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FIFTH PROGRESS REPORT ON
THERMAL AND RELATED PHYSICAL PROPERTIES OF MOLTEN MATERIALS

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CONTENTS

Abstract

Problem Status

Authorization

ABSTRACT

Further studies of reactions of sodium hydroxide with container materials are reported. Some measurements on diffusion of H_2 through thin-walled nickel tubes are given. The thermal conductivity measurements of lithium metal are being replaced on the schedule with measurements on $MoSi_2$, for which apparatus is essentially complete. Apparatus for mixed salts will be fabricated and used also for the sodium hydroxide measurements. After minor calibrations, the new high temperature furnace for heat capacity will be used for measurements on the disilicide.

PROBLEM STATUS

This is an interim report; work is continuing on this problem.

AUTHORIZATION

Cross Servicing and Acceptance Order 52-829; NRL Problem No. 32C11-06

Reactions of NaOH With Container Materials

The work of the Analytical Unit has been confined to loose ends and incidentals relative to previously reported data. This work included: (1) A search for the source of gold plating on nickel test strips used for sodium hydroxide-nickel melts in gold tubes, (2) Analysis of the products of complete reaction of both sodium hydroxide and sodium monoxide with nickel, (3) An investigation of the permeability of nickel tubing to hydrogen, helium, and nitrogen, (4) A brief test of the effect of sodium hydroxide on copper, and (5) Preliminary work on the electrical resistivity of sodium hydroxide melts.

Results

The nickel test strips immersed in sodium hydroxide melts in gold containers were invariably gold plated in the areas covered by hydroxide. This condition existed even under hydrogen when all NaOH-Ni reaction was inhibited.

The first test to determine the conditions of plating consisted in the heating of a nickel strip in gold with no hydroxide present. No plating occurred, indicating the effect was not the result of distillation or other strictly thermal sources. The next test involved the immersion of the test strip in a hydroxide melt during the heating period and magnetically raising it clear of the melt during cooling. Again no plating resulted. A third test, similar to the second, in which the strip was raised only partially clear of the melt resulted in plating only on the immersed area. It is evident that the plating results as a secondary effect of the gold-hydroxide reaction and appears only upon cooling from a given reaction temperature. As previously reported, the Au-NaOH reaction is not inhibited by the presence of hydrogen.

Chemical analysis of typical Na_2O-Ni and NaOH-Ni ultimate reaction products have established their identity with reasonable certainty. The products were obtained in relatively pure form by driving the equilibriums to the right by the continuous removal from the reaction zone of sodium and/or hydrogen in the case of NaOH-Ni and sodium in the case of Na_2O-Ni. Tests were made at 900-1000°C.

Under the conditions stated above, Na_2O reacts with Ni according to the equation:

1) $Na_2O + Ni \rightarrow NiO + 2Na\uparrow$

Stoichiometric yields of NiO and Na were obtained by this Laboratory in a study of reaction (1). No other reaction products were found.

A similar study of the NaOH-Ni system under continuous evacuation, and with metallic nickel powder as the source of Ni, resulted in the discovery of a stepwise reaction. First, the system was quenched at a point just prior to the complete evolution of available hydrogen and the product analyzed for metallic sodium, total alkali, combined nickel and metallic nickel. The data confirms the following equation:

2) $2NaOH + Ni \rightarrow Na_2NiO_2$* $+ H_2 \uparrow$

*The analysis confirmed a 1 to 1 molecular ratio of Na_2O to NiO. X-ray and electron diffraction studies now in progress may determine whether or not a compound of the formula shown exists or whether it is merely a mixture of Na_2O and NiO. For a reason discussed later, the formula Na_2NiO_2 will be assumed and used in this report.

Further runs were identical to the first except that the heating period was extended for arbitrary lengths of time (one to three hours) after the cessation of hydrogen evolution. The analyses following these runs revealed the following had occurred after the hydrogen evolution indicated in equation (2).

3) $Na_2NiO_2 + Ni \rightarrow 2NiO + 2Na \uparrow$

The summation of (2) and (3) gives the following equation, which represents the <u>apparent</u> ultimate reaction.

4) $NaOH + Ni \rightarrow NiO + Na \uparrow + 1/2\ H_2 \uparrow$

Stoichiometric yields in support of these equations have been obtained by this Laboratory.

It should be borne in mind that the above is true only for the conditions stated. If the hydrogen is not removed, the equilibriums and semi-reversals previously reported will occur.

The Na_2NiO_2 produced by reaction 2 reacts, at least partially, with water, thus:

5) $Na_2NiO_2 + 2H_2O \rightarrow 2NaOH + Ni(OH)_2$

This reaction (5) proceeds slowly after an initial rapid reaction because of the deposition of insoluble nickel hydroxide on the surface of the unreacted Na_2NiO_2. The writers are of the opinion that Na_2NiO_2 is a nickelite type compound of the form shown rather than a double salt of the form $Na_2O \cdot NiO$. Basis for this assumption is the lack of direct reaction of NiO with either H_2O or aqueous NaOH to give $Ni(OH)_2$; a compound repeatedly identified in past experiments as one hydrolysis product of the NaOH-Ni reaction product.

Permeability

The permeability to H_2, He, and N_2 of 1/8" and 1/16" wall nickel L tubing was studied on a semi-quantitative basis. The data is not quantitative because of the existence of a temperature gradient in the hot zone of the apparatus. For this reason, effective areas for a given temperature are not known and specific diffusion values cannot be calculated. On a relative basis, the data is significant, however. The data and conditions are given in Table I.

Table I

Diffusion Rates Through 1/16" Wall Ni L Tubing

Temperature* °C	Diffusion Rates** (cc/min)		
	H_2	He	N_2
500	0.11	None Detected	None Detected
640	0.31	" "	" "
725	0.56	" "	" "
815	0.85	" "	" "
900	1.39	" "	" "
940	1.82	" "	" "

* Temperatures shown are at the hottest part of the tube

** (a) Total tube area in furnace 30-40 cm^2
(b) Internal gas pressure = 600-700 mm Hg
(c) External atmosphere = air at 760 mm Hg

The rates shown in Table I are for 1/16" wall tubing. Rates for 1/8" wall are approximately one quarter of those shown.

This permeability work was done on a new stock of 1/16" wall tubing preparatory to incorporating it into an experiment. Because of the rather high rates, it is not being used. All past work at this Laboratory has been performed with 1/8" to 1/4" wall thicknesses and at much lower pressures than those shown. (The effect of lower pressures is being investigated.)

It seems evident that the external oxide coating is sufficient to prevent the diffusion of both helium and nitrogen.

A single test of the effect of sodium hydroxide on copper yielded data on hydrogen evolution and equilibrium pressures nearly identical with those previously reported for the NaOH-Ni reaction. The solid products of reaction were not investigated, although copper hydroxide was observed in the hydrolyzed leachings.

Electrical Conductivity of NaOH (Liquid)

Because of the important applications of electrical data to many physical and chemical properties, an attempt is being made to measure the electrical resistivity of molten sodium hydroxide. The apparatus will consist of a reinforced teflon cup for containing the hydroxide and two gold electrodes of standard dimensions which will be dipped into the molten bath. The entire assembly will be contained in an inert atmosphere. Preliminary measurements will be made with a 60 ~ resistance bridge. and if the results are encouraging, a 1000 ~ high precision instrument will be substituted.

Thermal Conductivity

Two uni-axial (guard-ring compensated) type apparatuses complete with furnaces, precision potentionmeters, and control equipment are available for this work. One furnace is designed for measurements to 800°C, and the other to 1000°C or higher. While this type apparatus is specifically designed for measurements on highly conducting materials, the main control system and couple measuring system for either apparatus can be converted with only slight modification to the operation of a radial heat-flow type apparatus for the measurement of low conducting liquids.

Molybdenum Disilicide

The uni-axial thermal conductivity apparatus (1000°C) will be used immediately for measurements on solid molybdenum disilicide. The method of measurement will be similar to that described in NRL Report No. 3835, where the liquid container is replaced by the solid sample. This sample, ground to appropriate size, will be furnished by NACA (Cleveland) and, for measurement, will be bonded between two machined bars of type 310 stainless steel. These metal bars are now being machined at this Laboratory and should be completed before receipt of the $MoSi_2$. The method employed will permit an absolute measurement of the heat flowing through the sample. The steel bars will permit a relative measurement of conductivity and, in addition, a double check on the condition and calibration of the primary thermocouples on the sample. Platinum thermocouples for this work have been calibrated. The apparent conductivity magnitude of the $MoSi_2$ would appear to make this apparatus ideally suited for these measurements.

Using powdered silica as insulation, conductivity figures should contain less than ±5% error to 1000 or 1100°C.

Salts

The feasibility of measuring the thermal conductivity of molten mixed salts in the uni-axial type apparatus has been investigated. We feel now that any measurement of these low conducting liquids in this apparatus would lead to uncertainties greater than ±10%. Therefore, a radial apparatus for this work has been designed and drafted. The apparatus was specifically designed for incorporation into the existing furnace and equipment (800°C). This apparatus, due to the consideration of time, is somewhat less refined than that described in 3230-201/52; however, preliminary calculations indicate that final results will be well within the required accuracy. Nickel container material has been received and shop work has begun on the apparatus.

Lithium

The actual measurement of molten lithium will be delayed until conclusion of the $MoSi_2$ work. However, distillation and purification work will continue. At the conclusion of purification studies, a sample of lithium will be introduced into a type 310 stainless test container for corrosion and solubility check at higher temperatures.

Sodium Hydroxide

This work will also be delayed until conclusion of the investigation of the other low-conducting salt mixtures. The specific type of radial apparatus for measuring sodium hydroxide can best be formulated after the work with the other salts has begun. However, it is anticipated that the same apparatus will serve equally well for the hydroxide.

Heat Capacity

The assembly of the new specific heat furnace is nearly complete. The first measurements will be made on 347 stainless steel blanks. A few runs will then be made on aluminum oxide to check the furnace and calorimeter. Upon completion of this work, the measurements on molybdenum disilicide will begin as soon as the material has been received.