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PROGRESS REPORT

Subcontract No. 501--Under W-7405-eng-26
Report for the Period January 1, 1953, through March 31, 1953

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the work conducted under Subcontract
No. 501--Under W-7405-eng-26.

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Reaction Studies. The battery of six Vycor reaction chambers - a part of the high vacuum system - has been put into operation. The volume of the manifold was determined by means of a gas burette. The volume of each reaction chamber and its auxiliary glass system was determined by measurement of the pressure change which resulted from permitting the known volume of gas in the manifold (which was at a known pressure) to equilibrate with the vacuum in the reaction chamber. The volume of each reaction system was calculated from the original and final pressures and the known volume of the manifold. It was assumed that the gas used (air) behaved as a perfect gas.

The vacuum system can be evacuated to a pressure of 10^{-6} mm Hg under continuous pumping. It has been shown several times that, if the reaction systems are isolated from the pumping system, the pressure increases to only 10^{-2} mm Hg or less after several days.

In order to facilitate the study of the sorption of hydrogen by the reaction products, the reactants, and the containing system, experiments were begun on the study of the effect of the surroundings on the over-all pressure of a known amount of gas in each reaction system. This procedure is necessary because not all parts of the entire system are at the same temperature during the reaction. The qualitative studies were of value, despite the fact that the absolute calibrations of the systems must be discarded because the Vycor vessels later collapsed slowly while being heated under vacuum at 950°C for several days.

A hydrogen pressure of approximately 77 mm Hg was introduced into the entire vacuum system at 28°C, after which each reaction system was isolated from the manifold. The pressure of each reaction system was determined as a function of the temperature of the reaction vessel. The results varied slightly because of the different volumes, but in each case the pressure was approximately 100 mm Hg at the time that the temperature reached about 900°C. When 196 mm Hg hydrogen pressure was introduced at 28°C, the pressure was 256 mm Hg at 900°C.

It was noted that the flow of water through the coils which cool the ball and socket joints of the reaction chambers alters the pressure of the system by 2 to 3 mm Hg when the systems are at room temperature.

A rise in room temperature (from 23°C to 30°C) caused a pressure increase of 2 to 3 mm Hg in the systems when the reaction chambers were at 25°C to 850°C; however, above 900°C, the pressure increase appears to be larger.

Further calibration and study of sorption were postponed in favor of a study of the hydrogen pressure which results from the nickel-sodium hydroxide reaction. No calibration is needed for this study because, if equilibrium pressures are attainable, the pressure should be independent of the volume and temperature of the external part of the system.

Under continuous pumping, different-sized samples of NaOH in nickel containers were heated to a temperature slightly above the melting point of NaOH to remove the water vapor and the trapped gases. Two samples of NaOH weighing 0.2 gm each, two of 2.0 gm, and two of 20.0 gm were studied. After the removal of water vapor, the samples were heated to some 400°C, and at this low temperature some gas was evolved. The pressure of this

gas increased slowly with time. However, because the pressures were too low to be measurable with a mercury manometer they were measured with a McLeod gage. At present it can be reported only that the gas pressure at 400°C was real and increased with time. Further investigations are under way.

After the gas formation at 400°C was observed, the temperatures of the reaction chambers were increased to approximately 600°C and the rate of pressure increase was determined. After 18 hours, the pressures were still increasing in all cases. No equilibrium pressures were found, and plots of pressure vs. time did not indicate that an equilibrium was being approached. The temperatures were increased to about 700°C, the reaction vessels which contained 20.0-gm and 2.0-gm samples of NaOH were evacuated and the rate of pressure increase was followed at this temperature. The vessels which contained 0.2-gm samples were not evacuated, but the temperature was increased and the resulting pressure increase was followed, starting with the pressures developed at lower temperatures.

The 0.2-gm samples gave pressures of 74 and 55 mg Hg, respectively, and the pressures remained essentially unchanged after $3\frac{1}{2}$ days at 700°C. When the systems were opened, no sodium hydroxide could be detected in the reaction vessels; the only reaction product (other than the gas) was a black material which gave an unidentifiable X-ray pattern.

The 2.0-gm and 20.0-gm samples heated at 700°C gave pressures which were still increasing after 6 days. The slope of the pressure-time curve was decreasing, but there was no evidence that an equilibrium pressure was being approached. One 2.0-gm sample was held in a system which contained a liquid nitrogen trap for the first $1\frac{1}{2}$ days. The trap then was removed,

and thereafter the pressure increased much more rapidly than did that from the 2.0-gm sample, which had never had a trap in its system. The trap was replaced on the sixth day. After this, the pressure fell considerably, but it did not approach that of the other 2.0-gm sample. Similar experiments were begun with the 20.0-gm samples, but the system containing the trap was broken after 10 hours. Table 1 contains a brief summary of the approximate pressures obtained from the 2.0- and 20.0-gm NaOH samples.

Table 1. Pressure changes of gas in high-vacuum system.

Weight of NaOH Sample	Pressure after 7½ hours	Pressure after 35 hours; trap re- moved	Pressure after 55 hours	Pressure after 97½ hours	Pressure after 155 hours	Pressure after 156 hours; with cold trap
	<u>mm Hg</u>	<u>mm Hg</u>	<u>mm Hg</u>	<u>mm Hg</u>	<u>mm Hg</u>	<u>mm Hg</u>
20.0-gm with trap - - -	34					
20.0-gm with- out trap -	49	81	129	174	222	194
2.0-gm with trap - - -	18	35	130	297	448	367
2.0-gm with- out trap -	29	46	84	134	173	156

X-ray analysis of the solid reaction products definitely identified NaOH in each instance, except in the case of the 20.0-gm sample in the system which shattered while it was hot. In that instance nickel oxide was identified. Other experiments designed to amplify and support these pressure experiments are in progress.

A graphite-lined nickel crucible is being prepared for use as a hydroxide container. It is hoped that the graphite will be unreactive, and, further, that any reaction products which may be formed if the NaOH diffuses through the graphite and comes in contact with the nickel will not diffuse back into the hydroxide melt. If the vessel is practicable, it will be used for phase studies. (R. V. Nauman and D. M. Mathews).

Dynamic Corrosion Studies. These studies were proposed as a means of determining the corrosive effects of molten sodium hydroxide on a rotating metal rod, weighed before and after each experiment, under various atmospheres and with the use of several different additives.

Experiments have been completed at 800°C and 900°C, with a nickel stirrer, under a flowing argon atmosphere. A temperature gradient at the stirrer caused a considerable deposition to take place there. The deposit at 800°C generally was small and made up of characteristic black, shiny crystals. At 900°C, the deposit usually was quite large and, in addition to the usual black crystals, there was a larger quantity of metallic nickel. Beneath this spongy deposit there was a small, hard deposit of metallic nickel. The gain in weight reported as a result of runs at 900°C was that of this hard deposit which remained after the removal of the spongy deposit and after the stirrer had been rubbed with steel wool.

Table 2 shows that, for short runs of like duration, the stirrer underwent a consistent weight gain at 900°C and a similar weight loss at 800°C. For longer runs, there was a weight gain at both temperatures, with a larger gain at the higher temperature for runs of like duration.

Table 2. Corrosion of nickel by molten sodium hydroxide under flowing argon.

Temperature	Duration	Weight of stirrer	Weight loss	Weight gain
<u>°C</u>	<u>hours</u>	<u>gm</u>	<u>gm</u>	<u>gm</u>
800 - - - - -	16	45.1915	-----	0.0490
800 - - - - -	16	45.3110	-----	.0345
800 - - - - -	16	45.1449	-----	.0291
800 - - - - -	16	45.2380	-----	.0230
900 - - - - -	16	45.0462	-----	.1561*
900 - - - - -	16	45.1357	-----	.3702
900 - - - - -	6	45.1532	-----	.0031
900 - - - - -	6	45.1505	-----	.0395
900 - - - - -	3	44.8921	-----	.0090
900 - - - - -	3	44.9501	-----	.0024
900 - - - - -	3	44.8993	-----	.0081
900 - - - - -	3	44.9520	-----	.0044
900 - - - - -	3	44.9057	-----	.0035
900 - - - - -	3	44.9553	-----	.0042
900 - - - - -	3	44.9071	-----	.0017
900 - - - - -	3	44.9568	-----	.0035
800 - - - - -	3	44.9083	0.0038	-----
800 - - - - -	3	44.9598	.0041	-----
800 - - - - -	3	44.9045	.0052	-----
800 - - - - -	3	44.9557	.0046	-----
800 - - - - -	3	44.8993	.0058	-----
800 - - - - -	3	44.9511	.0086	-----

*(1.3592, including spongy deposit)

Because a temperature gradient exists in this system and prevents quantitative measurement of corrosion of the stirrer, it is recommended that a crucible and a stationary cold finger be used. A hydrogen atmosphere also will increase the validity of the results. (J. K. Carlton).

X-ray Analysis. The X-ray reflections ascribed to beta-NaOH may be indexed on the basis of a cubic unit cell with $a = 11.0 \text{ \AA}$. West's allegation that beta-NaOH is cubic thus appears to be justified. Observed d values are compared with those based on a cubic cell with $a = 11.0 \text{ \AA}$ (Table 3).

Table 3. Calculated and observed X-ray spacings of beta-NaOH.

Index	Calculated	Observed	Index	Calculated	Observed
	$\text{\AA}$	$\text{\AA}$		$\text{\AA}$	$\text{\AA}$
111 - - - -	6.35	6.4	331 - - - -	2.53	2.54
200 - - - -	5.50	5.6	420 - - - -	2.46	2.46
210 - - - -	4.92	5.0	421 - - - -	2.40	2.40
211 - - - -	4.50	4.6	332 - - - -	2.35	2.35
220 - - - -	3.89	3.9	500, 430 - - - -	2.20	2.20
310 - - - -	3.48	3.5	520, 432 - - - -	2.05	2.06
222 - - - -	3.18	3.18	522, 441 - - - -	1.91	1.90
320 - - - -	3.05	3.07	611, 532 - - - -	1.78	1.78
321 - - - -	2.94	2.94	621, 540, 443 - -	1.72	1.72
400 - - - -	2.75	2.73			

Products from the reaction apparatus (Mathews) have been examined at room temperature. In experiments where NaOH was heated in nickel to 700°C, material which gave an unfamiliar powder pattern was isolated.

NaOH and nickel were heated in the high-temperature X-ray furnace (modified to eliminate creep) to 650°C. At this temperature only the nickel pattern was observed. At room temperature unfamiliar lines appeared in the pattern. These lines did not correspond to those produced by products obtained by Mathews. (R. F. Kruh).

Microscopy. The apparatus used in microscopic work was improved in order that a hydrogen atmosphere may be used for observation. Principal improvements include the design of a heating element which can withstand higher temperatures and the use of a copper cooling coil on the standard taper joint of the unit.

Solubility studies of nickel oxide in molten sodium hydroxide were begun. Under a flowing hydrogen atmosphere of approximately 100 cc/min, a mixture of 1.5 per cent by weight of nickel oxide in sodium hydroxide

was observed at 600°, 700°, 800°, and 900°C. Observations were made over two-hour periods for all except the 900°C temperature test, the observation time for which was 30 minutes. Nickel oxide at a concentration of 1.5 per cent was not completely soluble over this temperature range.

Some solubility was evidenced by the dark green appearance of the melt. The melt began to take on a green coloration at a temperature between 525° and 550°C and the color was so intense at temperatures of 700°C and higher that the bottom of the crucible could not be seen through a solution thickness of one-eighth inch. After the melt was heated to higher temperatures and cooled slowly, the green hue became gradually less pronounced until at 525°C no color remained. The intense green color of the melt necessitates the use of quite small quantities of sodium hydroxide so that the nickel oxide may be seen in the bottom of the crucible. Experiments are planned at a lower concentration of nickel oxide. (J. K. Carlton).

Differential Thermal Analysis. An apparatus in which larger samples could be heated in a closed system was built. Inequalities of heat flow produced a very poor "base line" when Al_2O_3 vs. Al_2O_3 was heated. This apparatus has been redesigned to eliminate these difficulties. (Yao Chiang).

Electrochemical Measurements

The purpose of measurements of thermo-galvanic potentials is the elucidation of transport processes of nickel ion, both in solution and in melts.

Solution Thermocells. Thermal potentials of nickel in NiCl_2 solutions are being studied. In general, the apparatus and experimental procedure are similar to that of Carr and Bonilla (J. Electrochem. Soc. 99,

475, 1952), who published their data for nickel in NiSO_4 at the time that preliminary work was in progress on this project.

Preliminary results in our laboratory indicate that values of dE/dT for 0.1 molar solutions are of the same order of magnitude in both NiSO_4 and NiCl_2 , which was to be expected.

It is considered of interest to determine the entropies of transport of nickel ion in solution. This can be done by use of the Eastman Thermo-cell equation. The procedure is that given by Goodrich, Cohan, Preston, and Young (J. Am. Chem. Soc. 72, 4411, 1950). This procedure requires a knowledge of thermopotentials for at least two different nickel salts and also their transference numbers. Because transference data are not known for either NiSO_4 or NiCl_2 , measurements will be made in the near future.

It is also planned to measure thermocells of nickel in aqueous NaOH . Measurements at uniform temperatures for this system have been made by MacGillavry, Singer, Rosenbaum, and Swenson (J. Chem. Phys. 19, 1195, 1499, 1951). These authors conclude that nickel electrodes in hydroxide solutions are highly polarized, that no measurable amount of nickel goes into solutions, and that hydroxyl ions are preferentially adsorbed in the double layer.

Thermocell: Nickel - Fused NaOH. The apparatus for the measurement of thermopotentials of nickel in fused NaOH is shown in Figure 1 and Figure 2. Experimental difficulties, particularly with respect to the construction of a leak-proof cell, have limited the work. However, preliminary experiments indicate the following:

- (a) Measurements must be carried out in the absence of oxygen and the nickel surface must be reduced before

the cell is filled. Potentials as large as 0.1 volt have been measured with the entire cell at uniform temperature when the nickel surface was partially oxidized.

(b) Conduction above 150°C in solid NaOH is sufficient to permit the measurement of thermopotentials. This would appear to indicate that the source of the potentials is a surface effect rather than one of differential solution of nickel in the hydroxide at different temperatures.

(c) The value of dE/dT is approximately constant from 250°C to 500°C and is equal to 0.1 mv/°C.

(K. H. Stern).

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Figure 1. THERMO-CELL FURNACE

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Figure 2. THERMO-CELL IN DETAIL

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