

STUDIES ON THE BASIC CARBONATES OF NICKEL

Part I: Factors Influencing the Precipitation of Nickel Carbonates

BY R. M. MALLYA AND A. R. VASUDEVA MURTHY

(Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore - 12)

Received on July 22, 1960

ABSTRACT

The precipitation of nickel from various systems of nickel salts and alkali carbonates has been followed under controlled conditions. The various factors that influence the precipitation process have been studied and the condition for reproducible precipitation has been described.

INTRODUCTION

When dilute solutions of sodium carbonate and nickel sulphate of equimolar concentrations are mixed in equal proportions it is found that only about 80% of the nickel is precipitated. The complete precipitation of the nickel from the solution takes place only if the alkali carbonate added is at least 2.5 times the amount of the nickel taken. It was of interest to study the factors that influence the course of precipitation, the compositions of the precipitates obtained under different experimental conditions and the physico-chemical behaviour of the precipitates formed. A detailed investigation was therefore undertaken.

REAGENTS USED

Solutions of Nickel Salts:—Stock solutions of nearly 1 molar nickel sulphate (Analar, B. D. H.), chloride (C. P., Merck) and nitrate (Analar, B. D. H.) were prepared and standardised by analysing them for their nickel content using the dimethyl glyoxime method. Exactly 0.05 molar nickel salt solutions were prepared by suitably diluting the stock solutions and the strengths of these solutions were also checked up by determining their nickel contents.

Alkali Carbonate Solutions:—Standard solutions (0.05M) of sodium carbonate and potassium carbonate were prepared in CO₂-free distilled water as recommended by K \ddot{u} lthoff and Stenger¹. The strengths of these solutions were periodically checked up by titration against standard hydrochloric acid using methyl orange indicator.

Temperature Control:—An electrically heated water thermostat with an electronic relay system and a toluene mercury biliquid regulator was employed to

maintain constant temperatures (25°C and 40°C) during the experiment. The bath temperature could be controlled to within $\pm 0.05^\circ\text{C}$. A mercury regulator was employed for the higher temperatures, 50° and 60°C. The precipitations at $97 \pm 1^\circ\text{C}$ were conducted by immersing the beaker in a boiling water bath. The precipitations at 0°C were conducted by employing a bath of melting ice.

MODE OF ADDITION OF PRECIPITANT

At laboratory temperature, when various mixtures of nickel sulphate and sodium carbonate solutions corresponding to different molar ratios of reactants were analysed for the amounts of nickel precipitated it was found that duplicate experiments gave results differing by as much as 8 to 10%. Consequently experiments were carried out to find out the influence of the method of addition of the reagents on the course of the precipitation meanwhile keeping other factors such as temperature and time constant.

Procedure I:—Exactly 25 ml. of 0.05 M nickel sulphate solution were taken in a 250 ml. pyrex beaker maintained at 25.0°C. To this solution, 25 ml. of 0.1 N sodium carbonate solution were added from a calibrated pipette. The solution was stirred with a glass rod for a minute and the contents were filtered immediately. The entire operation was carried out in three minutes. The precipitate was washed with distilled water and then dissolved in dilute hydrochloric acid (1:1) and the nickel content of the precipitate determined gravimetrically as the dimethylglyoxime complex.

Even when the precipitations were carried out as described above reproducible values for the amounts of nickel precipitated could not be obtained. For instance, in five such experiments, the values of the nickel contents of the precipitates obtained were 4.92, 4.67, 4.73, 5.02 and 4.54 (in 10^{-4} g. atoms) out of 12.50×10^{-4} g. atoms of nickel in the salt solution taken. This gives a mean value of 4.78 and a relative mean deviation of 33.47 parts per thousand. This deviation is much too large to be attributed to experimental error since the method of analysis is both accurate and precise. With this low order of reproducibility it is difficult to compare and draw any inferences from the experimental values. It is therefore necessary to adopt a method which gives reproducible and accurate results.

The non-reproducibility could be attributed to the concentration gradients prevailing in the immediate vicinity of the added drop of the precipitant^{2,3}. This causes the non-uniformity of the complex that is produced when alkali carbonate is added to the nickel salt. In order to minimise the gradient effects, each drop of the alkali carbonate added should be immediately dispersed and distributed homogeneously throughout the solution. The precipitation then takes place under uniform conditions which may be reproduced easily whereas heterogeneous conditions are difficult to reproduce. The rapid dissolution of

the precipitant could be facilitated by slow and dropwise addition and quick dissolution of each drop, by stirring.

It was found out that efficient stirring was essential for quick dispersion of the precipitant. Otherwise the amount of nickel precipitated varies with the rate of stirring. For instance, if during the dropwise addition of the alkali carbonate solution from the burette, the solution was stirred with a glass rod by hand, the amount of nickel precipitated was found to be 4.98×10^{-4} g. atoms $\pm 0.20 \times 10^{-4}$ whereas the amount of nickel precipitated when the solution was stirred mechanically at 600 r. p. m. was 5.92×10^{-4} g. atoms (± 0.05). When the rate of stirring was decreased to nearly 200 r. p. m. with the same design of the stirrer, the amount of nickel precipitated was 5.23×10^{-4} g. atoms. After several trials the following method was found to be satisfactory for the present work.

Procedure II:—The precipitations were conducted under the same conditions as earlier except that the addition was done drop by drop from a calibrated burette during the course of an interval of 15 minutes. The stirrer consisted of a glass rod the tip of which was flattened out and twisted twice. The stirrer rod was mounted on the shaft of an electric motor. The contents of the beaker were stirred continuously at 600 r. p. m. In five successive experiments the amounts of nickel present in the precipitates were found to be 5.94, 5.98, 5.86, 5.96 and 5.87×10^{-4} g. atoms, with a mean value of 5.92×10^{-4} . This gives a relative mean deviation of 8.45 parts per thousand which is considered as reasonably satisfactory for analytical purposes.

In all subsequent experiments, therefore, this latter procedure was adopted.

Another factor that influences the extent of precipitation is the period for which the solution is stirred. The amount of nickel precipitated increased

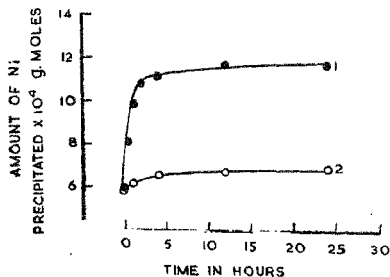


FIG. 1

Precipitation from an Equimolar mixture of NiSO_4 and Na_2CO_3 Solutions

1. With Mechanical Agitation; 2. Without Mechanical Agitation.

[Amount of Ni Taken = 12.50×10^{-4} g. moles.]

rapidly with increase of time up to two hours' stirring and therefore the increase in the amount of nickel precipitated was not very marked as shown in curve one, Figure I. Within a period of two hours' agitation nearly 86 per cent of the nickel was precipitated. If on the other hand, the solution in the beaker was not stirred during the period of ageing, the amount of nickel precipitated is increased only slightly on ageing. Thus on keeping for a period of four hours the amount of nickel precipitated is only 6.54×10^{-4} g. moles. This corresponds to curve two in the same figure.

From the foregoing, it may be inferred that unless uniform conditions of precipitation are maintained it is not possible to make any comparison with precipitation experiments. The conditions adopted for all further experiments in the present studies were: (1) maintenance of constant temperature, (2) dropwise addition of precipitant and (3) efficient mechanical stirring of the solution during the addition of the precipitant and for a period of two hours thereafter.

EXTENT OF PRECIPITATION OF NICKEL CARBONATE WITH VARYING AMOUNTS OF ALKALI CARBONATE

It has already been observed that when a nickel salt solution is mixed with a solution of alkali carbonate in stoichiometric proportions, only about 86% of the nickel carbonate is precipitated in two hours' time. In order to find

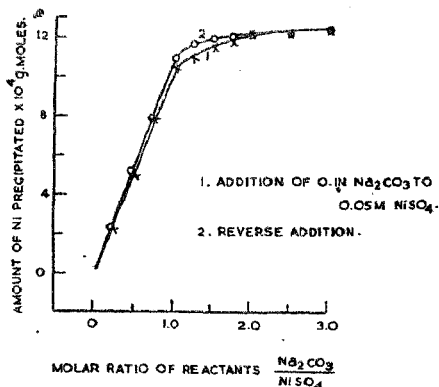


FIG. II

Precipitation of Nickel from the system $NiSO_4-Na_2CO_3$ at $25^\circ C$ with Mechanical Agitation for 2 hours

out the amount of carbonate required to remove the nickel completely from solution, various quantities of alkali carbonate solution were added to known amounts of nickel salt solution corresponding to definite molar ratios of reactants. The precipitation was carried out under uniform conditions as described earlier and the precipitate filtered and washed. The excess of alkali in the filtrate was determined by titration against standard hydrochloric acid and the nickel content of the precipitate and the filtrate determined gravimetrically by the dimethylglyoxime method. For the system nickel sulphate-sodium carbonate the plot of the amount of nickel precipitated versus molar ratio of reactants is shown in Figure II, curve one.

It can be made out from these results that complete precipitation of nickel takes place only when the amount of alkali carbonate added is more than 2.5 times the molar quantity of nickel salt taken.

When the reactants are in equimolar quantities, about 85% of the nickel is thrown out of the solution. Up to this ratio, the amount of nickel precipitated is a linear function of the amount of alkali added. In the region of molar ratios of reactants 1.0 to 2.5 there appears to be a process whereby nickel is retained in solution and only a very small increase in the amount of nickel precipitated per mole of sodium carbonate added is observed. Thus, in this range, 18.75×10^{-4} g. moles of sodium carbonate are required to precipitate nearly 2×10^{-4} g. atoms of nickel from the solution.

Similar observations were made when 25 ml. of other nickel salt solution were added to different amounts of alkali carbonate solution, the other experimental conditions being the same. The corresponding results are shown in Figure II, curve two. It was also found that the results obtained were similar when the nickel salt employed was the chloride or the nitrate or when the precipitant employed was potassium carbonate instead of sodium carbonate.

INFLUENCE OF TEMPERATURE ON THE COURSE OF PRECIPITATION OF NICKEL CARBONATES

All the precipitation experiments described above were carried out at the constant temperature 25°C. It was of interest to find out the effect of temperature on the extent of precipitation of nickel for the various systems of nickel salt and alkali carbonate. The precipitations were studied for the equimolar mixture in the same manner as described above at various constant temperatures ranging from 0°C to 97°C. The results for the system nickel nitrate-sodium carbonate are presented in the different curves given in Figure III. It can be made out from the results that with increase of time, there is no rapid increase in the amount of nickel precipitated at 0°C. Thus on agitation of the solution for a period of four hours the amount of nickel precipitated increased from 7.86×10^{-4} to 8.82×10^{-4} g. atoms. At higher temperatures, however, the amount of nickel precipitated was found to increase rapidly with time. For example, within an interval of one hour, the amounts of nickel precipitated in the

system nickel nitrate-sodium carbonate, at the temperatures of 0°, 25°, 40°, 50°, 60° and 97°C were 8.17, 9.83, 10.75, 11.37, 11.87 and 12.50 in 10^{-4} g. atoms

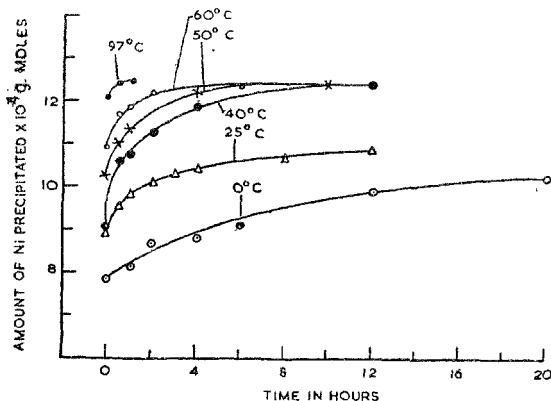


FIG. III

Precipitation from an Equimolar mixture of $\text{Ni}(\text{NO}_3)_2$ & Na_2CO_3 Solutions at various temperatures

respectively, out of 12.50×10^{-4} g. atoms of nickel taken. The time required under these experimental conditions, to completely precipitate all the nickel from equimolar mixtures increases as the temperature of the experiment is lower as indicated below:

Temp.	97°	60°	40°
Time for complete precipitation of nickel in equimolar solutions	1 hour	5 hours	12 hours

It has already been indicated that more than 2.5 moles of alkali carbonate are required to precipitate one mole of nickel from solution at 25°C. As the constant temperature at which the precipitation was conducted, was raised, it was found that less of alkali carbonate was consumed in completely throwing out nickel from solution. The results for the system nickel nitrate-sodium carbonate are presented graphically in Figure IV. The molar ratios $\text{Na}_2\text{CO}_3/\text{Ni}(\text{NO}_3)_2$, at which precipitation was complete in a period of two hours, at 0°, 25°, 50°, 60° and 97°C were 3.50, 2.50, 2.00, 1.50 and 1.00 respectively. In all cases, however, up to a molar ratio of 1.0, the amount of nickel precipitated is a linear function of the amount of alkali carbonate added.

These results are explained in subsequent communications on the basis of several physico-chemical factors involved in the process of precipitation⁴.

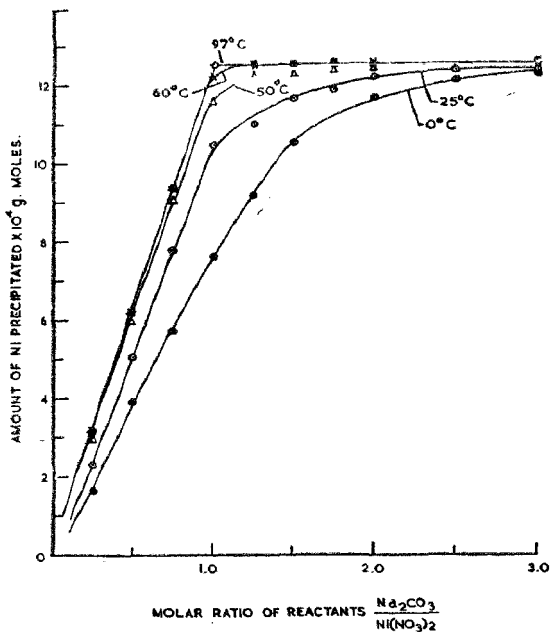


FIG. IV

Influence of temperature on the Precipitation of Nickel at various molar ratios of reactants

ACKNOWLEDGEMENT

The authors thank Prof. K. R. Krishnaswami and Prof. M. R. A. Rao for their great interest in this work.

REFERENCES

1. Kolthoff, I. M. and Stenger, V. A. . . ' Volumetric Analysis' Vol. II, (New York, Interscience), 1947.
2. Gordon, L. *Anal. Chem.*, 1952, 24, 459.
3. Willard, H. H. and Tang, N. K. . . *Ind. Engg. Chem. Anal. Ed.*, 1937, 9, 357 ;
J. Am. Chem. Soc., 1937, 59, 1190.
4. Mallya, R. M. and Vasudeva
Murthy, A. R. *J. Indian Inst. Sci.*, 1961, 43, April, (in Press).