more concentrated of these two solutions, and the three to which chloride was added, the solutions of the experiments of Fig. 2 were all between 0.082 and 0.090 M in total ammonia and the ionic strength was varied by the addition of potassium nitrate. The values of $-\log (K')^{1/2}$ for these experiments all lie on Curve B. It is evident that K' is not a function of ionic strength alone, and the activity coefficients calculated from the experiments of Randall and Halford cannot be true ones for the complex salt. When a fairly dilute ammonia solution was used and potassium chloride added, K' falls between the two curves, showing that the value of K' depends on the chloride ion concentration. Extrapolation to zero ionic strength should eliminate the effect of the chloride ion, and the constant of Randall and Halford should be without error from this source.

Summary

Previous measurements of the solubility of silver iodate in solutions of potassium nitrate have been checked.

The solubility of silver iodate in ammonia solutions has been determined. The instability constant of the diammine-silver ion calculated from the solubility data agreed with the best of the previous results.

Assumption of equality of the activity coefficients of the silver and diammine-silver ions gave consistent results.

Measurements of the solubility of silver chloride in ammonia solutions containing potassium nitrate or potassium chloride showed that the solubility is dependent on the chloride ion concentration as well as on the ammonia concentration and the ionic strength.

DURHAM, NORTH CAROLINA RECEIVED JULY 28, 1941

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI]

A Study of the Products Obtained by the Reducing Action of Metals upon Salts in Liquid Ammonia Solution. VI. The Reduction of Nickel Salts

BY WAYLAND M. BURGESS AND JOHN W. EASTES[1]

Introduction

The reduction of metal salts by solutions of sodium (or potassium or calcium) in liquid ammonia forms first the free metal in a finely divided state. This may act as an efficient catalyst for the reaction between sodium and ammonia or it may take part in other reactions such as the formation of an intermetallic compound with sodium.[2-6]

With nickel salts that furnish a nickel cation, reactive metallic nickel has been prepared. Calcium as a reducing agent gave the most active form of precipitated metal. No intermetallic compound was formed. When salts containing nickel in the anion were reduced, free nickel was not a product. Since different results were obtained with the two types of nickel compounds, their reduction will be presented in two sections. The present article deals with the reduction of nickel cations.

Preparation of Nickel Salts.—Nickel salts (chloride, bromide, iodide, thiocyanide, acetate, cyanide) with ammonia of crystallization were used in this work. Nickel hexammine acetate and nickel triammine cyanide, were formed by washing the hydrated salt with liquid ammonia, then removing the excess ammonia by evacuation at about 20 mm. of mercury. No reference has been found in the literature to these particular ammines.

Nickel hexammine acetate is of a light violet color, stable in dry ammonia or dry air, but quite unstable in moist air.

Anal. Calcd. for $Ni(C_2H_3O_2)_2 \cdot 6NH_3$: Ni, 21.04; NH_3, 36.65. Found: Ni, 21.3; NH_3, 36.4.

Nickel triammine cyanide is also of a light violet color but is stable in ordinary air.

Anal. Calcd. for $Ni(CN)_2 \cdot 3NH_3$: Ni, 36.27; CN, 32.16; NH_3, 31.57. Found: Ni, 36.4; CN, 32.3; NH_3, 32.9.

Reduction Reactions Using Potassium.—The apparatus employed was essentially the same as described in previous articles.[2,5]

Two reactions occurred concurrently as may be represented by equations (1) and (2).

$$2K + NiBr_2 \longrightarrow 2KBr + Ni \qquad (1)$$

$$2K + 2NH_3 \longrightarrow 2KNH_2 + H_2 \qquad (2)$$

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[1] This article is based upon the thesis presented to the Faculty of the Graduate School, University of Cincinnati, by John W. Eastes in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1936.

[2] Burgess and Rose, THIS JOURNAL, **51**, 2127 (1929).

[3] Burgess and Smoker, *ibid.*, **52**, 3573 (1930).

[4] Burgess and Smoker, *Chem. Rev.*, **8**, 265 (1931).

[5] Burgess and Holden, THIS JOURNAL, **59**, 459 (1937).

[6] Burgess and Holden, *ibid.*, **59**, 462 (1937).

The amount of potassium used in reaction (2) was determined by the collection and analysis for hydrogen of the gaseous products. The gram atoms of potassium (corrected for that used in reaction (2)) divided by the gram moles of nickel salt employed should be 2. Experimentally values between 2.2 and 2.5 were obtained for this ratio.

In a typical run, 0.1732 g. of potassium reduced 0.2999 g. of $NiBr_2 \cdot 6NH_3$ and liberated 25.7 cc. of hydrogen. The ratio is 2.28.

This high value for the ratio of reactants was due to the adsorption of an appreciable amount of hydrogen by the precipitated nickel (as much as 100 cc. of hydrogen per gram of nickel). The nickel, first washed with liquid ammonia to remove all potassium amide, was heated in a closed system connected to a Toepler pump. At temperatures below 360°, adsorbed hydrogen and ammonia were given off slowly, even at pressures below 1×10^{-4} mm. of mercury (as measured on a McLeod gage). Above 360°, hydrogen was evolved rapidly. When the hydrogen so obtained was added to that collected during the reaction, the new ratio of reactants for five runs was 2.00 ± 0.03. This confirms the reactions represented by equations (1) and (2).

In the above example, 2.7 cc. of hydrogen was obtained from the heated nickel. This gave a ratio of 2.02.

Reduction Reaction with Sodium.—When sodium was used as the reducing agent, the difficultly soluble sodium amide could not be removed from the precipitate by washing. Ammonium bromide was added after reduction to react with the sodium amide and form soluble sodium bromide and ammonia. An unexpected result of this addition was that part of the adsorbed hydrogen was then evolved. Still more hydrogen was usually obtained when the precipitate was heated as described above. When all the hydrogen found was used to determine the sodium used in reaction (2), then one mole of nickel salt required two gram atoms of sodium for reduction.

The hydrogen evolved upon addition of ammonium bromide did not appear to come from a reaction with the precipitated nickel. The amount of hydrogen so formed was limited and in no case more than that lost by adsorption. Ammonium bromide added to the precipitate formed by reduction with potassium gave similar results.

Reduction Reactions Using Calcium.—The nickel formed when calcium was used as the reducing agent was so effective a catalyst that the first nickel precipitate converted most of the calcium added to calcium amide. Only a small portion of the nickel salt could be reduced, since 90–95% of the calcium added reacted with ammonia. The greater activity of metals prepared by reduction with calcium has been observed before.[6]

Formation of Nickel Amide.—In numerous experiments a small amount of a red material was observed mixed with the black precipitated nickel. This red substance was found only when unreduced nickel salt and sodium amide or potassium amide were both present. Nickel amide is known to be red in color and has been formed by the reaction of alkali amides and nickel salts.[7] The presence of an excess of potassium or sodium during reduction prevented the formation of this red compound.

Reduction of Nickel Thiocyanate.—Nickel thiocyanate and nickel nitrate are the only nickel salts that can be reduced in solution, but here the anion is also reduced. Reduction of the thiocyanate with sodium or potassium occurred without the formation of hydrogen and the precipitate was the most finely divided sample prepared. It was not pyrophoric and was the least efficient as a catalyst. Using calcium, hydrogen was liberated as soon as reduced nickel was formed. This nickel was pyrophoric.

The cause of this decreased activity may be due to the presence of sulfides formed in the reduction of the thiocyanate anion. The activity of the precipitated metal does vary, however, with the salt. Thus, using sodium, the nickel from nickel chloride was less active than that from nickel iodide and this, in turn, less active than that from nickel bromide.

There was no evidence that the acetate anion was appreciably reduced by potassium although the ratio of reactants here was 2.09, somewhat higher than with the halides.

Reduction of Nickel Cyanide.—When sodium or potassium was added to a suspension of nickel triammine cyanide, the solution turned red for a brief instant before it became black with precipitated nickel. Careful inspection of the washed and dried precipitate from the reaction showed the presence of small amounts of a red material. That this is not nickel amide was apparent when the treatment of the precipitate with water gave a cherry-red solution. Further research showed that this red product is a univalent nickel compound—a report on the formation of which by the reduction of potassium nickelocyanide will be given in a later article.

Properties of the Precipitated Nickel.—All attempts to obtain a sample of high purity nickel by reduction of a nickel salt failed. The presence of adsorbed substances made it impossible to obtain a precipitate with a nickel content over 95% nickel. A typical analysis of such a precipitate showed nickel 93.3%, ammonia 4.0%, potassium 3.0%.

The gas adsorbed by the nickel was held very tenaciously. Only a small fraction of the adsorbed hydrogen was given off from a sample kept in a closed system under a pressure of 1×10^{-4} mm. at room temperature for a period of two weeks. A sample kept at 320° for a period of 135 hours did not give up all its hydrogen. All the adsorbed hydrogen was evolved quickly when the sample was heated above 360° under reduced pressure. At this temperature, which is the transition temperature for magnetic and non-magnetic nickel, the color of the precipitate changed to gray.

The precipitated nickel reacted vigorously when exposed to air or moisture. The only sample not found to be pyrophoric was that prepared by reduction of soluble nickel thiocyanate, with the nickel salt always in excess so that no hydrogen was evolved during the reduction. Such a product had but a trace of adsorbed hydrogen. This indicates a close connection between the adsorbed hydrogen and the property of pyrophoricity. Samples prepared by the reduction of nickel thiocyanate using excess alkali metal or calcium were pyrophoric. Here hydrogen was evolved during the reaction.

The sample heated at 320° for 135 hours was pyrophoric after the heating. Samples heated to or above 360° were

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[7] Bohart, *J. Phys. Chem.*, **19**, 537 (1915).

not pyrophoric and did not regain their black color or pyrophoric property by allowing them to cool in an atmosphere of hydrogen.

Summary

Nickel salts are reduced by sodium, potassium or calcium to free nickel. It is pyrophoric and an excellent catalyst for the reaction between sodium (potassium or calcium) and ammonia. Small amounts of nickel amide are formed when the nickel salt is present in excess. The reactivity of the nickel is greater when calcium is the reducing metal. The pyrophoric property appears to be due to adsorbed hydrogen.

CINCINNATI, OHIO RECEIVED JULY 9, 1941

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, INDIANA UNIVERSITY]

Transference Numbers of Sulfuric Acid in Anhydrous Methanol at 25°[1]

BY E. W. KANNING AND J. E. WALTZ

Transference numbers of sulfuric acid in aqueous solutions have been estimated[2] from a combination of the data of the electromotive force of cells without liquid junctions and of concentration cells with transference. Measurements are reported for the cells

$$\mathrm{Pt(H_2)\ |\ H_2SO_4\ |\ Hg_2SO_4\ |\ Hg} \qquad \text{(I)}$$

and

$$\mathrm{Hg\ |\ Hg_2SO_4\ |\ H_2SO_4}(m_1)\ ||\ \mathrm{H_2SO_4}(m_2)\ |\ \mathrm{Hg_2SO_4\ |\ Hg} \qquad \text{(II)}$$

Activity coefficients have been calculated from data obtained with Cell I. Moreover, the difference of various combinations of Cell I may be represented as the electromotive force of concentration cells without transference.[3] The relation is expressed in differential form as

$$dE = (-3RT/2F)d(\ln a)$$

where a is the geometric mean activity of the ions. The differential expression for the potential of Cell II is given as

$$dE_t = (-3RT/2F)t_{H^+}\ d(\ln a)$$

where t_{H^+} is the transference number of the ions to which the electrodes are not reversible. If dE and dE_t were plotted as the ordinates against $d(\ln a)$ as abscissa, the transference number, t_{H^+}, can be estimated by computing the ratio of the slopes of the two curves.

The purpose of this investigation was to study the applicability of this method for the determination of transference numbers of sulfuric acid in other than aqueous solutions. Some preliminary studies are here reported on solutions in anhydrous methanol.

Experimental

Materials.—About 5 g. of sodium hydroxide and 15 g. of iodine were added to each liter of methanol to be purified; the mixture was allowed to stand for twenty-four hours. The solution was then refluxed for six hours and distilled. After this treatment the methanol showed a negative test for aldehydes and ketones when warmed with an equal volume of 6 *N* sodium hydroxide solution saturated with mercuric cyanide. The water was removed by the method of Lund and Bjerrum.[4] Basic impurities were removed by a final distillation from sulfanilic acid. The sulfuric acid used (m. p. 10.4°) was prepared by the method of Kendall and Carpenter.[5] The mercury–mercurous sulfate electrodes were made from twice distilled C. P. mercury and electrolytically prepared mercurous sulfate.[6] The hydrogen electrodes were platinized and treated according to the directions of Popoff, Kunz and Snow.[7]

Procedure.—Measurements of the potentials of Cells I and II were made with a Leeds and Northrup type K-2 potentiometer, a type R galvanometer, and an Eppley standard cell which was certified by its manufacturer and checked frequently with another certified cell. Cell I was of the H-type with two electrodes in each half-cell. The stoppers were fitted with stopcocks and interchangeable ground glass joints in order that the cell could be flushed with hydrogen and filled without the solution coming into contact with air. Purified tank hydrogen was used. A saturating bottle containing the cell solution was interposed between the purification train and the cell. In the concentration range for which measurements are reported, the potentials of this cell were constant and reproducible to about 0.1 mv. Cell II, with some modifications, was essentially the same as that described by MacInnes and Beattie.[8] The junction was formed in the center of a 34/45 Pyrex ground glass joint through 12-mm. tubing drawn to 4 mm. at the junction, with the tips about 5 mm. apart.

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[1] This paper is constructed from a dissertation presented by Joseph Elmer Waltz to the Faculty of the Graduate School of Indiana University in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry.

[2] Harned and Hamer, THIS JOURNAL, **57**, 27 (1935); Hamer, *ibid.*, **57**, 662 (1935).

[3] D. A. MacInnes, "Principles of Electrochemistry," Reinhold Publishing Corporation, New York, N. Y., 1939, pp. 168–169.

[4] Lund and Bjerrum, *Ber.*, **64**, 210 (1931).

[5] Kendall and Carpenter, THIS JOURNAL, **36**, 2498 (1914).

[6] See Carhart and Hulet, *Trans. Am. Electrochem. Soc.*, **5**, 59 (1904).

[7] Popoff, Kunz and Snow, *J. Phys. Chem.*, **32**, 1056 (1928).

[8] MacInnes and Beattie, THIS JOURNAL, **42**, 1117 (1920).