CCX.—*Some Properties of Fused Sodium Hydroxide.*

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THE amount of information available concerning fused sodium hydroxide is very small considering the enormous quantities which are produced and used every day in the chemical industry.

Certainly for one period in its production, and often continuously in its use sodium hydroxide is in the fused condition, and as such possesses many characteristic chemical properties, some of which are quite distinct from the properties of sodium hydroxide in solution.

This paper is a collection of some results obtained in the course of everyday working and experimenting with the fused material. It is divided into three sections.

Section A.—Estimation of moisture contained in sodium hydroxide.

Section B.—Action between sodium hydroxide and metals when heated in air.

Section C.—Action between metals and mixtures of sodium hydroxide and sodium peroxide.

A.—Estimation of the Moisture contained in Sodium Hydroxide.

The fact that sodium hydroxide, even when fused, contains moisture is quite well known, and various methods are available for removing it. Among these are

(1) The addition of sodium.

(2) Prolonged heating at 700° (Neuman and Bergve, *Zeitsch. Elektrochem.*, 1915, **21**, 143).

(3) Electrolytic decomposition.

None of these methods is easily applicable for a quantitative estimation. The suggestion of a suitable method came from some observations made when sodium hydroxide was being fused in a vacuum. An iron boat containing this material was placed in a horizontal glass tube connected with a mercury pump. The apparatus was evacuated and the sodium hydroxide slowly fused. As soon as the hydroxide melted, an extraordinarily vigorous bubbling and spitting took place. So much sodium hydroxide was thrown from the boat that the glass tube became quite opaque. This continued for some time, and then the alkali which was left in the boat became quiet, and it was seen that in the cooler portions of the tube moisture had condensed. By weighing the sodium hydroxide used and by absorbing the water in a weighed phosphoric

FIG. 1.

(a) Silica tube. (b) Metal tube and boat. (c) Glass plugs. (d) Airtight sealing-wax joints. (e) Phosphoric oxide tube with pressure-tubing joints (e_1e_1). (f) Portion of tube heated.

oxide tube, the percentage of moisture could easily be obtained. This method with some modifications was used and the arrangement is shown in Fig. 1. A silica tube was used to minimise the risk of cracking. A metal tube was introduced in order to protect the silica, and the rounded glass plug with which the tube was sealed enabled a view of the boat to be obtained. The sodium hydroxide used, which had been fused for some weeks before being poured into the boat, was weighed with all possible speed. By handling the hydroxide quickly while it was warm, it could be got into the tube without taking any appreciable quantity of moisture from the air. When the boat had been placed in the tube and the apparatus evacuated, the tube was gradually heated to approximately 500° and this temperature was maintained for about an hour. Long before this time had elapsed all ebullition had ceased. After the apparatus had cooled, the phosphoric oxide tube was detached and weighed. It was found that the amount of moisture varied in different samples of sodium hydroxide. The lowest value observed was 0.9, the highest was 1.2, whilst the average value was 1.1 per cent.

It is interesting to note that if white, crystalline sodium hydroxide is put into the boat at the beginning, it will still be white at the end of the experiment. Had the fusion at 500° taken place in an iron boat in air, the sodium hydroxide would have become distinctly green. It was further observed that when green sodium hydroxide has been put into the boat initially, the hydroxide which remains in the boat at the end of the experiment has become pure white. These observations indicate :

(a) That air (or oxygen) is necessary to effect any solvent action between iron and sodium hydroxide at temperatures up to 500° .

(b) That in a vacuum, iron is capable of acting as a reducing agent in fused sodium hydroxide in the same way as sulphur, sodium, etc.

B.—Reaction between Sodium Hydroxide and Metals when Heated in Air.

Analysis of sodium hydroxide, even of the white, finished product, always reveals the presence of metallic impurities, usually oxides of iron, aluminium, nickel, manganese, calcium, and magnesium.

Sodium hydroxide fused in an iron vessel is invariably coloured, due to these metallic impurities (except immediately after treatment with some reducing agent, usually sulphur). The colour of the sodium hydroxide varies with the temperature and the relative proportion of metals dissolved. For example, if iron is predominant, then the sodium hydroxide has a green colour up to about 450 — 500° . At higher temperatures, it becomes blackish-yellow. If copper is predominant, the sodium hydroxide is coloured an intense blue, and so on.

It is interesting to note, in passing, that the amount of metals in solution is always very small, and that a very small percentage of metallic impurity produces a very strong coloration in the sodium hydroxide.

We have had occasion to examine many samples of commercial sodium hydroxide, which were in most cases very pure so far as other sodium salts are concerned, and we have never found the total percentage of metallic oxides to be more than 0.05 per cent. The bulk of this is usually iron and manganese, yet these small quantities are sufficient to colour the sodium hydroxide very deeply. In order to obtain a more complete knowledge of the behaviour of fused sodium hydroxide with metals, we conducted the several series of experiments given below.

1. Action of Fused Sodium Hydroxide on Iron at Various Temperatures.

Two sets of experiments were performed :

(a) With spun iron laboratory crucibles.

(b) With cast crucibles made from the iron used in the manufacture of ordinary melting pots for sodium hydroxide.

The sodium hydroxide used was of the best quality, never containing more than 1 per cent. of total impurity, of which the greatest part was sodium carbonate. The hydroxide was in the form of large, glistening crystals taken from the middle of a large mass, and small pieces of these were placed in the crucible.

The apparatus used is shown in Fig. 2, and with these arrangements it was possible to keep the temperature fairly constant to within 10° .

FIG. 2.

(a) Firebricks. (b) Iron pot. (c) Iron crucibles. (d) Gas ring.
(p) Pyrometer.

The *modus operandi* was the same throughout the experiments. Two crucibles were placed in the furnace together and were used, when possible, throughout the series. Before each experiment, the insides of the crucibles were cleaned and burnished. Fifty grams of solid sodium hydroxide were introduced, and the crucibles were covered by loose lids, placed in the furnace, and kept at the required temperature for four hours. By heating the furnace to the required temperature before the crucibles were put in, a steady condition could be obtained within an hour.

At the end of four hours the crucibles were removed and the contents poured into nickel moulds. Each crucible was then thoroughly washed out and the washings were added to the solution of the main quantity of the sodium hydroxide. The total iron in the resulting liquid was estimated. Wherever possible, the amount

Observations made with Sodium Hydroxide and Laboratory Crucibles.

Temp.	No. of expts.	Colour of fused sodium hydroxide.	Condition.	Cooling phenomena.	Suspended matter.	Residue.	Iron in solution per cent.	Grams of iron removed from the crucible.
350°	9	Colourless.	Very turbid.	—	Red iron oxide.	None.	—	0.4
	1	"	Crystal clear.	—	None.	"	—	—
400	8	"	Very turbid.	—	Red iron oxide.	"	—	0.425
	2	Pale green.	"	—	"	"	—	0.425
450	8	Green.	Quite clear.	—	None.	Red iron oxide.	0.02-0.04	0.2-0.3
500	6	Almost colourless.	Clear.	Became turbid owing to the formation of a yellow ppte. as the hydroxide cooled.	"	Very small amount of red oxide.	0.014-0.024	0.2-0.3
550	2	Bright green.	"	No ppte.	"	"	0.018-0.028	0.2-0.3
	3	Almost colourless.	"	Became turbid owing to the formation of a yellow ppte. as the hydroxide cooled.	Small yellow crystals resembling lead iodide crystallised from water.	"	0.02	0.4-0.48
600	5	Dark greenish-brown.	Almost opaque.	No ppte. seen.	None.	"	0.048	0.09
	6	Dark yellowish-green.	"	"	Large quantity of crystals.	None.	0.068	0.3
650	1	Dark brown.	"	"	Very few crystals.	"	0.068	0.13
	1	Dark yellowish-green.	Opaque.	"	Large quantity of crystals.	Red iron oxide.	"	"

Note.—One experiment was performed in which a crucible containing sodium hydroxide was heated to 350°. After four hours the contents were examined and found to be red and turbid. The furnace was closed and allowed to cool very slowly. The final product was a solid mass of white sodium hydroxide in which all the red oxide had collected at the bottom.

of iron dissolved in the sodium hydroxide was estimated independently. The experiment was repeated three or four times at each particular temperature.

Table I gives the observations and data collected from the experiments conducted with laboratory crucibles. Particularly from 500° upwards, the action of sodium hydroxide and iron seems to be very complex, and at each of the temperatures taken we were met with absolutely different phenomena under what were, so far as we knew, the same conditions. The term "Frequency" in the table indicates for each particular temperature the number of times the phenomena described were met with. We are without any satisfactory explanation why this variation in the phenomena occurred.

Results with Cast Iron Crucibles.

The qualitative results were the same as those described in the case of spun crucibles, except in one particular. The sodium hydroxide obtained at 550°, when dissolved in water, gave a large quantity of purple precipitate, which yielded ferric hydroxide on keeping, or on the addition of water and was probably sodium ferrate. The total amount of iron removed was, however, much larger, and on the whole the tendency seemed to be for the quantity to rise with the temperature.

As in the previous experiments, the formation of the scintillating crystals was associated with a considerable rise in the total quantity of iron removed. The iron in solution was estimated and the quantity found to be of the same order as that estimated in the sodium hydroxide used with the other crucibles.

In generalising the results of these observations it should be clearly understood that they might be different if a period of heating other than four hours had been fixed upon. Practical experience, however, has shown that, in these experiments, the quantities of iron dissolved in the sodium hydroxide are of the same order as those contained in hydroxide which has been fused in iron pots for several weeks.

The quantitative results obtained with cast iron crucibles and those given in the table, are shown graphically in Fig. 3.

The important conclusions to be drawn from the table and the curves are as follows :

1. At temperatures up to and including 400° the ferric oxide formed by the action of sodium hydroxide and iron remains in suspension for at least several hours and practically no iron is dissolved.
2. Between 400° and 500° the amount of iron removed is much

smaller. The red oxide formed settles to the bottom very quickly, except for a small amount which dissolves in the sodium hydroxide.

3. Between 500° and 550° , a soluble substance is formed which settles out as a yellow precipitate when the sodium hydroxide cools. This does not always occur.

4. At 550° and above, a yellow, crystalline substance is formed which is insoluble in sodium hydroxide at temperatures up to 650° .

FIG. 3.

Laboratory iron crucibles.—(1) Quantity of iron dissolved. (2) Quantity of iron removed (a) when yellow precipitate and crystals are not formed; (b) when yellow precipitate and crystals are formed.

Cast iron crucibles.—(3) Quantity of iron removed (a) when yellow precipitate is not formed; (b) when yellow precipitate is formed.

5. The graphs of the quantitative data show clearly that

(a) The amount of iron dissolved is very small compared with the amount removed.

(b) The amount dissolved increases with the temperature.

(c) With laboratory iron crucibles the amount removed falls rapidly from 400° to 600° , except when yellow crystals are formed. In these cases the amount is greatly increased.

(d) With cast iron crucibles the tendency is for the amount removed to increase steadily with rise of temperature.

Isolation of the Crystalline Substance observed at 550° and above.

By the methods described above, it was impossible to isolate any of the crystals, as they were spread through the mass of the solid sodium hydroxide obtained in the mould, and treatment with water always gave a precipitate of ferric hydroxide, from which the crystals could not easily be separated. A new method had to be adopted.

The crucibles were treated exactly as before, the sodium hydroxide was introduced, and the crucibles were heated to 500—600° and left for four to eight hours. The gas was then turned off, the crucibles left in the furnace to cool slowly, and, when cold, the solid block of sodium hydroxide was tapped out of the crucible. The first result of this method was to reveal the presence of some dark

FIG. 4.

(a) Red crystals. (b) Yellow crystals. (c) Red iron oxide.

red crystals which had not been seen before. The solid block of hydroxide was split vertically and gave a section sketched in Fig. 4. It will be observed that the red oxide and the yellow crystals had settled out very conveniently for purposes of separation, and that the dark red crystals were found at the point where air, iron, and sodium hydroxide meet.

The bottom of the block was split off and a piece of sodium hydroxide was thus obtained containing all the yellow crystals with a compact layer of red oxide on the bottom. This was completely scraped off with a knife, and the sodium hydroxide dissolved in water. A solution was obtained, with the yellow crystals and a small amount of the red oxide in suspension. The final separation was accomplished by spinning the solution round and then holding the beaker still. The red oxide rapidly settled out in a little heap on the bottom while the crystals were still carried round with the liquid. The latter was rapidly decanted off and carried the major

portion of the crystals with it, while the red oxide was left in the beaker.

A sample of the dark red crystals was easily obtained by breaking off the sodium hydroxide at the edges, which was quite free from the red oxide, and dissolving it. Being at the edge, the crystals could be removed with only a very small amount of sodium hydroxide.

In this way a fairly large quantity of the yellow crystals was obtained, and a small quantity of the darker crystals. The yellow crystals consist of iron, sodium, and oxygen, and their chemical properties are identical with those of the red crystals described on p. 1854. The presence of sodium was first indicated in an attempt to estimate the oxygen by reduction in a stream of hydrogen. Very varying results were obtained, and in all cases the boat (both platinum and silica were used) showed signs of having been acted on. This disproved the suggestion that the yellow crystals might be crystalline oxides of iron.

The analysis of the crystals proved very unsatisfactory. The estimation of the iron was effected without difficulty, but even here the results obtained were never within the limits of experimental error, although they were always fairly close to one another. The estimation of the sodium was completely unsatisfactory, the difficulty being to obtain a suitable method. This difficulty was overcome later and the method finally employed to estimate the sodium will be fully dealt with in section *C*.

Several analyses were performed (Found : Fe = 56.3 ; Na = 14.8 ; O = 28.9 per cent.), but the figures correspond with no simple formula ($\text{Na}_3\text{Fe}_5\text{O}_9$ is the simplest), and cannot be regarded as giving more than an indication of the composition of the crystals.

Owing to the trial of one method after another, our sample was almost exhausted. Our old crucibles were worn out, and we had to wait many months before new ones could be obtained (1917—18). When we did get them, we were totally unsuccessful in our attempts to prepare anything like reasonable quantities of the crystals. The reason for this is not evident. The matter was allowed to rest there until another series of experiments was performed, which is described in section *C*.

2. Action of Fused Sodium Hydroxide on Nickel at Various Temperatures.

Ordinary laboratory nickel crucibles were used, and the gas-fired furnace was replaced by an electrically-heated muffle. In each experiment two crucibles containing 150 grams of sodium hydroxide

TABLE II.
Observations made with Sodium Hydroxide and Nickel.

Temp.	No. of expts.	Colour of fused sodium hydroxide.	Condition.	Cooling phenomena.	Suspended matter and residue.	Nickel in the solution per cent.
<i>Series 1 with new crucibles.</i>						
360°	8	Very pale green.	Clear.	Set to white solid with purple tint.	None.	0.01-0.02
	4	Pale green.	Clear, with slight scum.	Black ppte. on cooling.	"	0.01-0.02
400	10	Colourless.	Clear.	No ppte.; set to pure white solid.	"	Trace.
	5	Pale green.	Clear, with slight scum.	No ppte.; set to yellow solid.	"	0.008
	1	Very pale green.	Clear.	—	Small quantity of small, silvery crystals floating in the sodium hydroxide.	0.014
	2	Greenish-yellow.	Clear, with scum.	Black ppte. on cooling.	—	0.02
<i>Series 2 with same crucibles as before.</i>						
350	4	Green.	Clear, with scum.	Black ppte. on cooling.	—	0.01-0.03
375	6	"	"	"	—	0.01-0.03
400	4	"	More scum.	"	—	0.01-0.02
450	4	"	No scum.	Much less ppte.	—	0.01-0.02
500	6	"	"	Very little ppte.	—	0.005-0.015

and fitted with fairly tight nickel lids were used. The nickel in the hydroxide was estimated by dissolving the product in hydrochloric acid and precipitating the nickel by dimethylglyoxime in the usual way. The phenomena observed were very inconsistent. Owing to this, one series of experiments was abandoned altogether, and another undertaken with the intention of raising the temperature by steps of 20° rather than 50° .

It is very difficult to sum up the reaction of nickel and sodium hydroxide. The most feasible line of explanation is that the inner surface of the crucible is oxidised in some way which is not very clear. It is well known that nickel oxide is only very slightly soluble in sodium hydroxide, and it would consequently form a protective covering. This would account for the small quantities of nickel found in the alkali and for the absence of anything comparable with the red oxide obtained with iron crucibles. The production of the silvery crystals observed in one isolated case will be fully dealt with in section *C*. In some cases, similar to what we once or twice obtained with iron crucibles, there seemed to be no action whatever. The explanation of such cases, in which the inside surface of the crucibles remained quite bright and clean, would seem to be one where the metal was in the passive state. It should be noted, however, that these negative results were not obtained after the crucibles had been used for a while.

3. *Action with Copper at Various Temperatures.*

A similar series of experiments to those performed with nickel was undertaken with two crucibles beaten out of $\frac{1}{8}$ -inch sheet.

With copper there seemed to be a very complex action, judging by the various phenomena which were observed. In contradistinction to iron, the phenomena were almost the same for various temperatures, but they became intensified as the temperature rose.

The following phenomena were observed at 350° , and in a greater degree at higher temperatures.

The fused sodium hydroxide was clear and intensely blue and contained a number of shiny scales floating in it. On pouring the melt into a cold mould, the first sodium hydroxide to touch the mould instantly became intensely yellow, whilst the rest of the hydroxide, cooling comparatively slowly, deposited a red substance. The final solid was dark red, with a bright yellow surface where it had been in contact with the mould. This yellow effect was without doubt due to the sudden cooling of the sodium hydroxide.

Several interesting phenomena were observed during the analysis of the sodium hydroxide. When the alkali was put into water, a vivid yellow substance was precipitated, and this was followed by

the precipitation of a bright red powder. After keeping, the whole precipitate turned red. The solution itself was of a blue colour, which deepened on keeping. The copper was estimated by precipitation with hydrogen sulphide in the usual way after the addition of hydrochloric acid. This precipitation was somewhat curious. The hydrochloric acid solution was yellowish-green and gave a precipitate only very slowly with hydrogen sulphide, in fact, a few minutes elapsed before the gas produced any precipitate at all. When, however, the acid solution was first boiled with a little sodium hydrogen sulphite, the hydrogen sulphide immediately gave a precipitate.

FIG. 5.

As the temperature rose, the colour of the fused sodium hydroxide deepened, and at 450° it had a distinctly brown tint. The number of shiny scales in the hydroxide increased considerably, and this probably accounts for the big increase in the percentage of copper in the alkali. No attempt was made to isolate any of the crystals, as they were invariably mixed with a red precipitate which accompanied the solution of the sodium hydroxide. They were also acted on by water, and after remaining for a short while were decomposed.

At 500° an interesting change was observed. The sodium hydroxide was very dark brown, and a large quantity of crystalline matter was found in the bottom of the crucible. The crystals were long and narrow, and quite different in shape and appearance from the scales observed at lower temperatures. At 550° still more of these crystals were formed. It was possible to pour off the sodium hydroxide and leave the crystals in the crucibles. They were removed, rapidly washed, and dried. In this way an impure sample was obtained, from which some large crystals were picked out.

The sodium hydroxide obtained at these high temperatures is very pretty when cooling in the mould, and finally gives a crystalline solid totally different in crystalline character from ordinary sodium hydroxide.

At the lower temperatures the total percentage of copper in the

PLATE 1. $\times 30$.

PLATE 2. $\times 30$.

PLATE 3. $\times 30$.

PLATE 4. $\times 30$.
Reflected light.

sodium hydroxide was 0.067 at 350°, 0.440 at 400°, and 0.536 at 450°. Since the scales were always found in suspension, the above figures do not represent the exact amount of copper dissolved in the sodium hydroxide, but they give some idea of the relative amounts of copper dissolved from the crucible. The data, shown graphically in Fig. 5, refer to 200 grams of sodium hydroxide heated for four hours.

As there was not sufficient picked material, the analysis of the crystals was made on the impure sample. It consisted of a mixture of very small crystals and a little amorphous copper oxide. The sample was dissolved in hydrochloric acid, the copper precipitated in the usual way, the filtrate evaporated to dryness, and the residue dissolved and titrated with standard silver nitrate. The precipitate of copper sulphide was redissolved, and the copper estimated electrolytically.

The following are the analytical data :

Weight of sample	1.1131 grams.
„ of copper found	0.8716 gram.
„ of sodium in the filtrate	0.00591 „

It is reasonable to assume that such a small amount of sodium must be present as an impurity—probably due to incomplete washing, in which case it would be present as sodium carbonate. The weight of carbonate present would be 0.0131 gram. On this assumption, the actual weight of the crystals was 1.1131 — 0.0131 = 1.100 grams. The percentage of copper in the crystals was therefore 79.2. This gives a final proportion of Cu : O = 1.247 : 1.3 = 1 : 1.04. From this it would seem that the crystals are a crystalline oxide of copper of the empirical formula CuO.

When examined with transmitted light, the crystals are quite opaque. From the photograph (Plate I, magnification 30 diameters) it is seen that they are long, needle-shaped crystals which have, in unbroken specimens, truncated ends.

Conclusions.

(1) Compared with iron and nickel, copper can be said to be readily attacked and dissolved by fused sodium hydroxide.

(2) The actual amounts are still quite small—the highest being in the sodium hydroxide heated at 450°, which contains approximately 0.8 per cent. of copper, but it will be seen that the actual quantities are much greater than in the case of either iron or nickel. Since copper is much more easily oxidised than the other two metals, this supports the view that all these reactions of fused sodium hydroxide with metals commence with the oxidation of the metal.

(3) Crystals are obtained in the sodium hydroxide at all tem-

peratures. At 350° to 500°, shiny scales are observed in the hydroxide. Above 500°, the scales disappear and long, thin crystals are seen floating in the liquid.

(4) These long crystals are readily soluble in acids, are decomposed by water after a while, and are quite different in character from the crystals obtained with iron and nickel. Their empirical formula is CuO.

C.—Action of Mixtures of Sodium Hydroxide and Sodium Peroxide on Metals.

1. Action with Iron.

In the previous section of this paper, reference was made to two kinds of crystals (yellow and red) produced by the action of sodium hydroxide on iron at temperatures above 550°. The second attempt to prepare any quantity of these, was, for some unknown reason, unsuccessful. It was thought that these crystals were the product of some oxidation process, and the lack of success in their preparation seemed to indicate the necessity for some stronger oxidising agent. To achieve this, it was decided to add sodium peroxide. A preliminary experiment was carried out in one of the crucibles used previously. A mixture of sodium hydroxide and 5 per cent. of sodium peroxide was heated in an iron crucible at 500 to 550° for four to eight hours. The crucible and contents were then allowed to cool very slowly in the furnace. When the sodium hydroxide was quite cold, it was found that a large quantity of red crystals had been formed. The crystals were found adhering to the crucible and the surface of the sodium hydroxide, and they were much larger and better formed than any obtained previously. The hydroxide was broken up, but no sign of the yellow crystals was seen. As the addition of sodium peroxide seemed to give a very promising result, a complete series of experiments was carried out at various temperatures. Unless otherwise stated, the sodium hydroxide in the following experiments always contained 5 per cent. of sodium peroxide.

Results obtained.

Temp.	Description of the sodium hydroxide.	Particulars of crystals observed.	Percentage of iron in the solution.
350°	Greenish-blue.	Quantity of very small crystals.	0·024
	Free from suspended matter.	Mixed with the red oxide.	
400	Free from suspended matter.	Mixed with the red oxide.	0·025
450	Very black; gave a yellow ppte. on cooling.	Large quantity of red crystals in suspension.	0·11

Results obtained at 500—550°

On one occasion a clear, dark green sodium hydroxide was formed which gave no yellow precipitate on cooling and in which there were no crystals of any kind. It contained 0.029 per cent. of iron in solution. This was quite evidently one of the exceptional cases which were met with every now and then.

The general results of heating sodium hydroxide with 5 per cent. of sodium peroxide in an iron crucible to 550° and leaving to cool slowly after about five hours' heating, were as follows :

(1) A large quantity of red crystals was formed.

(2) The sodium hydroxide was a dark, almost black, quite soft solid which dissolved in water very readily, usually with evolution of gas. The solution was deep purple, which rapidly became deep green, a large quantity of ferric oxide being precipitated. The green solution seemed permanent when very concentrated.

(3) When the sodium hydroxide was dissolved in a minimum quantity of water and the concentrated solution poured off after the insoluble matter had been allowed to settle, a mixture of substances was found in the sediment. In this, which was principally ferric oxide, there were a few red crystals and two substances different in appearance from anything we had seen previously. The separation of the latter substances was not attempted on any scale, but a few specimens were picked out and examined microscopically. Of the two new substances, one was in the form of long, narrow, blood-red crystals (almost opaque) with peculiar truncated ends, which were rapidly decomposed by water and deliquesced in the air. The other, of which there was a moderate quantity, consisted of small, flat pieces of rust-coloured matter. It was difficult to tell whether these were crystalline or not. They generally had a peculiar red sheen with reflected light.

An excellent sample of the red crystals was obtained by carefully cutting off the masses of crystals which had collected at the edge of the solid sodium hydroxide and dissolving in water. The crystals were so thick that they could be detached with very little adhering sodium hydroxide.

Results at Higher Temperatures.

Two iron crucibles containing sodium hydroxide with 5 per cent. and 10 per cent. of peroxide respectively were heated at 720° and allowed to cool very slowly in the furnace.

The hydroxide containing 5 per cent. of peroxide set to a green solid. On dissolving in water, a large quantity of the long, red

crystals with truncated ends was observed along with a small quantity of red crystals.

The hydroxide with 10 per cent. of peroxide set to a dark purple solid, and red crystals had been deposited in considerable quantity on the sides of the crucible. A large quantity of the long crystals and a small quantity of the red variety were seen when the sodium hydroxide was dissolved. It is seen from this that the long crystals are the product of reactions carried out at the higher temperatures.

Results obtained with the Use of Pure Sodium Peroxide.

It was found that the employment of larger quantities of sodium peroxide than those used, resulted in the crucibles being attacked very vigorously. Ordinary laboratory crucibles were usually eaten right through. In addition to this, it was found that as the amount of peroxide used was increased, the amount of crystals of all kinds diminished until with large amounts, such as 50 per cent., no crystals were found at all.

A thick cast-iron crucible containing sodium peroxide only was heated at 500—550° for about four hours, and left to cool in the usual way. The final product was a mass of long, very dark crystals which dissolved in water very readily, yielding a deep purple solution which deposited ferric oxide and turned green on keeping. These crystals were probably pure sodium ferrate.

Properties of the Red Crystals formed at 500°.

1. When examined under the microscope, it was seen that the crystals tended to be very perfect hexagons. All the available evidence, microscopic as well as chemical, showed that the yellow crystals and the red crystals are both modifications of one substance. The crystals are transparent and of a reddish-brown colour, the intensity varying with the thickness of the crystal. They have a refractive index slightly greater than that of oil of cinnamon ($n = 1.58$). Most of the crystals are lamellar and are really basal cleavage plates of hexagonal crystals which have a very perfect basal cleavage. With convergent light they readily give optical figures which show that the crystals are uniaxial and optically negative. A microphotograph (Plate 2, magnification 30 diameters) is given, in which the crystals, being red, appear quite black, and which shows the regular hexagon shape of the untouched crystals.

2. They are unacted upon by boiling water, boiling sodium hydroxide solution, and cold dilute mineral acids.

3. They are readily dissolved by hot concentrated acids.

4. They are stable up to at least 720° in fused sodium hydroxide.
5. They consist of sodium, iron, and oxygen. In view of this composition their stability is remarkable.

Analysis.

A known weight of the crystals was washed with water and the amount of Na_2O in the washings estimated.

The washed crystals were dissolved in hydrochloric acid, and the solution was carefully evaporated to dryness in either a platinum or porcelain dish. The residue was then gently heated until a constant weight was obtained, indicating that all the ferric chloride had been converted into oxide. The final residue was boiled with water, and the sodium chloride in the resulting liquor estimated by titration with silver nitrate. The sodium oxide estimated in the washings was assumed to be carbonate, and allowance was made for this in calculating the results. The solution of the crystals in acid was made up to 250 c.c. and 50 c.c. taken for each sodium estimation. The sodium figures for various estimations on the same solution agreed fairly well, showing that the method was satisfactory. The analysis of the crystals was never satisfactory.

The following are the average results of an analysis made immediately after the crystals were isolated : $\text{Fe} = 52.2$; $\text{Na} = 14.55$; $\text{O} = 30.25$ per cent.

Analyses made on a washed sample twelve months after its formation gave an iron content larger than the above by approximately 6 per cent.

It seems fairly definite that the crystals are composed of a mixture of oxides of sodium and iron, the latter probably functioning in an acidic capacity. The variations in the analyses are most likely due to the crystals themselves undergoing slow decomposition, which would of course introduce differences. This is shown by the fact that no matter how carefully the crystals are washed, if they be kept for any length of time and then rewashed, the washings will always contain a further quantity of sodium. No weight can therefore be put on the analysis for the purpose of obtaining a molecular formula, but it seems possible that immediately after the removal they have a composition represented by the formula $\text{Na}_2\text{Fe}_3\text{O}_6$.

2. Action with Nickel.

A series of experiments similar to those with iron crucibles were carried out with nickel. These experiments were made at the

TABLE III.
Results with Nickel and Sodium Hydroxide containing Sodium Peroxide.

Temp.	Sodium peroxide per cent.	Colour of fused sodium hydroxide.	Condition.	Cooling phenomena.	Suspended matter.	Percentage of nickel in the sodium hydroxide.
350°	5	Dark green.	Clear, with slight scum.	Black ppte. on cooling.	None.	0.0024
400	"	Brown.	Clear.	Large black ppte. and vigorous bubbling on cooling.	Large quantity of silvery crystals.	0.0135
450	"	"	"	"	"	0.0131
500	"	"	"	Large black ppte., but no bubbling.	Larger quantity of crystals.	
720	"	Allowed to cool slowly in the furnace.			Few crystals on the surface. None in the mass of the sodium hydroxide.	
10		Grey solid. Allowed to cool slowly in the furnace. Shiny black mass of sodium hydroxide and silvery crystals, more like graphite than sodium hydroxide. Apart from the crystals, the hydroxide had crystallised in a kind of check pattern, totally different from anything seen before.				

same time as the second series of experiments with sodium hydroxide and nickel, the crucibles all being in the furnace together. The principal aim was to ascertain if the silvery crystals observed on one occasion in the first series would be produced in any quantity by the addition of sodium peroxide to the hydroxide.

From Table III it is seen that this object was accomplished, and from the mass of silvery crystals obtained at 720° a large sample was prepared.

These crystals were much more easily separated than the corresponding iron ones, as there was practically no precipitate when the sodium hydroxide dissolved in water, and nothing analogous to the red oxide. A little nickel oxide was present, but this was easily got rid of by swirling the solution and decanting the liquor containing the bulk of the crystals. There were no signs of any other crystalline substances.

Examination of the Crystals.

(1) When examined under the microscope with transmitted light, these crystals are quite opaque. They are, however, very similar in form to the crystals obtained with iron crucibles, that is, they crystallise in regular hexagons, as is shown from a single crystal on Plate 3. If, however, they are examined with reflected light, it is seen that the crystals are regularly etched. Frequently the etching is seen as parallel bands, very similar in appearance to the parallel twin bands of plagioclase. At times, however, more or less complete equilateral triangles are seen (Plate 4), which shows that the crystals have symmetry of the hexagonal system.

(2) The crystals are stable in fused sodium hydroxide up to 750° and are unacted on by water and cold dilute acids.

(3) They are readily dissolved by hot concentrated acids, and liberate chlorine from hydrochloric acid.

(4) They consist of nickel, sodium, and oxygen.

Analysis.

This analysis was again unsatisfactory, but an average analysis gives $\text{Ni} = 53.6$; $\text{Na} = 8.4$; $\text{O} = 38.0$ per cent.

The sodium was estimated in the manner described for the iron compound. The nickel chloride was very readily reduced to the oxide. The percentage obtained was the average of several results obtained on four lots of the solution, namely, 8.38, 8.7, 8.5, 8.46. The nickel was estimated by the glyoxime method, and the oxygen by difference. The average analysis indicates an empirical formula

TABLE IV.
Results with Copper and Sodium Hydroxide containing Sodium Peroxide.

Temp.	Sodium peroxide per cent.	Description of the sodium hydroxide.	Behaviour with water.	Crystals observed.	Percentage of copper in the solution.
350°	5	Dark brown and clear.	Dissolved readily with evolution of gas, giving clear, colourless solution.	None.	Trace.
400	"	" " "	" " "	"	0.013
450	"	" " "	Pale blue solution.	"	0.08
500	"	" " "	" " "	Large quantity of brown, shiny scales similar to those obtained with sodium hydroxide alone at 350–500°.	
550	"	" " "	" " "	A few long crystals in suspension.	
350	10	Greyish solid with the "check" crystalline appearance previously noted.	Clear blue solution.	None.	0.05
400	"	Black solid.			0.14
450	"	" " " crystalline appearance very pronounced.		A few crystals adhering to the crucible.	

of $\text{Na}_2\text{Ni}_5\text{O}_{13}$. It was found that the crystals were unstable over long periods of time and in this respect were similar to the iron crystals already described. When crystals which had been very thoroughly washed with water were kept for a period of, say, a week, sodium compounds were always found in the washings when they were rewashed. This will account for the unsatisfactory analysis.

3. *Action with Copper.*

A parallel series of experiments to those described with copper and sodium hydroxide was carried out in similar crucibles with sodium hydroxide and 5 per cent. of sodium peroxide. A few additional experiments with 10 per cent. of peroxide were performed. The results obtained (see Table IV) were quite unexpected, being the reverse of those obtained with iron and nickel. There, the action on the metal was much increased by the addition of peroxide, whilst with copper the action was considerably reduced.

Conclusion.

So far as the formation of crystalline substances and the removal of copper from the crucibles are concerned, the addition of the peroxide seemed to have a prohibiting effect, in marked contrast to that produced by peroxide with iron or nickel crucibles.

Summary.

The chemical properties of fused sodium hydroxide have been studied in three respects.

(1) *The Water Content.*

By fusing sodium hydroxide in a vacuum, it has been found that it has an average water content of 1.1 per cent. In connexion with these experiments, it is evident that the presence of oxygen is necessary before the fused hydroxide becomes coloured in its usual manner. In a vacuum, the iron of the containing vessel is able to act as a reducing agent on the small quantities of impurities in the hydroxide.

(2) *Action on iron, nickel, and copper in air.*

(a) These reactions have been studied between 350° and 600° .

(b) In no case is the amount of metal dissolved in the sodium hydroxide very high. The maximum amount, which was obtained with copper, was 0.73 per cent.

(c) Iron is less vigorously attacked than copper, and more vigorously than nickel.

(d) The formation of crystalline substances by the action of fused sodium hydroxide on each of these metals has been noted and their separation described.

(3) *Action of iron, nickel, and copper with sodium hydroxide containing 5 per cent. of sodium peroxide.*

(a) This action has been studied at temperatures ranging from 350° to 720°.

(b) The formation of crystalline substances previously noted is found to be facilitated in the case of iron and nickel at certain temperatures between 500° and 700°. The substances formed in the largest quantities have been described and analysed. In the case of copper, the formation of crystals is retarded.

(c) The reaction between sodium hydroxide, sodium peroxide, and iron or nickel is almost certain to have a parallel with similar metals such as cobalt, chromium, or manganese, and it is extremely probable that research with other metals on the lines indicated would reveal the presence of new crystalline substances, similar to those we have described.

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