CXII.—*The Spontaneous Crystallisation of Solutions of Potassium Chloride, Bromide, and Iodide.*

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In the investigation of the spontaneous crystallisation of solutions of the nitrates of potassium, rubidium, and cæsium, one of the authors had observed (Jones, T., 1908, **93**, 1739) a relation between the extents of the metastable regions in aqueous solutions of these salts having a common anion. The work recorded below was undertaken with a view to determine whether in the case also of similar salts with a common cation any similar relation exists. The salts chosen, namely, potassium chloride, bromide, and iodide, were suitable for the purpose, as they all crystallise in the anhydrous condition and in the cubic system; they are, further, moderately soluble, and the viscosity of their supersaturated solutions should not offer serious hindrance to spontaneous crystallisation.

The work was begun and almost finished before that of Young on the mechanical stimulus to crystallisation (*J. Amer. Chem. Soc.*, 1911, **33**, 148) had come to our notice. Young's work affords strong evidence that no "metastable limit" exists; its apparent existence depends on the fact that in the experiments of Miers, Hartley, Jones, and others to determine the supersolubility curves of various solutions, the amount of mechanical stimulus afforded by shaking the solutions with hard substances (glass or garnet) has coincided with a "transitional" value. By plotting the temperatures of crystallisation against the energies of the shocks employed to induce crystallisation in water, benzene, and fused hydrated calcium chloride, curves of a hyperbolic character were obtained, which indicated that during a certain small range of temperature—the "transitional" region—shocks of considerably varying intensity would bring about crystallisation. Above this region the curve is asymptotic to the energy axis, indicating that a very large additional shock is necessary to raise the temperature of crystallisation by a small amount; below, the curve is asymptotic to the temperature axis, indicating that the supercooled liquid or solution is in a state very sensitive to shock, in which crystallisation is brought about by very small stimuli The supersolubility curves are explained by Young as corresponding with these "transitional" regions; and so far as it goes the explanation appears to accord well with the facts. It is interesting that the "transitional" region found by Young for pure water lies in the neighbourhood of $-0.6°$, the value obtained for the point of spontaneous crystallisation of ice by the shaking method.

Young's explanation of the supersolubility curves cannot, however, be considered complete, for although the intensity of the stimulus applied may be a large, perhaps the main, factor in bringing about crystallisation, it is likely that other, as yet undetermined, influences are at work, perhaps those of the nature suggested by Hartley and Thomas (T., 1906, **89**, 1031). For if the intensity of the shock were the only factor to be considered, it is difficult to understand why in such closely similar salts as the nitrates of potassium, rubidium, and cæsium, the supersolubility curve should be coincident with the solubility curve in the last case, and at an average distance of 4° and 1° in the two others; or, as is shown in the present paper, the corresponding values for the chloride, bromide, and iodide of potassium should be 10°, 12°, and 3°. It would also be a curious coincidence if in all cases investigated by the shaking method, varying in character from Glauber's salt dissolved in water to triphenylmethane dissolved in benzene and comprising "metastable regions" varying in extent from nothing to 35 Centigrade degrees, the investigators should always have chosen just those conditions of mechanical stimulus which correspond with the "transitional" regions of Young. It would be expected that for substances of widely differing character the stimuli necessary to produce crystallisation and corresponding with the "transitional" region should also vary widely. This, indeed, Young has shown to be the case. It might not unreasonably be expected, then, that in some cases at least among those investigated by the shaking method, where the stimuli employed were all of the same order of magnitude, the "transitional" stimulus would have been greater than that actually employed.

Again, assuming that Young's curves, which are based on three points only in every case, represent the real relation between the energy of the stimulus and the temperature of crystallisation, it is seen that the "transitional" region covers a range of temperature of several degrees. It would be expected, then, that the observed temperatures of crystallisation obtained by the shaking method should also vary through this range. This has not been found, the observed temperatures almost always agreeing closely, even over wide ranges of temperature and concentration, within a few tenths of a degree, in spite of the fact that no attempts were made to keep constant the vigour of the shaking. In the present investigation the rapidity and violence of the shaking were purposely varied through a considerable range.

That other than purely mechanical factors enter into the problem is indicated by the fact that if the solubility-temperature coefficient of the salt is positive, the supersolubility curve runs closely parallel

to the solubility curve with a tendency to diverge from it at high temperatures and concentrations; whereas if the coefficient is negative (Na_2SO_4 or Na_2CO_3,H_2O), the supersolubility curve converges towards the solubility curve with increasing temperature, that is, decreasing concentration.

It would appear, then, justifiable to conclude that no specifically "metastable" region exists within which spontaneous crystallisation (that is, without the presence of crystal nuclei) *cannot* take place. At the same time, however, the supersolubility curves do mark a somewhat sudden change in properties in the supercooled liquids or supersaturated solutions. They do not mark a "metastable limit," yet they indicate a remarkably sharp change in conditions from a state (labile) where the tendency is for crystallisation not to occur except under very violent stimuli, to a state (metastable) in which with moderate shaking, whereby the hindering effect of viscosity is probably largely obviated, separation of the solid phase will *invariably* take place within a very short time. Young's explanation of the supersolubility curves does not diminish their practical importance in defining the boundary between these two states, nor does it take into account those factors, other than purely mechanical, which would appear to play some part in the phenomenon. Whether the explanation advanced by Hartley and Thomas account for these other factors cannot as yet be said to be proved. It does at least invoke the aid of the kinetic theory, which in a problem of this nature it would be unwise to ignore completely. The influence of time as a factor in bringing about the "accident of crystallisation" is also doubtless not to be neglected.

In the present investigation on the chloride, bromide, and iodide of potassium, all three salts have given well-defined supersolubility curves under the conditions of experiment, slow cooling and moderate agitation and mechanical shock. The supersolubility curves for both the ice and the salt phases have been traced.

EXPERIMENTAL.

The method used was the same as that employed in previous investigations (Hartley, Jones, and Hutchinson, T., 1908, **93**, 825; Jones, T., 1908, **93**, 1739; 1909, **95**, 1672). The tubes were shaken by various means: by hand, by an electric-bell shaker, by a mechanical shaker worked by a hot-air motor, or by a highly-geared hand-turned machine. The energy of the shaking was then widely varied, but the manner and vigour of the shaking seemed to have little or no effect on the temperature of crystallisation. The shape and material of the tube also appeared to be without influence on the temperature of crystallisation. The bulbs of the tubes were

blown as thin as was consistent with safety to allow of their contents assuming the temperature of the bath as rapidly as possible. The same results were obtained whether ordinary or Jena glass was used, but perhaps the crystallisation phenomena were most definite in tubes of Jena glass with conical bulbs, this shape giving somewhat greater opportunity for mechanical shock during shaking. Mechanical friction or stimulus was promoted by adding small crystals of garnet (about 2 mm. across); this made the phenomenon of crystallisation much more definite than was the case in the absence of solid substances. Fragments of Jena glass were first used, since, being amorphous, they could have no inoculating effect, but they were found to be unsatisfactory, as they broke up on shaking, giving rise to minute fragments, the presence of which hindered the observation of the first appearance of the crystals, which they closely resembled. Since in all cases the solutions had to be cooled well below the saturation point before crystallisation could be induced, it may be supposed that the garnets, too, although crystalline, had but very small, if any, inoculating effect.

The influence of the rate of cooling of the bath on the temperature of crystallisation was investigated. It was found that so long as the rate was kept reasonably slow, not more than $1°$ in ten minutes, crystallisation always occurred at the same temperature within a few tenths of a degree (compare Jaffé, *Zeitsch. physikal. Chem.*, 1903, **43**, 585). More rapid cooling caused a lowering of the apparent temperature of crystallisation, due probably to the fact that the temperature fall within the bulb lagged somewhat behind that of the surrounding bath. Slower cooling up to about $1°$ in half an hour or more had no appreciable effect on the temperature of crystallisation. The rate generally employed was about $1°$ in fifteen minutes.

Every tube before cooling in the bath was heated in boiling water in order to get rid of all possible solid crystal nuclei. The time during which the tube was heated had apparently no influence on the crystallisation temperature so long as it was more than a certain minimum value of about ten to fifteen minutes, which appeared to be the time necessary to dissolve all traces of solid crystals. A tube heated for periods varying from twenty minutes to three hours would give the same crystallisation temperature at every deter-mination.

The observation of Jaffé (*loc. cit.*), that " the temperature at which spontaneous crystallisation appears sinks very slowly and steadily with the number of times a tube is experimented with," was not confirmed in the present work. The contents of the same tube would crystallise at a definite temperature even after repeated

observations extending over four months. Jaffé, however, used neither solids to promote friction nor mechanical shaking, and his results are therefore perhaps hardly comparable with ours.

The separation of the salt phase from the solution almost always took place in the same way. One or two very small crystals, often visible only through a pocket lens, would appear, and these after a short time would multiply rapidly either at the same temperature or on cooling through one or two tenths of a degree. The detection of the first appearance of the crystals was often a matter of some difficulty, and sometimes of a little uncertainty, since even the garnets would occasionally give rise to very minute, colourless fragments easily confounded with minute salt crystals. They could be distinguished, however, by watching whether they grew or not on lowering the temperature. "Showers" of crystals were only rarely observed, and these only in the more concentrated solutions.

The influence of the solvent action of the water on the glass upon the temperature of crystallisation was investigated, and found to be very small. Two tubes of similar size and shape were made, one of Jena and the other of ordinary glass. Solutions of potassium chloride were prepared and sealed up in the ordinary way, and the crystallisation points determined immediately. They gave salt crystals at $38\cdot2°$ and $29\cdot5°$ respectively. On repeating the experiments four months later, they were found to be $38\cdot2°$ and $29\cdot9°$. Similarly, a tube containing $4\cdot12$ parts of chloride to 100 of water gave ice at $-3\cdot8°$ after four months, whilst a freshly prepared tube containing $3\cdot99$ parts of chloride gave ice at $-3\cdot6°$. The effect of the dissolution of the glass was evidently very small.

Crystallisation of Potassium Chloride.

Table I gives the highest temperatures at which potassium chloride crystallised from aqueous solutions of various strengths. The results
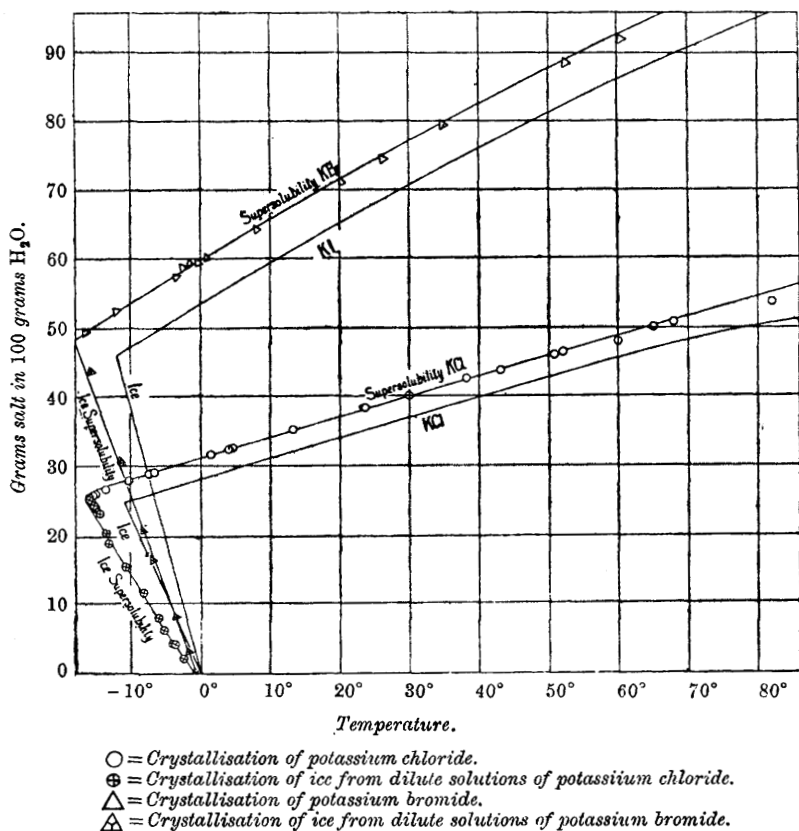
TABLE I.

Grams of potassium chloride in 100 grams of water.	Temperature of crystallisation of potassium chloride.	Grams of potassium chloride in 100 grams of water.	Temperature of crystallisation of potassium chloride.
54·09	81·9°	35·55	13·3°
51·03	67·9	32·75	4·7
50·33	65·0	32·54	4·3
48·32	60·0	31·84	1·2
46·63	52·2	29·08	− 6·5
46·37	50·9	28·92	− 7·4
44 02	43·2	27·93	− 10·2
44·00	43·2	26·72	− 13·5
42·94	38·2	25·97	− 14·9
40·32	29·9	25·87	− 15·2
38·65	23·6	25·54	− 15·5

are plotted in Fig. 1, which shows both the solubility and super-
solubility curves.   The phenomenon of crystallisation was very
definite, successive determinations often agreeing within one-tenth,
and always within three or four tenths, of a degree.   The super-
solubility curve runs practically parallel to the solubility curve at
an average distance from it of 10°.

FIG. 1.

Solubility and supersolubility curves of potassium chloride and bromide in water.

O = *Crystallisation of potassium chloride.*
⊕ = *Crystallisation of ice from dilute solutions of potassium chloride.*
△ = *Crystallisation of potassium bromide.*
⊿ = *Crystallisation of ice from dilute solutions of potassium bromide.*

Crystallisation of Ice from Solutions of Potassium Chloride.—
Table II shows the temperatures at which ice separates spontaneously
from dilute solutions of potassium chloride.   The tubes were at first
shaken in a freezing mixture contained in a vacuum vessel, which
enabled the crystallisation to be observed without removing the
tube from the bath, the cooling being brought about by the addition

of ice or salt when necessary. It was not, however, easy in this way to secure a regular rate of cooling, nor to maintain the temperature uniform throughout the bath. It was therefore abandoned in favour of a well-stirred toluene bath surrounded by a freezing mixture of ice and salt. The production of the ice phase was quite a definite phenomenon, and the temperatures of crystallisation are seen to lie on a well-defined supersolubility curve (Fig. 1). The ice- and potassium chloride-supersolubility curves give rise to a hypertectic point at about $-15 \cdot 7°$. The region in the neighbourhood of the hypertectic point was thoroughly investigated, and a tube containing 25·51 grams of potassium chloride in 100 grams of water gave a mixture of ice and salt crystals at $-15 \cdot 7°$.

The temperature at which ordinary pure distilled water crystallised in tubes containing garnets was found to be $-0 \cdot 6°$, a value agreeing well with those previously obtained: Hartley, Jones, Hutchinson, $-0 \cdot 5°$; Miers, $-0 \cdot 4°$; Jones, $-0 \cdot 7°$.

TABLE II.

Grams of potassium chloride in 100 grams of water.	Temperature of crystallis- ation of ice.	Grams of potassium chloride in 100 grams of water.	Temperature of crystallis- ation of ice.
0·00	$-0 \cdot 6°$	18·77	$-13 \cdot 0°$
2·00	$-2 \cdot 4$	20·40	$-13 \cdot 5$
3·99	$-3 \cdot 6$	23·44	$-14 \cdot 4$
4·12	$-3 \cdot 8$	24·09	$-15 \cdot 1$
6·03	$-5 \cdot 1$	24·30	$-15 \cdot 3$
7·99	$-6 \cdot 0$	24·96	$-15 \cdot 5$
11·73	$-8 \cdot 1$	25·19	$-15 \cdot 7$
15·48	$-10 \cdot 5$	25·51	$-15 \cdot 7$

Crystallisation of Potassium Bromide.

The temperatures of spontaneous crystallisation of solutions of potassium bromide are given in table III, and are plotted in Fig. 1. The character of the phenomena was quite similar to that in the case of the chloride.

The supersolubility curve runs almost exactly parallel to the

TABLE III.

Grams of potassium bromide in 100 grams of water.	Temperature of crystallisation of potassium bromide.	Grams of potassium bromide in 100 grams of water.	Temperature of crystallisation of potassium bromide.
112·90	$107 \cdot 0°$	64·39	$8 \cdot 1°$
92·18	$60 \cdot 4$	60·61	$0 \cdot 9$
88·78	$52 \cdot 6$	59·89	$-0 \cdot 1$
79·85	$34 \cdot 9$	59·64	$-1 \cdot 3$
77·49	$30 \cdot 5$	58·96	$-2 \cdot 3$
74·97	$26 \cdot 2$	57·37	$-3 \cdot 5$
71·72	$20 \cdot 2$	52·79	$-11 \cdot 9$
67·61	$12 \cdot 1$	49·60	$-16 \cdot 4$

solubility curve at an average distance from it of about 12°.   The
data for both the ice and salt solubility curves at temperatures
below 0° are contradictory and untrustworthy.   In drawing the
curves the average values given by Seidell have been adopted.

Crystallisation of Ice from Solutions of Potassium Bromide.—
Table IV gives the temperatures of spontaneous crystallisation of
ice from dilute solutions of the bromide; they are plotted on Fig. 1,
where the ice- and salt-supersolubility curves are seen to intersect
at the hypertectic temperature of about −18°, the solution then
containing about 49 parts of salt to 100 of water.

TABLE IV.

Grams of potassium bromide in 100 grams of water.	Temperature of crystallisation of ice.	Grams of potassium bromide in 100 grams of water.	Temperature of crystallisation of ice.
0·00	− 0·6°	21·00	− 8·2°
3·12	− 1·9	31·15	− 11·3
8·17	− 3·5	44·01	− 15·3
16·49	− 6·8		

Crystallisation of Potassium Iodide.

In the case of the iodide the "metastable region" appears to be
considerably smaller than in the case of the chloride and bromide,
namely, about 3° as against 10° and 12°.   This made the detection
of the first crystals a matter of greater difficulty, since the "relief
of supersaturation" on crystallisation was relatively much smaller.
Moreover, the crystallisation was a comparatively slow process.   The
first crystals to appear were only visible through a lens, and always
very few in number; they did not themselves grow rapidly, nor as
a rule induce rapid crystallisation through the rest of the solution.
It was often, in fact, necessary to lower the temperature a few
tenths of a degree to make certain that the crystals would grow.
Successive determinations of the temperature of first appearance of
the crystals, however, gave quite concordant results.   For example,
tube No. VI (179·6 parts of potassium iodide to 100 parts of water)
gave crystals at 63·0°, 63·0°, 63·1° in successive experiments;
No. VII (173·7) gave crystals at 54·7°, 55·0°, 55·0°; No. VIII (186·7)
gave crystals at 71·8°, 71·7°, 71·7°; No. XIII (141·7) crystallised
between 14·2° and 15·3° (preliminary determination), at 14·5° (not
at 14·9°), at 14·6° (not at 14·8°).   All the tubes showed after heating
that hydrolysis had taken place by the brown colour of the liberated
iodine; and this was the more noticeable in the more highly con-
centrated solutions.   The amount of chemical action was, however,
probably not sufficient materially to affect the temperature of
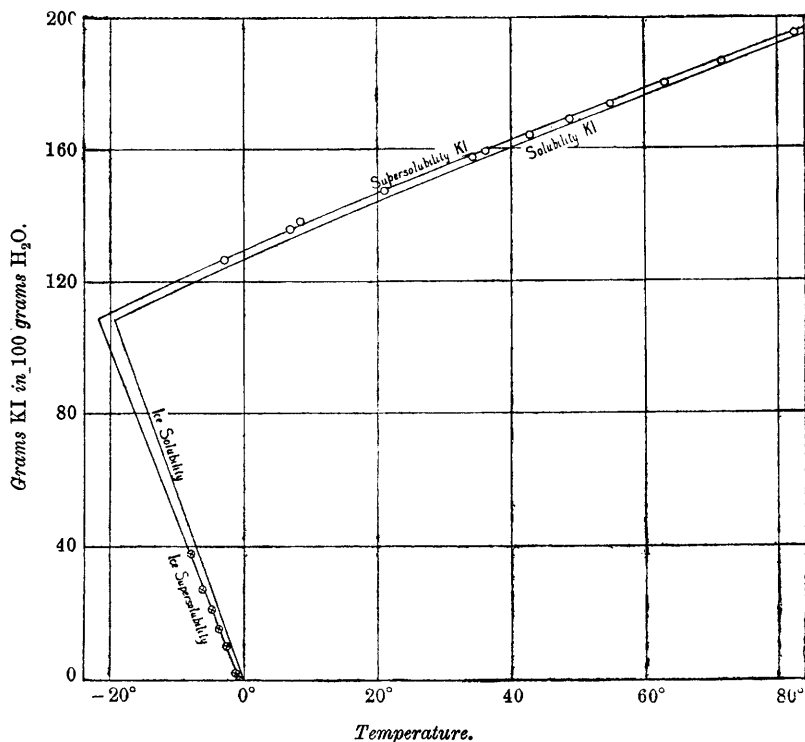crystallisation.

The results are given in table V and plotted in Fig. 2, where the supersolubility curve is seen to be nearly parallel to the solubility curve.   As in the case of the bromide, the ice- and salt-solubility curves given in the figure are based on rather discordant data.

FIG. 2.

Solubility and supersolubility curves of potassium iodide in water.

Temperature.

$\bigcirc$ = *Crystallisation of potassium iodide.*
$\oplus$ = *Crystallisation of ice from dilute solutions of potassium iodide.*

TABLE V.

Grams of potassium iodide in 100 grams of water.	Temperature of crystallisation of potassium iodide.	Grams of potassium iodide in 100 grams of water.	Temperature of crystallisation of potassium iodide.
195·3	82·7°	157·7	34·2°
186·7	71·7	147·2	21·1
179·6	63·1	145·9	19·5
173·7	55·0	141·7	14·6
169·2	48·9	138·0	9·4
164·3	43·0	135·7	7·0
159·3	36·2	126·9	− 2·9

Crystallisation of Ice from Solutions of Potassium Iodide.—The results are given in table VI, and are plotted in Fig. 2. The ice- and salt-supersolubility curves would seem to meet on prolongation at a hypertectic point of about $-22°$, the solution at that temperature having a concentration of about 108·5 parts of salt to 100 of water.

TABLE VI.

Grams of potassium iodide in 100 grams of water.	Temperature of crystallisation of ice.	Grams of potassium iodide in 100 grams of water.	Temperature of crystallisation of ice.
0·00	$-0·6°$	21·51	$-4·8°$
1·94	$-1·3$	27·20	$-6·3$
10·18	$-2·8$	37·84	$-7·8$
15·30	$-3·9$		

The work was done in the laboratories of the Government and Forman Christian Colleges, Lahore, India.

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