[CONTRIBUTION FROM THE CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY]

Isotopic Exchange Reactions of Neptunium Ions in Solution. II. The Np(IV)–Np(V) Exchange

BY J. C. SULLIVAN, DONALD COHEN AND J. C. HINDMAN

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The isotopic exchange reaction between Np(IV) and Np(V) has been measured in perchloric acid as a function of hydrogen ion concentration, metal ion concentration, ionic strength and temperature. The complex hydrogen ion dependence of the exchange rate was resolved into two regions of constant hydrogen ion dependence. In each region metal ion orders and heats of activation were determined. The over-all rate equation may be expressed as $R = k_1[NpO_2^+]^2[H^+] + k_2[Np^{+4}]^{1.5}[NpO_2^+]^{0.5}[H^+]^{-2}$. At $\mu = 1.2$ and 25°, for the high acid path, $k_1 = 6.61 \times 10^{-4}$ l.^{2} mole^{-2} min.$^{-1}$, $\Delta F^* = 24.2$ kcal. mole^{-1}, $\Delta H^* = 17.6$ kcal. mole^{-1} and $\Delta S^* = -22.2$ cal. deg.$^{-1}$ mole^{-1}. At $\mu = 1.2$ and 25°, for the low acid path, $k_2 = 3.87 \times 10^{-6}$ mole liter^{-1} min.$^{-1}$, $\Delta F^* = 27.2$ kcal., $\Delta H^* = 36.8$ kcal., $\Delta S^* = 32.2$ cal. deg.$^{-1}$ mole^{-1}.

The isotopic exchange reaction between Np(V) and Np(VI) was discussed in the first communication[1] of this series. This paper concerns itself with the kinetics of the exchange between Np(IV) and Np(V) in perchloric acid. The most interesting feature of this study was the complex dependence of the exchange rate on the hydrogen ion concentration. Over the range 0.05 to 1.0 *M* hydrogen ion concentration, at constant metal ion concentration, the rate can be depicted as a continuous function with a maximum in the region $-\log [H^+] = 0.4$. It has been found possible to reproduce this function by considering the exchange reaction as the sum of two reactions proceeding by different paths.

Experimental

As in the first communication of this series[1] Np^{239}, a β-emitter with a 2.33 day half-life was used as the tracer. It was prepared and purified in the manner previously described. Np^{237} solutions were purified by solvent extraction techniques and were spectroscopically pure. The tracer was added to a solution of Np^{237} and a stock Np(V) solution in 1 *M* perchloric acid was prepared.[2] A Np(IV) solution was prepared electrolytically.[3]

The perchloric acid solutions were prepared by diluting G. Frederick Smith double vacuum-distilled 72% perchloric acid with triple distilled water. The sodium perchlorate was prepared by dissolving chemically pure sodium carbonate in perchloric acid. This sodium perchlorate failed to give a test for chloride ion. The thenoyltrifluoroacetone (TTA) was a product of the Dow Chemical Co.

The hydrogen ion concentrations of the Np(IV) and the Np(V) stock solutions were measured by direct titration of aliquots with standard sodium hydroxide using methyl orange as the indicator. For the Np(IV) stock solution a correction had to be made because of the reaction between the hydroxide ion and the cation. The magnitude of this correction was determined by dissolving a sample of pure $NpCl_4$, prepared by J. Malm of this Laboratory, in a known volume of standard perchloric acid to give a solution similar to the Np(IV) stocks. Various aliquots of this solution were titrated with the standard sodium hydroxide. Three equivalents of hydrogen ion were found necessary for each equivalent of Np(IV) ion to titrate the solution to a *p*H of four.

The exchanges were carried out in a constant temperature bath which was controlled to ±0.05°. The reaction vessel was made entirely of Teflon with a tight fitting stopper that penetrated an inch into the vessel itself leaving a volume of 2.5 ml. for the reaction solution. Thus, the entire volume of the cell was thermostated in the constant temperature bath under such conditions that at the higher temperatures there was very little tendency for water vapor to condense and form distinct droplets in the cell with the concomitant change in concentrations of the reaction mixture. Precautions of this type were necessary because of the long half-times involved in some experiments.

Each run was set up by using appropriate aliquots of the stock solutions of Np(IV), Np(V), perchloric acid, sodium perchlorate and sufficient water to bring the volume up to two ml. At discrete time intervals an aliquot, about 0.01 ml., of this solution was withdrawn with a Teflon pipet and was delivered into a Teflon test-tube containing one ml. of 1 *M* perchloric acid and two ml. of a 0.5 *M* TTA in benzene solution. The solvent extraction was carried out in this Teflon test-tube and the two phases were separated by centrifugation. An aliquot of the organic phase was plated on a five-mil tantalum plate and counted in the manner described in the first paper of this series. All counting was carried out to a statistical accuracy of 1% standard deviation.

Treatment of the Data

Applying the exponential rate law for isotopic exchange[4] to the system under consideration we have

$$Rt = -\frac{[Np(IV)][Np(V)]}{[Np(IV)] + [Np(V)]} \ln (1 - F) \quad (1)$$

where *R* is the rate constant in mole l.$^{-1}$ min.$^{-1}$, *t* is the time in minutes and *F* is the fraction exchanged.

For each experiment the fraction exchanged was measured at five to ten time intervals. For each measurement the value of *R* was calculated using equation 1. The results of a single experiment are tabulated in Table I. The precision of the data as in all the cases reported is given in terms of standard deviation.

TABLE I

RATE OF Np(IV)–Np(V) EXCHANGE

1.00 *M* $HClO_4$ at 47°; 0.0492 *M* Np(IV), 0.0211 *M* Np(V)

Time, min.	Fraction exchanged, %	$R \times 10^5$, moles l.$^{-1}$ min.$^{-1}$
100	8.55	1.32
200	16.50	1.33
230	18.41	1.31
260	20.65	1.31
290	23.38	1.36
320	24.43	1.29
350	27.68	1.37
390	28.22	1.29
		1.32 ± 0.02

A duplicate experiment gave a value of $R = 1.36 \pm 0.03 \times 10^{-5}$. It must be pointed out that the internal consistency of the data, as measured by the standard deviation within a run or by the standard deviation between duplicate runs made from the same stocks of starting materials, indicated

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[1] D. Cohen, J. C. Sullivan and J. C. Hindman, THIS JOURNAL, **76**, 352 (1954).

[2] R. Sjoblom and J. C. Hindman, *ibid.*, **73**, 1744 (1951).

[3] D. Cohen and J. C. Hindman, *ibid.*, **74**, 4679 (1952).

[4] H. McKay, *Nature*, **142**, 997 (1938).

a smaller probable error than was found when duplicate runs from different stock preparations were compared.

Results and Discussion

The Effect of Hydrogen Ion.—Applying the general procecure used in chemical kinetics and assuming the rate law to be represented by

$$R = k[\mathrm{Np(IV)}]^a[\mathrm{Np(V)}]^b[\mathrm{H}^+]^c \qquad (2)$$

where k is the specific rate constant, we may independently vary the hydrogen ion concentration and evaluate c from the slope of the log R *vs.* log $[\mathrm{H}^+]$ curve. This plot is shown in Fig. 1. An inspection of this figure shows that in the region $0 \leq -\log [\mathrm{H}^+] \leq 0.35$ a straight line with the slope of +1 and in the region $0.5 \leq -\log [\mathrm{H}^+] \leq 1.4$ a straight line with the slope of −2 adequately represents the data. Thus for constant neptunium ion concentrations the rate law has the form

$$R = k_1'[\mathrm{H}^+] + k_2'[\mathrm{H}^+]^{-2} \qquad (3)$$

In these experiments sodium perchlorate was added so that the sum of $[\mathrm{H}^+] + [\mathrm{Na}^+]$ was 1.00 *M*. The ionic strength was 1.23.

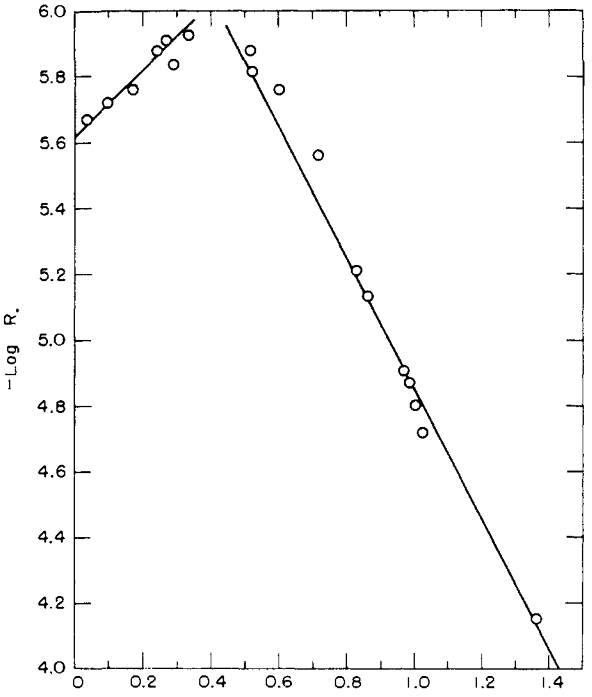

Fig. 1.—Plot of log $[\mathrm{H}^+]$ against log R for Np(IV)–Np(V) exchange at 47.4° with 0.0203 *M* Np(IV) and 0.0225 *M* Np(V), $\mu = 1.2$.

The Effect of Ionic Strength. High Acid Path.—The exchange reactions were carried out in 1.00 *M* perchloric acid. A series of experiments was run at 47° in which the only variable was the ionic strength. This was accomplished by adding sodium perchlorate to each of the reacting solutions. The results are given in Fig. 2 which shows a plot of ionic strength *vs.* R. The plot is a smooth curve of increasing R with increasing ionic strength.

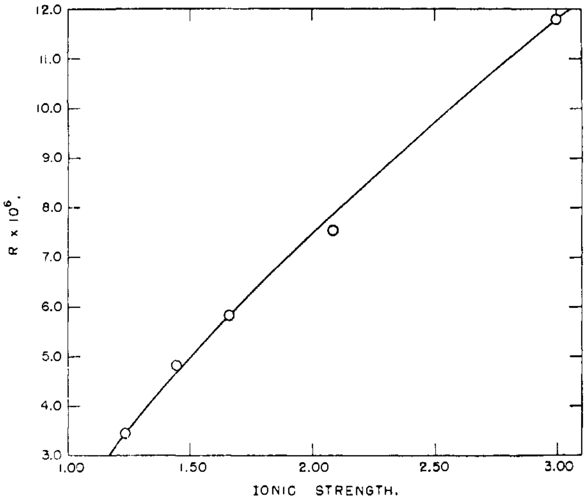

Fig. 2.—The effect of ionic strength on R for the Np(IV)–Np(V) exchange in the high acid region at 47.4°; 1.00 *M* $\mathrm{HClO_4}$, 0.0211 *M* Np(IV) and 0.0245 Np(V).

The Effect of Metal Ion Concentration. High Acid Path.—For the series of experiments from which the Np(IV) order was elucidated the ionic strength was kept constant at $\mu = 2$. The variation of R with Np(IV) concentration (corrected to ionic strength 1.2) is presented in Table II. Inspection of these data suggests that the rate of exchange is independent of the Np(IV) concentration over most of the range. Whether the slight increase in −log R noted at the lowest Np(IV) concentration is significant has not been established. The experimental data have the greatest uncertainty at these low Np(IV) concentrations.

Table II

Rate of Np(IV)–Np(V) Exchange

1 *M* $\mathrm{HClO_4}$ at 47°; $\mu = 1.2$ and 0.0246 *M* Np(V)

Np(IV), moles/l.	− log R
0.00394	5.63
.00789	5.47
.0118	5.48
.0211	5.46
.0316	5.44

The variation of R with Np(V) concentration is presented in Table III. These experiments were performed at an ionic strength of approximately 1.2. The effect of the change in Np(V) concentration on the ionic strength was neglected. Since this amounted to only 3% any error introduced should be negligible. The least squares straight line computed for a log–log plot of the data has a slope of 1.89 ± 0.07. It is considered that the data are adequately represented by a second-

Table III

The Dependence of R on the Np(V) Concentration

47.4°; 1.00 *M* $\mathrm{HClO_4}$ and 0.0211 *M* Np(IV)

Np(V), moles/l.	R	Np(V), moles/l.	R
0.0133	1.17×10^{-6}	0.0245	3.78×10^{-6}
.0148	1.35×10^{-6}	.0247	2.96×10^{-6}
.0246	3.59×10^{-6}	.0492	1.32×10^{-5}
.0246	3.49×10^{-6}	.0492	1.36×10^{-5}

order dependence of the Np(V). The rate equation for this high acid region is

$$R = k_1[\mathrm{H}^+][\mathrm{Np(V)}]^2 \qquad (4)$$

At 25° and $\mu = 1.2$, k_1 is $6.61 \pm 0.37 \times 10^{-4}$ l.^{2} mole^{-2} min.$^{-1}$.

The Temperature Effect. High Acid Path.—The variation of R with respect to temperature is shown in Fig. 3. From the data, the Arrhenius heat of activation was calculated to be 18.2 ± 0.2 kcal. by the methods of least squares. The related quantities ΔH^* and ΔS^* were calculated from the relation

$$k = \frac{ekT}{h}\, e^{-\Delta E/RT} e^{\Delta S^*/R} \qquad (5)$$

where $\Delta H^* = \Delta E - RT$.[5] These data are given in Table IV.

TABLE IV

THE FREE ENERGIES, HEATS AND ENTROPIES OF ACTIVATION FOR THE Np(IV)-Np(V) EXCHANGE PROCESSES AT 25°

Reaction path	ΔF^*, kcal. mole^{-1}	ΔH^*, kcal. mole^{-1}	ΔS^*, cal. deg.$^{-1}$ mole^{-1}
Low acid	27.2	36.8	32.1
High acid	24.2	17.6	−22.2

Catalytic Effects.—Some difficulty was experienced at the outset of this investigation in obtaining reproducible data. In this system any reactant that could oxidize the Np(IV) would cause difficulty. It was at first feared that during the sampling, air oxidation was occurring. To check this, gaseous oxygen was bubbled through one of the solutions for a period of 15 minutes without causing any change in R within the limits of error of the experiment. However, a trace of ferric ion immediately increased the rate of exchange. When glass systems were abandoned for the Teflon reaction vessels and intensive solvent extraction purification of the neptunium stocks were undertaken the difficulties were decreased.

The intimation that the reaction was surface catalyzed in the high acid region was verified in the following manner. Four identical experiments were run in Teflon cells. Metallic platinum foil, metallic gold foil and Pyrex helices were added to three of the reaction vessels. The data in Table V which gives the results of these runs indicate surface catalysis of the exchange reaction in 1 M $HClO_4$.

Effect of Metal Ion Concentration. Low Acid Path.—Most of the experiments were carried out in 0.110 M perchloric acid. The sum of the perchloric acid and sodium perchlorate concentrations was adjusted to 1.00 by the addition of sodium perchlorate. The effect of changing the neptunium ion concentration was neglected since the rate of exchange was found to be constant within experimental error over the range of $\mu = 0.78$ to $\mu = 1.70$.

TABLE V

THE EFFECT OF PYREX, PLATINUM AND GOLD ON THE RATE OF EXCHANGE

1 M $HClO_4$ at 47°; 0.0211 M Np(IV) and 0.0247 M Np(V)

Substance added	$R \times 10^6$, mole l.$^{-1}$ min.$^{-1}$
. . . .	3.46
Pyrex helices	4.67
Pt foil (9 cm.^{2})	4.93
Au foil (7 cm.^{2})	5.51

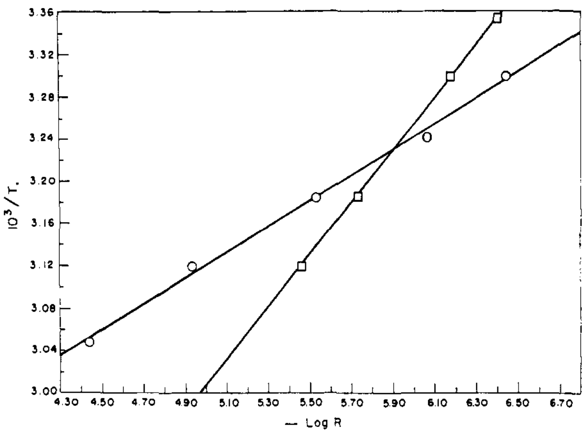

Fig. 3.—The temperature dependence of the Np(IV)-Np(V) exchange: ○, 0.110 M $HClO_4$, 0.0205 M Np(IV) and 0.0227 M Np(V); □, 1.00 M $HClO_4$; 0.0211 M Np(IV) and 0.0246 M Np(V).

The data used to evaluate the variation of R with Np(IV) concentration are shown in Table VI. Log R' is log R normalized to unit hydrogen ion concentration utilizing the experimentally determined second-order hydrogen ion effect on the rate. It was necessary to treat the data in this manner because of the occasional variation of hydrogen ion concentration from 0.110 M. The least square straight line computed from a log-log plot of these data had a slope of 1.54 ± 0.07. It is therefore considered that the data are consistent with a Np(IV) order of 1.5.

TABLE VI

THE DEPENDENCE OF THE EXCHANGE RATE ON THE Np(IV) CONCENTRATION

0.110 M $HClO_4$ at 47.4°; 0.0227 M Np(V)

Np(IV), moles/l.	− log R'	Np(IV), moles/l.	− log R'
0.00420	7.938	0.0315	6.617
.00420	7.876	.04205	6.434
.0204	6.925	.04205	6.380
.0205	6.841	.1051	7.507
.0206	6.825	.1051	7.399
.0210	6.839		

Table VII contains the data from which the variation of R' with Np(V) concentration was elucidated. The least squares straight line computed for a log-log plot of the data had a slope of

TABLE VII

THE DEPENDENCE OF THE EXCHANGE RATE ON THE Np(V) CONCENTRATION

0.110 M $HClO_4$ at 47.4°; 0.0205 M Np(IV)

Np(V), moles/l.	− log R	Np(V), moles/l.	− log R
0.00494	7.129	0.0227	6.825
.00494	7.216	.0227	6.841
.00988	7.064	.0228	6.839
.0132	7.000	.0395	6.759
.0227	6.925	.0448	6.757

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[5] S. Glasstone, K. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, pp. 197-199.

0.46 ± 0.04. It is considered that a straight line with a slope of 0.5 adequately represents the data. The general rate equation can now be written as

$$R = k_1[\mathrm{NpO_2}^+]^2[\mathrm{H}^+] + k_2[\mathrm{Np}^{+4}]^{1.5}[\mathrm{NpO_2}^+]^{0.5}[\mathrm{H}^+]^{-2} \quad (6)$$

Effect of Temperature. Low Acid Path.—The temperature variation of the exchange rate is depicted graphically in Fig. 3. From these data a heat of activation of 37.4 ± 0.5 kcal. for the reaction was determined by least squares. Values of ΔF^*, ΔH^* and ΔS^* for the exchange are summarized in Table III. The value of k_2 was found to be 3.87×10^{-6} mole liter^{-1} min.$^{-1}$ at 25° and $\mu = 1.2$.

Catalytic Effects. Low Acid Path.—There was apparently no surface catalysis in this acid region as an experiment with a piece of Pt foil of approximately the same surface area as the one used in the high acid region failed to change the exchange rate.

Mechanisms of the Exchange Reactions.—The mechanisms of the exchange reactions in both acid regions appear to be complex. The molecularity of the reaction for the high acid path is the same as that observed for the disproportionation of uranium(V),[6,7] suggesting that the rate of the exchange is governed by the equilibrium between neptunium(V) and the activated complex, X*, in the exchange mechanism

$$2\mathrm{Np^*O_2}^+ + \mathrm{H}^+ \rightleftharpoons [\mathrm{X}^*]^{+3} \rightleftharpoons \mathrm{Np^*O_2}^{+2} + \mathrm{Np^*O_2H}^+ \quad (7)$$

$$\mathrm{Np^*O_2H}^+ + \mathrm{Np(OH)_2}^{+2} \rightleftharpoons \mathrm{NpO_2H}^+ + \mathrm{Np^*(OH)_2}^{+2} \quad (8)$$

It is of interest to note that the molecularity of the disproportionation reaction 7 does not have the same form as has been adduced for the disproportionation of neptunium(V) from equilibrium and kinetic data on the Np(IV)–Np(VI) reaction.[8] However, it is quite probable that the latter reaction should be represented as

$$2\mathrm{NpO_2}^+ + \mathrm{H}^+ \rightleftharpoons [\mathrm{X}^*]^{+3} \longrightarrow \mathrm{NpO_2}^{+2} + \mathrm{NpO_2H}^+ \quad (9)$$

followed by

$$\mathrm{NpO_2H}^+ + \mathrm{H}^+ \longrightarrow \mathrm{Np(OH)_2}^{+2} \quad (10)$$

with the rate-determining step being reaction 9. Although the stoichiometry of the rate of the dismutation has not been experimentally investigated, the free energy, heat and entropy of activation are known.[8] Within experimental error, the heat of activation for the exchange process ($\Delta H^* = 17.6 \pm 0.2$ kcal. mole^{-1}) and the dismutation ($\Delta H^* = 17.1 \pm 1.6$ kcal. mole^{-1}) of Np(V) are identical. Despite the fact that the exchange process must involve a dismutation reaction of Np(V) with an activation energy equal to that found for the net change in the Np(V) disproportionation, the exchange proceeds at a much more rapid rate ($\Delta F^* = 24.2 \pm 0.2$ kcal. mole^{-1}) than does the gross reaction ($\Delta F^* = 28.5 \pm 1.6$ kcal. mole^{-1}). From the available data no statement can be made as to which temperature independent factors are involved.

The mechanism for the exchange in the low acid region also presents an interesting problem. The observed rate

$$R = k_2[\mathrm{Np(IV)}]^{1.5}[\mathrm{Np(V)}]^{0.5}[\mathrm{H}^+]^{-2} \quad (11)$$

can be expressed in terms of the following simple reactions. First, the equilibrium

$$\mathrm{Np}^{+4} + \mathrm{Np^*O_2}^+ \rightleftharpoons \mathrm{Np^*O_2}^{++} + \mathrm{Np}^{+3} \quad (12)$$

whence

$$[\mathrm{Np^*O_2}^{++}] = [\mathrm{Np}^{+3}] = K^{0.5}[\mathrm{Np}^{+4}]^{0.5}[\mathrm{Np^*O_2}^+]^{0.5} \quad (13)$$

also the hydrolytic equilibrium

$$\mathrm{Np}^{+4} + 2\mathrm{H_2O} \rightleftharpoons \mathrm{Np(OH)_2}^{+2} + 2\mathrm{H}^+ \quad (14)$$

with exchange

$$\mathrm{Np(OH)_2}^{+2} + \mathrm{Np^*O_2}^{++} = [\Omega] = \mathrm{Np^*(OH)_2}^{+2} + \mathrm{NpO_2}^{+2} \quad (15)$$

Reactions 14 and 15, correspond in stoichiometry to the kinetics found for the formation of Np(V) from Np(IV) and Np(VI).[8] In the exchange mechanism as written above, the reproportionation reaction 16 is the rate determining process. Both the

$$\mathrm{Np(OH)_2}^{++} + \mathrm{NpO_2}^{++} \rightleftharpoons \Omega \longrightarrow 2\mathrm{NpOOH}^{+2} \quad (16)$$

value[9] of the equilibrium constant, K, for reaction 12 and the value of the rate constant,[8] k_1^0 for reaction 16 have been determined

$$-\frac{\mathrm{d}[\mathrm{Np}^{+4}]}{\mathrm{d}t} = k_1^0[\mathrm{Np}^{+4}][\mathrm{NpO_2}^{++}][\mathrm{H}^+]^{-2} \quad (17)$$

whence

$$R = k_2[\mathrm{Np}^{+4}]^{1.5}[\mathrm{NpO_2}^+]^{0.5}[\mathrm{H}^+]^{-2} = K^{0.5}k_1^0[\mathrm{Np}^{+4}]^{1.5}[\mathrm{NpO_2}^+]^{0.5}[\mathrm{H}^+]^{-2} \quad (18)$$

Simple algebra shows that

$$\frac{k_1^0}{k_2} = \sqrt{\frac{1}{K}} \quad (19)$$

but substitution of the measured values

$$\frac{2.69}{3.87 \times 10^{-6}} \neq \sqrt{\frac{1}{25 \times 10^{-10}}} \quad (20)$$

As in the case of the exchange for the high acid path, the exchange reaction for the low acid path proceeds at a much faster rate than would be calculated assuming the same mechanism as observed in the net reaction of Np(IV) and Np(VI) to give Np(V). The calculated values of the free energy, heat and entropy of activation for the exchange are: $\Delta F^* = 30.6 \pm 1.6$ kcal. mole^{-1}, $\Delta H^* = 41.5 \pm 1.6$ kcal. mole^{-1}, and $\Delta S^* = 37.1$ cal. deg.$^{-1}$ mole^{-1}. The observed values for the exchange are $\Delta F^* = 27.2 \pm 0.5$ kcal. mole^{-1}, $\Delta H^* = 36.8 \pm 0.5$ kcal. mole^{-1}, and $\Delta S^* = 32$ cal. deg.$^{-1}$ mole^{-1}. In this case, however, the entropy factor favors a slower rate for the exchange reaction, and the increased rate observed must be attributed to a lower activation energy for the complex formed in the exchange reaction.

The fact that in both cases the exchange reactions proceed at a much more rapid rate than the related net reactions, although for different reasons, raises

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(6) D. M. H. Kern and E. F. Orlemann, THIS JOURNAL, **71**, 2102 (1949).

(7) H. G. Heal and J. G. N. Thomas, *Trans. Faraday Soc.*, **45**, 11 (1949).

(8) J. C. Hindman, J. C. Sullivan and D. Cohen, THIS JOURNAL, **76**, 3278 (1954).

(9) D. Cohen and J. C. Hindman, *ibid.*, **74**, 4682 (1952).

the question of how far one can go in utilizing the results of exchange experiments to deduce the gross rate of reaction. Further experimental and theoretical work would be strongly indicated.

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[CONTRIBUTION FROM THE CHEMISTRY DIVISION OF OAK RIDGE NATIONAL LABORATORY]

Phase Equilibria of Uranium Trioxide and Aqueous Hydrofluoric Acid in Stoichiometric Concentrations[1]

BY WILLIAM L. MARSHALL, J. S. GILL AND C. H. SECOY

RECEIVED APRIL 12, 1954

A phase study of the liquid–solid equilibria for aqueous solutions containing two moles of hydrofluoric acid per mole of uranium trioxide from the ice eutectic at -13° to the critical temperature of the saturated liquid at 377° is presented. Some observations on vapor–liquid equilibria are included and their significance is discussed. The system displays three solid phases of uranyl fluoride hydrates stable with respect to the saturated solution in the temperature ranges -13 to 150°, 150 to 240°, and above 240°, respectively. There is some evidence to indicate that these solids are all allotropic modifications of uranyl fluoride dihydrate but this is not certain. In the dilute region at temperatures above approximately 200° a solid phase appears which is apparently a solid solution between $UO_2(OH)_2$ and $UO_2(OH)F \cdot {}^1/_2H_2O$. A two-liquid phase region occurs from approximately 23 to 66 weight per cent. uranium trioxide. The critical solution temperature of the two-liquid phase region is 320° while the upper limit is the temperature of the invariant system solid–liquid I–liquid II–vapor, at 333°. The vapor–liquid critical temperature of the water-rich liquid phase saturated with respect to the high temperature solid is 376°, thus indicating a significant but small solubility in the critical fluid.

Introduction

Some solubility data for uranyl fluoride in water from 0 to 100° have been determined both by Kunin[2] and by Dean and Eidinoff.[2] Freezing point data for uranyl fluoride in water have been presented by Johnson and Kraus,[3] of this Laboratory. It was our objective to determine a phase equilibria picture for this system from the ice eutectic to the critical temperature of the aqueous phase. In carrying out this research we have found that some portions of the system at the higher temperatures cannot be considered as a simple two-component system but must be considered as a three-component system, probably best represented by UO_3, F_2O_{-1} and H_2O. This is true for two reasons: first, because the vapor phase undoubtedly contains HF as well as H_2O and second, because of the occurrence of a basic salt, $UO_2(OH)F \cdot {}^1/_2H_2O$, as a constituent of the solid. In this study the vapor phase has been neglected, compositions being those determined at 25°. In brief, the data presented herein indicate the phase changes which occur when stoichiometric uranyl fluoride solutions are heated in a closed system the volume of which is approximately 50% vapor at room temperature. Also, considerable insight into the general nature of the true phase diagram is obtained.

Experimental

Anhydrous uranyl fluoride was obtained both from the Harshaw Chemical Company and from the Y-12 Plant, Oak Ridge, Tennessee. A spectrographic analysis of both materials showed negligible impurities. The fluoride to uranium mole equivalent ratios were found by the Y-12 Plant Analytical Division to be 1.983 and 1.998, respectively.

Solubility data below 0° were obtained by standard methods of thermal analysis. A copper–constantan thermocouple was used for temperature measurements. Analytical solubility determinations were made from 0 to 90°. Solutions which were saturated with respect to solid were analyzed directly for uranium by ignition at 900° to U_3O_8; the precision of duplicates was within $\pm 0.15\%$. Samples analyzed after four hours stirring time agree with those obtained after 24 hours or longer and thus indicated a fairly rapid equilibrium attainment.

The first work above 100° was carried out in sealed silica and Pyrex tubes using the technique described by Secoy.[4] Later, additional data were obtained in sealed tubes using a semi-micro technique described by Marshall, Wright and Secoy.[5] Both of these procedures entailed the synthetic method in which the temperature of a solution of known composition is changed and the point recorded at which a phase transition occurs. By this method solubility points were checked to ±1° for the rapidly reversible equilibria.

Owing to a very low temperature coefficient of solubility the synthetic method was not effective for concentrated solutions in the range 150 to 240°. Therefore, an analytical approach was attempted in which saturated solution and excess solid sealed in silica tubes were rocked in an aluminum heating block at a constant temperature, the variation in temperature being of the order of ±2°. The tubes were rapidly cooled in an ice-bath, opened, and both the gel-solid (originally liquid phase) and the crystalline-solid analyzed for uranium. Above 150° the saturated solution is very viscous but will flow in 5 millimeter, inside diameter, tubing. Below this temperature, if it is not shaken on cooling, the solution forms a translucent gel. The assumption was made that equilibria attainment during the cooling period is sufficiently slow under conditions of such high solution viscosity as to not materially change the solid and solution compositions.

The compositions of the solid phase in the dilute region JF of Fig. 1 were obtained by removing the solution from a steel pressure vessel at the equilibration temperature by means of steel capillary tubing, cooling the bomb to room temperature, removing the crystalline solid and analyzing it for uranium and fluoride.

Analysis for fluoride was carried out by dissolving the solid in a measured amount of standard acid, removing uranyl ion on a cation-exchange resin and titrating the resultant acid solution with standard base.[6]

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[1] Presented in part before the Division of Physical and Inorganic Chemistry at the 119th Meeting of the American Chemical Society, Cleveland, Ohio, April 8–12, 1951.

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