LXI.—*The Hydrates of Sodium, Potassium, and Lithium Hydroxides.*

By Spencer Umfreville Pickering, M.A., F.R.S.

One of the chief reasons which induced many chemists to look with distrust on the conclusions I drew from my work on sulphuric acid was the large number of the hydrates represented as existing in solution. Possibly no exception would have been taken if these hydrates had not exceeded four or five, but the existence of some 18 or 20 was regarded as highly improbable, although, as a matter of fact no data existed on which an estimate of the probable number present in such a case could be based. The ground of this objection, however, will be removed if it is found that in other cases a similarly large number of hydrates not only exist, but can be extracted from the solution in a solid, crystalline condition.

Sodium hydroxide has been found to be thus prolific in crystalline hydrates. In the case of sulphuric acid, between the limits of 1 and $7H_2O$ (inclusive) to each H_2SO_4, indications of five hydrates in solution (two of them isolable) were obtained, whereas between these same limits, in the case of sodium hydroxide, no less than eight have been actually isolated, and it is very probable that two others which have not been isolated also exist within these limits.

The results with this substance are given in Table I and Fig. 1. The determinations were made in the manner already described (this vol., p. 144): a small quantity of a strong solution was taken and diluted by successive additions of water; the amount of water added being determined by measuring it, and also by weighing the tube, with its contents, at intervals, and, as a further precaution, the solution obtained at the end of each series was titrated. The soda used was made from sodium.

In the table, each series is distinguished by a different Roman numeral, and different portions of the same series will be found in different parts of the table, according to which hydrate crystallises from the solution in question.

A glance at the figure will show that it is made up of a series of independent curves; each of these represents the crystallisation of a different hydrate, except in the region from 0 to 20 per cent., throughout which water crystallises. The elaboration of such a complicated figure was naturally a work of considerable time and labour. The first series performed in the region where the complications exist (Series II) gave only two or three points on each of the curves, and the result was an apparently hopelessly irregular figure; but, from the appearance of the crystallisation, it was evident that

FIG. 1.—Freezing Points of Solutions of Sodium Hydroxide.
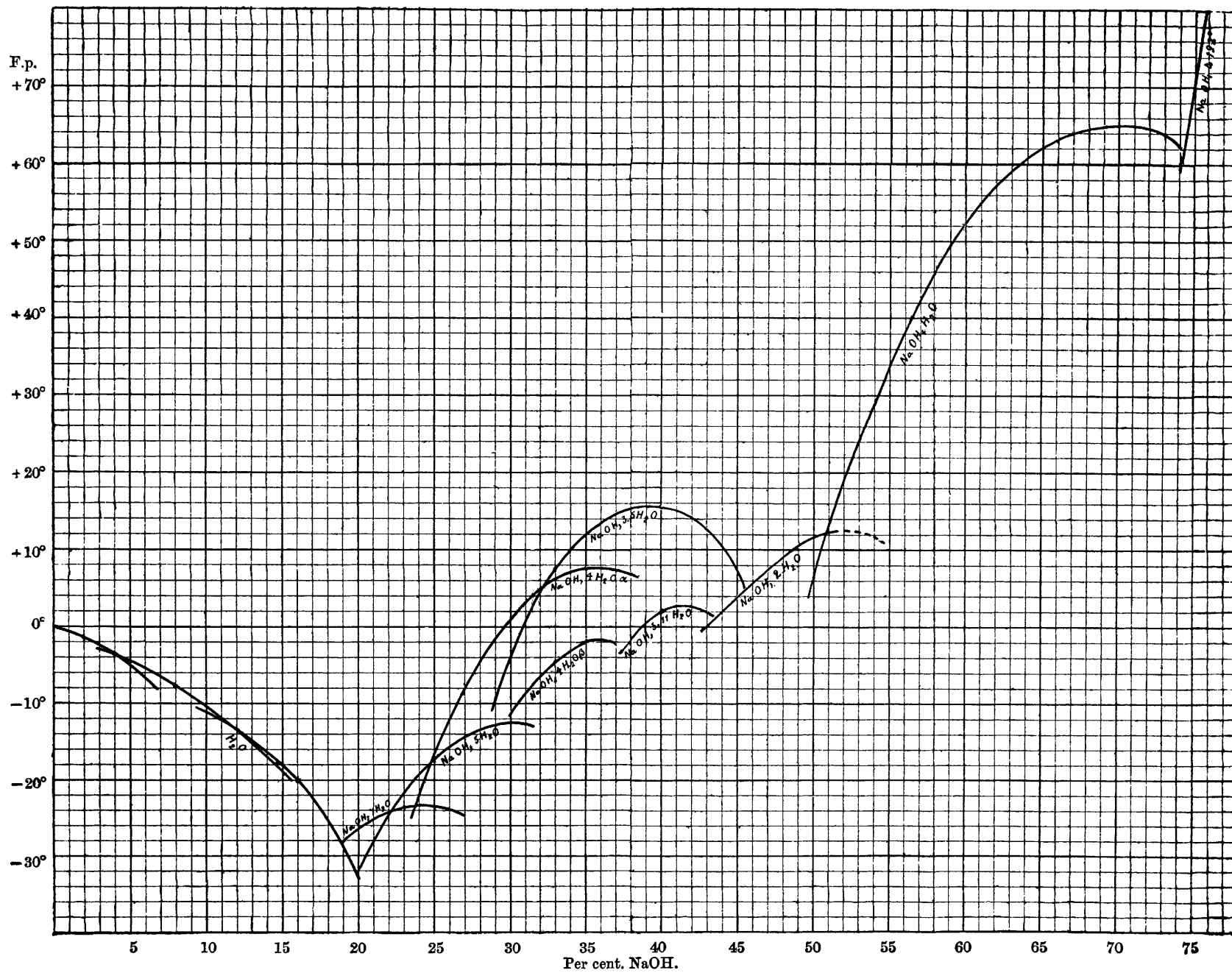
the same substance was not separating throughout, and another fuller series was performed, which led to the performance of yet other and fuller series, till before the nature of the figure was successfully elucidated no less than 34 series, comprising nearly 500 determinations, had been made.

The first few series were made with an alcohol thermometer, which, owing to the difficulty which there generally is in observing the moment when the crystals are all but melted in the liquid (the true freezing point), yields results as concordant as a mercurial one does. Its use, however, has this disadvantage, namely, that sometimes the temperatures obtained in a series on one occasion will be throughout uniformly lower or higher than those obtained on another occasion. This is not due to any alteration in the zero point, as the latter was determined at the end of each series, but probably to the fact that an alcohol thermometer with a large bulb always lags perceptibly behind the temperature of the liquid in which it is immersed, and as the temperature of the latter may rise at different rates on different occasions, the lag of the thermometer may also be different. From this cause the series with the alcohol thermometer should each be treated separately for diagrammatic purposes, and the actual temperatures indicated are always somewhat doubtful. These remarks do not apply to the series with the mercurial thermometers : they are marked by asterisks in the tables.

In observing the freezing points in the present case, we have most of the difficulties which are usually met with in such cases : viscous liquids which tend to become filled with air-bubbles, and prevent accurate observation of the moment when the crystals are just disappearing, also the invisibility of the crystals, owing to their refractive index being nearly the same as that of the liquid. In addition to these we have the fact that several different crystallisations may take place in the same liquid, and that to obtain the one required in a particular instance necessitates care and experience, and even then is often attended with provoking failure. When a particular crystallisation occurred, which happened to be the one required, and of which the curve had to be followed, care was taken that the crystals were never entirely melted while taking the freezing point, and while more water was being added; in this way the same crystallisation was ensured throughout the series. At temperatures below about $-15°$, this method of procedure was impossible, as the water which was added congealed on the thermometer bulb, and the liquid had to be heated to nearly $0°$ before it could be melted. Attempts were made to work in the opposite direction, that is, to start with a weak solution and add successive amounts of a stronger solution, but these attempts failed, as the drops of this strong solution crystallised

before they became mixed with the weaker solution, and caused the whole to crystallise as some hydrate other than the one required. The only successful method of working was found to be to touch off each solution separately with some of the required crystals kept at a suitable temperature for the purpose.

It was eventually ascertained that when any solution from which two or more crystallisations are possible is cooled to a very low temperature, or is kept for some time at a moderately low temperature, those crystals are obtained of which the freezing point is highest. For instance, liquids from 22·5 to 25 per cent., when thus treated, always yield the pentahydrate, and not the hepta- or tetra-hydrate, and they may be used for touching off other liquids in order to obtain the rest of the pentahydrate curve (see Fig. 1). The knowledge of this fact can naturally, however, be properly utilised only after the general nature of the results has been fairly well elucidated, and this preliminary elucidation is the main difficulty. It would be almost an impossibility, if the appearance of the crystallisation did not help in showing when the substance crystallising changed. After a little practice we can tell with certainty when the change occurs, the grittiness, flocculence, opacity, or size of the crystals being the main features in which one hydrate differs from another. These terms, of course, have but a relative meaning, as crystals which appear flocculent when separated during the rapid cooling of a small mass of liquid might be hard and gritty if formed slowly in larger masses; nevertheless, they describe with sufficient accuracy the very palpable changes which occur in determinations such as the present.

The determinations vary in accuracy, not only according to the nature of the hydrate crystallising, but also according to which portion of any particular curve is being examined. Near the maximum part of a curve small differences of temperature produce comparatively less effect on the amount of crystals present, and the determinations are proportionately more accurate.

The composition of the hydrates was determined by ascertaining the strength of solution which gave the maximum freezing point. This maximum must correspond with the composition of the crystallising substance (see this vol., p. 142).

The position of various maxima are given in Table II, and with two exceptions, which will be discussed separately, they coincide almost exactly with simple molecular proportions: the differences range only from 0·005 to 0·03 H_2O, or from 0·02 to 0·27 in the percentage of anhydrous soda present. The positions were determined from the smoothed curves drawn with the help of a bent lath through the experimental points.

The maxima can, in most cases, be attained only by performing

special series—using the "touching off" method, if necessary—for the purpose, except in the cases of the hydrates with H_2O, $3 \cdot 11H_2O$, and $4H_2O\ \beta$, where the maxima are attained without using any special methods. When a full series of determinations is made with solutions of successive strengths from 70 per cent. downwards, we get freezing points of the other hydrates on the left-hand branches of the curves only (see Fig. 1). The hydrates marked $NaOH,H_2O$, $2H_2O$, $3 \cdot 11H_2O$, and $4H_2O\ p$ crystallise in succession, the freezing points falling on the whole throughout, then at about 32 per cent. there is a sudden rise from $-5°$ to $+5°$, when we get the hydrate $NaOH,4H_2O$ crystallising; then the pentahydrate crystallises, and a point or two on the heptahydrate curve may or may not be obtained accidentally. At about 20 per cent. the crystallisation of water begins, and the freezing points gradually rise to $0°$.

The $3 \cdot 5H_2O$ hydrate is not usually obtained, though it may always be obtained by excessive cooling. It is the only one of the hydrates here isolated which have been previously described. It was obtained by Rose in 1863, and again by Hermes (*Ann. Phys. Chem.*, **119**, 170), though it was not fully examined by either of them. Hermes gives its melting point as $7 \cdot 0°$, whereas it is really $15 \cdot 5°$; and he also differs from Rose as to its crystalline form. It is possible that what he obtained and analysed was the tetrahydrate (m. p. $7 \cdot 6°$) contaminated with mother liquor.

Starting with the strongest solutions, and a freezing point of $+192°$, we get what is probably *anhydrous soda*, or some low hydrate crystallising. This portion of the figure, however, I have examined only superficially. The freezing points from $+192°$ to $+60°$ form an approximately straight line.

The *monohydrate* then crystallises, the freezing points rising to $+64 \cdot 3°$ and subsequently falling to $+4 \cdot 5°$. This hydrate crystallises very easily in large, pointed, and semi-transparent crystals. It is surprising that no description of it has yet been published, for it always forms in large crystals whenever a hot concentrated solution of soda is allowed to cool. Professor Dunstan informs me that it was obtained and analysed in his laboratory some years ago. Series I was of too rough a character to afford any satisfactory evidence as to the position of the maximum.

The *dihydrate* crystallises in semi-transparent crystals, much less well formed than the monhydrate, and they do not feel at all gritty when rubbed against the tube. The various determinations in this case are only of an approximate character, for the separation of the crystals is, especially in the stronger solutions, accompanied by the formation of a mass of air bubbles which renders accurate observations impossible.

In this case (the only case in the whole series), it was not found practicable to extend the results quite as far as the maximum. The position of this maximum, which is obtained by extending the figure formed by the determinations by a bent lath curve, must, therefore, be doubtful, the exactness of the concordance which it shows with the composition of the dihydrate being a chance; but I do not think that there can be much doubt that the hydrate really is the dihydrate.

The next hydrate is one to which special interest attaches. The mean position of the maximum is at 41·68 per cent., which is not far from the composition of a trihydrate, this containing 42·55 per cent. But I do not think that it is possible to regard it as such : of the six series which are available for the determination of the maximum, every one gives its position to be very appreciably lower than 42·55 per cent., and the three series with the mercurial thermometer, which were performed with special care, clearly show that the freezing points at 42 to 43 per cent. are lower than those at 41 per cent. Moreover, the accuracy with which the maxima in the case of other hydrates coincide with simple molecular proportions precludes the idea of there being any mistake as to the composition of the solution which would amount to a whole unit in the percentage values.

We can but conclude, therefore, that the hydrate is one of complex character. All the series are very concordant, those with the mercurial thermometer especially so, and the mean value given for the position of the maximum (allowing half weight to those series made with an alcohol thermometer) is 41·677 per cent., which represents exactly $9NaOH,28H_2O$. Such a composition may appear, according to our present notions, to be somewhat improbable, but if we represent the hydrate as a compound of the tetrahydrate with a trihydrate not yet isolated, the improbability disappears, the hydrate becoming a comparatively simple compound of $8(NaOH,3H_2O)$ with $NaOH,4H_2O$. Additional countenance is given to this view by the fact that we have another hydrate which either is, or may be regarded as, a molecular compound of these two hydrates, namely, $NaOH,3·5H_2O$ or $NaOH,3H_2O + NaOH,4H_2O$. The actual isolation of a hydrate of this complex character is of special interest in connection with my work on sulphuric acid, for I found two breaks indicating the existence of complex hydrates containing about 6 mols. of the monohydrate to 1 of sulphuric acid and to 1 of water respectively.

This hydrate forms in very bulky, transparent crystals, which feel only very slightly gritty.

The 3·5-*hydrate* forms large, well-defined, transparent and gritty crystals. The curve representing its crystallisation extends over a considerable region, as will be seen from Fig. 1.

The existence of two different *tetrahydrates* is another matter of considerable interest. It was thought, at first, that one of them was the tetrahydrate and the other a complex hydrate differing from it but slightly in composition. But if this is so the difference is too slight for detection in experiments such as the present, and is certainly less than $0.05H_2O$. The two series which are most to be relied on for the position of the maxima in the two cases are XXII and XVIII respectively, and they each give exactly the same value, namely 35·8 per cent., corresponding with $NaOH,3.985H_2O$. (Series XIX and IX have not been included in the means in Table II owing to their meagreness.)

The freezing points of the two tetrahydrates differ considerably, being $+7.57°$ and $-1.7°$ respectively. Both hydrates form in small, acicular crystals, those of the α-hydrate (that with the highest melting point) being considerably more gritty than those of the β-hydrate.

It is an interesting matter for speculation as to what the difference between two such hydrates can be, whether it is a difference of molecular structure or whether it is a case of polymerisation, and, if so, whether it occurs in the liquid hydrate or in the solid hydrate only. The fact that the freezing point of the α-tetrahydate is exceptionally high as compared with the other hydrates, and that it appears to be more analogous to the 3·5-hydrate, which must contain at least $2NaOH$, suggest, at first sight, that it may be a polymeride containing also $2NaOH$, that is, $2NaOH,8H_2O$. But the position of the 3·11-hydrate does not bear out the suggestion that a complexity of structure is accompanied by a rise in the freezing point, and we know so little about the freezing points of any series of hydrates that we are scarcely justified in even speculating on the subject.

There seem to be other instances known of the existence of two modifications of the same hydrate. One is in the case of calcium chloride, and there also it is the tetrahydrate (Lefévre, *Compt. rend.*, **70**, 684; Hammerl, *Wien Sitzungsber.* II. *Abth.*, **72**, 667; and Rooze-boom, *Rec. Trav. Chim.*, **8**, i, 9), but the freezing point curves in this case were not traced up to their maxima, and the analyses on which the composition of the crystals were based would not have distinguished between a tetrahydrate and a moderately complex hydrate approaching it in composition. There are also said to be two modifications of the heptahydrate of sodium carbonate, having different solubilities, and in connection with these I may recall my own observations as to the evidence of three modifications of the anhydrous double sulphates of the type $M''SO_4,K_2SO_4$ (Trans., 1886, **49**, 1) and of two modifications of anhydrous sodium sulphate (Trans., 1884, **45**, 686).

The *pentahydrate* forms in crystals which feel only slightly gritty near the maximum of the figure, and not gritty at all in the lower regions of the curve; here they appear as a fine opaque crystallisation, which is easily distinguishable from the *heptahydrate*, which forms small, gritty and non-transparent crystals.

From Table II it will be seen that the maximum attained by the pentahydrate (30·03 per cent.) does not coincide exactly with the calculated composition of such a hydrate, which is 30·77 per cent., and it is most probable that we have here another case of a complex hydrate similar to the 3·11-hydrate.   But the difference in the percentage composition between the values found and those calculated for a simple molecular proportion is smaller than in the former case, and, owing to the more gradual manner in which the maximum is attained, there is greater difficulty in determining its exact position. I have thought it safer, therefore, not to insist on the reality of the difference observed, but to regard this hydrate provisionally, at any rate, as a pentahydrate.   The mean position of the maximum found corresponds to $NaOH, 5\frac{2}{11}H_2O$, or a complex hydrate, which might be represented as consisting of 10 mols. of a pentahydrate, united with 1 mol. of the heptahydrate.   If this is really its composition, then there would also exist a pentahydrate which has not been isolated.

Between 19·9 and 20·5 per cent. (see Table I), four freezing points were observed, which did not appear to belong to any of the crystallisations described so far.   They gave a very opaque, flocculent crystallisation, more nearly approaching in appearance to that of water than to that of the hydrates, but not nearly so opaque as that of water, and easily distinguishable from it.   The three consecutive determinations in Series X suggest that the maximum of this crystallisation is at about 20·2 per cent., and the hydrate might be a nonohydrate, which contains 19·80 per cent.   The observations, however, are too few in number to permit of any feeling of certainty as to the reality of this as a separate crystallisation.

From about 20 per cent. downward water crystallises, and the curve which represents the results indicates the existence of two well marked changes of curvature at about 12·3 and 4 per cent respectively; these correspond to hydrates containing 16 and $53H_2O$.

In the figures representing the crystallisation of the various hydrates, indications of changes of curvature may also be seen (though to simplify matters I have not depicted them in the woodcut), and these indications occur at points corresponding with the composition of hydrates which have actually been isolated.   Thus, in the curve of the 3·5-hydrate, there are changes of curvature corresponding with the 3·11-hydrate and the tetrahydrate ; also the curve

of the α-tetrahydrate shows a break corresponding to the pentahydrate, indeed, I was led to infer the existence of the pentahydrate from this break long before I ascertained that I had actually isolated it. Thus further evidence is obtained, unintentionally in this case, of the connection between changes of curvature and existing hydrates. There appear to be some indications both in the pentahydrate and heptahydrate curves of a break corresponding to an octohydrate, but there are none corresponding to a hexahydrate, the absence of which in such a complete series is very noticeable.

I have already pointed out (Trans., 1890, **57**, 340) that when we extract a hydrate from a solution, we have a very strong argument that some molecules of that hydrate exist in the solution. The only alternative hypothesis is that the water and the substance are thrown out of the solution the instant these combine together, that is, that the hydrate is insoluble, a most unacceptable view, even if we did not know that whenever two substances are thrown out at the moment of their combination with each other, as in the precipitation of insoluble salts, they are invariably thrown out in the amorphous, and not in the crystalline condition. We may safely conclude, therefore, that in solutions of soda we have, at least, as many hydrates, eight, as have been extracted from the solutions, and, as a very superficial study of the literature on hydrates will show that hydrates are often obtained from solutions only under special conditions, it is highly improbable that by the simple means adopted in the present case we should have succeeded in isolating all the existing hydrates. Indeed there are good grounds for concluding that there are three more hydrates, the trihydrate and the two higher hydrates indicated by the breaks in the water curve, and some grounds for concluding that there are yet three others, those with 5, 8, and $9H_2O$. The possible total is thus 14, and this is in a case where only three-quarters of the whole available range of solutions has been investigated, and where also no suitable examination of the extreme dilute solutions has been made, which solutions in the case of sulphuric acid I found to be prolific in hydrates. This will show that there is no improbability attaching to my former conclusions that sulphuric acid in the whole range of its solutions forms about 20 hydrates, especially when we remember that sulphuric acid is a substance which, as far as we can tell, possesses a much stronger affinity for water than soda does. Why in the case of soda such a much larger number of hydrates should be isolable than in that of sulphuric acid we do not know; it is probably dependent on some peculiar property of sodium in combination, for sodium salts generally, as is well known, are especially prolific in hydrates.

There is one other very important point on which the present

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experiments throw some light, namely, the number of hydrates co-existing in a solution of a given strength. In some cases as many as four hydrates have actually been obtained from the same solutions (30—32 per cent.), and if the curves representing the various crys-tallisations had been followed further (and we may prolong them with a bent lath with a fair degree of certainty), it is evident that often five, and perhaps sometimes six, hydrates could have been separated from, and therefore must have existed in, the same solu-tions. Hence, solutions must be very complicated in their con-stitution, and this is why Mendeléeff's theory as to the rectilineal character of the rate of change of the densities with change of percentage composition should have proved to be incorrect (see Trans., 1887, **51**, 779; 1890, **5 7**, 79), since it was founded on the sup-position that only two hydrates were present simultaneously in a given solution.*

Potassium Hydroxide.

The results with potash are of a much simpler character than those with soda. They are given in Table III and Fig. 2, ABC.

Three hydrates only were obtained, containing 1, 2, and $4H_2O$ respectively; their freezing points were $+143°$, $+35.5°$, and $-32.7°$ (mean of $-32.45°$ and $-33.0°$). Of these the dihydrate is the only only one which has been previously described† (Walter, *Pogg. Ann.*, **39**, 192). Solutions containing less water than the monohydrate were not investigated.

The *monohydrate* crystallises in large, radiating crystals. The maximum of the freezing points is reached at 76.3 per cent., which represents $KOH,0.97H_2O$, the monohydrate requiring 75.68 per cent.

The *dihydrate* forms in small, gritty crystals. The maximum obtained by prolonging the curve with a bent lath is found to be at 60 per cent., representing $KOH,2.08H_2O$; the theoretical percentage is 60.87. If this hydrate had not been previously known, the present experiments would scarcely have been sufficient to establish the position of the maximum with certainty.

The *tetrahydrate* crystallises in large, transparent crystals, and its crystallisation extends over but a small region. The maximum is just attained before the crystallisation of the dihydrate begins. The two series gave 44.3 and 44.0 per cent. respectively (mean 44.15) as

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* I feel somewhat doubtful whether it would be rectilineal even if two hydrates only were present.

† Mendeléeff in his *Principles of Chemistry* (English translation, **1**, 542, foot-note), speaks of $KOH,4H_2O$ as being the hydrate of potash which has been isolated. This is evidently a misprint for $KOH,2H_2O$, or else a mistranslation of the old formula $KO,5HO$.

the position of the maximum. This corresponds with $KOH,3\cdot94H_2O$, the theoretical composition of the tetrahydrate being $43\cdot75$ per cent. Attempts were made by cooling in various ways to obtain another modification of the tetrahydrate similar to that existing in the case of soda, but without success.

FIG. 2.—Freezing Points of Solutions of Potassium and Lithium Hydroxides.
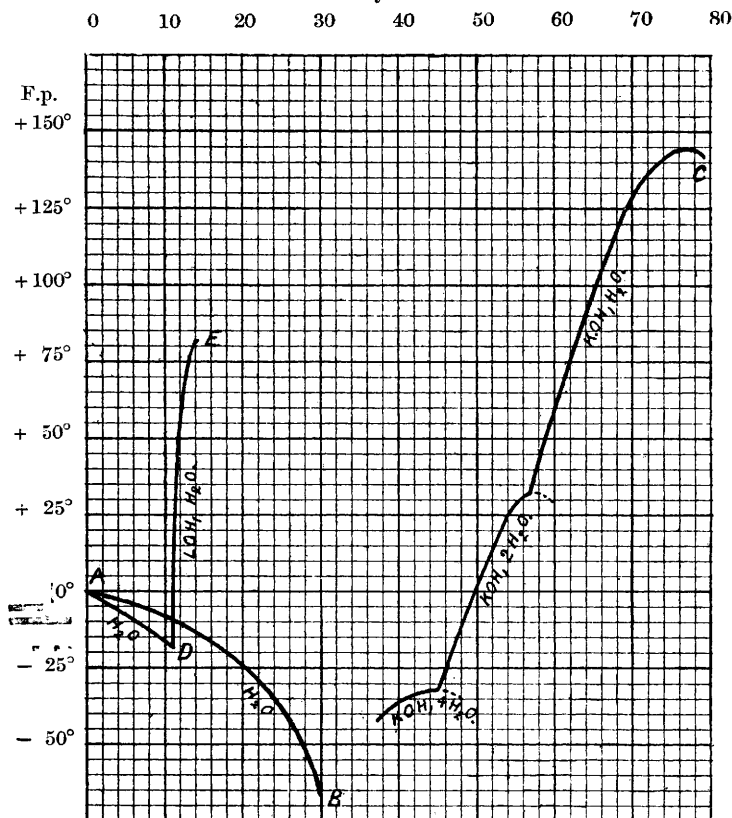
After the tetrahydrate, water crystallises, and the curve obtained does not show any special peculiarities; it was not, however, investigated very fully.

Lithium Hydroxide.

The results with lithia are still simpler than those with potash. Water crystallises from 0 to 11 per cent. (see Table IV and Fig. 2,

TABLE I.—*Freezing Points of Aqueous Solutions of Sodium Hydroxide.*

Per cent NaOH.	F. p.	Per cent. NaOH.	F. p.
The anhydrous (?) hydroxide crystallises— I.*		The monohydrate crystallises—*cont.* XII.*	
		72·06	+63·5
		70·76	+64·3
83·87	+192	69·37	+64·4
81·09	+159	67·92	+64·2
78·51	+110	66·45	+63·23
75·83	+ 80	64·61	+61·0
74·15	+ 60	62·85	+57·8
		60·55	+53·0
		57·95	+45·75
The monohydrate crystallises— I.*		55·13	+34·75
71·17	+ 63	The dihydrate crystallises— II.	
68·45	+ 64	49·11	+10·3
66·37	+ 63	45·78	+ 4·8
64·27	+ 61		
62·06	+ 55·5	III.	
59·20	+ 49	49·24	+10·0
		47·65	+ 7·0
		46·04	+ 5·0
II.*		44·37	+ 2·3
71·59	+ 64·5	42·77	(
69·85	+ 65·5		
67·45	+ 64·5	V.	
64·87	+ 61·5	49·07	+11·75
62·13	+ 55·55	48·57	+11 0
		48·10	+10·4
		47·59	+ 8·0
V.		47·03	+ 6·85
51·70	+ 18	46·52	+ 6·8
50·99	+ 13·5	46·01	+ 6·5
50·34	+ 9·0		
49·70	+ 4·5	VI.	
		46·76	+ 7·2
		45·71	+ 5·85
XI.*		44·60	+ 4·35
		43 54	+ 2·5
67·67	+ 63·3		
66·04	+ 62·25	VII.	
64·61	+ 61·05	49·95	+10·7
62·98	+ 58·4	49·26	+10·9
61·31	+ 55·1	48·59	+ 9·9
59·31	+ 50·2	47·95	+ 9·05
57·76	+ 44·65	47·30	+ 7·8
56·44	+ 40·25	46·72	+ 6·8
		46·06	+ 4·6
		45·42	+ 3·9
		44·77	+ 2·9
		43·90	+ 1·5
		42·97	+ 0·35

* A mercurial thermometer was used in these series.

TABLE I—*continued.*

Per cent. NaOH.	F. p.	Per cent. NaOH.	F. p.
The dihydrate crystallises—*cont.* VIII.		The 3·11-hydrate crystallises—*cont.* VII.	
51·70	+ 12·7	42·97	+ 2·1
50·72	+ 11·7	42·47	+ 2·9
49·81	+ 11·6	41·95	+ 2·9
49·05	+ 10·35	41·45	+ 2·9
47·89	+ 9·4	40·90	+ 2·35
47·02	+ 8·7	40·37	+ 1·85
46·22	+ 6·7	39·81	+ 1·1
45·39	+ 5·3	39·21	+ 0·4
44·60	+ 3·5	38·42	− 0·55
43·74	+ 1·3	37·67	− 1·8
XV.		VIII.	
		42·95	+ 1·8
		42·30	+ 2·6
43·95	+ 1·6	41·67	+ 2·1
		41·00	+ 2·3
XVII.		40·27	+ 2·3
		39·61	+ 1·2
44·01	+ 2·1	38·98	+ 0·15
43·42	+ 1·3	XV.*	
		43·25	+ 2·00
		42·50	+ 2·60
The 3·11-hydrate crystallises— II.		41·79	+ 2·75
		41·08	+ 2·53
		40·37	+ 2·25
42·16	+ 2·8	39·69	+ 1·38
38·47	− 2·2	38·74	+ 0·20
		37·34	− 2·0
III.		XVII.*	
41·26	+ 2·5	42·71	+ 2·19
40·31	+ 1·5	42·09	+ 2·61
39·04	+ 0·5	41·35	+ 2·68
37·67	− 2·5	40·64	+ 2·43
		39·95	+ 2·00
V.		39·32	+ 1·49
		38·72	+ 0·50
42·50	+ 3·0	38·05	0
41·97	+ 3·0	XVIII.*	
41·44	+ 2·9	37·66	− 1·72
VI.		XXI.*	
42·48	+ 2·5	43·54	+ 1·35
41·45	+ 3·1	42·72	+ 2·3
40·44	+ 3·0	41·94	+ 2·7
39·53	+ 1·8	41·14	+ 2·63
38·55	+ 0·25	40·31	+ 2·3
37·68	− 0·7		

TABLE I—*continued.*

Per cent. NaOH.	F. p.	Per cent. NaOH.	F. p.
The 3·5-hydrate crystallises— V.		The *a*-tetrahydrate crystallises— III.	
45·52	+ 7·0	31·29	+ 2·7
44·96	+ 9·3	30·21	+ 1·35
44·38	+ 11·05	29·13	− 2·0
43·76	+ 12·3	28·16	− 4·0
43·18	+ 12·3	27·19	− 6·0
42·50	+ 14·0	26·20	− 9·85
		25·47	−12·6
		24·64	−18·25
XIII.*			
41·86	+ 14·95	IV.	
40·80	+ 14·9		
39·51	+ 15·35	26·12	−13·2
38·22	+ 15·25		
37·02	+ 14·5	IX.	
35·51	+ 13·2		
34·12	+ 10·95	31·23	+ 2·4
32·64	+ 7·03	30·82	+ 2·1
31·04	+ 0·3	30·38	+ 1·65
29·50	− 4·2	29·95	+ 0·7
		29·53	− 0·15
XVI.*		29·10	− 1 62
44·80	+ 8·75	28·70	− 2·6
44·22	+ 10·75	28·31	− 4·0
43·60	+ 12·0	27·90	− 5·3
42·96	+ 13·25	27·46	− 6·35
42·28	+ 13·95	26·94	− 8·75
41·60	+ 14·5	26·42	−10·5
40·98	+ 15·2	25·92	−12·8
40·34	+ 15·5	25·46	−14·95
39·63	+ 15·5	24·95	−17·2
38·99	+ 15·6		
38·32	+ 15·6	X.	
37·52	+ 15·25		
36·65	+ 14·5	25·72	−14·1
35·77	+ 13·4		
34·70	+ 11·75	XIV.*	
33·68	+ 9·5		
32·39	+ 6·5	26·91	− 8·45
30·84	+ 2·0	26·25	−10·3
		25·58	−13·65
XX.*		24·97	−16·75
34·02	+ 10·1	24·33	−19·1
32·97	+ 7·0	23·80	−21·35
31·82	+ 3·9		
30·58	− 1·1		
29·58	− 6·45		
29·07	− 8·75		

TABLE I—*continued.*

Per cent. NaOH.	F. p.	Per cent. NaOH.	F. p.
The α-tetrahydrate crystallises—*cont.* XIX.*		The β-tetrahydrate crystallises— II.	
34·02	+ 6·7	34·78	− 2·1
34·02	+ 6·8	32·54	− 5·85
33·18	+ 6·4	29·85	−14·45
32·58	+ 5·95		
31·98	+ 5·2		
31·38	+ 4·33	III.	
30·89	+ 3·3		
30·31	+ 1·9	36·54	− 2·15
29·76	+ 1·27	35·74	− 1·8
29·14	− 1·05	35·03	− 1·95
28·68	− 2·05	34·19	− 2·5
28·22	− 3·95	33·35	− 3·6
27·69	− 5·27	32·49	− 5·7
26·90	− 7·1	31·29	− 7·5
25·94	−12·25		
25·06	−17·4		
		VI.	
XXI.*		36·76	− 1·7
		35·93	− 1·0
37·05	+ 7·3	35·10	− 0·95
36·41	+ 7·47	34·20	− 1·5
35·97	+ 7·6	33·17	− 2·18
35·47	+ 7·55	31·74	− 4·8
34·93	+ 7·4	30·18	− 7·95
34·35	+ 7·2		
33·66	+ 6·83	IX.	
32·92	+ 6·05		
		34·17	− 3·3
		33·06	− 4·35
XXII.*		32·09	− 5·9
		31·23	− 7·9
38·25	+ 6·6		
37·50	+ 7·08		
36·80	+ 7·4	XV.*	
36·10	+ 7·55		
35·42	+ 7·54	35·45	− 1·65
34·71	+ 7·35	33·01	− 3·75
33·99	+ 7·00	31·51	− 7·08
33·26	+ 6·50		
XXVIII.*		XVIII.*	
		37·14	− 2·25
27·72	− 6·3	36·64	− 1·93
27·28	− 8·15	36·14	− 1·8
26·75	−10·25	35·61	− 1·75
26·50	−12·0	35·13	− 1·9
25·47	−15·58	34·67	− 2·1
		34·24	− 2·5
		33·78	− 2·85

TABLE I—*continued.*

Per cent. NaOH.	F. p.	Per cent. NaOH.	F. p.
The pentahydrate crystallises— II.		The pentahydrate crystallises—*cont.* XXVI.*	
25·16	−18·2	28·26	−13·1
23·31	−21·7	27·80	−13·2
III.		27·24	−13·8
22·03	−25·5	26·48	−15·1
		25·42	−16·3
IV.		XXVII.*	
25·34	−16·7	20·94	−28·85
24·86	−17·6	20·42	−30·85
24·39	−18·7		
23·86	−20·1	XXVIII.*	
23·34	−21·7	31·19	−12·6
22·44	−23·7	30·49	−12·25
22·06	−25·0	29·85	−12·15
21·70	−25·9	29·20	−12·35
21·00	−28·2	28·59	−12·50
IX.		27·81	−13·10
24·44	−18·9	26·94	−14·10
23·97	−19·55	24·35	−18·8
23·48	−21·45	23·56	−21·0
X.		22·59	−23·4
24·52	−18·8	20·98	−27·7
24·02	−19·9	20·52	−29·9
23·64	−20·8	20·10	−31·6
23·24	−22·2	XXX.*	
22·84	−23·6	31·09	−12·5
22·46	−24·0	30·62	−12·28
22·07	−25·4	30·08	−12·20
21·73	−26·8	29·55	−12·42
21·06	−29·25	28·99	−12·48
20·76	−30·3	28·44	−12·80
XIV*.		24·34	−18·88
23·28	−21·0	23·53	−20·4
22·80	−21·75	20·98	−27·9
21·43	−26·28	20·07	−31·9
21·04	−27·6	XXXI.*	
20·67	−28·3	31·44	−12·75
20·27	−30·0	30·97	−12·47
19·91	−31·4	30·46	−12·25
XXIV.*		29·97	−12·29
26·27	−15·0	29·48	−12·25
25·73	−15·6	28·97	−12·50
25·27	−16·85	28·45	−12·78
24·61	−18·3	27·94	−13·15
24·09	−20·55		
23·48	−20·8		
23·20	−20·8		

TABLE I—*continued.*

Per cent. NaOH.	F. p.	Per cent. NaOH.	F. p.
The heptahydrate crystallises— II.		The heptahydrate crystallises—*cont.* XXVII.*	
		22·62	−24·0
21·53	−24·2	22·13	−24·2
19·80	−25·7	21·56	−24·8
		20·94	−25·25
III.		19·92	−26·4
23·75	−23·0		
23·22	−23·3	XXXII.*	
22·63	−23·7		
21·55	−24·8	26·91	−24·77
21·02	−24·9	26·25	−24·2
20·43	−26·15	25·59	−23·75
		25·02	−23·85
IV.		24·42	−23·5
		23·70	−23·65
22·86	−23·4	23·02	−23·85
21·33	−25·45	22·30	−24·1
20·64	−25·0	21·43	−25·0
20·30	−25·4	20·52	−25·5
19·98	−26·0	19·69	−26·5
19·63	−26·7		
19·39	−26·7	XXXIII.*	
X.		20·98	−25·15
		20·59	−25·25
21·40	−24·6	19·46	−26·4
XIV.*		A hydrate crystallises-- X.	
22·32	−24·1	20·44	−32·15
21·85	−24·3	20·16	−31·9
		19·88	−31·95
XXII.*			
22·06	−24·5	XXII.*	
21·56	−24·5		
21·10	−25·2	20·01	−32·15
20·97	−25·25		
20·62	−25·6	Water crystallises— II.	
19·84	−27·0		
19·44	−27·7	18·07	−26·7
19·00	−28·25	16·34	−21·9
XXV.*		14·06	−16·9
		10·47	−10·9
25·44	−23·75	3·69	−3·1
24·87	−23·45		
24·20	−23·5		
23·56	−23·8		
22·93	−23·8		
22·22	−24·45		
21·48	−25·5		

TABLE I—*continued.*

Per cent. NaOH.	F. p.	Per cent. NaOH.	F. p.

Water crystallises—*cont.*
III.

Water crystallises—*cont.*
XXIX.*

Per cent. NaOH.	F. p.	Per cent. NaOH.	F. p.
19·88	−32·6		
18·85	−28·7	20·52	(−33·0)
17·56	−25·0	19·69	−31·4
15·62	−20·25	19·28	−29·25
14·11	−17·2	18·69	−27·50
12·51	−14·5		
10·68	−10·9		XXXIII.*
9·10	− 8·5		
7·63	− 7·0	18·45	−26·25
6·36	− 5·6		
5·29	− 4·4		XXXIV.*
3·59	− 3·0		
2·24	− 1·7	10·03	−10·29
1·37	− 0·8	9·52	− 9·62
0·81	− 0·6	8·84	− 8·82
		7·97	− 7·72
	XIV.*	6·89	− 6·42
		5·78	− 5·27
19·53	−31·0	4·70	− 4·07
19·19	−29·5	3·68	− 3·07
		2·75	− 2·32
	XXII.*	2·15	− 1·77
		1·46	− 1·12
18·59	−26·0	0·89	− 0·62
18·17	−25·3	0·46	− 0·30
17·63	−24·05		
16·93	−22·0		
16·12	−20·4		
15·27	−18·5		
14·07	−16·0		
12·66	−14·0		
11·11	−11·75		
10·10	−10·3		
8·88	− 8·6		
7·56	− 7·05		
6·30	− 5·7		
5·15	− 4·50		
4·05	− 3·7		
2·97	− 2·28		
1·97	− 1·52		

ADE), after which a hydrate, which by analysis was found to be the monohydrate, crystallises. The maximum for the freezing points of this hydrate was not reached, as the solution boils before it is attained. The hydrate has been already described by Muretow (*Ber.*, **5**, 331).

The "water" curve indicates a somewhat feeble break at 6·2 per cent. (mean of 6·0 and 6·4 per cent. in the two series) corresponding to about $LiOH,13H_2O$.

TABLE II.—*Position of the Maxima attained by the Hydrates of Sodium Hydroxide.*

Series.	Position of maxima, per cent. NaOH.	Molecular composition indicated.	Percentage composition calculated.	Freezing point.
II* XI* XII*	69·5 68·6 } 69·17 69·4	$NaOH,0·99H_2O$	$NaOH,H_2O = 68·97$	+65·4 +63·3 } +64·3° +64·5
VII VIII All the series	51·2 54·6 } 52·8 52·6	$NaOH,1·995H_2O$	$NaOH,2H_2O = 52·63$	+11·7 +13·4 } +12·5° +12·4
VI VII VIII XV* XVII* XXI*	41·4 41·9 (41·63) 41·6 } 41·677 41·75 41·70 } 41·70 41·65	$NaOH,3·11H_2O$	$NaOH,3·1H_2O = 41·67$ $(NaOH,3H_2O = 42·55)$	+3·2 +2·85 +2·65 +2·75 } +(2·90°) +2·70 +2·73
XIII* XVI*	39·0 } 39·10 39·2	$NaOH,3·47H_2O$	$NaOH,3·5H_2O = 38·83$	+15·4 } +15·55 +15·7
XIX* XXI* XXII*	[34·7] 35·9 } 35·85 35·8	$NaOH,3·98H_2O$	$NaOH,4H_2O = 35·71$	[6·9] +7·68 } +7·57° +7·57
III VI IX XV* XVIII*	35·6 35·4 [35·15] } 35·61 35·65 35·8	$NaOH,4·02H_2O$	$NaOH,4H_2O = 35·71$	-1·8 -0·9 -2·95 } -1·70° -1·65 -1·75
XXVIII* XXX* XXXI*	29·9 30·2 } 30·03 30·0	$NaOH,5·17H_2O$	$NaOH,5\frac{5}{2}H_2O = 30·01$ $(NaOH,5H_2O = 30·77)$	-12·15 -12·25 } -12·22° -12·25
III XXV* XXVII* XXXII*	24·1 24·4 } 24·12 23·7 24·3	$NaOH,6·99H_2O$	$NaOH,7H_2O = 24·10$	-23·2 -23·5 } -23·51° -23·9 -23·45

TABLE III.—*Freezing Points of Aqueous Solutions of Potassium Hydroxide.*

Per cent. KOH.	F. p.	Per cent. KOH.	F. p.
First Series.		*Second Series.*	
KOH,H_2O crystallises.		KOH,H_2O crystallises.	
66·415	110·0°	71·84	+ 139·15°
64·573	105·0	70·22	+ 134·65
62·499	88·5	68·54	+ 127·9
60·423	70·0	66·72	+ 118·6
58·516	49·0	64·61	+ 105·8
		62·46	+ 90·0
		60·29	+ 69·75
$KOH,2H_2O$ crystallises.		58·83	+ 53·7
		57·84	+ 41·8
56·716	32·8		
54·986	27·5		
53·388	22·5	$KOH,2H_2O$ crystallises.	
51·852	17·0		
50·467	8·8	56·82	+ 32·5
48·142	− 5·8	55·81	+ 30·0
45·874	−23·2	54·94	+ 28·0
		53·89	+ 24·0
		52·77	+ 20·0
$KOH,4H_2O$ crystallises.		51·37	+ 12·5
		49·90	+ 3·5
43·092	− 32·7	48·12	− 9·0
40·095	− 35·0	45·81	about − 27
37·327	− 42·2		
34·352	none at − 75	$KOH,4H_2O$ crystallises.	
		44·29	− 33·0
		43·12	− 33·0
Water crystallises.		41·87	− 34·2
		40·66	− 36·2
30·833	−65·2		
27·029	−44·2		
22·661	−30·5		
18·496	−20·7		
12·966	−11·2		
6·839	− 4·6		
3·509	− 2·2		

TABLE IV.—*Freezing Points of Aqueous Solutions of Lithium Hydroxide.*

Per cent. LiOH.	F. p.	Per cent. LiOH.	F. p.
First Series.		*Second Series.*	
$LiOH,H_2O$ crystallises.		$LiOH,H_2O$ crystallises.	
13·20	+ 78·5°	13·31	+ 81·1°
12·60	+ 72·0	13·01	+ 77·3
11·91	+ 58·0	12·69	+ 71·85
		12·36	+ 66·5
		12·03	+ 58·5
Water crystallises.		11·68	+ 45·5
		11·36	+ 33·5
9·45	−14·8	11·28	+ 10·0
8·77	−13·4		
8·07	−12·5		
7·40	−11·5	Water crystallises.	
6·66	−10·6		
5·86	− 9·5	10·65	−17·4
4·99	− 7·5	10·38	−16·75
4·05	− 6·0	10·12	−16·45
3·20	− 4·4	9·84	−15·6
1·39	− 1·85	9·53	−14·9
		9·21	−14·18
		8·82	−13·25
		8·52	−12·95
		8·12	−12·1
		7·70	−11·45
		7·23	−10·5
		6·70	− 9·7
		5·99	− 8·7
		5·44	− 7·8
		4·89	− 6·75
		4·31	− 5·9
		3·59	− 4·9
		2·83	− 3·8
		2·00	− 2·7
		1·16	− 1·5