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UNIVERSITY of ARKANSAS
Institute of Science and Technology
FAYETTEVILLE

W⁰43367

PROGRESS REPORT

Subcontract No. 501--Under W-7405-eng-26
Report for the Period April 1, 1953, through June 30, 1953

8413-1

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PROGRESS REPORT

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Report for the Period April 1, 1953, through June 30, 1953

Summary

Static tests in a NaOH-Ni system demonstrated that equilibrium, as measured by a constant pressure above the system, could be established at temperatures of 600 to 850°C after 40 to 200 hours. Cooling the system to 730 and 620°C showed that constant pressures could be obtained in from 10 to 20 hours. It is possible that the rate of the reaction

is much more rapid toward the left.

A graphite-lined nickel crucible was not a suitable container for sodium hydroxide because the nickel that had been in contact with graphite and hydroxide became brittle and porous. Preliminary data on the

system, as studied by thermal analysis, showed that a binary compound is formed and that there is a solid-state transformation in mixtures containing approximately 90 mole per cent of sodium hydroxide.

Microscopic investigation revealed the solubility of nickel oxide in sodium hydroxide to be approximately 0.25 weight per cent. The solubility of UO_3 is approximately 0.15 per cent.

High temperature X-ray investigation of NaOH-Ni mixtures heated to 700 and cooled to approximately 300°C showed a reproducible series of lines which could not be identified.

Measurement of thermogalvanic potentials between powdered nickel metal

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electrodes and 0.1 molar solutions showed, after cooling the system, a residual potential that was constant for a considerable time. Preliminary results from a thermocell containing nickel electrodes in fused sodium hydroxide show that potentials as great as 0.1 volt may be developed. Apparatus for determining the ion transference numbers of selected nickel salts is being constructed.

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Reaction Studies: D. M. Mathews and R. V. Nauman

Results reported by the Naval Research Laboratory indicate that the pressures above a NaOH-Ni system are less than this laboratory reported previously and that equilibrium, as measured by a constant gas pressure, may be reached in a relatively short time.

We repeated experiments described in the last quarterly report¹, finding the measured pressures of hydrogen above the reacting NaOH-Ni less than those previously reported. After heating for 90 hours at 730°C, the pressures on two systems were 52 and 75 mm and were increasing slowly.

After evaluating the results in this laboratory we decided that there may have been gaseous diffusion through the vycor containers at high temperatures, actual leaks in the system, or gases sorbed on the nickelware which could be evolved on heating. In previous experiments some leaks, which developed at high temperatures, were found after the systems had cooled, but this was true only for one or two of the six reaction chambers.

To check the possibility of gaseous diffusion at higher temperatures three of the vycor cells were replaced by quartz cells and the pressure in each was reduced to 3×10^{-5} mm. After standing at room temperature for 67 hours the pressures in the 6 cells ranged from 0.02 mm to 0.07 mm. This was considered a satisfactory vacuum, so the cells were heated to 650°C. The pressures, after the system was maintained at that temperature, indicated no appreciable gaseous diffusion.

¹Progress Report, University of Arkansas Institute of Science and Technology; January 1, 1953 through March 30, 1953

The nickelware was then placed in one of the cells and heated to 535°C. Gases were given off when the system was under vacuum, but after four days at this temperature the pressure did not increase further.

Two quartz cells containing nickelware, heated as described above to remove sorbed gases, were loaded with sodium hydroxide and heated to approximately 600°C without a cold trap in the system. The gas pressure in cell 5 appeared to approach a constant value, but that in cell 3 was still increasing (Fig. 1). After 40 hours the temperature was increased to approximately 650°C on cell 5.

After 65 hours heating the two cells were evacuated and the temperature was increased to approximately 750°C. After 60 hours at this temperature the pressures appeared to be approaching a constant value (Fig. 1).

The two cells were evacuated again and heated to approximately 850°C. After 200 hours at this temperature the pressure in cell 5 appeared essentially constant while that in cell 3 was still increasing (Fig. 2).

At this time the temperature was decreased to approximately 730°C. The pressure in the cells decreased rapidly and soon reached a value which remained essentially constant (Fig. 3). After 40 hours at this temperature the system was again cooled to approximately 620°C. The pressure again rapidly approached a constant value (Fig. 3).

The results of these experiments indicate that, on heating, a constant gas pressure may be reached at a given temperature after a rather long period of time; however, there are indications that a constant gas pressure value at a given temperature might be rapidly obtained by first heating the system to a high temperature and then successively decreasing the temperature in

desired intervals. The reaction may be shown as

The pressure measurements indicate that the rate of the reverse reaction may be much faster than the rate of the forward reaction.

System NaOH-Ba(OH)₂: R. V. Nauman

The study of the system NaOH-Ba(OH)₂ by thermal analysis was begun to obtain new information while testing the usefulness of graphite-protected nickelware as containers for molten hydroxides. We knew that graphite is porous to molten hydroxides and will not contain them, but we thought that nickel covered by graphite might be a useful container. We assumed that the molten hydroxide would pass through the graphite and react with the nickel. It was thought that the products of the nickel-hydroxide reaction might not pass through the graphite, but would clog the graphite pores so that further diffusion of hydroxide in either direction would be prevented; thus a container that would not react with the hydroxide would be obtained.

The containing vessel (Fig. 4) consisted of a nickel cylinder closed at one end, into which was snugly fitted a similar graphite cylinder. We placed a closed-end graphite tube into the center of this container. Inside the graphite tube a nickel thermocouple protection well was tightly fitted. Into this nickel tube was inserted a ceramic insulator through which the thermocouple wires passed.

For comparison, measurements were made using nickel container and thermocouple well without any enclosing graphites. Within experimental error the same freezing temperatures were obtained with both containers.

A few experiments with sodium hydroxide indicated that the graphite shielding around the nickel container was not useful. It was not determined whether the graphite prevented the diffusion of nickel reaction products into the hydroxide melt. We found that the nickel thermocouple well became very porous to hydroxide after contact with the graphite and hydroxide at high temperatures. Similar experiments without the graphite showed that the nickel did not become porous to the hydroxide even after hundreds of hours of contact. The nickel which had been in contact with graphite and hydroxide at high temperatures became very brittle, broke easily under pressure, and appeared extremely porous and crystalline at a break. When the hydroxide passed through the nickel tube, the thermocouple was attacked and false temperatures were recorded. As a result of this nickel porosity the graphite lining was abandoned and most of the NaOH-Ba(OH)_2 system was studied in nickel alone. This is possible because, at the temperatures necessary for studying the system, the nickel-hydroxide reaction is slow and probably unappreciable.

To complete this investigation would require much more work, but it appears that the phase diagram can be tentatively explained by saying that somewhere in the 35 to 55 mole per cent Ba(OH)_2 region there is a eutectic mixture of Ba(OH)_2 and a not yet identified compound.

A solid-state transition occurs in mixtures containing about 90 mole per cent sodium hydroxide. Kruh substantiated this result by high temperature X-ray analysis, but the nature of the transition has not been established.

Chemical Microscopy: J. K. Carlton

Observations were continued on the solubilities of selected metal oxides

in molten sodium hydroxide. Under a flowing hydrogen atmosphere (250 cc/min), samples containing approximately 0.5 per cent nickel oxide (by weight) were not completely soluble in sodium hydroxide at 800°C. Further tests showed that the solubility is probably slightly less than 0.25 weight per cent.

Solubility studies were conducted on various concentrations of UO_3 in sodium hydroxide. A flowing hydrogen atmosphere was used initially but, because of the apparent reduction of UO_3 as shown by a color change, a flowing argon atmosphere was used for all subsequent observations. The solubility of this compound in sodium hydroxide is approximately 0.15 per cent (by weight) at 800°C.

Studies will be continued on UO_2 , Fe_2O_3 and other metal oxides.

X-ray Analysis: R. F. Kruh

Experimental work on the NaOH-Ni reaction has reached a point where analytical results are necessary to identify the reaction products. X-ray patterns obtained on a mixture heated to 700°C under flowing argon and then examined at approximately 300°C show the presence of substances for which no patterns have been reported (Table 1).

Table 1. High temperature X-ray Data on Reaction Products
from NaOH-Ni Heated to 700°C and Cooled to 300°C

Spacing	Intensity	Spacing	Intensity
$(\sin\theta)/\lambda$		$(\sin\theta)/\lambda$	
0.0948	medium	0.1942	medium
.0965	medium	.2055	weak
.1080	weak	.2192	weak
.1571	strong	.2230	weak
.1696	weak	.2358	medium
.1909	weak	.2562	weak
		.2991	weak

There is a superficial resemblance to some of the patterns given by the various nickel oxides described by Glemser and Einerhand (Z. anorg. Chem. 261, 26-51 [1952]).

No agreement between these results and those obtained from reaction cells operated by Mathews has been found.

Thermogalvanic Potentials: K. H. Stern

(1) In Solution

Measurements of thermocells containing powdered nickel electrodes and 0.1 molar NiCl_2 solutions are continuing. The results obtained agree generally with those of Carr and Bonila (J. Electrochem Soc. 99, 475 [1952]) for NiSO_4 solutions. In contrast to the work of these authors, however, we observed that the same curve is not followed on decreasing as on first in-

creasing the temperature (Fig. 5). It is improbable that the residual potential results from the Soret effect, since it remains constant when the entire system remains at the same temperature for several weeks. It is possible that some irreversible electrode effect occurs at elevated temperatures in these solutions.

Since large amounts of hydrogen are absorbed by the nickel in the preparation of the nickel electrodes, the residual potential may be the result of a change in the amount of absorbed gas when the electrode is heated. It is known that electrode potentials may change after the absorption of gas by electrodes.

(2) In Melts

The lack of a suitable container hampers measurements of thermocells containing nickel electrodes in fused NaOH. Some experiments indicate that potentials as great as 0.1 volt may be set up between pieces of nickel in hydroxide melts--even at constant temperature--if the condition of the nickel surface is not carefully controlled.

Transference Measurements: K. H. Stern

In order to apply the Eastman thermocell equation to measurements of thermopotentials, the ion transference numbers must be known. Since these are not available in the literature for the nickel salts used in this study, measurements are being planned. A modification of the apparatus used by MacInnes and Dole (J. Am. Chem. Soc. 53, 1357 [1931]), using the Hittorf method, has been constructed (Fig. 6).

Density Measurements: K. H. Stern

Density measurements of solutions used in the above studies are in pro-

gress. These will be used in the calculation of transference numbers and for the determination of partial molal volumes.

W. J. Smothers
W. J. Smothers, Associate Professor
Institute of Science and Technology

Date 7-30-53

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Figure 1. GAS PRESSURE ABOVE NaOH-Ni SYSTEM AS A FUNCTION OF TIME AT GIVEN TEMPERATURES

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Figure 2. GAS PRESSURE ABOVE NaOH-Ni SYSTEM AT 850°C

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Figure 3. GAS PRESSURE ABOVE NaOH-Ni SYSTEM
ON COOLING TO GIVEN TEMPERATURES

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Figure 4. GRAPHITE-LINED NICKEL CONTAINER
FOR MOLTEN SODIUM HYDROXIDE

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Figure 5. THERMOCELL: Ni-NiCl₂ (0.1M)

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Figure 6. EQUIPMENT TO BE USED FOR
TRANSFERENCE MEASUREMENTS.

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There is submitted herewith for your
consideration a Progress Report on
the work conducted under Subcontract
No. 501--Under W-7405-eng-26.

Date _____

For W. W. Grigorieff, Director
University of Arkansas
Institute of Science and Technology

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