at a temperature of about 1200°. A 20 mole per cent. mixture of BaO in NiO gave a somewhat diffuse pattern when quenched from 1200° but a sharp pattern when quenched from 1150°. The composition of the eutectic was not determined.

Intersolubility of NiO, NiO·BaO and NiO·3BaO is small. Mixtures with composition nearly equimolar, when quenched from 1050°, produce sharp patterns of the expected phases. The melting point of NiO·BaO was observed to be about 1240°.

A eutectic between NiO·BaO and NiO·3BaO occurs at a temperature of about 1080°. The composition of the eutectic was not determined.

The melting point of NiO·3BaO is about 1160°. A sample quenched from 1100° gave a sharp X-ray pattern of the single phase.

The melting point of BaO is taken as 1923°. A mixture of 10 ml. per cent. NiO in BaO quenched from 1250° gave a pattern of well developed crystals of BaO and NiO·3BaO. The cell constant of BaO was changed by less than 0.1 per cent. It appears therefore that NiO is not very soluble in BaO at 1250°, and that there is no eutectic between NiO·3BaO and BaO.

MURRAY HILL, N. J. RECEIVED MAY 12, 1950

[CONTRIBUTION FROM THE BELL TELEPHONE LABORATORIES, INC.]

Barium–Nickel Oxides with Tri- and Tetravalent Nickel

BY J. J. LANDER AND L. A. WOOTEN

The compound $BaNiO_3$ and intermediates with composition ranging between $Ba_3Ni_3O_8$ and $Ba_2Ni_2O_5$ have been prepared. $BaNiO_3$ is black, stable in alkali, and has a structure made up of layers identical with the 111 planes of a perovskite but stacked in a close-packed hexagonal fashion. At 730° in 730 mm. of oxygen, the structure changes to that associated with the series $Ba_3Ni_3O_8$ to $Ba_2Ni_2O_5$ in which the oxygen content appears to decrease continuously with temperature increasing to 1200°, at which point sharp melting is observed. These materials are black and stable in alkali with an hexagonal structure for which the details have not been determined. Resistivities and magnetic susceptibilities are reported. A wide range in composition, temperature and reaction atmosphere was studied but only one additional compound was observed. Attempts to isolate this compound were not successful.

1. Introduction.—Nickel is bivalent in the vast majority of its known compounds, but higher oxides of nickel have been the subject of considerable work and discussion (ref. Mellor, Vol. XV, p. 391). The compounds Ni_3O_4, Ni_2O_3, NiO_2 and several intermediates have been reported. One infers from the existence of these higher oxides and from reports to be found in the literature of other higher valent nickel compounds that a variety of such compounds, stable in the solid state, can be prepared. This paper is concerned with the preparation and properties of a barium–nickel oxide in which nickel is formally tetravalent and one in which the average valence of nickel is approximately three. The crystal structures of the compounds will be described in another paper.[1]

The formation of barium–nickel oxides in which nickel has a valence greater than two has been reported by E. Dufau.[2] His compound $BaNi_2O_5$ has not been observed in the present work. D. K. Goralevich[3] fused NiO and $Ba(NO_3)_2$ and describes the products $BaNiO_3$ and $BaO_2{\cdot}NiO_3$. Petrav and Ormont,[4] however, report that they found no hexavalent nickel product in attempts to synthesize $BaO_2{\cdot}NiO_3$. E. A. Thurber[5] observed that NiO and $BaCO_3$ react in oxygen to form several compounds which gave negative tests for peroxide but a positive test for higher valent nickel. J. D. Struthers, in unpublished work done in this laboratory, confirmed the work of Thurber and also found that one or more such compounds can be made by heating BaO_2 and NiO.

2. Materials and Apparatus.—Mixtures of BaO_2 and NiO were used in most of the preparations. The BaO_2 contained about 86% peroxide and 1.3% silica as an impurity. Pure phases prepared for tests of chemical and physical properties were generally prepared from $Ba(OH)_2$ and NiO. The $Ba(OH)_2$ was very pure except for water, the amount of which was determined immediately before use. The NiO was a 99.8+% grade with oxygen content very close to stoichiometric. Nickel boats were used for reaction vessels and the various atmospheres used were dry and CO_2-free oxygen, CO_2 free oxygen saturated with water at room temperature, and nitrogen.

Heats were made in the center portion of a 1.25″ alundum tube which was surrounded by a nichrome heater. Temperatures were measured with a chromel–alumel thermocouple placed beside the reaction boat.

3. Preparation of $BaNiO_3$.—Mixtures of BaO_2 and NiO having the mole ratios 3/1, 2/1, 1/1, 1/2 and 1/3 were thoroughly ground and heated in wet oxygen at various temperatures. Heats below 900° were normally run for 24 hours. At about 450° all the mixtures, which were green, rapidly turned black. X-Ray examination showed that at temperatures below 730° only one new phase was produced in the mixtures and that phase was obtained pure from the 1/1 mol ratio mixture. The other mixtures gave patterns of this phase plus either BaO_2 or NiO. Moreover it was found that mixtures containing a ten percentage excess of either NiO or BaO_2 yielded the new phase plus the component in excess. The new phase is $BaNiO_3$. Its X-ray powder pattern is reproduced in Fig. 1.

A purer product was prepared by slowly heating an equimolar mixture of $Ba(OH)_2$ and NiO to 700° in wet oxygen. The material was maintained under these conditions for 24 hours after which the atmosphere was changed to dry oxygen. After several hours exposure at 700° to dry oxygen the product was removed. This treatment produces a black powder which gives sharp X-ray lines free from traces of any impurity, but on analysis is found to be about 90% oxidized. However several of the products from BaO_2 and NiO gave spotty powder patterns, indicating that a somewhat larger crystal size may be obtained using these reagents, and were found to be 98% oxidized.

Attempts were made to grow single crystals in a flux of $Ba(OH)_2{\cdot}xH_2O$ the melting point of which depends on the amount of water present. Heating to about 650° yielded no $BaNiO_3$ crystals large enough to handle conveniently. Under the conditions of the experiment water was rapidly lost and within a few minutes the flux solidified. It seems likely that

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[1] J. J. Lander, to be published in *Acta Crystall.*

[2] E. Dufau, *Compt. rend.*, **123**, 495 (1896); *Ann. chem. phys.*, **7**, 12 (1897).

[3] D. K. Goralevich, *J. Russ. Phys.-Chem. Soc.*, **62**, 879, 1165, 1577 (1930).

[4] B. A. Petrav and B. Ormont, *J. Gen. Chem.* (*U. S. S. S R.*), **8**, 563 (1938).

[5] E. A. Thurber, Thesis, Polytechnic Inst. of Brooklyn, 1937.

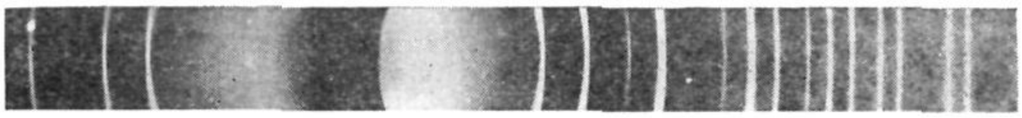

Fig. 1.—X-Ray powder pattern of $BaNiO_3$.

large single crystals could be grown by this method if the $BaNiO_3$ and flux were maintained in a closed system.

Single crystals were not obtained from a $Ba(NO_3)_2$ flux. This salt melts at 592°. After melting and cooling slowly a homogeneous solid was obtained. This product was not investigated.

Single crystals of $BaNiO_2$ were heated at 700° in wet oxygen for 48 hours in an attempt to convert them to single crystals of $BaNiO_3$. X-Ray examination of the products showed that although reaction had proceeded in the anticipated direction the crystals obtained were far from perfect.

The composition of the best $BaNiO_3$ prepared has been determined in several ways. The ratio of Ba to Ni must be very near unity because it is found by X-ray analysis that this ratio yields the pure phase. There is little change in weight in the reaction of BaO_2 and NiO. It was found by gravimetric analysis that one lot contained 1.021 moles of Ba, 0.984 mole of Ni and the figure for oxygen by difference was 3.11 moles. A determination of the amount of oxygen which reacts with hydrogen when the sample is heated to 1000° gave the figure 14.7%. The theoretical amount (assuming that BaO is not reduced) is 13.1%. Determination of chlorine released by dissolving $BaNiO_3$ in HCl gave the result 0.981 mole per mole of compounds. The chlorine was distilled into potassium iodide solution and the iodine released was titrated with thiosulfate in accordance with a method developed by J. D. Struthers. Finally the determination of crystal structure is in agreement with the formula $BaNiO_3$.

4. **Preparation of Intermediates.**—An equimolar mixture of BaO_2 and NiO held in wet O_2 at 730° for 24 hours yielded a mixture identified by X-ray analysis as $BaNiO_3$ plus a new phase. The new phase was obtained pure by heating to 800°. Moreover the 3/1, 2/1, 1/2 and 1/3 mole ratio mixtures of BaO_2 and NiO all gave the new phase plus the component in excess when heated at 800°.

Two samples of $BaNiO_3$, prepared from $Ba(OH)_2$ and NiO as described above, were heated to 850° and weight losses measured. The losses were 2.1 and 2.2%. The theoretical loss in the reaction $4BaNiO_3 \rightarrow 2Ba_2Ni_2O_5 + O_2$ is 3.29%. Change in weight of the oxidized boat during reduction of $BaNiO_3$ is the principal error in the method. This error was made small by using boats made of thin nickel sheet and heating the empty boat for twenty-four hours at 850°. Compounds made above 730° were cooled rapidly through the range 730 to 450° to avoid oxidation.

It was found that heating the compound at the temperatures 900, 1000 and 1100° in oxygen produced small changes in the X-ray powder patterns but no radically different crystalline phase. Patterns are reproduced in Fig. 2. Changes in the relative intensities of some reflections as well as small displacements are to be observed. These results can probably be correlated with oxygen content in terms of small rearrangements of nickel oxygen groups.

Single crystals with composition very near $Ba_2Ni_2O_5$ were grown by mixing the material obtained at 850°, as described above, with barium chloride, heating to 1000° and cooling slowly. An equimolar mixture was found to be satisfactory. The crystals developed as long black needles having a diamond shaped cross-section with acute angles very near 60°. In contrast to the powder materials, an X-ray diffraction study of these crystals revealed that they were not truly hexagonal but were slightly distorted. They could be indexed using an orthorhombic cell.

5. **Investigation of the Composition of Intermediates.**—The X-ray diffraction patterns and the results of oxygen determinations indicate a variable oxygen content, in the range from 730 to 1200°, for the solid phase with composition near that given by $Ba_2Ni_2O_5$. The question which arises is whether there is more than one stable phase in this region (*e.g.*, $Ba_3Ni_3O_8$ and $Ba_2Ni_2O_5$) or one which has a continuously variable oxygen content, accompanied by continuous but small over-all change in structure. Titration of iodine liberated in potassium iodide solution by oxygen in excess of that given by the formula $BaNiO_2$ provides a sensitive test for the degree of oxidation.

A series of oxygen determinations, designed to answer the problem proposed above, has been carried out by J. Armstrong of these laboratories. A thoroughly mixed equimolar mixture of $Ba(OH)_2$ and NiO, converted to $BaNiO_3$ by heating at 650° in wet oxygen for several days, was heated in dry oxygen at increasing temperatures, spaced by about 50°, through the range 700 to 1200°. The sample melted at 1200°. After heating at a temperature for about 24 hours (or several hours if above 1000°), small samples were removed, dissolved in HCl–KI solution, and titrated with thiosulfate according to a standard procedure. Two separate runs were made.

The results give a linear variation of percentage oxidation with temperature between 730 and 1200°. Percentage oxidation is here used as percentage of that required to oxidize $BaNiO_2$ to $BaNiO_3$. At 800° the percentage oxidation was 68 and at 1180° it was 51. The maximum deviation of any result from the average was 2%. It therefore appears that the oxygen content in this range is continuously variable from that given by $Ba_3Ni_2O_8$ to that given by $Ba_2Ni_2O_5$. At 700° the percentage oxidation of samples with structure corresponding to that shown in Fig. 1 was found to be 82 with a maximum deviation of about 2%. More complete oxidation can be obtained in the range 550 to 650°.

6. **Other Phases in the System.**—The five mixtures with mole ratios 3, 2, 1, 1/2 and 1/3 where heated in oxygen and in nitrogen to maximum temperatures of about 1150°. X-Ray analysis revealed only one additional phase and this was observed when the mixtures with 2/1 and 3/1 mole ratio BaO_2 to NiO were heated above 1050° in nitrogen (not prepurified). This phase was not obtained pure. Data from the X-ray pattern are given in the crystal structure paper. No indication of other compounds was observed in any of these studies.

7. **Properties of $BaNiO_3$.**—$BaNiO_3$ was obtained in the form of a black powder. At 730° (±10°) it decomposes in oxygen at a pressure of 730 mm. It is insoluble in base but reacts with acid, for example in dilute hydrochloric the reaction $BaNiO_3 + 2HCl \rightarrow Cl_2 + BaNiO_2 + H_2O$ proceeds quantitatively and with concurrent solution of the product $BaNiO_2$. $BaNiO_3$ is not a peroxide. It reacts negatively to the titanium sulfate and the perchromic acid tests. Its density, calculated from X-ray data, is 6.22 g./cc. Its structure has been determined and is given in the crystallographic paper.

A sample of the material was found to be an N-type conductor and this confirms the theory that the nickel has a valence higher than two. A mixed oxide–peroxide or a compound with excess oxygen would be expected to be a P-type conductor. The resistivity of a pressed disc was found to be 5×10^4 ohm-cm. Effects of stoichiometric deviations were not studied.

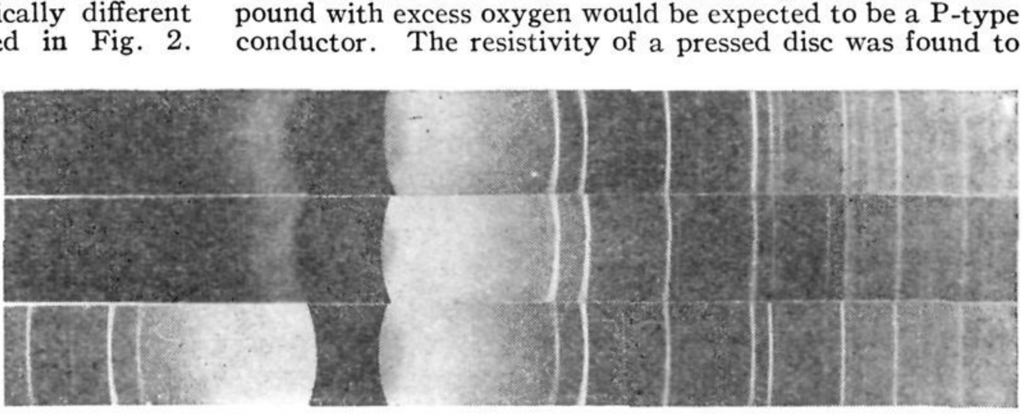

Fig. 2.—X-Ray powder patterns of material with approximate composition $Ba_2Ni_2O_5$. The patterns in descending order are from materials heated at 850, 950 and 1070° in oxygen.

The magnetic susceptibility, measured by F. Morin of these laboratories, was found to be very low and it obeyed the Curie–Weiss law in the range 50 to 300°K. The observed susceptibility per gram of nickel at 300°K. was 0.68 and a good fit was obtained with Δ equal to 210°. The calculated number of unpaired spins per nickel atom is 0.82.

8. **Properties of Intermediates with Composition near $Ba_2Ni_2O_5$.**—At 730° in oxygen at 730 mm. pressure the structure associated with $BaNiO_3$ changes to that associated with $Ba_2Ni_2O_5$ and the product obtained is black. It may be heated in oxygen to 1200° (where it melts) without further gross change in structure. These materials give negative tests for peroxide and liberate chlorine from dilute hydrochloric acid. The study described in Section 5 revealed no tendency toward higher stability of certain definite compositions.

All these intermediates have almost identical hexagonal unit cells with barium ions in an hexagonal close-packed arrangement. The nickel and oxygen positions were not obtained from the powder pattern data. The calculated density of a product obtained at 850° is 6.40 g./cm.^{3}, the formula $Ba_2Ni_2O_5$ being assumed.

The electrical resistivity of a pressed disc made from the 800° product was found to be 7×10^8 ohm-cm. It was an N-type conductor.

The magnetic susceptibility per g. of nickel at 300°K., measured by F. Morin, was 1.24 and data obtained between 50 and 300°K. fit the Curie–Weiss law with $\Delta = 100$°K. The calculated number of unpaired spins per nickel atom is 0.97.

MURRAY HILL, N. J. RECEIVED MAY 12, 1950

[CONTRIBUTION FROM STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

A New Calorimetric Method[1,2]

BY ANNE BUZZELL[3] AND JULIAN M. STURTEVANT

An apparatus suitable for the measurement of the heat effects of slow chemical reactions in aqueous solutions is described. Twin calorimeters serve as a thermal balance to compare the chemical energy evolved or absorbed with automatically adjusted electrical energy, and analog computers are used to evaluate the electrical energy. The functioning of the apparatus is illustrated by determinations of the heat of the inactivation of pepsin.

Introduction

It has long been recognized that the twin calorimetric method first employed by Joule[4] is particularly well-suited in principle to the observation of the heat effects accompanying slow processes. However, this method, with electrical compensation, has not been applied to slow chemical reactions largely because of the difficulty of integrating the varying electrical power required for compensation.

In the twin calorimetric method as applied to exothermic chemical processes, the chemical energy liberated in one calorimeter is duplicated electrically in the other. In the case of an endothermic process, sufficient electrical energy is introduced into the calorimeter in which the process takes place to prevent any temperature change. The two calorimeters can be made very similar in thermal properties. If they are supported within an "adiabatic" shield, the differential method of operation permits the uncertainty of any remaining calorimetric corrections to be reduced to a very low value.

We have employed electromechanical computers to overcome the problem of measuring the electrical compensation energy. In the present report we discuss the general method employed and the instrumentation involved. It will be evident that different designs of the calorimeters themselves, devised for a variety of purposes, can be used with the instrumentation to be described.

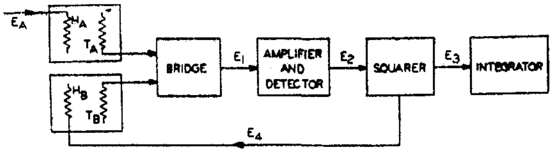

Fig. 1.—Simplified block diagram of apparatus.

Outline of Method

Figure 1 gives a simplified block diagram of the apparatus. Calorimeters A and B are each equipped with constant resistance electrical heaters H_A and H_B, and resistance thermometers T_A and T_B. The thermometers are in adjacent arms of a 25-cycle Wheatstone bridge, the output of which is proportional to the temperature difference between the calorimeters. The bridge output is amplified and detected, the detector output is continuously squared by a computer, and the squared voltage is integrated. The squarer also produces an unsquared voltage, E_4, proportional to its input E_2. This voltage is fed back to the heater of that calorimeter which requires electrical heat. The integrator output is proportional to the total electrical energy fed back.

If the ratio of the heater voltage, E_4, to the bridge output voltage, E_1, which produces it is sufficiently large, and if the over-all feedback system is stable (*i.e.*, does not oscillate), then the temperature difference between the calorimeters will always be held to small values. It is evident that under these circumstances there is no need to measure the actual temperature difference. The accuracy of the calorimetric observations is then determined, so far as the instrumentation is concerned, by the accuracy of the squaring and integrating computers. These are of a type to ensure reliability and stability of calibration.

As is always the case with feedback systems which include a thermal link, careful attention has to be paid to minimizing the thermal lag between heaters and thermometers in order to be able to employ a reasonably high sensitivity without oscillation of the system.

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[1] The apparatus described in this paper was developed in a program of calorimetric investigations of protein reactions aided by grants from the American Cancer Society on recommendation of the Committee on Growth of the National Research Council.

[2] Presented in part at the Meeting of the American Chemical Society, Chicago, September, 1950.

[3] Research fellow under grants from the American Cancer Society.

[4] J. P. Joule, *Mem. Proc. Manchester Lit. Phil. Soc.*, **2**, 559 (1845).