sults yield further confirmation of the validity of the Nernst limiting equation.

The diffusion coefficients of the three unsymmetrical type electrolytes, lithium sulfate, sodium sulfate and calcium chloride at concentrations below 0.005 *M* exhibit considerable individualistic behaviors. Assuming for the time being that the theoretical computations are correct, we find that lithium sulfate conforms with theory. On the other hand, the observed values of sodium sulfate are somewhat higher than those calculated while those for calcium chloride lie considerably below the theoretical values. These observations prove that the explanation of the deviations does not reside in the unsymmetrical nature of these salts but in specific interactions between the ions themselves or between the ions and the solvent molecules.

NEW HAVEN, CONN. RECEIVED DECEMBER 4, 1950

[CONTRIBUTION FROM THE BELL TELEPHONE LABORATORIES, INC.]

The Phase System BaO–NiO

BY J. J. LANDER

The phase system BaO–NiO has been studied largely by means of X-ray diffraction. The two compounds NiO·BaO and NiO·3BaO occur in the system. Their preparation and properties are described. NiO·BaO is black, stable in air, orthorhombic, and melts at 1240°. NiO·3BaO is gray-green, unstable in air, hexagonal, and melts at 1160°. A eutectic melting at 1080° is observed between these compounds, but none between NiO·3BaO and BaO. Intersolubility of all solid phases in the system is small, even at high temperatures, but quantitative data have not been obtained.

1. **Introduction.**—The purpose of this paper is to give an account of the preparation and properties of phases in the system bivalent nickel ion, oxygen ion and barium ion. The following paper describes the synthesis and properties of compounds containing oxygen ion, barium ion and nickel in higher states of oxidation.

2. **Chemical Background.**—BaO may be obtained by decomposition of $BaCO_3$, BaO_2, $Ba(OH)_2$, etc. It may then be mixed with NiO and heated until reaction takes place. But one would like to mix BaO and NiO in a predetermined ratio. Since BaO rapidly absorbs moisture, techniques for doing this are generally not convenient. $BaCO_3$ is, from this point of view, a more convenient starting material, and moreover it can be obtained very pure. It has been found that decomposition of the carbonate and reaction with NiO proceed rapidly if the mixture is maintained in vacuum (1 mm. or less) at 900° or higher. Reaction between several grams of material in a small volume is then complete in a few hours.

The atmosphere in which reaction takes place is critical. The products react with oxygen at temperatures above 450°. In one atmosphere of oxygen and below 730° divalent nickel compounded with oxygen and barium is oxidized to the tetravalent state. Between 730° and about 1200° it is also oxidized. But at high temperatures and in the absence of oxidizing agents divalent nickel compounded with oxygen and barium is reduced to metallic nickel. Exact conditions for the stability of divalent nickel products containing barium and oxygen have not been determined.

Reactions carried out in vacuum at a high temperature may easily result in reduction of the nickel. The residual atmosphere in a vacuum system tends to be reducing and when $BaCO_3$ is a starting material, once decomposition of the carbonate is complete, reduction of nickel may take place. Above 900° this danger becomes increasingly acute. Reactions carried out in nitrogen present much the same problem.

The danger of oxidation or reduction is largely avoided by starting with large amounts of anhydrous BaO and NiO and either fusing rapidly, or reacting below the fusion temperature in a small closed system. However, it may also be avoided, if $BaCO_3$ is used, by exercising simple precautions. Use of a vacuum system eliminates the danger of oxidation. Reduction of nickel or incomplete decomposition of the carbonate may be avoided by monitoring the decomposition (measuring the pressure of released CO_2). In a well-mixed sample reaction with NiO and decomposition of the carbonate are completed simultaneously. If the reaction mixture is loosely packed the pressure drop is fairly sharp. If the products are immediately cooled carbon dioxide and/or nickel are normally found in no more than trace amount.

3. **Materials and Apparatus.**—All chemicals used were highly pure except BaO_2. The grade of BaO_2 available and used in a few experiments contained 89% peroxide and about 1% silica.

Two types of furnaces were used. Heats made at atmospheric pressure were run either in a 1.25″ i.d. long alundum tube the center portion of which was surrounded by a nichrome heater, or in a 0.5″ i.d. alundum tube wound with Pt–Rh heater wire and inserted in the larger alundum tube. Vacuum heats were made in a Pt–Rh wound vacuum furnace of conventional design.

Both platinum and nickel crucibles were used. In general platinum crucibles were used for vacuum heats and nickel crucibles for heats carried out at atmospheric pressure. These latter heats generally had for purpose the fusion of products in a flux in order to obtain single crystals and comparatively large amounts of material were used.

4. **Technique.**—In the initial and largest phase of the work weighed amounts of $BaCO_3$ and NiO were mixed in acetone in a ball mill. A platinum crucible was filled loosely with several grams of the dried material and slowly heated in the vacuum furnace. After several hours heating at 900 to 950° the pressure normally dropped in a few minutes from about 1 mm. to about 0.1 mm. The furnace was then turned off.

When cool the furnace was opened and the reaction products transferred rapidly to a small vial. A fraction of a gram was placed under a few drops of dried pump oil in an agate mortar and ground. This material was drawn into a thin walled 15 mil glass capillary and an X-ray powder pattern obtained from it. CuKα radiation was used. It was found that this capillary-immersion in oil technique

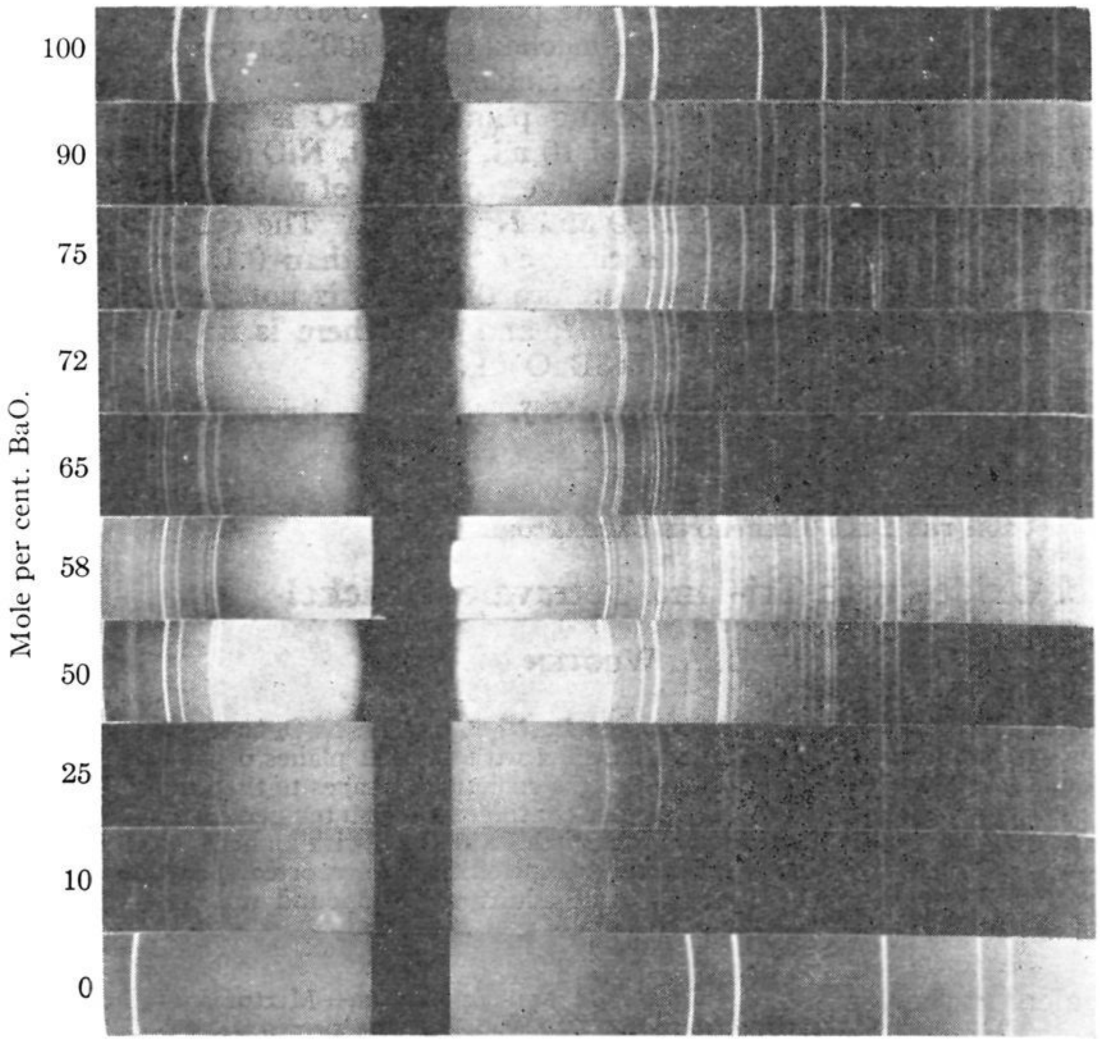

Fig. 1.—X-Ray diffraction patterns of products of reaction between BaO and NiO.

gave the protection necessary to obtain excellent powder patterns of BaO. Products of mixtures containing one or more moles of NiO per mole of BaO were found to be stable in air at low temperatures so that the oil immersion step could be omitted.

5. Phases Observed at Room Temperature.—In a routine survey, tests were made of fifteen mixtures with composition roughly equally spaced between 0 and 100 mol per cent. BaO. Some of the X-ray patterns, plus those of NiO and BaO, are given in Fig. 1. Two reaction products are to be observed. The patterns were measured and it was found that the new phases were obtained pure at 50 mole per cent. BaO and 75 mole per cent. BaO, respectively. Mixtures with exactly 50 mole per cent. and 75 mole per cent. were among the fifteen prepared. These preparations have each been repeated several times.

Strong additional support for the formulas NiO·BaO and NiO·3BaO is obtained from structure determinations. These will be reported in detail.[1] NiO·BaO is orthorhombic and NiO·3BaO is hexagonal (rhombohedral). The X-ray patterns are completely accounted for by the structures reported, which require the above compositions.

6. Properties of NiO·3BaO.—Pure NiO·3BaO is gray-green. A small excess of NiO, exposure to oxygen at temperatures above 450°, or a small amount of reduction of the nickel ion changes the color from green to black. Its chemical properties are those expected of a solution of NiO in BaO. It is soluble in acid and alkali and it rapidly absorbs moisture from air. Its density has not been determined experimentally but that calculated from the X-ray data is 6.05. That of BaO is 5.86. Incipient melting of material with composition NiO·3BaO is observed at 1160°, precautions being taken to avoid oxidation or reduction.

The hexagonal (rhombohedral) unit cell of NiO·3BaO has the axes a_0 = 7.85 Å. and c_0 = 16.50 Å. It contains 18 molecules of BaO and 6 molecules of NiO. Although the structure is a distorted NaCl type, it has an unusual coordination of oxygen and nickel—three oxygen ions in triangular arrangement with a nickel ion at the center.

7. The Properties of NiO·BaO.—All preparations with composition at or near NiO·BaO have appeared black by reflected light and rust-colored by transmitted light. Single crystals of NiO·BaO are easily grown at about 1000° in nitrogen. $BaCl_2$, $Ba(OH)_2$ or $BaO·2BaCO_3$ may be used as flux. The crystals have a plate-like habit. At room temperature they are orthorhombic with a_0 = 5.73 Å., b_0 = 0.20 Å. and c_0 = 4.73 Å. The structure is pseudohexagonal with barium ions in a hexagonal close-packed arrangement. Each nickel ion is at the center of a square array of oxygen ions. Whether or not transitions take place at high temperatures has not been determined.

The compound is soluble in acid and insoluble in water and alkali. It is easily obtained pure. For example, fusion and slow cooling of a mixture containing excess BaO yields crystals of NiO·BaO in a matrix of NiO·3BaO. The matrix may be dissolved in water. An observed density of single crystals is 5.99. The density calculated from X-ray data is 6.11. Crystals rapidly heated in N_2 were observed to melt at 1240°.

A pressed-powder disc was observed to be a P-type electrical conductor with a resistivity equal to 300 ohm-cm. Wide variations in resistivity have been observed and since correlation with stoichiometric deviations has not been attempted, exact figures are of little value. D.C. resistivities in the range of 10 to 100 ohm-cm. were most frequently observed and a measurement of a single crystal gave 24 ohm-cm.

The magnetic susceptibility of powdered material was measured by F. Morin of these laboratories. The material obeyed the Curie–Weiss Law with the susceptibility per gram of nickel atom at 300°K. equal to 3.82 and Δ = 180. The calculated number of unpaired electrons per nickel atom is 1.83.

8. The High Temperature Region of the Phase Diagram.—Data concerning the behavior of the system in the upper temperature range have been obtained in two ways. The temperature of incipient melting of a large sample in a nitrogen atmosphere has been found by heating until fusion was observed. Approximate solubilities and a further check on fusion temperatures have been obtained by quenching material in closed $^1/_{16}''$ nickel tubes and examining by X-ray diffraction.

A fairly complete phase diagram is given in Fig. 2. The melting point of NiO is taken as 1650°. The solubility of BaO in NiO is very small. A mixture of 3 mol per cent. BaO in NiO quenched from 1100° gave a pattern of NiO and well crystallized NiO·BaO.

A eutectic between NiO and NiO·BaO probably occurs

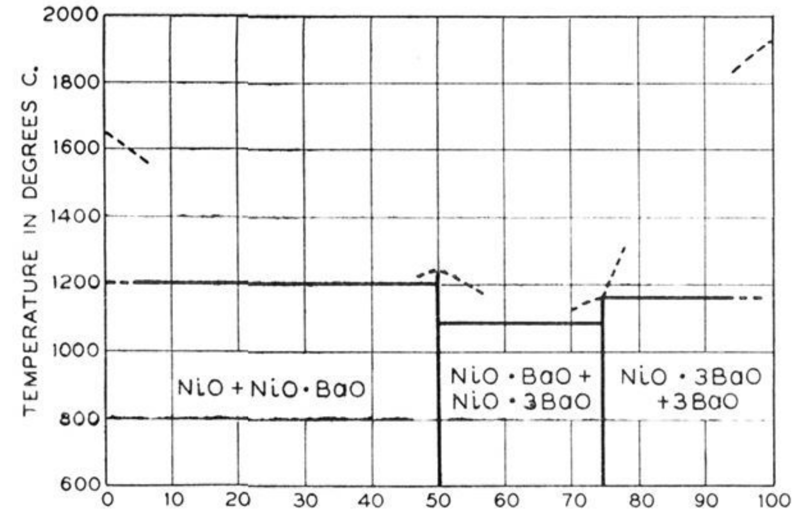

Fig. 2.—The phase system BaO–NiO.

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[1] To be published in *Acta Crystall.*

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. R.*), **8**, 563 (1938).

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