XXXIV.—*Solubilities of the Calcium Salts of the Acids of the Acetic Series.*

By JOHN S. LUMSDEN, D.Sc., Ph.D.

IT is well known that many calcium salts are more soluble in water at low than at high temperatures. This is not in accordance with the usual experience that the solubility of a solid increases with rise of temperature, yet the matter has never been submitted to careful investigation.

For the purpose of obtaining more information on the subject, it seemed best to select a series of acids, to prepare the calcium salts in a crystalline state, and to determine the solubility of each salt for a range of temperature between 0° and 100°.

The acetic series of organic acids was chosen and the calcium salts of the first nine normal acids and of *iso*butyric and *iso*valeric acids have been prepared and examined.

In order to obtain accurate results, the estimation of the solubility of a substance must be done with very great care. The difficulties to be overcome are: the maintenance of a constant temperature for many hours, the production of complete saturation and the removal of the solution from contact with the solid to another vessel without change or loss.

The apparatus used to obtain a constant temperature is shown in Fig. 1 (p. 352). The thermostat is an enamelled iron vessel supported on bricks and heated from below by a luminous gas jet and a ring air burner.

The temperature regulator consists of two bottles filled with water or calcium chloride solution, one of which is shown at *A* connected with an ordinary mercury gas cut-off, *B*. By means of Y glass connections, the gas flame, the ring burner, and the fan jet, *C*, are supplied with gas from the tap, *D*.

For high temperatures, the luminous gas flame connected with the regulator does not produce sufficient heat and the ring burner is then used, being set to keep up a constant temperature less than that required and the gas flame then raises the temperature to the exact point and regulates it.

The water level is kept constant by the syphon, *E*. When the water sinks below the bell-mouthed tube, air enters and water flows from the bottle until the level rises and shuts off the supply of air.

The stirrer, *F*, is mounted on a steel point running in a hole in a glass stopper and moved by a wheel made of Japanese fans. At low temperatures, the fan jet is required, but at high temperatures the heated air from the apparatus causes a sufficiently rapid rotation.

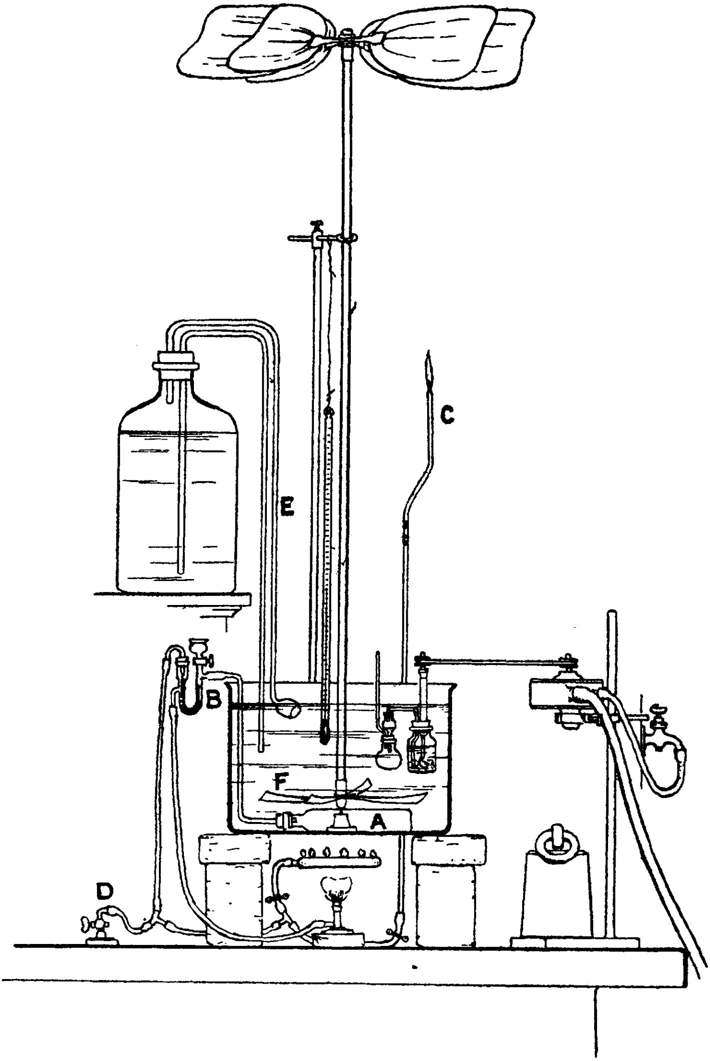
The thermometer used reads to tenths of a degree, and for temperatures between 20° and 90° the water in the thermostat can be kept without variation of more than one-fifth of a degree for many hours. Below 20°, constant temperatures were obtained by running a continual stream of water from the laboratory tap into the vessel. On different days the temperature varied, but on the same day it was sufficiently constant for six hours. Temperatures down to 6° were got in this way. For estimations at the freezing point a mixture of ice and water was used and boiling water was employed for the determinations at 100°.

The apparatus used to obtain complete saturation of the solution and to remove the saturated liquid is shown in Fig. 2 (p. 353), and on a small scale in Fig. 1 (p. 352).

The object in view when this apparatus was devised was to carry out all the operations under the surface of the water in the thermostat and therefore exactly at the temperature of estimation.

The saturating vessel, *G*, is a bottle or small flask into which excess of finely powdered solid is placed along with the solvent. A glass stirrer running in a glass collar and passing down the outer tube, *H*, is driven by

FIG. 1.

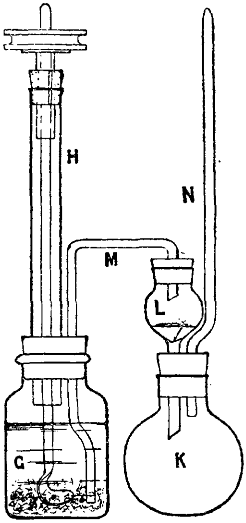


a water motor as shown in Fig. 1. *K* is the flask or bottle into which the saturated liquid is to be filtered. The bulb, *L*, is the filter and contains a very small filter paper filled with cotton wool, which keeps the paper in position and also acts as a filter plug. Connection is made with the saturating vessel by the tube *M*, and the tube *N*, rising above the water level, is the suction tube. The filter flask is not attached to the saturating vessel until a short time before filtering, since at high temperatures water is liable to distil through the tube *M*. The end of that tube is therefore plugged while saturation is taking place.

All the stoppers are of rubber except that which bears the neck of the stirrer, and this has a notch to prevent increase of pressure in the bottle.

After saturation has been attained, which at low temperatures is only after many hours but at high temperatures is complete in an hour, the filter flask is attached, ten minutes are allowed for heating to the temperature of the bath, then suction is applied by the mouth to *N*, and the liquid passes over and filters quite clear into the flask. As much as possible of the liquid is filtered, to reduce any error due to absorption by the filter or moisture in the connecting tube.

FIG. 2.



After filtration, the flask is quickly detached, corked and immediately cooled to the temperature of the laboratory by running water on the outside. This quick cooling prevents evaporation taking place and consequent concentration of the solution.

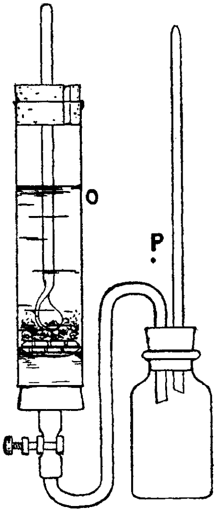
It is necessary to know the exact composition of the solid of which a saturated solution is being made, as the solid may undergo change. An anhydrous salt, when placed in water, may become a crystalline hydrate and a salt containing water of crystallisation may lose water in contact with a hot solution. As a salt and its hydrates are essentially different substances, they have different solubilities, and analysis is necessary to determine the substance being dealt with.

The apparatus used for separating the solid at any temperature from the saturated solution is seen in Fig. 3 (p. 354). The tube *O*, used as the saturating vessel, has a rubber stopper fitted to the lower end, and through a hole in this passes a glass tube which makes connection with the filter bottle. A rubber connection with a screw clip keeps the tube closed until filtration is to take place. On the rubber stopper rest two perforated porcelain plates with a filter paper between. The solid is placed in the tube, the solvent added, and saturation attained at the desired temperature. The clip is then opened, the tube

P attached to a filter pump, and while suction is going on the solid is rammed down tightly to express as much solvent as possible. The apparatus is then quickly removed from the thermostat and the solid placed on a warmed porous plate. Drying is speedily effected, and after an hour in a desiccator the solid is analysed before any change can take place. With all precautions, it is difficult in many cases to get exact quantitative results: either the solid is insufficiently dried or water of crystallisation is lost, but there is no difficulty in getting results which show decidedly whether the solid is one or other of two hydrates.

The saturated solutions obtained in these determinations and the solids containing calcium had to be analysed, and this is a tedious and difficult process unless the following method is adopted.

FIG. 3.



It was found most exact to convert the calcium compounds always into calcium sulphate. From 5 to 10 grams of the solution were placed in a platinum crucible and weighed, then somewhat less than the quantity of concentrated sulphuric acid required to complete the change to calcium sulphate was added. When the crucible was heated on a water-bath, the organic acid rapidly evaporated, and a hard residue was obtained in an hour. This was carefully ignited, and the dried mass, consisting of oxide, sulphide, and sulphate of calcium, was treated again with concentrated acid and heated until fumes ceased to be evolved and the residue was pure white.

The calcium salts employed in the following determinations were prepared from the pure acids obtained from Kahlbaum and from precipitated calcium carbonate. A quantity of the acid was largely diluted with water, enough water being used in the case of the higher acids, which are only slightly soluble, to form a complete solution, and this was then poured on excess of calcium carbonate contained in a large flask. After the first action ceased, heat was applied for some time, and the liquid was then filtered.

This filtered solution was always slightly acid, and it was found that when organic acids become very dilute they cease to act on calcium carbonate. Since all the acids are volatile, the acidity disappeared during evaporation of the liquid. The solid obtained by evaporation over a water-bath was dissolved in water, and crystals obtained by placing the vessel in a warm place, and occasionally removing and drying those which separated.

Most of these calcium salts are soluble in hot dilute alcohol, and it was found easiest to obtain good crystals of the higher members from such a solution.

Solubility of Calcium Formate, $(HCO_2)_2Ca$. *Curve No.* 1.

Calcium formate crystallises from solution in water or dilute alcohol in anhydrous, hard, glass-like, rhombic crystals. Attempts to obtain a hydrated salt by spontaneous evaporation of a solution in water at a low temperature were unsuccessful:

0·9616 crystals gave 1·0021 $CaSO_4$. Ca = 30·7.
$(CHO_2)_2Ca$ requires Ca = 31·2 per cent.

The solubility curve of calcium formate between 0° and 100° is a straight, upwardly inclined line, representing a steadily increasing solubility with rise of temperature.

The weights of solid dissolved by 100 parts by weight of water are as follows:

t.	Parts.	t.	Parts.	t.	Parts.
0°	16·15	40°	17·05	80°	17·95
10	16·37	50	17·27	90	18·17
20	16·60	60	17·50	100	18·40
30	16·82	70	17·72		

Formula for this range of temperature, 16·15 + 0·0225t°.

Solubility of Calcium Acetate, $(CH_3\cdot CO_2)_2Ca,2H_2O$ *and* $(CH_3\cdot CO_2)_2Ca,H_2O$. *Curve No.* 2.

From a cold solution, calcium acetate crystallises in long, silky, transparent needles which contain 2 mols. of water of crystallisation. These effloresce readily, and the ordinary white solid contains only 1 mol. of water:

1·066 gave 0·8230 $CaSO_4$. Ca = 22·71.
$(C_2H_3O_2)_2Ca,H_2O$ requires Ca = 22·73 per cent.

In solution, the change from the salt with $2H_2O$ to that with $1H_2O$ takes place at 84°.

The solubility at 0° is 37·40 parts in 100 parts of water; it then diminishes until about 60°, when the solution contains only 32·70 parts, then rises until the transition point is reached at 84°, when 33·80 parts are dissolved. From 84°, the solubility of the new salt diminishes rapidly to 100°, when the solution contains 29·65 parts.

The weights of solid, calculated as anhydrous salt, dissolved by 100 parts of water, are as follows:

	t.	Parts.		t.	Parts.		t.	Parts.
($2H_2O$)	0°	37·40	($2H_2O$)	35°	33·50	($2H_2O$)	70°	32·98
	5	36·65		40	33·22		75	33·22
	10	35·98		45	33·00		80	33·50
	15	35·32		50	32·82	T	84	33·80
	20	34·73		55	32·70	(H_2O)	85	32·85
	25	34·20		60	32·70		90	31·05
	30	33·82		65	32·78		95	30·20
							100	29·65

Solubility of Calcium Propionate, $(CH_3{\cdot}CH_2{\cdot}CO_2)_2Ca,H_2O$.

Curve No. 3.

The crystals of calcium propionate are thin, glistening plates containing 1 mol. of water of crystallisation, which is only given off above 100°.

The solubility curve is markedly convex to the temperature axis. At 0°, as much as 42·80 parts of the salt dissolve in 100 parts of water, but the solubility quickly diminishes until, at about 55°, only 38·20 parts are in solution. Above this temperature, the solubility increases and at 100° 48·44 parts are dissolved.

To make sure that the solid in contact with the solution was the same on the descending and ascending parts of the curve, it was filtered off at various temperatures and analysed. The results showed that at all temperatures the solid contained 1 mol. of water:

At 12°, 0·1739 gave 0·1159 $CaSO_4$. Ca = 19·61.
„ 90°, 0·3895 „ 0·2591 $CaSO_4$. Ca = 19·57
$(Ca_3H_5O_2)_2Ca,H_2O$ requires Ca = 19·61 per cent.

The weights of solid dissolved by 100 parts of water are as follows:

t.	Parts.	t.	Parts.	t.	Parts.
0°	42·80	35°	38·75	70°	38·75
5	41·70	40	38·45	75	39·20
10	40·95	45	38·35	80	39·85
15	40·35	50	38·25	85	40·80
20	39·85	55	38·20	90	42·15
25	39·40	60	38·25	95	44·25
30	39·05	65	38·40	100	48·44

Solubility of Calcium Butyrate, $[CH_3{\cdot}(CH_2)_2{\cdot}CO_2]_2Ca,H_2O$.

Curve No. 4.

Calcium butyrate crystallises by spontaneous evaporation in long, ribbon-like leaves containing 1 mol. of water, and this is the composition of the solid in contact with the solution at all temperatures below 100° :

0·4940 gave 0·2898 $CaSO_4$. Ca = 17·26.
$(C_4H_7O_2)_2Ca,H_2O$ requires Ca = 17·24 per cent.

The solubility of this substance has been determined by Hecht (*Annalen*, 1882, **213**, 65) and by Chancel and Parmentier (*Compt. rend.*, 1887, **104**, 474). Their results are slightly lower than those given below.

The weight, calculated as anhydrous salt, in 100 parts of water is as follows :

t.	Parts.	t.	Parts.	t.	Parts.
0°	20·31	35°	16·70	70°	14·92
5	19·75	40	16·40	75	14·90
10	19·15	45	16·00	80	14·95
15	18·65	50	15·70	85	15·10
20	18·20	55	15·40	90	15·25
25	17·75	60	15·15	95	15·50
30	17·25	65	15·00	100	15·85

Solubility of Calcium Valerate, $[CH_3\cdot(CH_2)_3\cdot CO_2]_2Ca,H_2O$.

Curve No. 5.

Calcium valerate is obtained from solution in hot water as a microcrystalline powder, but if a cold solution is allowed to evaporate, fine, interwoven crystals are obtained, and from dilute alcohol long, ribbon-like plates readily separate out.

One mol. of water is always present below 100° :

0·4219 crystals gave 0·2210 $CaSO_4$. Ca = 15·41.
$(C_5H_9O_2)_2Ca,H_2O$ requires Ca = 15·38 per cent.

The solubility for each 10° is as follows :

t.	Parts.	t.	Parts.	t.	Parts.
0°	9·82	50°	7·85	70°	7·80
10	9·25	55	7·76	80	7·95
20	8·80	57	7·75	90	8·20
30	8·40	60	7·78	100	8·78
40	8·05				

The point of lowest solubility is 57°, when only 7·75 parts of solid are in solution.

Solubility of Calcium Caproate (Hexoate), $[CH_3\cdot(CH_2)_4\cdot CO_2]_2Ca,H_2O$.

Curve No. 6.

This salt separates from water in small, leafy crystals, but long, thin plates are obtained from hot dilute alcohol. One mol. of water is present up to 100°:

0·4580 gave 0·2162 $CaSO_4$. Ca = 13·89.

$(C_6H_{11}O_2)_2Ca,H_2O$ requires Ca = 13·89 per cent.

The solubility curve, although very flat, distinctly shows a descending and an ascending part, the point of lowest solubility being about 55°.

The solubility for each 10° is as follows:

t.	Parts.	t.	Parts.	t.	Parts.
0°	2·23	40°	2·15	80°	2·30
10	2·20	50	2·10	90	2·45
20	2·18	60	2·15	100	2·57
30	2·17	70	2·20		

Solubility of Calcium Œnanthate (Heptoate), $[CH_3\cdot(CH_2)_5\cdot CO_2]_2Ca,H_2O$.

Curve No. 7.

The crystals from dilute alcohol are long, monoclinic prisms forming a fibrous, silky mass. They contain 1 mol. of water:

0·098 gave 0·0424 $CaSO_4$. Ca = 13·52.

$(C_7H_{13}O_2)_2Ca,H_2O$ requires Ca = 12·88 per cent.

The solubility is as follows:

t.	Part.	t.	Part.	t.	Part.
0°	0·95	40°	0·82	80°	0·98
10	0·90	50	0·80	90	1·10
20	0·86	60	0·82	100	1·26
30	0·84	70	0·90		

Solubility of Calcium Caproate (Octoate), $[CH_3\cdot(CH_2)_6\cdot CO_2]_2Ca,H_2O$.

Curve No. 8.

As caproic and pelargonic acids are very slightly soluble in water, the calcium salts were prepared by first making the ammonium salts and then adding calcium chloride solution. The precipitated salts were well washed and crystallised from dilute alcohol.

The crystals of calcium caproate are long, thin rhombic needles containing 1 mol. of water.

0·3420 gave 0·1350 $CaSO_4$. Ca = 11·61.

$(C_8H_{15}O_2)_2Ca,H_2O$ requires Ca = 11·62 per cent.

The greatest solubility is at 100°, when 0·5 part dissolves in 100 parts of water; the lowest is about 60°, where 0·24 part is in solution:

t.	Part.	t.	Part.	t.	Part.
0°	0·33	40°	0·28	80°	0·32
10	0·32	50	0·26	90	0·40
20	0·31	60	0·24	100	0·50
30	0·30	70	0·28		

Solubility of Calcium Pelargonate (Nonoate), $[CH_3\cdot(CH_2)_7\cdot CO_2]_2Ca,H_2O$. *Curve No.* 9.

Calcium pelargonate forms long, transparent, leafy crystals which, massed together, resemble white satin in lustre. The crystals are readily obtained from solution in hot dilute alcohol. One mol. of water is present:

0·3208 gave 0·1170 $CaSO_4$. Ca = 10·73.
$(C_9H_{17}O_2)_2Ca,H_2O$ requires Ca = 10·75 per cent.

The solubility is now very small:

t.	Part.	t.	Part.	t.	Part.
0°	0·16	40°	0·13	80°	0·15
10	0·15	50	0·13	90	0·18
20	0·14	60	0·12	100	0·26
30	0·14	70	0·12		

Solubility of Calcium iso*Butyrate*, $[(CH_3)_2CH\cdot CO_2]_2Ca,5H_2O$ *and* $[(CH_3)_2CH\cdot CO_2]_2Ca,H_2O$. *Curve No.* 10.

From solution at low temperatures, calcium *iso*butyrate crystallises in long, thick, prismatic needles containing 5 mols. of water of crystallisation:

0·5648 gave 0·2516 $CaSO_4$. Ca = 13·10.
$(C_4H_7O_2)_2Ca,5H_2O$ requires Ca = 13·16 per cent.

The crystals filtered from a saturated solution above 80° contain 1 mol. of water:

0·5062 gave 0·2964 $CaSO_4$. Ca = 17·22.
$(C_4H_7O_2)_2Ca,H_2O$ requires Ca = 17·24 per cent.

The transition point from one salt to the other is at 62·5°, and the solubility is represented by two curves.

The weights of anhydrous salt dissolved by 100 parts by weight of water are:

t.	Parts.	t.	Parts.	t.	Parts.
($5H_2O$) 0°	20·10	($5H_2O$) 35°	24·55	(H_2O) 65°	28·25
5	20·52	40	25·28	70	27·75
10	21·10	45	26·05	75	27·32
15	21·70	50	26·80	80	27·00
20	22·40	55	27·60	85	26·70
25	23·10	60	28·40	90	26·48
30	23·80	T 62	28·70	95	26·28
				100	26·10

The solubility of calcium *iso*butyrate was determined in 1887 by Chancel and Parmentier (*Compt. rend.*, 1887, **104**, 474). At low temperatures, their values approximate to those now found, but although they knew that above 80° the salt contained only 1 mol. of water, yet they show no transition point, but represent the solubility by a simple curve, concave to the temperature axis. Possibly by joining a few distant points, they missed the transition point.

Solubility of Calcium iso*Valerate,* $[(CH_3)_2CH{\cdot}CH_2{\cdot}CO_2]_2Ca,3H_2O$ *and* $[(CH_3)_2CH{\cdot}CH_2{\cdot}CO_2]_2Ca,H_2O$. *Curve No.* 11.

Calcium *iso*valerate crystallises in two forms: in long, thick, well-formed, prismatic needles containing 3 mols. of water, and from a hot solution in thin plates containing 1 mol. of water :

0·2796 gave 0·1289 $CaSO_4$. Ca = 13·56.
$(C_5H_9O_2)_2Ca,3H_2O$ requires Ca = 13·52 per cent.

The crystals filtered from a saturated solution above 80° were pressed on a porous plate and placed in a desiccator until they showed signs of efflorescence :

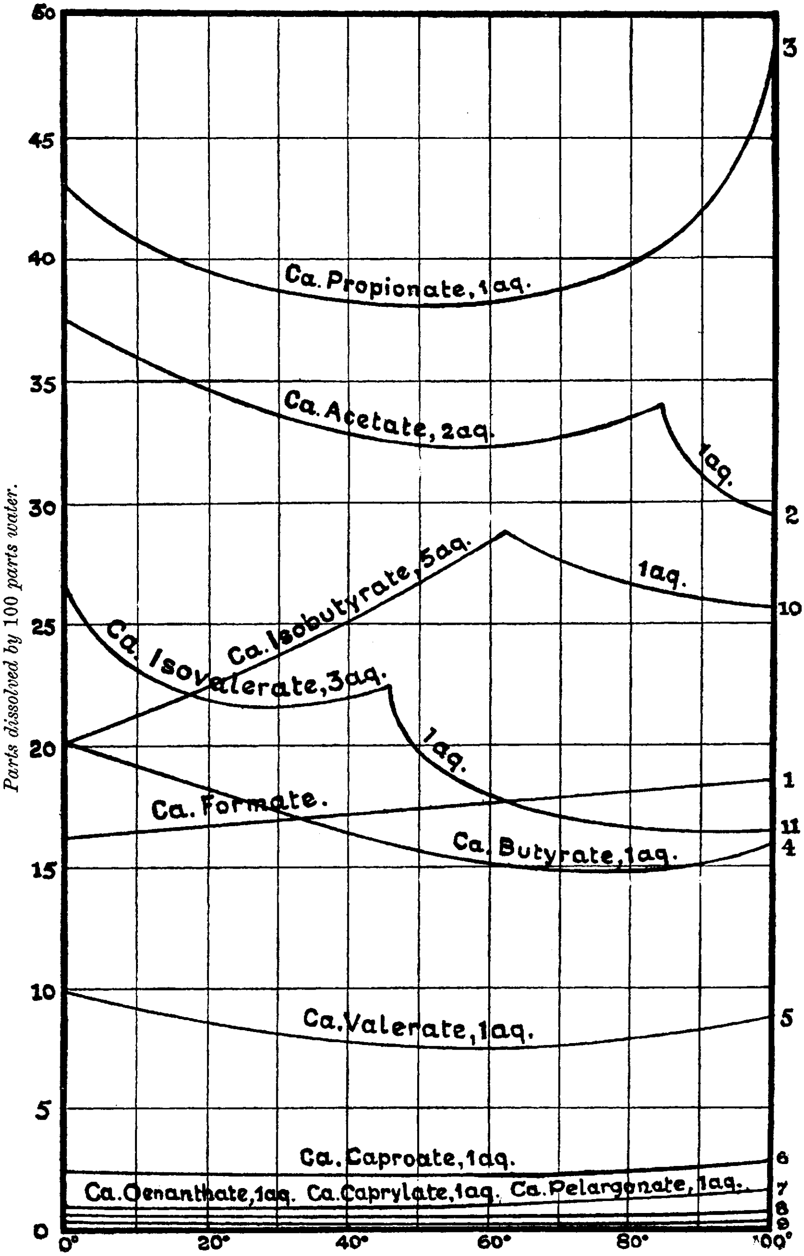
0·8758 gave 0·4626 $CaSO_4$. Ca = 15·53.
$(C_5H_9O_2)_2Ca,H_2O$ requires Ca = 15·38 per cent.

The solubility is shown by two well-marked descending curves, the transition point being at 45·5°.

The weights of anhydrous solid in 100 parts of water at different temperatures are as follows :

t.	Parts.	t.	Parts.	t.	Parts.
$3H_2O$ 0°	26·05	($3H_2O$) 40°	22·00	(H_2O) 70°	17·40
5	23·75	45	22·30	75	17·10
10	22·70	T 45·5	22·35	80	16·88
15	22·15	(H_2O) 50	19·95	85	16·75
20	21·80	55	19·00	90	16·65
25	21·68	60	18·38	95	16·58
30	21·68	65	17·85	100	16·55
35	21·80				

FIG. 4.



Solubility curves of the calcium salts of acids of the acetic series.

The examination of the collected solubility curves (Fig. 4, p. 361) shows the following points :—Calcium formate, the salt of the lowest acid of the series, is peculiar; it consists of anhydrous crystals, and shows a simple ascending curve of solubility. All the other calcium salts crystallise with water, and all with rise of temperature first diminish in solubility then reach a minimum point, and thereafter the solubility steadily increases.

Of the salts of the normal acids, only calcium acetate changes from one crystalline state to another between 0° and 100°, while both calcium *iso*butyrate and calcium *iso*valerate have double curves. It will also be noticed that, with the exception of calcium formate, all the salts which have been investigated, when in contact with their saturated solutions at 100°, consist of crystals which contain 1 mol. of water.

Whilst it is difficult to compare a series of salts with respect to solubility, since one may be more soluble than another at one temperature, but less soluble at a different temperature, and different hydrates are not truly comparable, yet in a general sense it may be said of the calcium salts under consideration that those formed from the normal acids increase in solubility from formate to acetate and propionate, then decrease quickly with the growth in the number of carbon atoms, and that the salts of the *iso*-acids are more soluble than those of the corresponding normal members of the series.

As the solubilities of these calcium salts with rise of temperature diminish, reach a minimum, and then increase, each curve is convex to the temperature axis, and it will be shown in the following paper that this is the normal shape of a solubility curve. Calcium salts will be found to be in no wise anomalous in diminishing in solubility with rise of temperature; they are simply peculiar in having the descending parts of their curves within the range of temperature between 0° and 100°, whilst the curves of most other solids are the ascending parts of convex curves, which would show a minimum and descending part if the determination of the solubility could be made at a low enough temperature.

UNIVERSITY COLLEGE, DUNDEE.
ST. ANDREW'S UNIVERSITY.