ture measuring instrument, it was calibrated over the range from −190 to 660° according to the recommendations for the International Temperature Scale (1948).[9] To extend the range of the thermometer to 62°K., the helium gas thermometer was used after the manner of Hoge and Brickwedde.[10] The tie-in between the two methods of calibration was made at the normal oxygen point.

Experimental Results

Heat Capacity of NaOH.—During these measurements the calorimeter contained 29.3602 g. of NaOH which, assuming the molecular weight of NaOH to be 40.005, corresponds to 0.7339 mole. The experimental values of the molar heat capacity obtained are given in Table I in the form of values picked from the smooth curve drawn through the actual experimental values. These values are based on the "defined calorie" which is assumed to have a value of 4.1840 absolute joules.

Entropy, Heat Content and Free Energy of NaOH.—The method recommended by Kelley[11] was used in the extrapolation of the heat capacity data to 0°K. Graphical integration of the data in the proper form yielded the absolute entropy of NaOH as entered in Table I. The contribution to the entropy of the extrapolated part amounts to 1.16 e.u. at 60°K. Following the practice of Kelley,[11] an uncertainty of 5–10% is assigned to this value. For record purposes, the entropy of crystalline sodium hydroxide can be assigned the value

$$S_{298.16} = 15.3 \pm 0.1 \text{ e.u.}$$

This value compares with the value of 13.8 ± 1.5 e.u. as obtained by Shibata[12] from cell measurements.

By suitable graphical integration, the heat content function was obtained, based upon its value at 0°K. By combining the entropy and heat content properly, the relative free energy function was then calculated. These two additional functions are given in Table I.

TABLE I

T, °K.	C_p, cal./degree mole	S_T, cal./degree/ mole	$(H_T^\circ - H_0^\circ)$, cal./mole	$-(F_T^\circ - H_0^\circ)$, cal./mole
60	2.075	1.16	51.6	18.2
75	4.417	1.97	106.3	41.6
100	6.877	3.61	251.1	109.4
125	8.553	5.33	447.4	221.6
150	9.870	7.01	680.8	370.5
175	10.92	8.61	940.9	566.1
200	11.76	10.13	1225	800.5
225	12.54	11.56	1529	1072
250	13.25	12.92	1821	1378
275	13.83	14.21	2190	1717
298.16	14.21	15.34	2534	2040
300	14.24	15.43	2541	2088

The several functions listed in Table I are given in four figures for possible future mathematical calculations only. The usual rounding off can then be done after calculation. By considering the deviations of the experimental heat capacities from the smoothed curve, a band of uncertainty can be drawn with the smoothed curve in the center. The area of this band is such that the maximum uncertainty at higher temperatures is approximately 1 in 500 for the entropy, 1 in 1000 for the heat content, and 1 in 200 for the free energy. At lower temperatures these would be doubled. Actually, however, it is felt that the real uncertainty will be considerably less than the above. However, because of the extrapolation below 60°K., the uncertainty in the entropy at 298.16°K. is estimated to be about 0.1 e.u. as indicated above.

PITTSBURGH, PENNSYLVANIA RECEIVED DECEMBER 16, 1950

[9] Stimson, *Natl. Bur. Standards J. Res.*, **42**, 209 (1949).

[10] Hoge and Brickwedde, *ibid.*, **22**, 351 (1939).

[11] K. K. Kelley, United States Bureau of Mines Bulletin, No. 447 (1949).

[12] Shibata, *J. Chem. Soc. Japan*, **50**, 523 (1929).

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

Millicoulometry. II. The Purported Reduction of Nitrate at the Dropping Mercury Electrode

BY LOUIS MEITES

The waves secured on adding nitrate to weakly acidic solutions of lithium or cerium(III) chloride, which have in the past been attributed to reduction of the nitrate ion, are shown to be due to a catalytic reduction of water or hydrogen ion.

Introduction

The behavior of nitrate ion at the dropping electrode was first investigated by Tokuoka,[1] and by Tokuoka and Ruzicka,[2] who reported the 45° tangent potentials of the waves secured by adding nitrate to 0.1 *N* solutions of the chlorides of a number of uni-, di- and trivalent metals. These fell into three groups, depending on the charge of the cation: *i.e.*, −2.2 v. (*vs.* S.C.E.) in lithium or tetramethylammonium chloride, −1.8 v. in calcium, magnesium or strontium chloride, and −1.3 v. in lanthanum or cerium(III) chloride. This effect was attributed to the formation of "ion pairs" in which the nitrate was in a more easily reducible condition than in the normal ion. A comparison of the diffusion currents of nitrate and cadmium ions indicated that the nitrate reduction consumed eight faradays per mole, giving ammonia as the product.

More recently it has been claimed[3] that the reduction of nitrate from lanthanum or neodymium chloride solutions required seven faradays per mole, corresponding to reduction to an equimolar solution

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[1] M. Tokuoka, *Collection Czechoslov. Chem. Communs.*, **4**, 444 (1932).

[2] M. Tokuoka and J. Ruzicka, *ibid.*, **6**, 339 (1934).

[3] S. I. Sinyakova and G. G. Karanovich, *Trudy Komisii Anal. Khim., Otdel. Khim. Nauk, Akad. Nauk S. S. S. R.*, [5] **2**, 65 (1949); *C. A.*, **44**, 9303 (1950).

of ammonia and hydroxylamine. In uranyl chloride solutions the reaction was found to be "more complicated than the formation of nitrogen."

Kolthoff, Harris and Matsuyama,[4] and Harris and Kolthoff[5] studied the catalytic effect of uranyl salts on the nitrate wave in 0.01 M hydrochloric acid solutions, but did not attempt to identify the reduction product.

With few exceptions, all of these studies have stressed the fact that the diffusion current of nitrate is not proportional to its concentration. This would seem to indicate either that the reduction is rate-controlled or that it is actually a catalytic process. The present investigation was undertaken to permit a decision between these alternatives, and to secure definite evidence concerning the oxidation state of the nitrogen after an electrolysis at the dropping electrode.

Experimental

Polarograms were made with the apparatus previously described,[6] using a modified H-cell.[7] All measurements were made in a water thermostat at 25.00 ± 0.02° except as otherwise noted.

Lithium chloride was recrystallized twice from 0.01 M hydrochloric acid and once from water: an 0.1 M solution of the air-dried product had the same pH as the water from which it was prepared, and contained no detectable amount of nitrate. Cerium(III) chloride was prepared from ammonium hexanitratocerate (G. F. Smith Chemical Company) by repeated evaporation to near-dryness with concentrated hydrochloric acid, followed by a double recrystallization from 6 M hydrochloric acid. Conductivity water was used for the preparation of all solutions. For the experiments in lithium salt solutions, lithium nitrate (Mallinckrodt Chemical Works) was used as the source of nitrate. Cerous ammonium nitrate (G. F. Smith Chemical Company), analyzed for nitrate by the method of Kolthoff, Sandell and Moskovitz,[8] was used in the work with cerium(III) solutions.

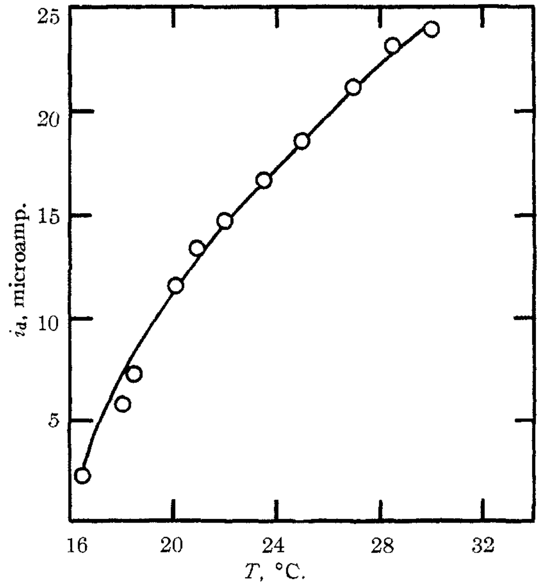

Fig. 1.—Effect of temperature on the diffusion current of 0.5 mM nitrate in 0.1 M lithium chloride.

Data and Discussion

Lithium Salt Solutions.—In 0.1 M lithium chloride the half-wave potential of the single well-defined nitrate wave is −1.59 ± 0.02 v. *vs.* S.C.E., which is much more positive than the value reported by Tokuoka and Ruzicka.[2] At pH 5.9 the value of i_d/C is not constant, but decreases considerably with increasing nitrate concentration. In one case i_d/C was 81 microamp./millimole/liter at a nitrate concentration of 0.03 mM, and decreased continuously to a value of 69 when the nitrate concentration was 2 mM. The diffusion current is very sensitive to traces of acid or base: it nearly doubles when the pH is lowered from 5.9 to 5.0 by the addition of hydrochloric acid, and the wave disappears completely if the pH is raised to 7.1 by the addition of a trace of ammonia.

Because of this sensitivity of i_d to small changes in pH, it was thought that the linearity of the diffusion current–concentration curve could be improved by the use of a buffered supporting electrolyte. Accordingly, lithium acetate and citrate buffers of pH 5.9 were prepared by mixing lithium carbonate and the appropriate acid, boiling to remove excess carbon dioxide, and diluting to a lithium concentration of approximately 0.1 M. In both of these media polarograms made in the presence of added nitrate were identical with the corresponding residual current curves, and this was also true when the pH of the supporting electrolyte was changed to 5.2 or to 6.5. The potential at which the residual current became equal to the expected nitrate diffusion current varied in these experiments from −1.70 to −1.85 v., showing that the failure to find a nitrate wave at −1.6 v. was not due to the prior discharge of hydrogen ion from the supporting electrolyte.

This suggested that the wave secured in unbuffered solutions might be due to the considerably higher concentration of hydrogen ion at the electrode surface, so that the pH there is considerably lower than in the bulk of the solution. This in turn led to the suspicion that the wave is actually due to the catalytic reduction of hydrogen ion.

The classical test for a catalytic reduction depends on the measurement of the temperature coefficient of the diffusion current of a wave. If this coefficient is approximately 1.5%/degree, the wave is considered to represent a normal reduction, but a much higher value is frequently associated with a catalytic reaction. The dependence of the diffusion current of nitrate in 0.1 M lithium chloride on the temperature between 16.5 and 28.5° is shown in Fig. 1. Over this range the average temperature coefficient of i_d is approximately 25%/degree. The derivative of this coefficient with respect to temperature is negative, so that the coefficient is 80% per degree between 16.5 and 18.5°, but is only 7.5%/degree between 22.0 and 28.5°.

It has been shown that, for a diffusion-controlled wave, the diffusion current constant[9] in the absence of gelatin is, in accordance with the Ilkovic equation,[10,11] independent of $m^{2/3}t^{1/6}$ or t at drop

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[4] I. M. Kolthoff, W. E. Harris and G. Matsuyama, THIS JOURNAL, **66**, 1782 (1944).

[5] W. E. Harris and I. M. Kolthoff, *ibid.*, **67**, 1484 (1945).

[6] L. Meites and T. Meites, *ibid.*, **72**, 3686 (1950).

[7] L. Meites and T. Meites, *Anal. Chem.*, in press.

[8] I. M. Kolthoff, E. B. Sandell and B. Moskovitz, THIS JOURNAL, **55**, 1454 (1933).

[9] J. J. Lingane, *Ind. Eng. Chem. Anal. Ed.*, **15**, 583 (1943).

[10] D. Ilkovic, *Collection Czechoslov. Chem. Communs.*, **6**, 498 (1934).

[11] D. Ilkovic, *ibid.*, **8**, 13 (1936).

times above about 2 sec.[12] It increases at lower drop times,[12] due to a stirring effect like that found in solutions containing gelatin.[13–15]

However, the diffusion current of nitrate in 0.1 *M* lithium chloride decreases only 25% as the drop time is increased from 1.2 to 4.8 sec., corresponding to a change in the effective pressure of mercury from 104.5 to 29.5 cm. Thus $i_d/h^{1/2}$, which is very nearly proportional to $i_d/m^{2/3}t^{1/6}$, increased about 40% over this range of drop times.

Table I contains the data of a typical millicoulometric electrolysis of a solution of nitrate in lithium chloride. Measurements were made with the millicoulometer whose construction, calibration, and use were described in a preceding paper.[16] A micro H-cell[17] was used.

TABLE I

ELECTROLYSIS OF NITRATE IN 0.1 *M* LITHIUM CHLORIDE

0.251 micromole of nitrate was initially present in 0.503 ml. of solution. $E_{d.e.} = -1.70$ v. *vs.* S.C.E., t = *ca.* 2.7 sec. The blank counting rate of the millicoulometer, including the residual current, was 0.2948 counts/sec. The values of *d* (galvanometer deflection, cm.) have been corrected for the residual current.

Time, sec.	Register	Counts	Counts cor.	Microfaradays	d_d, cm.	n
0	98943	0	0	0	23.53	..
1541	99734	791	336.7	0.153	23.30	62.4
1939	99938	995	423.4	.192	23.20	54.5
8183	02916	3973	1561	.708	22.57	69.1
10491	04060	5117	2024	.919	22.00	56.3
12480	05049	6106	2427	1.10	21.78	58.9
14989	06272	7329	2910	1.32	21.45	59.5
23271	09610	10667	3807	1.73	21.13	67.6
					Mean	61.2 ± 4.4

A number of runs in 0.04–0.5 *M* lithium chloride at 25° gave values of *n* between 55 and 65 faradays per mole of nitrate: the relatively poor reproducibility of the results is attributable to the extreme sensitivity of the diffusion current to small changes in the composition of the solution near the electrode, which cannot be avoided in a prolonged electrolysis. At 20°, where the diffusion current is about half that at 25°, the values of *n* were slightly lower, averaging about 45.

It is clear from these results that, even if the nitrate ion is reduced, the major portion of the current must be due to the catalytic reduction of water or hydrogen ion.

Three aliquots of a 1 m*M* solution of lithium nitrate in 0.1 *M* lithium chloride were electrolyzed at −1.70 v. *vs.* S.C.E. until the millicoulometer showed that 150–300 faradays had been used per mole of nitrate. Two of the resulting solutions were analyzed for nitrate by a modification of the method of Kolthoff, Sandell and Moskovitz[8] in which the excess ferrous ion was titrated potentiometrically with standard ceric sulfate. The two titrations indicated that 93 and 99% of the nitrate initially added was still present in that form. Similar titrations of two portions of the original solution showed 94 and 102% of the nitrate known to be present. The differences among these values are not significant.

Portions of the third solution after electrolysis were tested for ammonium and nitrite ions with negative results. Another portion was slightly acidified and treated with a measured volume of standard potassium permanganate, and its optical density at 525 millimicrons was compared with those of two portions of the original solution similarly treated. A Beckman Model B spectrophotometer was used for the comparison. The optical density of the electrolyzed solution was almost exactly equal to the mean of the two "blank" solutions, showing that little, if any, hydrazine, hydroxylamine or nitrite had been formed.

Cerium(III) Salt Solutions.—The polarography of nitrate in cerium(III) chloride solutions differs in many important details from that in lithium chloride media. In 0.05–0.5 *M* cerous chloride the half-wave potential is −1.60 ± 0.02 v., substantially identical with the value found in lithium chloride, but nearly 0.3 v. more negative than the figure reported by Tokuoka and Ruzicka.[2,18] This agreement between the half-wave potentials in different media seems to invalidate the "ion pair" theory of Tokuoka and Ruzicka.

In 0.10 *M* cerous chloride the diffusion current constant of nitrate, measured at −1.70 v. *vs.* S.C.E. with a capillary for which t was 2.22 sec. and $m^{2/3} \cdot t^{1/6}$ was 2.069 mg.$^{2/3}$ sec.$^{-1/2}$, is 17.6 at a nitrate concentration of 0.055 m*M*, and decreases to 12.5 when this concentration is increased to 0.65 m*M*. At the same drop time, the diffusion current constant of cadmium, by interpolation from previously published data,[6,12] is 3.59 in 0.1 *M* potassium chloride—0.1 *M* hydrochloric acid, or 3.53 in 0.1 *M* potassium nitrate. Accordingly, the ratio of the diffusion current of nitrate to that of an equimolar concentration of cadmium is not exactly 4, as claimed by Tokuoka and Ruzicka, but 3.5 to 5.0, depending on the nitrate concentration. From these data, therefore, the reasoning of Tokuoka and Ruzicka (which involves the indefensible assumption that the diffusion coefficients of the nitrate and cadmium ions are equal) would lead to the conclusion that the nitrate reduction requires from 7 to 10 faradays per mole, and that the reduction product changed as the concentration was varied.

Table II shows the dependence of the diffusion current of nitrate in 0.25 *M* cerous chloride on the applied pressure of mercury. In contrast to the data in lithium chloride solutions, which showed a large increase in $i_d/h^{1/2}$ with decreasing h, the present data show that $i_d/h^{1/2}$ is independent of h at drop times between 1.5 and 4.6 sec. in cerous chloride solutions, and that it is only slightly higher at 6.1 sec. This seems to indicate that the reduction in cerous chloride solutions is diffusion-controlled, a

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[12] L. Meites, THIS JOURNAL, **73**, 1581 (1951).

[13] J. J. Lingane and B. A. Loveridge, *ibid.*, **66**, 1425 (1944).

[14] H. Strehlow and M. v. Stackelberg, *Z. Elektrochem.*, **54**, 51 (1950).

[15] L. Meites and T. Meites, THIS JOURNAL, **73**, 395 (1951).

[16] S. Bogan, L. Meites, E. Peters and J. M. Sturtevant, *ibid.*, **73**, 1584 (1951).

[17] T. Meites and L. Meites, *Anal. Chem.*, in press.

[18] Lingane and Davis (unpublished experiments, described in I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941, p. 315) recorded polarograms of nitrate in lanthanum chloride solutions. The value of $E_{1/2}$ in the polarogram in 0.017 *M* lanthanum chloride shown by Kolthoff and Lingane is also much more negative than that reported by Tokuoka and Ruzicka. Dr. Charles L. Rulfs (private communication) found $E_{1/2}$ of nitrate in 0.04 *M* lanthanum chloride to be −1.58 ± 0.04 v. at 25°, in very good agreement with the results reported here.

conclusion which would appear to be substantiated by measurements of the temperature coefficient of the diffusion current. Between 17.0 and 37.5° this coefficient is, within the limit of precision of the measurements, independent of temperature, and it is equal to 2.2%/degree. This, although only one-tenth of the corresponding value for lithium chloride solutions, is still slightly higher than the expected value of 1.3 to 1.6%/degree, but the difference is not sufficiently great to deserve much emphasis.

TABLE II

EFFECT OF APPLIED PRESSURE ON DIFFUSION CURRENT OF NITRATE IN 0.25 M CEROUS CHLORIDE

The nitrate concentration was 0.4 mM, $E_{d.e.}$ = −1.70 v.

Applied pressure, cm.	t, sec.	i_d, microamp.	$i_d/h^{1/2}$
104.5	1.50	21.84	2.13
89.5	1.77	20.40	2.15
74.5	2.14	18.08	2.09
59.5	2.71	16.36	2.12
46.5	3.50	14.44	2.12
35.5	4.64	12.80	2.15
27.5	6.06	11.56	2.20

One explanation for these differences between lithium and cerium(III) chloride solutions is based on the fact that the latter are much more acidic. Our cerous chloride solutions had pH values of about 3.5, compared to 5.9 for the lithium chloride solutions. Therefore the region surrounding the dropping electrode in a cerous solution will contain much more hydrogen ion than nitrate, while the reverse is probably the case in a lithium chloride solution. As a result, one would expect that the rate-determining step in a cerium(III) solution would be the diffusion of nitrate up to the electrode surface, while in a lithium chloride solution the current is probably primarily governed by the rate of the catalytic reaction. Whether or not this hypothesis is valid can, of course, only be settled by proof that, on the one hand, the "deposition" of nitrate in a cerous solution proceeds normally and requires eight or fewer faradays per mole, or on the other hand, that this wave too corresponds to the reduction of water or hydrogen ion, and that the nitrate concentration decreases slowly or not at all during a prolonged electrolysis.

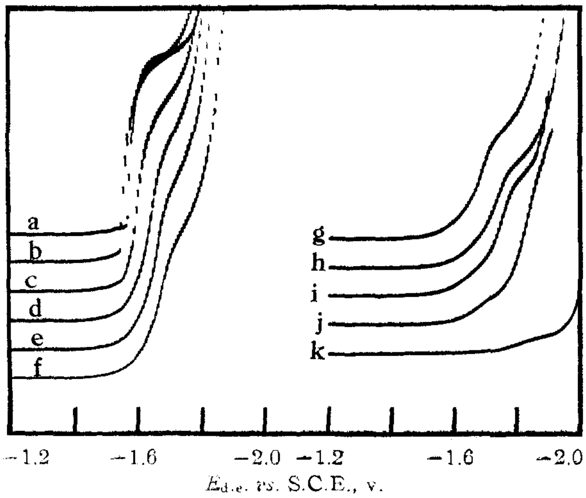

Fig. 2.—Polarograms of 0.4 mM nitrate in 0.1 M cerous chloride with (a) 0, (b) 0.64, (c) 1.5, (d) 2.5, (e) 4.2, (f) 8.1, (g) 28, (h) 47, (i) 83, (j) 175 and (k) 530 mM sodium sulfate.

The "reduction" of nitrate from a lanthanum chloride solution has recently been studied by Rulfs, who writes: "I tried in vain to get meaningful results on nitrate by macrocoulometry: apparently hydrogen is evolved and lanthanum hydroxide precipitation is the major process in the solution. Macro tests showed no ammonium ion after a long run."[19] This shows that the catalytic reduction of water or hydrogen ion is the predominating process, at least at a large stirred mercury cathode, but it does not provide conclusive proof that nitrate is not the reducible species at the dropping electrode.

Table III shows typical data on the millicoulometric electrolysis of a solution of nitrate in 0.1 M cerous chloride. The electrolysis was carried out until 6.07 microfaradays had been passed through a solution containing initially 0.112 micromole of nitrate, so that 54.2 faradays had been used per mole of nitrate. As shown by the last line in the table, the diffusion current was then approximately 30% higher than at the beginning of the experiment. During the course of the electrolysis, the diffusion current rose continuously until about 2 microfaradays had been passed, when it was nearly 2.4 times its initial value, and then began to fall slowly. The rate of decrease of the diffusion current during the latter part of the electrolysis, on comparison with the quantity of electricity used, corresponds to an apparent consumption of about 55 faradays per mole of nitrate. This is sufficiently close to the value found in lithium chloride solutions to show that the electrode process must be the same in both media.

TABLE III

ELECTROLYSIS OF NITRATE IN 0.1 M CERIUM (III) CHLORIDE

0.112 micromole of nitrate was initially present in 0.440 ml. of solution. $E_{d.e.}$ = −1.70 v. *vs.* S.C.E., t = *ca.* 2.8 sec. The blank counting rate of the millicoulometer, including the residual current, was 0.2953 ± 0.0001 counts/sec. The values of d (galvanometer deflection, cm.) have been corrected for the residual current.

Time, sec.	Register	Counts	Counts, cor.	Micro-faradays	d_d, cm.
0	11710	0	0	0	18.31
4783	14957	3247	1835	0.833	27.43
6496	16127	4417	2499	1.13	29.14
10135	18467	6757	3764	1.71	35.90
11817	19484	7774	4284	1.94	43.50
13314	20689	8979	5047	2.29	39.94
15453	22468	10758	6194	2.81	37.66
17354	23963	12253	7128	3.23	34.49
19534	25634	13924	8156	3.70	32.74
22124	27455	15745	9212	4.18	27.52
31713	34449	22739	13374	6.07	24.04

The position of the unexpected maximum in the electrolysis curve is of some importance. In 0.02 and 0.1 M cerous chloride containing 0.05 to 0.50 mM nitrate, the number of microfaradays required to attain this maximum current appears to be independent of the nitrate concentration. It varies

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(19) C. L. Rulfs, private communication.

with the cerous concentration, being slightly higher at the higher concentration of supporting electrolyte, and it increases linearly with the volume of the solution. A similar, though smaller, increase of the diffusion current was also produced by the addition of small amounts of sodium hydroxide to a fresh solution. These phenomena may be related to the formation of a partially hydrolyzed cerium(III) species.

Typical polarograms of nitrate in 0.1 *M* cerous chloride in the presence of various concentrations of sodium sulfate are shown in Fig. 2. Even very low concentrations (*ca.* 1.5 m*M*) of sulfate radically alter the shape of the wave, transforming it into the form shown in curve b. With higher sulfate concentrations the sharp "break" at the foot of the wave disappears completely. With 0.5 *M* sulfate a large precipitate is formed, presumably of cerous sulfate, and the wave practically disappears.

These results are difficult to explain on the basis of the "ion pair" theory of Tokuoka and Ruzicka. It seems very improbable that 1.5 m*M* sulfate should be able to replace most of the nitrate from the cerous nitrate complex in the presence of a large excess of cerium(III).

Acknowledgment.—This work was supported by Contract Number AT(30-1)-842 between the U. S. Atomic Energy Commission and Yale University.

NEW HAVEN, CONNECTICUT RECEIVED JANUARY 15, 1951

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENTS, BROOKHAVEN NATIONAL LABORATORY AND CORNELL UNIVERSITY]

Determination of Dissociation Constants of Complex Ions by a Radioactive Indicator Method[1a]

BY C. M. COOK, JR.,[1b] AND F. A. LONG[1b]

A radioactive indicator method for determining the dissociation constants of highly stable complex ions can be used when the complex ion is formed from the conjugate base of a weak acid with known ionization constants and when the complex ion interchanges its central metal ion only slowly. The method involves a determination of the metal ion concentration in a complex solution of sufficient acidity so that partial dissociation has occurred. Application of the method to ferroin gives a K_d value of 8×10^{-22} which agrees fairly well with the value obtained by Kolthoff and co-workers. A similar investigation of $NiEdt^{=}$, the complex formed from nickel ion and ethylenediaminetetraacetic acid, gives $K_d = 1 \times 10^{-19}$.

The determination of dissociation constants of highly stable complex ions is frequently a matter of some difficulty, particularly if the complex ion is only weakly colored or if the metal ion does not form a reversible electrode with its metal. A procedure which involves the use of radioactive indicators and which should have utility for certain common types of complex ions is outlined below; also given are results of the application of this method to two complex ions, ferroin and ethylenediaminetetra-acetato nickelous ion.

Consider a complex ion, MeA_x, formed from a metal ion and the conjugate base of a weak acid. In acid solutions this complex will undergo partial dissociation caused by removal of A by hydrogen ions. If the ionization constants of the weak acids formed from A are known, the dissociation constant of the complex can be calculated from the concentration of Me ions present in an equilibrated MeA_x solution of known acidity; this Me ion concentration can be determined by use of a radioactive indicator.

Suppose the undissociated complex ion will undergo radioactive exchange with added Me ions only slowly. (This will commonly be true for complex ions of high stability.) If one adds Me ions to an acidified and equilibrated solution of MeA_x which has been made from isotopically labeled Me of known radioactivity, and subsequently removes from solution a portion of the Me ions, one finds that this is radioactive due to mixing of the inactive Me with active Me from dissociation of the complex. The increase in specific radioactivity is an easily calculated function of the moles of added Me and of that present as such in the original solution. Consequently a measurement of this specific radioactivity decrease permits a calculation of the concentration of Me ions.

The addition of the radioactive Me will shift the equilibrium of the complex ion toward less dissociation. A basic assumption is that mixing of the radioactive and inactive Me precedes this shift in the equilibrium.

Bjerrum[2] has demonstrated that, in the case of many coördination complexes, the formation of the complexes will take place in stepwise fashion, so that in the acid-induced dissociation of MeA_x the species MeA_{x-1}, MeA_{x-2}, . . ., as well as Me may be present. If these intermediate complexes are present as a sizeable fraction of the total complexed Me in the equilibrium solution, their presence will complicate the interpretation of the data and the calculation of the dissociation constant. For some complex ions this difficulty obviously will not enter. For other cases, however, it may be necessary to investigate this intermediate complex formation problem before the method can be safely applied.

Specific illustrations of the application of this technique are given in the next sections.

Dissociation Constant of Ferroin

The dissociation of this complex of ferrous ion and orthophenanthroline, $FePh_3^{++}$, has been studied by Lee, Kolthoff and Leussing[3a] who report a

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(1) (a) Work carried out in part under the auspices of the Atomic Energy Commission. (b) Department of Chemistry, Cornell University, Ithaca, N. Y.

(2) J. Bjerrum, *Chem. Revs.*, **46**, 381 (1950).

(3) (a) T. S. Lee, I. M. Kolthoff and D. L. Leussing, THIS JOURNAL, **70**, 2348 (1948); (b) I. M. Kolthoff, D. L. Leussing and T. S. Lee, *ibid.*, **72**, 2173 (1950).