included in the entropy and free energy function. The estimated probable error in the entropy, heat content and free energy function is 0.1% above 100°K., but in order to make the table internally consistent some of the values are given to one more figure than is justified by the estimated probable error.

Magnetic Entropy of Uranium Tetrafluoride.—The heat capacity of uranium tetrafluoride as determined by Brickwedde, Hoge and Scott[4] from 20 to 350°K. has been included in Fig. 1 for comparison with that of thorium tetrafluoride. The heat capacity of thorium tetrafluoride, as discussed above, is considered to be a good approximation for the contribution of the lattice vibrations to the heat capacity of uranium tetrafluoride. At all temperatures the heat capacity of uranium tetrafluoride is greater than that of thorium tetrafluoride, the difference presumably being the magnetic contribution.

The magnetic entropy of uranium tetrafluoride, which is also shown in Fig. 1, was obtained by subtracting the entropy of thorium tetrafluoride from the total entropy of uranium tetrafluoride[4] at the same temperature. Although there is no hump in the heat capacity curve of uranium tetrafluoride down to 20°K., there is an appreciable magnetic contribution to the entropy, increasing with temperature and amounting to 2.17 cal. $deg.^{-1}$ $mole^{-1}$ at 298.16°K. This is very nearly equal to the spin-only value for the magnetic entropy at high temperatures, $R \ln (2S + 1) = R \ln 3 = 2.18$ cal. $deg.^{-1}$ $mole^{-1}$, but at higher temperatures the magnetic entropy exceeds the spin-only value.

The entropy calculations for uranium tetrafluoride involve an extrapolation of the heat capacity curve from 20 to 0°K., and there is, of course, a possibility that the extrapolation may be incorrect. In connection with this possibility it should be noted that the magnetic entropies of uranium dioxide and neptunium dioxide exceed the spin-only values by 0.86 and 0.85 cal. $deg.^{-1}$ $mole^{-1}$, respectively, at 298.16°K. The lower value for the magnetic entropy of uranium tetrafluoride suggests that there may be an anomaly in the heat capacity curve below 20°K. that causes the entropy to be greater than the tabulated values.[4] It therefore seems advisable to measure the heat capacity of uranium tetrafluoride below 20°K., and this work is now in progress.

Acknowledgments.—The authors wish to thank M. L. Sjoholm for the thorium analysis, the Chemical Engineering Analytical Group of this laboratory for the fluorine analysis, and Joseph Goleb for the spectrochemical analysis.

LEMONT, ILLINOIS

[CONTRIBUTION OF THE INTERNATIONAL NICKEL COMPANY'S MULTIPLE FELLOWSHIP, MELLON INSTITUTE]

Composition of Basic Nickel Carbonates

BY JONATHAN T. CARRIEL AND WILBUR J. SINGLEY, JR.

RECEIVED MARCH 4, 1954

Basic nickel carbonates were formed at constant *p*H and room temperature by the addition of standard nickel chloride and potassium hydroxide solutions to a reaction medium containing a 10-fold excess of potassium carbonates. The composition of the precipitates may be expressed $Ni(OH)_2 \cdot 3$ to $4NiCO_3$ in the *p*H range 8 to 10.5; above *p*H 10.5 the ratio of carbonate to hydroxide in the precipitate decreases rapidly. Essentially no chloride is absorbed by the precipitate. A previously developed method of precipitation at constant *p*H was adapted to permit calculation of the composition of the precipitate directly from buret readings.

Introduction

Basic nickel carbonates are frequently used as catalyst intermediates. Rather minor changes in preparative procedure have been known to influence the behavior of the ultimate reduced nickel catalyst. Fundamental data were sought as a step in the elucidation of problems connected with catalyst preparation. More specifically the objective was to determine the influence of *p*H of the reaction medium on the composition of the basic nickel carbonates formed. Previously a volumetric method was described for determining the composition of basic metal salts such as basic sulfates, nitrates, chlorides formed at constant *p*H.[1] This method had the advantage of avoiding possible changes in precipitate composition as a result of the washing and drying process required to prepare the materials for elemental chemical analysis. Briefly the composition of basic salts, formed at constant *p*H by the addition of standard alkali and metal salt solutions to an alkaline reaction medium, has been shown to be calculable from buret readings. The alkali added to maintain constant *p*H is an immediate measure of the hydroxide content of the precipitate.

With some modification of method, the composition of basic metal carbonates formed at constant *p*H by the addition of standard metal salt and alkali solutions to an alkaline reaction medium containing an excess of total carbonate is also calculable from buret readings. In the latter case, the calculation is slightly more complicated since the alkali added must not only compensate for hydroxide ion consumed by the precipitate but also must neutralize the acid hydrogen which may have been associated with carbonate ion consumed by the precipitate. It is assumed that precipitates are formed only by reaction of metal ions with carbonate ions, CO_3^{-2}, and that consumption of these ions by the precipitate is accompanied by equilibrium shifts tending to restore the relative concentrations among the various carbonate species. For example, if a

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(1) J. T. Carriel and W. J. Singley, Jr., THIS JOURNAL, **75**, 778 (1953).

mole of carbonate ion is removed from a reaction medium consisting essentially of bicarbonate ions, one mole of hydrogen ion would be liberated: $HCO_3^{-1} \rightleftarrows H^+ + CO_3^{-2}$. Therefore, to maintain constant *p*H, one mole of alkali must be added. In like manner, if the predominant carbonate species were carbonic acid, two moles of alkali would be required for every mole of carbonate precipitated: $H_2CO_3 = 2H^+ + CO_3^{-2}$. On the other hand, no alkali would be required for neutralization purposes if the carbonate ion consumed were drawn from a solution containing only carbonate ions. In actual solutions, all three of these carbonate species exist and their relative concentrations change continuously with *p*H. Let Z be defined as the moles of alkali required to neutralize the acid formed when one mole of carbonate ion is consumed by the precipitate. Then

$$Z = \frac{2[H_2CO_3] + [HCO_3^{-1}]}{T} \qquad (1)$$

where $[H_2CO_3]$ and $[HCO_3^{-1}]$ are the molar concentrations of these carbonate species in the reaction medium and T is the total molar concentration of all the carbonate species

$$T = [CO_2] + [H_2CO_3] + [HCO_3^{-1}] + [CO_3^{-2}] \qquad (2)$$

For the purposes of this treatment it is unnecessary to distinguish between dissolved, unhydrated CO_2 and H_2CO_3 since there are no acidimetric changes associated with the hydration reaction[2]: $CO_2 + H_2O \rightarrow H_2CO_3$. Hereinafter it will be understood that the quantity $[H_2CO_3]$ refers to the sum of the concentrations of both the hydrated and unhydrated carbon dioxide species.

In the experiments to be described, standard nickel chloride and potassium hydroxide solutions were added to a solution of potassium carbonates. The composition of the precipitate formed may be represented in general as: $A\text{Ni(OH)}_2 \cdot B\text{NiCO}_3 \cdot C\text{NiCl}_2$. It will be subsequently demonstrated that C for this system is zero; and, hence, it is only necessary to calculate A and B from the buret readings to determine the composition as precipitated. Let N = total equivalents of nickel in the precipitate and P = total equivalents of KOH required to maintain constant *p*H. Then $N = 2(A + B)$ and $P = 2A + ZB$. Solving for A and B simultaneously

$$A = \frac{2P - ZN}{4 - 2Z} \quad \text{and} \quad B = \frac{N - P}{2 - Z}$$

Values of N and P may be determined from the buret readings and the normality of the standard nickel chloride and potassium hydroxide solutions used. It remains, therefore, only to calculate Z as a function of *p*H in order to determine the composition by this method. This may be done as follows. The relative concentration of the various species is specified by the equilibrium equations

$$H_2CO_3 = H^+ + HCO_3^{-1};\ K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} \qquad (3)$$

$$HCO_3^{-1} = H^+ + CO_3^{-2};\ K_2 = \frac{[H^+][CO_3^{-2}]}{[HCO_3^-]} \qquad (4)$$

Substituting equations 3 and 4 in equation 2 and solving, one obtains

$$[H_2CO_3] = \frac{[H^+]^2T}{[H^+]^2 + [H^+]K_1 + K_1K_2} \qquad (5)$$

$$[HCO_3^{-1}] = \frac{[H^+]K_1T}{[H^+]^2 + [H^+]K_1 + K_1K_2} \qquad (6)$$

If equations 5 and 6 are substituted in equation 1, Z can be expressed in terms of hydrogen ion concentration

$$Z = \frac{2[H^+]^2 + K_1[H^+]}{[H^+]^2 + K_1[H^+] + K_1K_2} \qquad (7)$$

A plot of Z, calculated from equation 7, is shown in Fig. 1. The values of K_1 and K_2 used were 4.31×10^{-7} [3] and 5.6×10^{-11},[4] respectively. Since K_1 and K_2 vary with temperature, the entire procedure is limited to temperatures for which K_1 and K_2 are known.

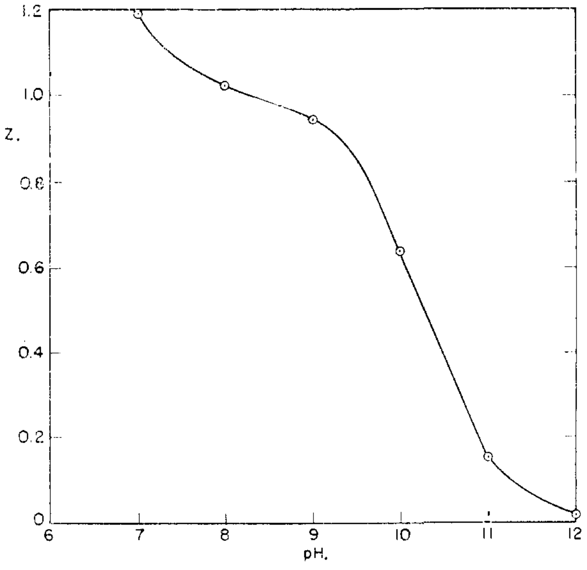

Fig. 1.—Plot of Z as a function of *p*H (calculated at points indicated).

Experimental

The precipitations were carried out in previously described apparatus,[1] using a Leeds and Northrup Universal *p*H meter. A special magnifying telescope was focused on the galvanometer needle in order to improve the observability of the smallest deflection and to minimize errors due to parallax.

In a typical titration, the reaction medium comprised one mole of a mixture of C.P. potassium bicarbonate and potassium carbonate dissolved in 1500 ml. of deionized water. The *p*H of the resultant solution, which depended on the relative amounts of the two carbonate salts used, was measured. A 3.31 *N* C.P., nickel chloride solution was added slowly from a buret; and, simultaneously, sufficient 3.47 *N*, C.P., potassium hydroxide solution was added in order to maintain essentially constant *p*H. At five or six well-spaced intervals during the course of addition of 50 ml. (0.165 equivalent) of the nickel chloride solution, the precipitation was interrupted and an exact restoration of the original *p*H was obtained usually by the addition of slightly more potassium hydroxide solution. Such buret readings were recorded and the precipitation continued. The temperature was within the range of 25 ± 2°.

The *p*H of the reaction mediums used varied between 8.2 and 11.6 which were the values obtained when 1.0 mole of pure potassium bicarbonate and 1.0 mole of pure potassium carbonate, respectively, were dissolved in 1500 ml. of water.

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(2) F. J. W. Roughton, THIS JOURNAL, **63**, 2930 (1941).

(3) T. Shedlovsky and D. A. MacInnes, *ibid.*, **57**, 1705 (1935).

(4) D. A. MacInnes and D. Belcher, *ibid.*, **55**, 2630 (1933).

Treatment of the Data.—The buret readings were plotted against each other, and usually straight lines were obtained. Linearity indicates that the composition of the solid is constant throughout the precipitation. The buret reading plots (Fig. 2) frequently did not extend exactly through the origin. Also, a few non-linear plots were obtained. The deviations from the origin and non-linearity were interpreted as being caused by instrumental errors in the *p*H meter which, in effect, suddenly change the calibration by an amount which is trivial for most purposes, but important in this application. Only the slope of the apparent best straight line through the observed points was used for the determination of compositions. The slope, *S*, multiplied by the ratio of the respective normalities of the nickel chloride and potassium hydroxide solutions gives the value of *R* which is the ratio of hydroxide to nickel equivalents consumed during the precipitation at constant *p*H.

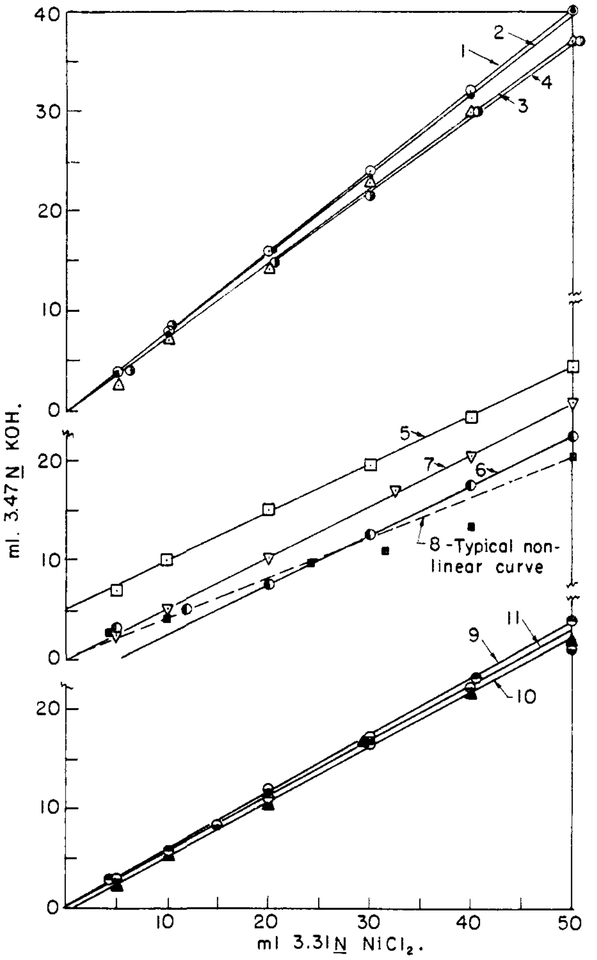

Fig. 2.—Typical plots of buret readings obtained during the precipitation of basic nickel carbonate at constant *p*H from mixed carbonate, bicarbonate solutions.

Curve	Symbol	Reaction medium Composition (moles/1.5 l. H_2O) $KHCO_3$	K_2CO_3	*p*H	Slope of curve, *S* (ml. KOH/ ml. $NiCl_2$)
1	⊙	0.0	1.0	11.61	0.804
2	●	.0	1.0	11.82	.803
3	◬	.1	0.9	10.80	.751
4	◑	.1	.9	10.80	.748
5	⊡	.25	.75	10.36	.490
6	◐	.25	.75	10.29	.502
7	▽	.5	.5	9.84	.519
8	■	.5	.5	9.84	.428
9	◒	.75	.25	9.32	.560
10	▲	.75	.25	9.45	.551
11	◓	1.0	1.0	8.32	.578

$$S\,\frac{\text{Normality KOH soln.}}{\text{Normality NiCl}_2\text{ soln.}} = \frac{P}{N} = R$$

Then

$$A = \frac{N(2R - Z)}{2(2 - Z)} \quad \text{and} \quad B = \frac{N(1 - R)}{(2 - Z)}$$

Results

The composition of the basic carbonate precipitates may be expressed in several different ways. In Fig. 3 it has been expressed as the ratio of hydroxide to nickel equivalents, or $A/(A + B)$. The data show that the composition does not change markedly with *p*H up to about 10.5 at which point the curve rises rapidly to approach the composition of pure nickel hydroxide at higher *p*H's. In the range *p*H 8.5 to 10.0, the composition changes from about $Ni(OH)_2 \cdot 4NiCO_3$ to about $Ni(OH)_2 \cdot 3NiCO_3$. Also plotted on Fig. 3 is the equivalent ratio of total hydroxide to nickel, *R*, as a function of *p*H. This curve shows a minimum at the point where decreasing alkali requirements for bicarbonate neutralization is equalled by increasing alkali requirements for hydroxide consumption by the precipitate.

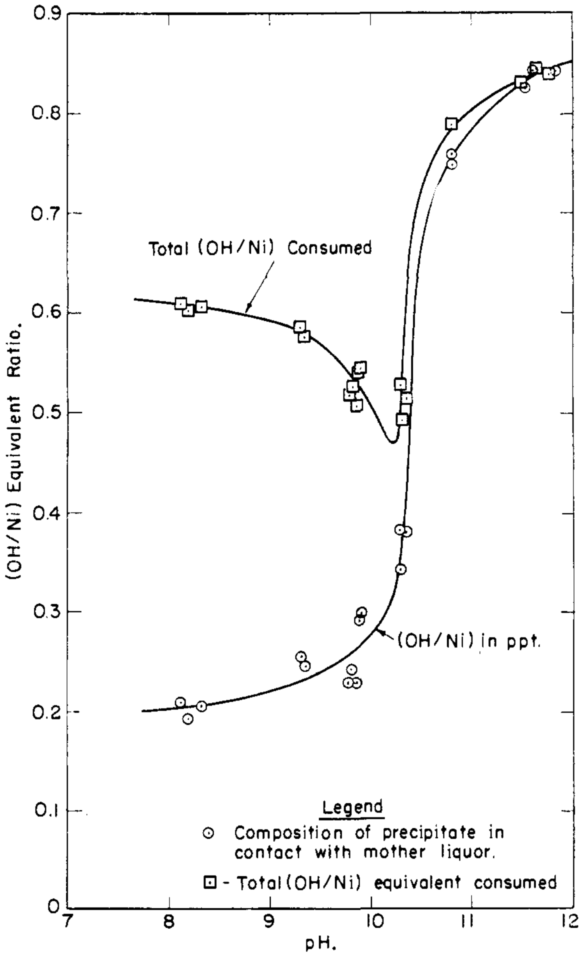

Fig. 3.—Effect of *p*H upon the composition of the precipitate and upon the total hydroxide to nickel equivalents consumed.

Chloride Content in Basic Nickel Carbonates.—It will be recalled that the basic nickel carbonate precipitates have been considered as being chloride-free. That this is essentially correct is indicated by the following experiment. After a normal precipitation at *p*H 8.23, a portion of the mother liquor was centrifuged, and eight analyses for chloride ion concentration were made on the clear supernatant liquid. The average concentration was 3.670 mg./ml., and the standard deviation was 0.006. If all the chloride ion added as nickel chloride remained in the mother liquor, the resultant chloride content may be calculated as 3.666 mg./ml. As a control, 50 ml. of the 3.31 *N* nickel chloride was added to 1500 ml. of deionized water and the resulting solution after mixing was analyzed eight times. The calculated chloride content was 3.785 mg./ml.; the experimental values averaged 3.812 with a standard deviation of 0.002. Although a possible uncertainty of less than 2% may be construed from these data, it has been concluded that no or essentially no basic nickel chloride is precipitated along with the basic nickel carbonates under the conditions of these experiments. Basic nickel chloride is more likely to contain high chloride content when formed at low rather than at high *p*H.[1]

Discussion of Experimental Error.—The reaction medium of these precipitations is highly buffered making the determination of the absolute equivalents of alkali required to maintain constant *p*H more difficult than for an unbuffered system. The minimum error associated with the individual experimental points on the plots of Fig. 2 is determined by the detectability of *p*H change, by the concentration and ionization constant of the buffer, and by the *p*H itself. The error may be computed in terms of ml. of the 3.47 *N* potassium hydroxide solution, for the arbitrary system used. This is numerically equivalent to a calculation of the maximum equivalents of acid, X, that can be added to a liter of mixed carbonates without producing more than the minimum detectable increase in hydrogen ion concentration, $\Delta[H^+]$. Nearly all of the acid added reacts according to $CO_3^{-2} + H^+ \rightarrow HCO_3^-$ which alters the equilibrium as indicated by

$$K_2 = \frac{([H^+] + \Delta[H^+])([CO_3^{-2}] - X)}{([HCO_3^-] + X)} \qquad (8)$$

Equation 8 is algebraically equivalent to

$$X = \frac{2.3 \times 10^{-pH} \times \Delta pH[CO_3^{-2}]}{10^{-pH}(2.3\Delta pH - 1) - K_2} = \frac{3.47}{1500} D$$

where ΔpH is the minimum detectable change in *p*H corresponding to $\Delta[H^+]$. The acid, X, to produce ΔpH is equivalent to the alkali required to restore the nominal *p*H and the latter may be expressed in terms of D ml. of 3.47 *N* KOH as indicated above. The value of D also depends on the carbonate ion concentration, but since there was a 10-fold excess of carbonate available in these experiments, the decrease in carbonate ion concentration during the course of a precipitation is less than 10%. The concentration of carbonate ion may be computed from the expression

$$[CO_3^{-2}] = \frac{K_1K_2T}{[H^+]^2 + [H^+]K_1 + K_1K_2}$$

which is obtained by combining equations 2, 5 and 6. Plots of D *vs.* *p*H are given in Fig. 4 for several different ΔpH's. The curves have a maximum when the *p*H equals pK_2 and maximum buffering is obtained.

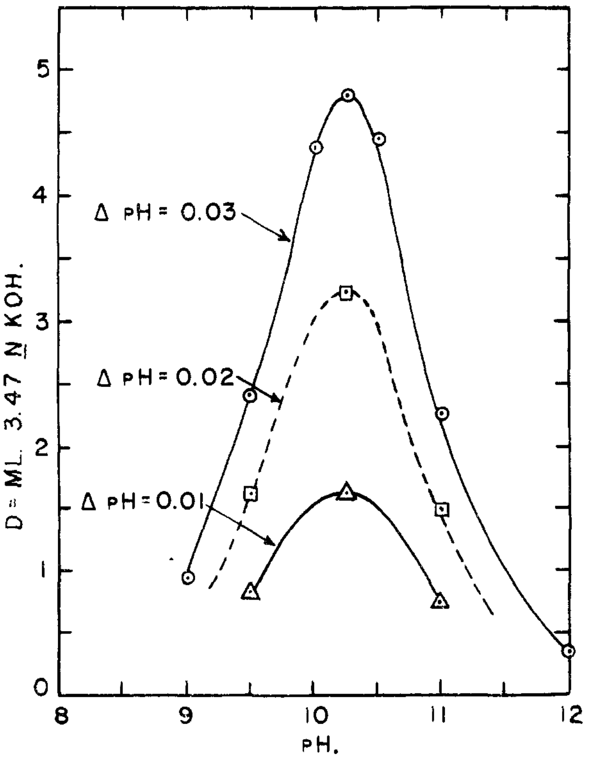

Fig. 4.—Plots of calculated error, *D*, expressed as ml. of 3.47 *N* KOH for uncertainties in *p*H, ΔpH's, of 0.01, 0.02 and 0.03 unit.

Several factors reduce the error in determining the slope of plots of buret readings so that the magnitude is not as great as that indicated in Fig. 4. First, the nominal *p*H during a precipitation was nearly always approached from the alkali-deficient side, which halved the error range by eliminating the plus from the plus and minus possibility. Secondly, there are error-leveling factors in operation during the selection of the best straight line. The observed linearity of these plots is equivalent to a ΔpH of not more than 0.01 unit in spite of the fact that absolute precision of that magnitude is not, of course, possible with the *p*H meter used. Deflections of the galvanometer on the *p*H meter were readily observed through the magnifying telescope when the actual change in *p*H producing the deflection was unreadable. The several cases of non-linear plots of buret readings were not reproducible and are believed to be the result of previously discussed instrument errors.[1]

Composition of Washed and Dried Precipitates.—Four precipitates prepared as described above, were filtered, washed with water until chloride-ion free, rinsed with acetone, and dried at room temperature under reduced pressure in a stream of dry air. Elemental analysis yielded the following data.

*p*H of precipitation	Ni, %	Co, %	K, %	Cl, %	Composition (OH/Ni)
8.2	41.5	32.2	0.9	0.00	0.23
8.2	40.5	32.8	.1	.00	.18
9.8	46.5	26.6	.03	.00	.44
11.5	58.1	12.7	.01	.00	.78

The compositions, expressed as the OH/Ni equivalent ratio above, may be directly compared with the "as precipitated" compositions given in Fig. 3. With the possible exception of the material precipitated at *p*H 9.8, the agreement is probably within the over-all errors involved. Near *p*H 10, the composition of these materials appears to be more unstable, and it is conceivable that the washing and drying could alter the composition to the extent observed.

X-Ray Diffraction by Basic Nickel Carbonates.—Debye–Scherrer patterns were obtained with both the washed and dried precipitates just described and with other representative precipitates wet with their mother liquor. Those prepared at *p*H's less than 10 produced only diffuse halos; faint lines due to nickel hydroxide were evident using samples precipitated at higher *p*H's.

Discussion of Results.—Attempts were made to relate in some logical way, the observed equivalent ratio of OH^{-1} to CO_3^{-2} absorbed by the precipitate to the concentration ratio of these groups as ions in the solution. Such efforts showed that the hydroxide content of the precipitates was always unaccountably too high. The rapid change in composition in the *p*H vicinity of pK_2 suggests an effect arising from the redistribution of carbonate species with *p*H. However, such influence, if correct, must be obscured by at least equally important unknown factors.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

Convection Controlled Limiting Currents (Convection Currents). I. The Platinum Wire Convection Electrode

BY I. M. KOLTHOFF AND JOSEPH JORDAN

RECEIVED DECEMBER 3, 1953

Under specified conditions of stirring a platinum convection electrode yields convection controlled limiting currents. These convection currents are defined by the equation $i_{\text{conv}} = nFA\tau C$ where nF denotes the number of coulombs per mole involved in the electrode process, A the area of the indicator electrode and C the concentration of the electroactive species. τ is the "convection coefficient" which depends on the efficiency of stirring and on the hydrodynamic characteristics of the electrolysis cell. While limiting currents at the dropping electrode and at conventional wire electrodes are diffusion controlled, the limiting currents at the convection electrode are independent of the diffusion coefficient of the electroactive species. The convection current of iodide increases 2.1% per 1° increase in temperature. Within wide limits it is independent of the viscosity of the medium. Upon a relative increase of 29% of the viscosity of a dilute iodide solution by addition of glycerol the convection current decreased only 1%. The convection electrode has the further advantage over diffusion electrodes that the relation between convection current and concentration need to be established by one reaction only as it holds for all other reactions.

Current–voltage curves of electroreducible or oxidizable substances at stationary, vibrating and rotating platinum wire electrodes[1] yield "waves" with a "limiting current region" at potentials where the rate of the electrode process is large as compared to the rate of supply of the electroactive species to the surface of the indicator electrode.[2,3] The ordinary type of limiting currents is diffusion controlled.[1,4,5] In a preliminary communication[6] we reported that, under specified conditions, convection controlled limiting currents can be obtained at the rotated platinum wire electrode. These "convection currents" do not depend on the diffusion coefficient of the electroactive species. When convection currents prevail, the thickness of the "boundary layer"[7] at the electrode becomes very small and attains a limiting value (v.i.).

Experiments presented in this paper indicate that limiting boundary layers are not attained with the customary rotated platinum electrode, but that with an auxiliary stirrer convection currents are observed within a wide range of stirring rates.

Experimental

Materials.—C.P. chemicals and conductivity water were used throughout.

Apparatus.—Current–voltage (c.v.) curves were recorded with a Sargent Model XXI polarograph at a chart speed of 2.53 cm./minute and a rate of change of applied potential, $\Delta V/\Delta t$, of 2.47 mv./sec. In manual current–voltage determinations potentials were measured with a Leeds and Northrup Type K2 potentiometer and currents with a General Electric Mirror and Scale Galvanometer (maximum sensitivity, 10^{-8} a. per scale division; period, 3.7 sec.), equipped with a suitable Ayrton shunt. Unless otherwise stated, all limiting current values reported have been corrected for residual currents.

Electrodes and Electrolysis Cell.—A Hume–Harris saturated calomel reference electrode (SCE) and salt bridge[8] were used in all experiments. Potentials reported in this paper are referred to this SCE.

Rotated platinum indicator electrodes were made of annealed platinum wire, approximately 0.3 mm. in diameter and 4 mm. in length. They were sealed into a glass tube into which an auxiliary stirrer could be concentrically mounted by means of a ground glass joint. The stirrer was made of glass in the form of a rectangular propeller with 4

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(1) For a review see: I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., pp. 402–419.

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