CCCLXI.—*The Stability of Magnesium* r-*Mandelate.*

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IN continuation of the study of the stability of racemates (J., 1928, 1768), determinations have been made of the solubility of magnesium *l*-mandelate and *r*-mandelate, as well as of the composition of the invariant system with these two salts as solid phases, at temperatures between 0° and 40°. The solubilities of the single salts at 16° had been determined by McKenzie (J., 1899, **75**, 964), who found the values 4·5 g. and 1·8 g. per 100 g. of water for the active and the racemic salt respectively. The solid salts were found by him to be anhydrous.

The magnesium salts used in this investigation were prepared by the neutralisation of mandelic acid with magnesium carbonate. The magnesium *l*-mandelate, crystallised from water, had $[\alpha]_{5900}^{15^\circ}$

—138°. The solubilities were determined by the method described by Campbell (this vol., p. 179), and the following values (g. of anhydrous salt per 100 g. of water) were obtained:

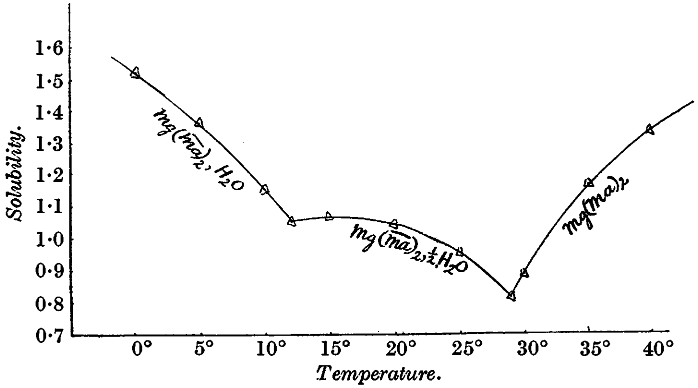
Temp.	0°	5°	10°	15°	20°	25°	30°	35°	40°
r-Salt	1·52	1·36	1·15	1·06	1·04	0·95	0·88	1·16	1·33
l-Salt	1·60	1·68	1·72	1·77	1·83	1·97	2·11	2·72	5·07

The composition of the solution in equilibrium with the active and the racemic salt as solid phases was determined polarimetrically, and the following values, expressed in terms of the two active salts (g. per 100 g. of water), were obtained:

Temp.	0°	5°	10°	15°	20°	25°	30°	35°	40°
l-Salt	1·94	2·12	1·59	2·66	2·23	1·96	2·16	2·40	2·50
d-Salt	0·24	0·55	0·32	0·60	0·39	0·41	0·49	0·49	0·50

If the solubility of the magnesium *l*-mandelate is plotted, a simple curve, rapidly ascending at temperatures above about 30°, is obtained. The solid phase was found to be anhydrous salt, in agreement with McKenzie. In the case of the *r*-mandelate, however, a three-branched solubility curve is obtained (Fig. 1), indicating the existence of hydrated salts. Further investigation showed that two hydrates exist, *viz.*, $Mg(Ma)_2,H_2O$ and $Mg(Ma)_2,\frac{1}{2}H_2O$, the former being stable up to about 12° and the latter between 12° and 29°. These temperatures are read from the solubility diagram. Above 29°, the salt is anhydrous.

Fig. 1.



Vapour Pressure of the Hydrates.—In order to determine the composition of the hydrates, the following method was pursued. A quantity of the moist solid phase was placed in a small bulb, which was connected by means of a well-lubricated ground joint with a manometer and a Hyvac pump. A small flask was inserted in the circuit to serve as an expansion chamber, and the pump was protected from moisture by a drying-tower. The bulb was immersed in a bath at constant temperature, and the vapour carefully pumped off, the vapour pressure during the process being read on the manometer. So long as saturated solution was present with the solid, the vapour pressure remained constant, but when all the solution had been evaporated, the pressure fell sharply to the value for the system, two solid phases–vapour. This point was approached with great care so as to dehydrate as little as possible any hydrate which might be formed; and immediately the pressure fell sharply, the bulb was detached, a sample of the solid removed, and the water of hydration determined by heating at 110°. The bulb was again attached to the manometer and pump, and the process of gradually pumping off vapour continued, until another sharp drop in pressure was observed. The following results were obtained :

At 6°, the pressure remained constant at 7·0 mm. (uncorr.) until all the water in the solution had evaporated; it then fell sharply to 5·0 mm. On dehydration, 1·066 g. of salt lost 0·0550 g., or 5·16% [Calc. for $Mg(C_8H_7O_3)_2,H_2O$: H_2O, 5·23%]. On further dehydration at 6·8°, the pressure remained constant until a sudden drop to 3·0 mm. occurred. On analysis, 1·0390 g. lost 0·0280 g., or 2·7% [Calc. for $Mg(C_8H_7O_3)_2,\frac{1}{2}H_2O$: H_2O, 2·69%]. On further dehydration, the pressure remained constant, and then dropped to zero.

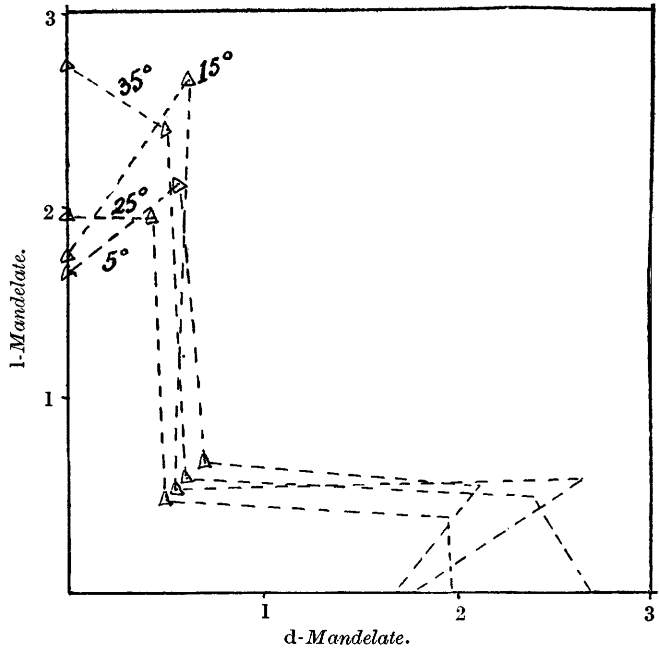
At 21°, similarly, after the saturated solution had been removed, there was a sharp drop in pressure to 17·0 mm. On dehydration at 110°, 0·9550 g. lost 0·0280 g., or 2·93%, showing that the solid was the hemihydrate. On further dehydration, the pressure at first remained constant, and then dropped to zero.

At 30°, after removal of the saturated solution, there was a sudden drop to zero pressure, and the solid was found to be anhydrous.

As the purpose of this investigation was to study the stability relations of magnesium *r*-mandelate, the composition of the solutions in equilibrium with *l*-mandelate, *r*-mandelate, and a mixture of *l*- and *r*-mandelates was plotted in rectangular co-ordinates (Fig. 2). The compositions are expressed as before. The experimental points are represented by triangles, and as the equilibrium curves of the ternary systems were not necessary for our present purpose and were not determined by us, the experimental points have been connected by straight (broken) lines. Although no determinations were made with magnesium *d*-mandelate, broken lines have been drawn so as to give a complete diagram symmetrical about the line bisecting the angle of the co-ordinates.

It is clear from an inspection of Fig. 2 that the magnesium *r*-mandelate exists as stable solid phase throughout the whole range of temperature of our experiments. As compared with other systems of a similar character, however, the diagram is complicated by the existence of racemate hydrates; and a crossing and re-crossing of the curves is indicated, owing to the way in which the solubility of these hydrates and of the anhydrous salt rises and falls with change of temperature. It becomes, therefore, practically impossible, from an examination of the change in the position of the invariant ternary system, to deduce the temperature of the transition point for the active antipodes and the racemate. Owing to the fact that the solubility of the higher hydrate of the racemate increases whereas the solubility of the active salt decreases with fall of temperature, the presumption is that the transition point lies at a fairly low temperature.

FIG. 2.



In view of the existence of racemate hydrates, it will be of interest to determine the actual position of the curve for ternary solutions in equilibrium with solid racemate and racemate hydrates. Such determinations, however, have had to be postponed owing to the departure of one of the authors.

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[*Received, June* 4*th*, 1930.]