results, the mean transition temperature for $Li_2C_4H_4O_6 \cdot 2H_2O \longrightarrow Li_2C_4H_4O_6 + 2H_2O$ results as 21.67°.

Solid Model.—In order to construct a solid model of the system, NH_4 *d*-tartrate–Li *d*-tartrate–H_2O, showing the behavior of the system with respect to temperature, it was also necessary to know the solubility curve of ammonium tartrate, since the solubility curves of the two simple salts form the boundaries of the model. The solubilities of ammonium tartrate were therefore determined and are expressed in Table III.

TABLE III

SOLUBILITY OF AMMONIUM TARTRATE

Temp., °C..........................	0.0	15.0	30.0	45.0	60.0
Ammonium tartrate per 100 g. of water, g.	43.916	58.101	63.813	79.450	87.171

An inspection of the solid model (not shown) reveals that the area representing stable existence of the double salt widens as the temperature increases, indicating that the double salt is more stable at higher than at lower temperatures.

At all temperatures between 0 and 60°, double salt formation takes place. In this temperature interval (a) ammonium tartrate is anhydrous; (b) lithium tartrate possesses two molecules of water of crystallization, which it loses at 21.67°; (c) the double salt is anhydrous. A rough extrapolation of the boundary lines of the area of stable existence of the double salt gives the transition temperature of $(NH_4)_2C_4H_4O_6\cdot Li_2C_4H_4O_6 \rightleftharpoons (NH_4)_2C_4H_4O_6 + Li_2C_4H_4O_6$ as $-80°$. An examination of the triangular diagrams also shows that the temperature interval investigated is outside of the transition interval, that is, that the double salt can be recrystallized from water without partial decomposition.

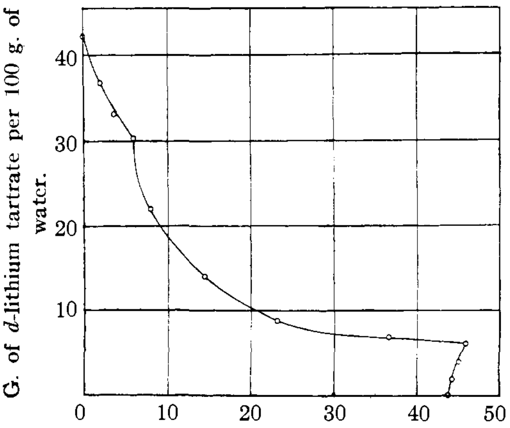

Fig. 4.—0°.

The System NH_4 Li *d*-Tartrate–NH_4 Li *l*-Tartrate–H_2O

The solubility of the inactive double salt was first determined by Schlossberg[9] who states that at 20° 100 g. of solution contains 13.104 g. of salt. This solubility is much higher than that which was obtained in this work. It is possible that Schlossberg's double salt contained some ammonium

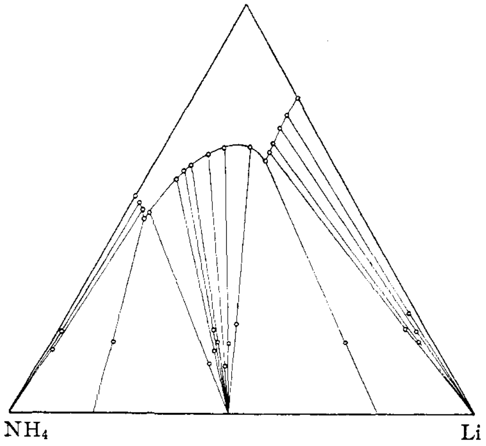

Fig. 5.—60° isothermal.

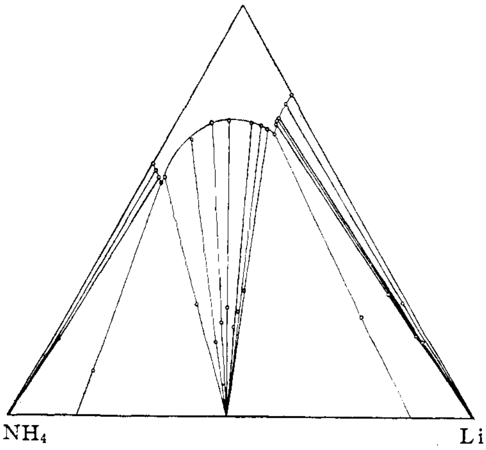

Fig. 6.—30° isothermal.

lithium mesotartrate, which is much more soluble than the corresponding salt of racemic acid. Schlossberg's figure for the solubility of the active double salt (14.186 g. per 100 g. of solution at 20°) is considerably lower than ours.

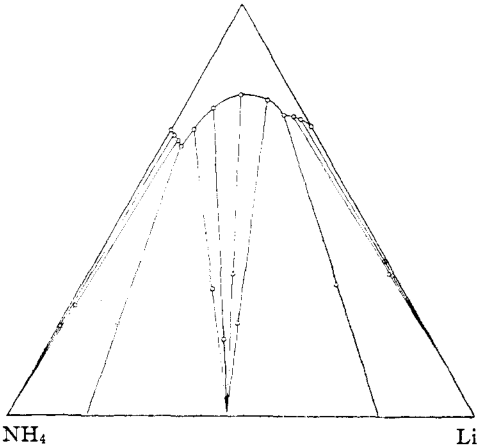

Fig. 7.—0° isothermal.

The experimental technique was the same as that of the previous system, except that the solutions and solid phases containing both active and inactive salt had to be analyzed polarimetrically. For this purpose it was necessary to determine the rotation of solutions of pure NH_4-Li *d*-tartrate at different concentrations. This was done for the sodium D line and at a controlled temperature of 30°, although it was subsequently found that the temperature coefficient of rotation for small changes of temperature is quite negligible. For experimental purposes, it was found simplest merely to plot observed rotation against the salt content of the solution, but for comparison with the literature, the figures are given as specific rotations.

TABLE IV

SPECIFIC ROTATIONS OF SOLUTIONS OF NH_4Li *d*-TARTRATE AT 30° AND FOR NA LIGHT

Concn. in g. per 100 cc. of soln.	4.00	12.00	16.00	20.00	28.00
Concn. in g. per 100 g. of H_2O	4.0829	12.7480	17.4080	22.3791	32.7772
$[\alpha]_D^{30}$	+33.0°	+32.1°	+31.3°	+31.4°	+31.2°

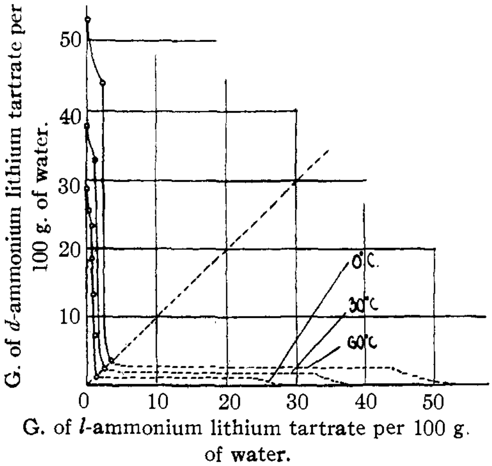

Fig. 8.

Since the object of this study was merely to find the transition temperature of NH_4Li *r*-tartrate to its active component, the 30 and 60° isotherms were not investigated in full, but only the three invariant points were determined. Such "stability curves" are hypothetical as to their curvature, but they are sufficient to define the boundaries of the area of stable existence of the racemate. At 0°, however, the isothermal was fully investigated, in order to determine the degree of hydration of the inactive double salt. The complete data are given in Table V.

TABLE V

Solid phase	Solubility in g. per 100 g. of H_2O 0°	30°	60°
d-	28.519	37.910	52.743
r- (total *d* + *l*)	2.806	6.542	11.480
d + *r*	*d* 23.250	*d* 32.917	*d* 44.103
	l 0.731	*l* 1.416	*l* 2.312

ISOTHERMAL 0°C.

Solubilities expressed as grams of salt per 100 g. of water and also as percentages

Liquid phase: Solubility in g./100 g. of H_2O *d*-form	*r*-form	Liquid phase: Percentages *d*-form	*r*-form	Solid phase: Percentages *d*-form	*r*-form
0.0	2.806	0.0	2.19	...	...
6.531	2.363	6.00	2.17	2.52	74.20
12.241	1.860	10.72	1.63	3.35	67.50
17.690	1.64	14.75	1.37	6.30	56.02
23.251	1.462	18.69	1.18	45.09	29.86
24.810	0.98	19.80	0.70	76.19	0.62
28.519	.0	22.19	.0	...	...

All racemic solubilities when plotted were divided in two and one-half added to the solubility of the *d*-form, and the other half plotted as total *l*-form.

The results are plotted on rectangular coördinates in Fig. 5, and the 0° isothermal on a triangular diagram in Fig. 6.

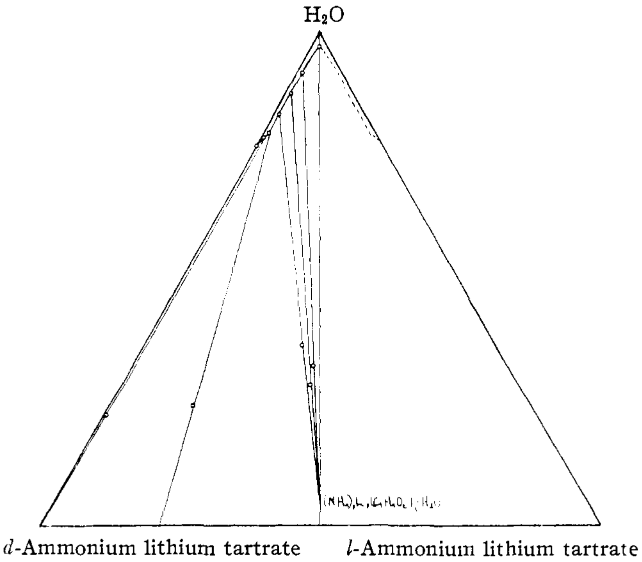

Fig. 9.—Isothermal at 0°.

The large intermediate portion of the rectangular graphs shows the racemate to be very stable at the temperatures investigated and that the transition point is well below 0°. When the solubilities of the inactive salt alone and of inactive salt plus active are plotted against temperature, the curves are found to intersect at a temperature of $-62°$. Consequently, if a solution of ammonium lithium racemate were allowed to crystallize below this temperature, it would deposit the two enantiomers. This is, of course, experimentally impossible owing to the solidification of the solvent.

The angle of intersection of the solubility curves for racemic and racemic plus active forms is large, indicating a large heat of formation.

The intersection of the double salt tie-lines on the 0° isothermal indicates for the inactive double salt the formula $(NH_4)_2Li_2(C_4H_4O_6)_2 \cdot H_2O$. This is in agreement with the findings of Scacchi and Schlossberg.[9] The hydrate also exists at 30° and quite possibly at 60°, although complete solubility measurements were not carried out to confirm this.

Summary

1. The solubility relations in the ternary systems ammonium *d*-tartrate–lithium *d*-tartrate–water and ammonium lithium *d*-tartrate–ammonium lithium *l*-tartrate–water have been determined at 0, 30 and 60°.

2. A double salt was found to be formed at all three temperatures, and its composition was established as $(NH_4)_2Li_2(C_4H_4O_6)_2$. The double salt is stable at all temperatures from 0 to 60°, becoming more stable as the temperature is raised. In the latter system a true racemate was found to exist at all three temperatures and its formula was established as $(NH_4)_2Li_2(C_4H_4O_6)_2 \cdot H_2O$.

WINNIPEG, CANADA

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