[CONTRIBUTION FROM CHEMISTRY DIV., NAVAL RESEARCH LAB.]

The Reactions of Molten Sodium Hydroxide with Various Metals[1]

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Under the conditions of the system geometry and at temperatures up to 1000°, the primary reaction of sodium hydroxide with the investigated metals appears to follow a pattern illustrated by the general equation (A) NaOH + Metal $\rightarrow$ Na_2O + Metal Oxide (or Sodium Metalite) + H_2. The various metals differ only in rate of reaction and valence state of the combined metal, each tending to form its most stable or common oxide. The secondary reactions digress, with only those metals having easily reduced or unstable oxides reaching a steady-state condition. Hence, chromium, iron, titanium, beryllium, tantalum, manganese and ferrous alloys exhibit only reaction (A). Nickel, copper, Monel, gold and probably silver and cobalt exhibit one or more of the following secondary reactions leading to a "steady-state" condition. (B) Metal Oxide + H_2 $\rightarrow$ Metal + H_2O; (C) $Na_2O + {}^1/_2H_2 \rightarrow NaOH + Na$; (D) $H_2O + Na \rightarrow NaOH + {}^1/_2H_2$. In the presence of nickel, copper, Monel and probably cobalt, reactions (B) and (C) are reversible. In the presence of gold and probably silver, reaction (C) is not reversible by reason of the formation of an alloy between the noble metal and the produced sodium metal. For the same reason and because of the stability of the alloy formed, reaction (D) is prevented. Therefore, only nickel, copper, and their alloys and probably cobalt will produce definite equilibria, since the summation of equations B, C and D is the exact reverse of the primary equation A. Only these metals are protected by hydrogen additions prior to heating. If reaction A proceeds to completion, with the hydrogen constantly removed by evacuation, and, if there is an excess of reacting metal present, all of the metals investigated will react further with the sodium oxide fraction of the primary reaction product (E) Na_2O + Metal $\rightarrow$ Metal Oxide + 2Na. Reaction E proceeds completely to the right only if provision is made to remove the metallic sodium from the reaction zone, either by distillation or alloy formation.

The application of liquid materials as high temperature heat transfer media is a field of growing importance. Current research has extended the area of interest beyond liquid metals[2] to molten salts. Among the obvious requirements for such materials are thermal stability and inertness with respect to the container material. The work now going on is a study of reactions of salts and container materials for possible use in the high temperature field.

One of the lower melting and more thermally stable materials is sodium hydroxide. While this chemical has long been handled as a liquid near its melting point, little is known of its behavior at more elevated temperatures. The most significant data in the literature were published by Le Blanc and Bergmann,[3] whose appraisal of their own work stipulated the need for further study. More recently, an ingenious corrosion study by Lad and Simon[4] has delineated serious phenomena of mass transport in ΔT systems employing sodium hydroxide in nickel. Their data show nickel to be resistant, though not inert, to attack by liquid hydroxide.

This paper presents chemical reaction data on metal–sodium hydroxide systems which explain corrosion and mass transfer in such systems.

Experimental

Apparatus.—With the work of Le Blanc and Bergmann as a guide, an apparatus was constructed, the simplicity of which aided in the interpretation of the data. The apparatus consisted of a vertical closed-end reaction tube made of the metal to be studied and a glass calibrated volume and a mercury manometer. A stopcock was located between the reaction tube and the remainder of the system. A cold trap was used to check for condensable gases. Temperatures were recorded and controlled by a Brown Electronik potentiometer equipped with a Pt, Pt-Rh thermocouple. Loading was accomplished through the glass and metal ball joint between the reaction tube and the glass system while purging through a stopcock which connected to a high vacuum manifold. Gas pressures were determined to the nearest mm., and were calculated to volume at STP. Upon completion of a run, solid non-volatile products were obtained by cutting the reaction tube at the melt line, and volatile products such as metallic sodium were to be found condensed on the cooler upper portion of the reaction tube.

Thus, in a given run, the existence and, in some cases the extent, of a reaction could be shown by pressure measurement alone. In addition, the establishment of pseudo-equilibrium or a "steady-state" (since the system was not isothermal) was made apparent if consecutively reproducible constant pressures were obtained. These consecutive readings were obtained by successive collection and evacuation of the gas. Reactions which gave "steady-state" conditions would be driven to completion by such incremental gas removal as well as by constant evacuation.

Most of the metals studied did not achieve a "steady-state" condition but continued to react until the reactants were consumed or until a protective coating of reaction products isolated the reactants. These metals were studied, therefore, on a basis of reaction product valence state by allowing a relatively small known weight of the metal to react completely with an excess of hydroxide. The gaseous yield (hydrogen) was calculable to only one valence state for the metal in question.

Material.—The sodium hydroxide used in the tests was ACS reagent grade pellets assaying 97.0% NaOH, 0.6% Na_2CO_3, plus the usual impurities, the bulk of which was water.

The effect of the carbonate impurity was considered negligible inasmuch as no reaction was observed when the metals studied were fused in pure sodium carbonate. In addition to this evidence, the carbonate was always recovered, seemingly unchanged, in the solidified melts. In the following data, all weights of original charges and reaction products have been corrected for carbonate content.

The water was removed from all charges by evacuation at 400° prior to higher temperature studies. In this connection, it should be noted that water is held tenaciously by molten hydroxide below 400°, even under reasonably high vacuum.

Sodium Hydroxide–Nickel Reactions.—Various grades of commercially available nickel metal ranging in purity from "A" nickel to electrolytic and vacuum cast pure nickel were used in this investigation. Little or no difference was found as regards the prime nickel–hydroxide reaction. Some surface leaching of impurities was found, but this had little effect on the final reaction mechanism. For this reason, all nickel runs are grouped together without regard to minor additives or "impurities."

Qualitative runs resulted in the establishment of the existence of the temperature and pressure sensitive "steady-state" condition shown in Fig. 1. Figure 2 is a plot showing rate of pressure development for three temperatures. These pressures are independent of the size of the free space in the system, equal values being obtained with the calibrated

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(1) Sponsored by Materials Laboratory, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio.

(2) "Liquid Metals Handbook," NAVEXOS P-733, U. S. Govt. Printing Off., June, 1952.

(3) M. Le Blanc and L. Bergmann, *Ber.*, **42**, [IV] 4728 (1909).

(4) R. A. Lad and S. L. Simon, *Corrosion*, **10**, 435 (1954).

volume being 2000, 1000 and 250 cc. High vacuum, McLeod gage runs established the fact that initial reaction occurred at about 475°, but the significant magnitude of 1 mm. pressure arbitrarily used in this study was not reached until 725°. The gas phase consisted of hydrogen and water vapor; while the solidified melt contained crystals of metallic nickel and black, green or brown nickel containing compounds that yielded alkaline filtrates and black precipitates upon hydrolysis. Some melts, which had been subjected to repeated evacuations or prolonged exposure to "steady-state" conditions, yielded sodium metal deposits on the upper tube walls.

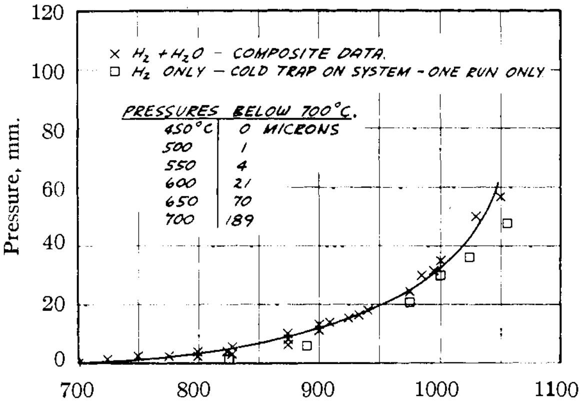

Fig. 1.—Steady-state pressure over NaOH–Ni system.

By repeated evacuation at a given temperature above 725°, the stoichiometric removal of the hydrogen contained in the original hydroxide charge was demonstrated.

Since conditions varied in the early runs, particularly with respect to time, the residual melts did not exhibit consistent or interpretable analytical results. It was determined, however, that neither the steady-state pressure nor incremental hydrogen yields were accurate measures of reaction extent.

The most reproducible step through which the reaction could be driven was the point of complete hydrogen removal. This was accomplished by the continuous evacuation of a nickel tube containing hydroxide at a temperature above 725°. A tared drying tube was placed "in-line" to detect and measure the water content of the evolved gas. The runs were stopped by quenching the system just as the oil vapor pump in the vacuum line began to reoperate smoothly after having been flooded by gas evolution. The tube was then cut at the melt line, weighed, leached in water and the empty tube dried and reweighed. Thus was obtained a sample, the dry weight of which was known. The hydrolyzed product was filtered and washed, the filtrate titrated for alkalinity and the residue analyzed gravimetrically (dimethylglyoxime) for nickel. These results calculated as various possible compounds (oxides) of sodium and nickel which could conceivably have resulted from an NaOH–Ni reaction were compared to the dry weight of the sample. The combination of a sodium compound and a nickel compound that agreed with the original weight was thus shown to be the probable molecular species of the melt. The tared drying tube was weighed for a check on water content, and the upper portion of the reaction tube was checked for metallic sodium by hydrolysis in a gasometric system.

When the reaction is driven rapidly to completion by constant evacuation, no water, sodium metal or nickel crystals appear in the reaction products. In addition, the solid residues analyze consistently to be an equimolar mixture of sodium and nickel monoxide. There was no way of determining from the data how or if these oxides were combined. The product may be a sodium nickelite (Na_2NiO_2) or simply mixed oxides. The Na_2O fraction is removed readily by hydrolysis, and, as will be shown later, the NiO portion is quantitatively converted to $Ni(OH)_2$ by the same process. Samples of the solid residue were subjected to X-ray diffraction, but the lines were too diffuse for identification. It was the opinion of the operator that the material was amorphous. Irrespective of these doubts as to actual product, the data show the prime NaOH–Ni reaction to be

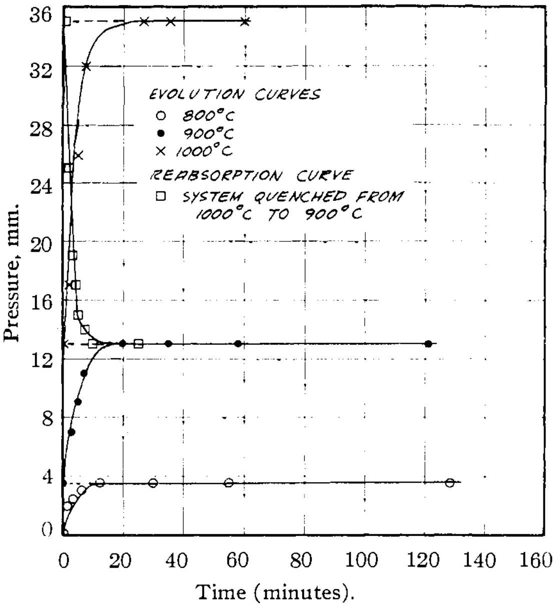

Fig. 2.—Rate of pressure development over NaOH–Ni system.

$$2NaOH + Ni \longrightarrow Na_2O + NiO\ (\text{or } Na_2NiO_2) + H_2 \quad (1)$$

The differences between these and previous runs were the length of time hydrogen remained in contact with the melt, and, in some cases, the extended time of heating after complete hydrogen removal. It follows that the appearance of water, nickel crystals and sodium metal must be related to these differences. To check these points, the apparatus was modified by adding an "in-line" drying tube (B_2O_3) between the reaction tube and the calibrated volume and a vacuum line connection above the manometer. The solid residues from reactions in this apparatus were subjected to magnetic analysis on a Gouy magnetic balance. This balance was used, not to determine paramagnetism, but as a qualitative tool for detecting traces of metallic nickel in the presence of non-ferromagnetic material.

The runs were made in the following manner: Sodium hydroxide was placed in the reaction tube and dehydrated under vacuum at 400°. The system was then isolated from the vacuum manifold and the temperature raised to a desired level. All evolved gas passed over the tared "in-line" drying tube. Thus, hydrogen was detected by pressure and water by the tared desiccant. Solid products were recovered, after quenching, by cutting the reaction tube and crushing the melt. This crushed sample was transferred to a tared glass tube for weighing both in and out of the magnetic field of the Gouy balance. The results of these runs are shown in Table I.

TABLE I

MAGNETIC MEASUREMENTS OF NaOH–Ni REACTION PRODUCTS

				Solid residue			
Temp., °C.	Time at temp., min.	H_2 press., mm.	H_2O, g.	Residue wt., g.	Wt. of Ni + NiO in residue, g.	Magnetic deflection, g.	Type of magnetism indicated
600	5	0	0.0000	0.9928	0.0000	−0.0007	Dia
800	10	4	.0000	1.1355	.0002	− .0010	Dia
850	10	14	.0000	1.1905	.0007	− .0003	Dia
900	80	7	.0007	1.0714	.0029	+ .0125	Ferro
920	30	10	.0006	1.6313	.0032	+ .0107	Ferro
950	60	14	0008	1 3629	.0018	+ .0051	Ferro
900	240	[a]	.0000	1.1261	.0000	− .0009	Dia
925	20	[b]	.0000	0.5802	.3174	− .0003	Dia

[a] 20 mm. added before heating. [b] Continuous evacuation.

Table II shows the type of deflection characteristic of dia-, para- and ferromagnetic materials. These data demonstrate that the very small nickel-containing fraction of the melts in Table I had to contain a dispersed ferromagnetic material (nickel) in order to have produced positive deflections of the magnitude shown.

TABLE II

TYPICAL MAGNETIC DEFLECTIONS

Material	Weight, g.	Total deflection, g.	Type of magnetism
KO_2 (80%)	1.1695	+0.0088	Para
NiO	12.3820	+ .1676	Para
NaOH	11.1621	− .0079	Dia
Ni	0.0005	[a]	Ferro

[a] Unweighable—pulled to pole piece and stuck.

Analyzing Table I, it is shown that no detectable reaction resulted at 600°; runs at 800 and 850° have produced hydrogen and some solid residue but no water or metallic nickel in ten minutes. Runs at 900, 920 and 950° extend the time element, and water and nickel appear simultaneously. The long run at 900° (240 min.) demonstrates that hydrogen added prior to heating completely suppressed reaction; and the last run shows again that continuous evacuation has produced only hydrogen and a non-ferromagnetic residue in accordance with equation 1. Thus, in a system which allows the evolved hydrogen to "equilibrate" with the melt, the following secondary reaction occurs.

$$NiO + H_2 \longrightarrow Ni + H_2O \qquad (2)$$

In these experiments, reaction 2 is driven to the right by the diffusion of water vapor into the free space of the system.

Earlier work at this Laboratory[5] established the fact that hydrogen and sodium monoxide react at temperatures up to 550° producing sodium hydroxide and sodium hydride. A repetition of this experiment at 700 and 900° was made in order to demonstrate a source of metallic sodium in the NaOH–Ni reaction. The runs were made, in the apparatus first described, by placing dry sodium monoxide in the reaction tube, purging, filling the calibrated volume with various pressures of hydrogen and heating to temperature before opening the stopcock between the reaction tube and the apparatus. The data on the rate of reaction are shown in Fig. 3.

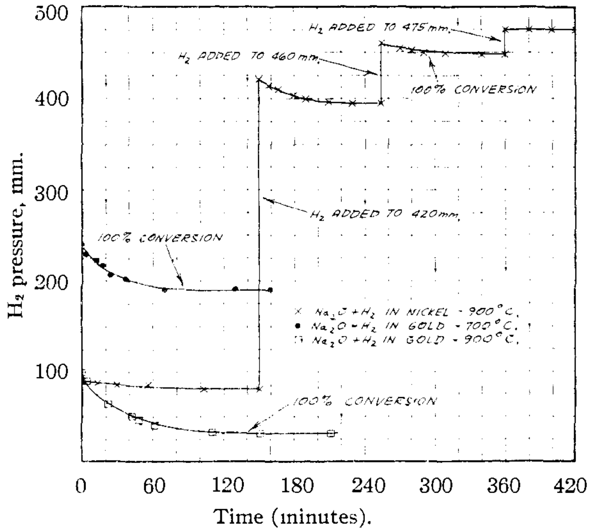

Fig. 3.—Rate of reaction between Na_2O and H_2.

The data in Table I and Fig. 3 show that the solid reaction product from equation 1 will equilibrate with the hydrogen produced by the same reaction. The NiO portion of the product reacts readily as in equation 2 with the production of metallic nickel and water vapor. The Na_2O portion of the residue reacts to produce NaOH and metallic sodium

$$Na_2O + {}^1/_2H_2 \longrightarrow NaOH + Na \qquad (3)$$

Both reactions tend toward the right in the system used in these studies, equation 2 by reason of the distillation of water and equation 3 by distillation of metallic sodium into the cooler parts of the system. Analytical results confirm the stoichiometry of equation 3. Evidently sodium hydride did not form under the conditions of this experiment. In the gold tube runs, the reaction proceeds readily to completion since the sodium produced immediately alloys with the gold tube. From the nickel runs, it follows that in a steady-state or equilibrated system in which equations 2 and 3 are progressing, their products would react further

$$H_2O + Na \longrightarrow NaOH + {}^1/_2H_2\uparrow \qquad (4)$$

The sum effect of reactions 2, 3 and 4 is the exact reverse of reaction 1, thus establishing the mechanism of equilibration in the non-isothermal, static system used for these experiments.

Additional proof of equilibrium in the NaOH–Ni system was demonstrated by isothermal capsule runs. The capsules were made by inert arc weldings 3-in. lengths of "L" nickel tubing after filling half full of predried hydroxide. The free space in the capsule was filled with argon. These capsules were heated in a muffle furnace four times and at temperatures corresponding to complete attack under vacuum conditions. The results are shown in Table III.

TABLE III

CAPSULE TESTS WITH NaOH IN NICKEL

Wt. NaOH, g.	Temp., °C.	Time, min.	Alkalinity in melt calcd. as NaOH, g.	NiO in melt, g.	Reaction product in melt, wt. %
2.3033	900	120	2.2800	0.0150	0.65
4.1790	1000	120	4.1540	.0349	.83
2.7510	800	90	2.7120	.0027	.10

These data (Table III) show that isothermal conditions with a small free space result in limited attack. The rate is probably dependent upon the rate of diffusion of hydrogen through the nickel.

The effect of atmosphere control on the NaOH–Ni system was also investigated. The runs were made in the original apparatus, and in crucibles equipped with close fitting lids containing inlet and outlet tubes. The data are in Table IV.

TABLE IV

ATMOSPHERE CONTROL

Atmosphere	Orig. press., mm.	Temp., °C.	Time, min.	Pressure rise as a result of reaction, mm.	Wt. of reaction residue after hydrolysis of melt, g.
H_2	760	950	120	0	0.0000
H_2	480	950	120	0	.0000
H_2	20	920	120	0	.0000
H_2	13	910	105	0	.0000
H_2	30	1000	60	7	.0240
N_2	760	800	15	[a]	.1682
N_2	25	900	30	1	.0682
A	760	900	20	[a]	.1351
Air	760	800	60	[a]	.4261

[a] Gas flowing over melt in covered crucible.

Table IV demonstrates that initially added hydrogen, in an amount in excess of the "steady-state" pressure required for a given temperature (Fig. 1), will inhibit NaOH–Ni reaction. Inert gas has no protective effect.

Further Reactions of the NaOH–Ni Reaction Products.—The solid residue produced by equation 1 exhibits at least two further reactions of interest. Of primary concern to an analyst wrestling with these materials is the fact that the Na_2O–NiO residue is stoichiometrically hydrolyzable, thus

$$Na_2O + NiO + 2H_2O \longrightarrow 2NaOH + Ni(OH)_2 \qquad (5)$$

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[5] Naval Research Laboratory Memo Report #33, June 1952.

However, if the Na_2O–NiO residue be heated for some time beyond the point of complete hydrogen removal (equation 1) and in the presence of an excess of nickel metal, a further reaction occurs which leaves a non-hydrolyzable residue of crystalline NiO. The reaction involves the Na_2O portion of the residue and proceeds as

$$Na_2O + Ni \longrightarrow NiO + 2Na \qquad (6)$$

The reaction goes completely to the right only if time and temperature allow for the complete distillation of the metallic sodium produced.

Table V is a compilation of the results of tests leading to the establishment of equation 6. The analyses in Table V are based on the hydrogen yield from the upper portion of the reaction tube when hydrolyzed in a gasometric analysis system.

TABLE V

REACTION OF Na_2O-NiO MIXTURE WITH EXCESS NICKEL *in vacuo*

Temp., °C.	Time at temp., min.	Na available, g.	Na found, g.	Na_2O reacted, %
830	75	0.575	0.092	16
910	60	.575	.259	45
910	105	.575	.390	59
910	180	.575	.407	70
910	290	.546	.424	78
955	110	.575	.488	85
955	110	.575	.501	87
1010	120	.575	.560	97
1050	120	.590	.585	99

Chemical analysis of residues from the last two runs in Table V confirm the percentage of reaction shown.

Table VI presents data on the hydrolysis of residues from equation 1 and equation 6. In addition, data are given for commercial crystalline NiO.

TABLE VI

HYDROLYSIS OF NaOH-Ni REACTION RESIDUES

Source of samples	Hydrolyzing soln.	Sample wt., g.	Alkalinity, calcd. as Na_2O, g.	NiO residue wt. after treatment: Ether dried	110°	500°	Remarks
Na_2O-NiO from eq. 1	H_2O	0.1905	0.0864	0.1408	0.1293	0.1042	Converted to $Ni(OH)_2$
NiO from eq. 6	H_2O	.7621	None	.7625	.7620	.7620	No effect
NiO from eq. 6	10% NaOH	.5325	....	.5332	.5320	.5321	No effect
NiO(Comm.)	10% NaOH	.4765	....	.4775	.4765	.4765	No effect
NiO(Comm.) in NaOH (fused)	H_2O	.1417	....	.1420	.1415	.1415	No effect

The solid hydrolysis product of equation 5 was pyrolyzed in a semi-micro train equipped with tared tubes containing P_2O_5, LiOH and P_2O_5, hot CuO, and hot Cu for determining H_2O, CO_2, H_2 and O_2, respectively. No CO_2, H_2 or O_2 was detected.

The weight gain of the water absorption tube was nearly identical to the weight loss of the sample at 500°. The chemical analysis of the pyrolysis residue established it to be NiO. These runs substantiate the data in Table VI and show the product to be $Ni(OH)_2$.

Certain tests were performed to check variables in the material and equipment used in the preceding experiments. For the sake of what little brevity can be salvaged they will be mentioned without accompanying data.

Total hydrogen diffusion through the nickel tubes used, at an arbitrarily selected average temperature of 900° and internal pressure of 12 mm., amounted to less than 0.5 mm. per hour. While this amount could have a decided long range effect, the times involved in the experiments herein reported make diffusion effects of minor import.

No evidence could be found of a reaction between NaOH and commercial NiO.

No evidence could be found of a reaction between Na_2CO_3 and nickel at temperatures up to 1000°.

Reaction 6 can be simulated by the use of separately prepared Na_2O in a Ni tube. Reaction times and temperatures are identical to those shown for the Na_2O–NiO mixture from equation 1. Capsule tests involving Na_2O in Ni show the existence of an equilibrium tending toward the left of the equation, less than 10% reacting in two hours at 950 to 1000°.

The role of certain reactive elements present in commercial nickel was investigated slightly. Carbon and iron, and probably all other impurities except copper and cobalt, are selectively leached from the surface of nickel by sodium hydroxide. The effect on the reaction of NaOH with nickel is so slight as to be undetectable; however, it is probable that corrosion data would find rate differences, depending upon impurity concentration and depth of leaching.

The Reaction of Copper and Monel with NaOH.—The runs with these metals were performed exactly as were the ones with nickel. The copper used was commercial tubing and the Monel was 66Ni–32Cu–2Fe.

With one exception, these metals exhibit the same reactions found for NaOH–Ni. The "steady-state" pressures shown in Fig. 1 apply to both the copper and the Monel systems. The one exception is the valence of the copper compound formed by initial NaOH–Cu reaction. In the case of pure copper, the oxide formed is Cu_2O, since this is the stable oxide in the presence of excess copper metal.[6] The prime reaction, hence, is

$$2NaOH + 2Cu \longrightarrow Cu_2O + Na_2O \text{ (or } 2NaCuO\text{)} + H_2 \qquad (7)$$

In the case of Monel, the copper compound formed is bivalent, evidently because the copper remaining in the alloy is not readily available. Monel reacts exactly as would be predicted for a mixture of nickel and copper

[6] J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. XV, Longmans, Green and Co., New York, N. Y., 1936.

$$(^2/_3\text{Ni}\cdot{}^1/_3\text{Cu}) + 2\text{NaOH} \longrightarrow (^2/_3\text{NiO}\cdot{}^1/_3\text{CuO}) + \text{Na}_2\text{O} + \text{H}_2 \quad (8)$$

The iron portion of the alloy reacts according to the equation developed later for pure iron. The total effect is a uniform reaction throughout the alloy, with little or no sign of pitting.

At the temperatures employed (700–900°), both Monel and copper exhibited deep non-protective external oxidation. The alloy oxidizes stoichiometrically and uniformly, with severe spalling occurring upon cooling.

The Reaction of Gold with NaOH.—In the work of Le Blanc and Bergmann,[3] gold was presumed to be non-reactive with NaOH at *ca.* 700° in spite of the recovery of macro quantities of gold flakes from their melts and certain unexplained gold plating effects on the metals tested in gold. The present investigation found gold to be resistant but not inert to NaOH.

The runs were made exactly as has been described for the nickel system. Gold was found to establish a "steady-state" pressure of hydrogen and water vapor somewhat lower than nickel and copper. Also, the proportion of water was considerably higher than in the case of nickel. The data are shown in Fig. 4. Another important difference was that the pressure developed is dependent upon the size of the free space in the system, whereas in the case of nickel and copper, no such dependence was found. Hence, the pressures shown in Fig. 4 apply only to a 200-cc. free space. This effect is no doubt related to the predominance of water vapor in the gaseous products, and to the solubility of reaction products in the melt.

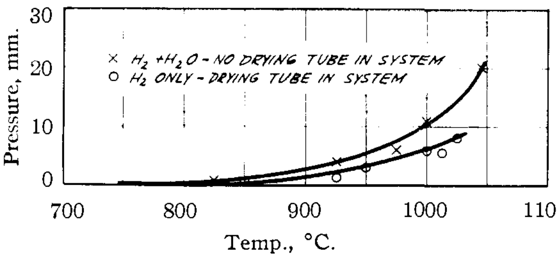

Fig. 4.—Steady-state pressure over NaOH–Au system.

The results of representative NaOH–Au reactions are shown in Table VII.

The data in Table VII show that water, hydrogen and gold compounds occur nearly simultaneously under all test conditions, except the run at 750° which was below the temperature of significant attack (see Fig. 4) and the run in an isothermal sealed capsule. It should be noted that two runs produced reaction products even under an excess of added hydrogen in contrast to the nickel and copper reactions.

The solid residues resulting from hydrolysis of the melts were subjected to analysis by pyrolysis with subsequent chemical analysis of this residue. In addition to the hydrolysis residue, a considerable fraction of all the total reacted gold was found as a soluble salt in the alkaline filtrate from the hydrolyzed melt. This compound separated as neutrality was approached during the titration of the filtrate with acid. The small weight involved and the preponderance of gold in the compounds prevented exact identification. The meager data indicated, however, that the reaction compound was Au_2O and that the hydrolysis residue was a hydrated oxide or hydroxide.

TABLE VII

NaOH-Au REACTION PRODUCTS

Temp., °C.	Time at temp., min.	Exptl. conditions	Reaction products: H_2O, g.	H_2	Au in hydrolysis residues,[a] g.
975	2	Constant evacuation	0.0017	Present	0.0005
1040	10	Constant evacuation	0.0031	Present	.0010
750	10	Static vacuum	None	None	None
910	240	20 mm. H_2 added	Present	.....	.0250
910	240	20 mm. H_2 added	Present	.....	.0180
1050	2	In air	.....	.....	.0110
900	60	Sealed capsule	.....	.....	None
800-1000	120	Static vacuum	0.0134	Present	.0390

[a] Combined and metallic gold.

A study was made of the gold plating on nickel strips in hydroxide melts reported by Le Blanc and Bergmann.[3] It was found that plating occurred only on strips which remained in the melt during cooling. The effect, therefore, must be related to the solubility and stability of the gold reaction compound in molten NaOH. As the melt cools, this compound, probably Au_2O, precipitates and thermally decomposes to metallic gold and oxygen, thus producing the metallic gold and plating effects reported by reference 3 and substantiated by this study. The apparent stability of this gold compound in solution at these elevated temperatures is somewhat striking.

An additional reaction affects this system. Any secondary reaction, such as Na_2O with H_2, which releases metallic sodium results in the formation of an Au–Na alloy. The metals combine readily and the alloy is very stable. The sodium is not completely removed even with repeated acid washing.

The following reactions can be postulated for the gold–NaOH system

$$2\text{NaOH} + 2\text{Au} \longrightarrow \text{Na}_2\text{O} + \text{Au}_2\text{O}\ (\text{or } 2\text{NaAuO}) + \text{H}_2 \quad (9)$$

$$\text{Au}_2\text{O} + \text{H}_2 \longrightarrow 2\text{Au} + \text{H}_2\text{O}\ (\text{or Au}_2\text{O} \longrightarrow 2\text{Au} + {}^1/_2\text{O}_2 \text{ and H}_2 + {}^1/_2\text{O}_2 \longrightarrow \text{H}_2\text{O}) \quad (10)$$

$$\text{Na}_2\text{O} + {}^1/_2\text{H}_2 \longrightarrow \text{NaOH} + \text{Na} \quad (11)$$

$$\text{Na} + \text{Au} \longrightarrow \text{Na–Au Alloy} \quad (12)$$

The prime reaction, number (9), is similar to the nickel and copper reactions. However, reaction 10 is not reversible and the reverse of reaction 11 is prevented by reaction 12. Thus, the "steady-state" system is not as predictable as in the case of nickel and copper, as, indeed, was found to be the case, particularly with respect to hydrogen inhibition.

Reaction of NaOH with Fe, Cr, Ti, Ta, Be, Mn, Ag, Co and Ferrous Alloys.—Except for silver and cobalt, the above metals were found to react completely with molten sodium hydroxide. The rate of reaction was dependent upon the availability of unreacted metal. These metals, therefore, were studied briefly to establish their valence state in the reaction products. Simultaneously, the absence of a "steady-state" and hydrogen inhibition was established.

The procedure used was a modified material balance technique in which a small weighed quantity of the metal reacted completely with an excess of sodium hydroxide contained in a nickel tube. The hydrogen yielded by the reaction was then balanced against the original weight of metal (after a chemical check of the residue to ensure complete reaction) and thus interpreted into which oxide of the metal could have resulted from the reaction.

The following equations summarize the results. The temperatures shown are approximate points of significant reaction

$$2Fe + 6NaOH \xrightarrow{600°} Fe_2O_3 + 3Na_2O + 3H_2 \quad (13)$$

$$2Cr + 6NaOH \xrightarrow{650°} Cr_2O_3 + 3Na_2O + 3H_2 \quad (14)$$

$$Ti + 4NaOH \xrightarrow{325°} TiO_2 + 2Na_2O + 2H_2 \quad (15)$$

$$2Ta + 10NaOH \xrightarrow{600°} Ta_2O_5 + 5Na_2O + 5H_2 \quad (16)$$

$$Be + 2NaOH \xrightarrow{650°} BeO + Na_2O + H_2 \quad (17)$$

$$Mn + 4NaOH \xrightarrow{600°} MnO_2 + 2Na_2O + 2H_2 \quad (18)$$

None of the runs resulting in the establishment of the above equations gave metallic sodium or water vapor as reaction products. They were, however, short time experiments. Prolonged exposure to hydrogen may result in the production of some water and sodium.

All of the solid products on the right in the above equations react with water, yielding hydroxides or hydrated oxides. In the case of tantalum, the hydrolysis product is completely soluble. In the case of chromium, when leached in air, part of the residue forms a soluble chromate.

Ferrous alloys (304 SS, 310 SS, 36% Ni–64% Fe alloy, and 64% Ni–17% Cr–17% Fe alloy) react as might be predicted from all of the foregoing. The iron and chromium fractions react completely as shown by their individual equations, while the nickel portion appears to remain unattacked, probably by reason of the protective effect of the produced hydrogen. The over-all effect on the alloy, however, is one of complete destruction. The mechanism of attack is one of severe penetration in contrast to the more or less uniform removal from the surface of nickel, copper and gold.

Meager data on the reaction of NaOH with silver indicates a similarity to gold. One exception is the fact that silver tubes become quite porous to molten NaOH after a few fusions.

Cobalt was investigated by a single test which showed "steady-state" pressures of hydrogen and water vapor identical to those shown for nickel. Its further reactions are assumed to be identical.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE KNOLLS ATOMIC POWER LABORATORY,[1] GENERAL ELECTRIC COMPANY]

The Titanium–Hydrogen System[2]

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The equilibrium pressure of hydrogen over titanium–hydrogen has been measured at 300, 400 and 500°. Similar measurements have been made of titanium–deuterium and titanium–tritium. At 500° no isotope effect was observed.

The titanium–hydrogen system is one of several metal–hydrogen systems which have been studied both from the practical standpoint because of the high hydrogen occlusion obtained and from the academic viewpoint because of the light which may be shed on the properties of metal systems. The high hydrogen concentrations (approximately 450 cc. (STP) H_2/g. titanium) obtainable in this system make it ideal for many storage applications. Among these are the following: 1. Separation of hydrogen and its isotopes from other gases; 2. Transfer of large quantities of gas in a small volume at low pressure; 3. Preparation of materials with high hydrogen density.

In the titanium–hydrogen system, as in the similar systems zirconium–hydrogen and hafnium–hydrogen, the occluded gas has apparently less metallic character than in the possibly unique palladium–hydrogen system, but more than in the uranium–hydrogen and thorium–hydrogen systems.

The dissociation pressures of the hydrides are the most convenient functions and have been extensively studied. Kirschfeld and Sieverts[3] and recently McQuillan[4] have studied the Ti–H system at pressures from 1 to 760 mm., and at temperatures below 1000°. Gibb, *et al.*,[5] have made measurements above 500° and at high as well as low pressures. No results have been reported, however, for the micron pressure region which includes low concentrations at 500° and nearly the entire range at 400 and 300°.

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[2] Presented before the Physical and Inorganic Division of the 127th National Meeting of the American Chemical Society, Cincinnati, Ohio, March, 1955.

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[5] T. R. P. Gibb, Jr., J. J. McSharry and R. W. Bragdon, THIS JOURNAL, **73**, 1751 (1951).