previous mechanism one might assume that the hydrogen molecule adds to the double bond in the quinoline ring. Since the cuprous atoms are probably solvated by the basic nitrogen atoms of the quinoline, a catalytic addition might occur although the exact mechanism is somewhat difficult to visualize. Such a partially hydrogenated quinoline would be expected to be thermodynamically unstable and a reversal of the formation would account for both the parahydrogen conversion and the deuterium exchange.

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Stabilities of +4 and +5 Oxidation States of the Actinide Elements—the Np(IV)-Np(V) Couple[1] in Perchloric Acid Solution

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RECEIVED SEPTEMBER 17, 1952

Equilibria in the reaction Np(IV) + Fe(III) = Np(V) + Fe(II) in perchlorate solutions were measured with hydrogen reference electrodes. The apparent equilibrium constant is inversely dependent on the fourth power of the hydrogen ion concentration. The formal potential of the reaction $Fe^{+3} + {}^1/_2H_2 = Fe^{+2} + H^+$ is 0.738 v. in 1 molar perchloric acid at 25°. The heat of reaction is −9.7 kcal. The formal potential of the reaction $NpO_2^+ + {}^1/_2H_2 + 3H^+ = Np^{+4} + 2H_2O$ in 1 molal perchloric acid is 0.7423 v. at 25°. The heat of reaction is −35.3 kcal. Consideration of disproportionation reactions for the +4 and +5 oxidation states of uranium, neptunium and plutonium leads to the prediction that the stability of the X^{+4} ion will decrease and the stability of the XO_2^+ ion will increase with increasing temperature. The extinction coefficient of the 723 mμ absorption band of Np(IV) decreases with increasing temperature.

As in the rare earths the properties of the +3 aqueous ions of the heaviest elements appear to differ only slightly and in a regular manner along the series.[2,3] The common occurrence of three higher oxidation states in the heavy element series poses the problem of the degree of similarity to be expected for these higher states. Heats and free energies of reactions relating +3, +4 and +6 states are known but no information was available at the time of this work on the thermal stability of a +5 state. From the practical point of view the disproportionation stabilities of the +4 and +5 states as functions of temperature were unknown.

To obtain a value for the relative entropy of a +5 state which would be useful with other data for predictions of approximate thermal stabilities, ΔH and ΔF for the reaction

$$Np(V) + {}^1/_2H_2 = Np(IV) + H^+ \qquad (1)$$

were determined in an e.m.f. cell. The stable ion of the +4 state is probably Np^{+4} in perchloric acid solution. If the +5 state is NpO_2^+, the complete form of reaction (1) should be

$$NpO_2^+ + {}^1/_2H_2 + 3H^+ = Np^{+4} + 2H_2O \qquad (2)$$

Preliminary to the heat of reaction determination, the predicted third power hydrogen ion dependence for reaction (2) was tested experimentally. Early work indicated that the Np(IV)–Np(V) couple does not establish an accurately measurable equilibrium at an inert metal electrode.[4] Reversible potential measurements with a hydrogen reference electrode were obtained in the present work in solutions containing Np(IV), Np(V), Fe(II) and Fe(III) ions in oxidation–reduction equilibrium. Equilibration times were known from previous kinetic data.[5] The concentration ratios at equilibrium were calculated from e.m.f. and spectrophotometric data. As a check on the e.m.f. apparatus the ΔH for the reaction

$$Fe^{+3} + {}^1/_2H_2 = Fe^{+2} + H^+ \qquad (3)$$

was obtained from potentiometric titrations at 15, 25 and 35°.

Experimental

E.m.f. Cell.—Ground glass stopcocks were sealed to the bottoms of two 15-ml. centrifuge tubes. The tubes were connected through the stopcocks by a short section of Tygon tubing for equalizing the liquid levels in the tubes.

The hydrogen electrode was fabricated from glass tubing, a one-hole rubber stopper and a strip of 1 mil platinum foil platinized at one end. The platinum strip was rolled along its length forming a semi-cylinder on a short piece of glass tubing with the platinized end projecting beyond the end of the tubing. The strip and tubing were held securely in the stopper. The stopper served as a closure for the hydrogen compartment of the cell as well as a support for the platinum electrode and hydrogen inlet. A glass sleeve surrounding the platinum and tubing was sealed to the assembly just below the stopper with Apiezon W. In operation the lower, open end of the sleeve was submerged in the electrolyte so that a portion of the platinized foil was exposed alternately to hydrogen and electrolyte as the gas bubbled from the end of the sleeve. The rubber stopper was slotted to vent the hydrogen. Tank electrolytic hydrogen was passed through a Deoxo purifier and presaturated with water vapor from a perchlorate solution of the same composition as that in the cell before the hydrogen entered the cell.

The two compartments of the cell with connecting tube were partially immersed in a water thermostat to a depth such that the water level was several centimeters above the level of electrolyte in the cell. The e.m.f. measurements were found to be independent of the depth of immersion with this arrangement. Bath temperatures were determined with a thermometer calibrated by the National Bureau of Standards.

The solution to be measured was placed in the open compartment of the cell. The stopcock below this compartment was greased only at the ends of the plug permitting electrical contact in the closed position through the thin film of electrolyte surrounding the plug. A platinum wire, wrapped on a glass stirring rod held in the chuck of a stir-

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(1) Presented in part before the Division of Nuclear Chemistry, XII International Congress of Pure and Applied Chemistry, New York, N. Y., September, 1951.

(2) K. Street, Jr., and G. T. Seaborg, THIS JOURNAL, **72**, 2790 (1950).

(3) S. G. Thompson, B. B. Cunningham and G. T. Seaborg, *ibid.*, **72**, 2798 (1950).

(4) J. C. Hindman, L. B. Magnusson and T. J. LaChapelle, *ibid.*, **71**, 687 (1949).

(5) J. R. Huizenga and L. B. Magnusson, *ibid.*, **73**, 3203 (1951).

ring motor, made electrical connection with the solution. The conventional electrical circuit was used with a Leeds and Northrup Type K potentiometer and sensitive galvanometer.

Preparation of Solutions.—Np(IV) perchlorate stock solutions were prepared by dissolving Np(V) hydroxide in known amounts of 8 *M* perchloric acid, diluting to 2 *M* acid and reducing with hydrogen and platinum black catalyst. The Np(IV) stock solutions were stable, no Np(V) being detectable over periods of several weeks. Neptunium concentrations were assayed by α-particle counting.

Ferric perchlorate stock solution was made by dissolving ferric hydroxide in 8 *M* perchloric acid. For the $E_{1/2}$ determination ferric perchlorate stock was diluted to the desired composition and reduced by hydrogen and platinum black catalyst prior to titration.

Stock solutions of 8 *M* perchloric acid were prepared by diluting distilled 12 *M* perchloric acid (The G. Frederick Smith Chemical Co.). They were standardized by titration of aliquots with sodium hydroxide solution. A pure stock solution of sodium perchlorate was made by neutralizing perchloric acid with sodium hydroxide.

Potentiometric Titrations.—Three ml. of 0.02 *M* ferrous perchlorate solution was placed in the open compartment of the e.m.f. cell. The stirrer bearing the platinum wire anode was lowered into the solution and the e.m.f. measured. The capillary tip of a calibrated 10-ml. buret was introduced into the solution and small aliquots of 0.005 *M* potassium dichromate solution added. The solution was thoroughly stirred after each addition before observing the e.m.f. The potassium dichromate, ferrous perchlorate and hydrogen reference electrode solutions were prepared with the same concentrations of perchloric acid and sodium perchlorate to maintain the ionic strength constant at 1.0. The same hydrogen electrode solutions were used in the measurement of the neptunium–iron equilibria as in the titrations.

Neptunium Equilibrations.—Weighed aliquots of the neptunium stock solutions were diluted to desired concentrations in calibrated flasks. Weighed aliquots (2.5 ml.) were placed in stoppered 1.00-cm. absorption cells for measurement in the Beckman spectrophotometer of the initial optical density at 723 mμ of the pure Np(IV) solutions. A small volume of ferric perchlorate solution (0.015–0.060 ml.) was added with stirring and the cell thermostated by sealing in a screw cap vial and submerging the vial in the e.m.f. water-bath. After equilibration the solution was transferred by pipet into the open compartment of the e.m.f. cell. The e.m.f. was observed between intervals of stirring until it was evident that the equilibrium e.m.f. was being measured. All samples gave constant readings within a minute or two with no change over periods of several hours. The solution was transferred back into the absorption cell and spectrophotometer compartment which was thermostated at the same temperature as the e.m.f. bath. The Np(IV)/Np(V) equilibrium ratio was calculated from measurement of the 723 mμ optical density. For the ΔH determinations the potentials of equilibrium solutions were measured at 15, 25 and 35°.

Results

Hydrogen Ion Dependence.—The potentiometric titration data for reaction (3) are summarized in Table I. The last column gives values for the formal potential, E_f, calculated from

$$E_f = E_{1/2} + \frac{RT}{F}\ln \mathrm{H}^+ - \frac{RT}{2F}\ln p \qquad (4)$$

where $E_{1/2}$ is the potential of the iron half-reaction at a Fe(III)/Fe(II) ratio of unity and p is the partial pressure of hydrogen.[6] The Fe^{+2}–Fe^{+3} couple is independent of hydrogen ion concentration as is expected. Another value of 0.7374 v. for the formal potential in 1.0 *M* $HClO_4$ at 25° is obtained from the ΔH data of Table IV. The value of 0.738 ± 0.001 v. from these data agrees satisfactorily with 0.7394 v. calculated by Connick and McVey for a hypothetical 1.0 *M* hydrogen ion concentration from data obtained from 0.5 *M* $HClO_4$ solutions.[7] The data of Schumb, Sherrill and Sweetser[8] indicate that the potential is less positive in 1.0 *M* $HClO_4$ than in 0.5 *M* $HClO_4$ by about a millivolt.

TABLE I

E.m.f. of the cell: Pt:H_2:M_1 $HClO_4$, M_2 $NaClO_4$; M_1 $HClO_4$, M_2 $NaClO_4$, Fe(II), Fe(III):Pt at 25° from potentiometric titration with $K_2Cr_2O_7$ soln. 10^{-2} *M* Fe(II + III), 0.95 atm. H_2.

$HClO_4$, *M*	$NaClO_4$, *M*	$E_{1/2}$	E_f
0.252	0.75	0.7735	0.7387
.482	.50	.7557	.7376
.937		.7396	.7386

TABLE II

E.m.f. of the cell: Pt:H_2:M_1 $HClO_4$, M_2 $NaClO_4$; M_1 $HClO_4$. M_2 $NaClO_4$, Fe(II), Fe(III), Np(IV), Np(V): Pt at 25°. 0.001–0.004 *M* Np(IV + V), 0.001–0.002 *M* Fe(II + III) 0.95 atm. H_2

$HClO_4$, *M*	$NaClO_4$, *M*	$E_{obsd.}$	Np(V)/ Np(IV)	K'	K
0.261	0.75	0.6980	7.90	149	0.69
.496	.50	.7165	2.57	11.8	.72
.961		.7230	0.435	0.830	.71

It was intended that the hydrogen ion concentrations in the neptunium–iron equilibria (Table II) be the same as in the hydrogen electrode solutions. A recalculation of the data after completion of the runs revealed differences as great as 4% (columns 1, Tables I and II). The e.m.f. of reaction (3) was found in a supplementary measurement to be essentially unchanged, however, by a variation of this magnitude in the perchloric acid concentration in the Fe^{+2}–Fe^{+3} compartment of the cell. Table II lists values of K', defined as

$$K' = [\mathrm{Np(V)}][\mathrm{Fe(II)}]/[\mathrm{Np(IV)}][\mathrm{Fe(III)}] \qquad (5)$$

where Fe(II)/Fe(III) is calculated from the observed e.m.f. at equilibrium and the corresponding $E_{1/2}$ from Table I. K' is plotted against H^+ with log–log coordinates in Fig. 1. The points fit a line of slope −4, indicating that the equilibrium reaction is correctly given by

$$Np^{+4} + Fe^{+3} + 2H_2O = NpO_2^+ + Fe^{+2} + 4H^+ \quad (6)$$

Values of the equilibrium constant for reaction (6) in terms of molar concentrations are given in the last column of Table II. An additional value of 0.73 is obtained from the formal potential of 0.738 v. for reaction (3) and the formal potential of 0.746 v. for reaction (2) from the data of Table V. The equilibrium constant of reaction (6) from these data is 0.72 ± 0.02 in 1.0 *M* perchlorate solution at 25°.

Effect of Temperature on 723 mμ Band.—The extinction coefficient of the Np(IV) 723 mμ absorption band was found to decrease with increasing temperature (Table III). No change was detectable in the wave length for maximum absorption. The molar extinction coefficient ϵ is defined as

$$\epsilon = d/M \qquad (7)$$

where d is the optical density of the solution for a

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[6] Values of the fundamental constants are from the report of the subcommittee of the Committee on Physical Chemistry, National Research Council, THIS JOURNAL, **74**, 2699 (1952).

[7] R. E. Connick and W. H. McVey, *ibid.*, **73**, 1798 (1951).

[8] W. C. Schumb, M. S. Sherrill and S. B. Sweetser, *ibid.*, **59**, 2360 (1937).

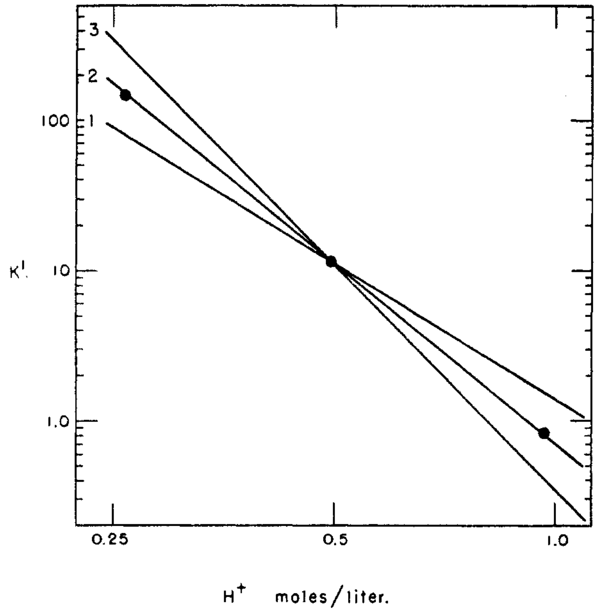

Fig. 1.—Hydrogen ion dependence of the ratios [Np(V)]·[Fe(II)]/[Np(IV)][Fe(III)] at equilibrium. Data from Table II: lines 1, 2 and 3 have slopes −3, −4 and −5, respectively.

1.0-cm. light path and M is the true molarity of Np(IV), *i.e.*, the molarity determined at 25° corrected for the change of volume with temperature. A similar effect has been reported for plutonium absorption bands.[9]

TABLE III

Molar extinction coefficient, ϵ, of the 723 mμ absorption band of Np(IV) at various temperatures; $2.62_2 \times 10^{-3}$ M Np(IV) at 25° in 1.0 M $HClO_4$; slit width 0.04 mm.

t, °C.	d	ϵ
14.8	0.353	134.3
25.3	.341	130.0
35.4	.329	125.9

Heats of Reaction.—Table IV gives data for reaction (3) at different temperatures obtained from the potentiometric titrations. The E' values of the last column are the mid-point potentials, $E_{1/2}$, corrected to 1 atmosphere hydrogen pressure. Corrections were applied for the change in water vapor pressure with temperature. The ΔH of reaction was determined by use of the equation

TABLE IV

E.m.f. of the cell: Pt:H_2:0.985 M $HClO_4$; 0.985 M $HClO_4$, Fe (II), Fe (III):Pt at various temperatures from potentiometric titration with $K_2Cr_2O_7$ soln. 10^{-2} M Fe (II + III).

T	$E_{1/2}$	p	E'
288.38	0.72693	0.97	0.72735
298.19	.73688	.95	.73752
308.53	.74775	.93	.74873

$$[\partial(E/T)/\partial(1/T)]_{P,N} = -\Delta H/nF \qquad (8)$$

where E is the electromotive force for the cell reaction, T the absolute temperature, n the number of electrical equivalents passing through the cell, F the faraday, and P and N refer to the restrictions of constant pressure and composition. E'/T is plotted against $1/T$ in Fig. 2. From the slope of the line, ΔH for reaction (3) is −9.7 ± 0.2 kcal. in *ca.* 1 M $HClO_4$. The value agrees within experimental error with either −9.95 ± 0.05 kcal. in 0.5 M $HClO_4$ reported by Connick and McVey[7] from e.m.f. data or −9.53 ± 0.04 kcal. in 0.5 M $HClO_4$ reported by Fontana from calorimetric data.[10,11]

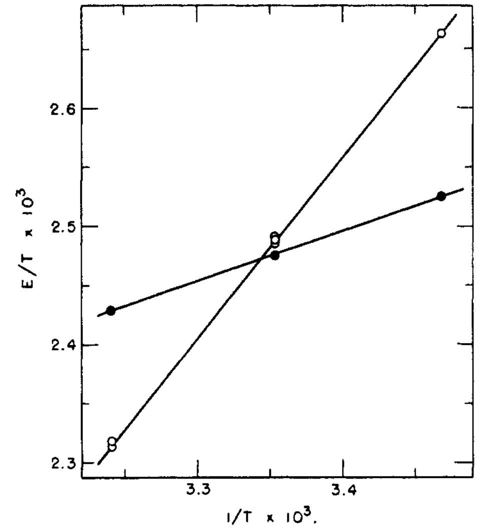

Fig. 2.—E/T *vs.* $1/T$: ●, ion data from Table IV; ○, neptunium data from Table V.

The e.m.f. data for reaction (2) are summarized in Table V. In a rigorous sense, eq. (8) is not applicable to the data since the composition of the solutions changes with the equilibrium shift. To calculate the e.m.f. of the cell at constant composition we make the same assumption as is implicit in the treatment of the equilibrium data for reaction (6). The assumption is that the activity coefficients of the reacting ions remain constant at any given temperature regardless of the position of equilibrium. It should be noted that the ionic strength of the solutions is determined mainly by the constant concentration of perchloric acid.

TABLE V

E.m.f. of the cell: Pt:H_2:$HClO_4(m_1)$; $HClO_4$ (m_2), Np(IV), Np(V), Fe (II), Fe (III): Pt at various temperatures: m_1 = 1.033 molal $HClO_4$, 2.7×10^{-3} molal Np(IV + V), 4.2×10^{-3} molal Fe (II + III).

Sample	T	m_2	p	Np(IV)/Np(V)	$E_{\text{obsd.}}$	E_f
1	288.38	1.033	0.97	2.446	0.7476	0.7678
2		1.033		2.515	.7470	.7679
3		1.024		1.915	.7530	.7679
1	298.19	1.034	0.95	1.357	.7366	.7424
2		1.035		1.324	.7376	.7427
3		1.027		0.845	.7470	.7415
1	308.53	1.036	0.93	.734	.7255	.7148
2		1.036		.734	.7243	.7141

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(9) R. E. Connick, M. Kasha, W. H. McVey and G. E. Sheline, "Transuranium Elements," NNES, Div. IV, Vol. 14B, McGraw-Hill Book Co., Inc., New York, N. Y., 1949, p. 559.

(10) B. J. Fontana, "The Chemistry and Metallurgy of Miscellaneous Materials," NNES, Div. IV, Vol. 19B, McGraw-Hill Book Co., Inc., New York, N. Y., 1950, p. 321.

(11) More precise measurement of the iron reaction heat was not attempted with the small scale titration apparatus used in this work.

In addition to the large change with temperature in the Np^{+4}/NpO_2^+ ratio small changes in hydrogen ion concentration were caused by the equilibrium shift. The e.m.f., E_f, of the cell at constant composition was calculated from the equation

$$E_f = E + \frac{RT}{F}\ln\frac{(Np^{+4})(H^+)}{(NpO_2^+)p^{1/2}} - \frac{4RT}{F}\ln(H^+)' \quad (9)$$

where E is the observed e.m.f., (H^+) the molal hydrogen ion concentration in the hydrogen half cell, $(H^+)'$ the hydrogen ion concentration in the neptunium half cell, p the partial pressure of hydrogen and the constants R, T and F have usual significance. Column 3 of Table V shows that small differences existed between the hydrogen ion concentration in the neptunium–iron equilibrium samples and the hydrogen electrode solutions. The corrections made for these differences by equation (9) turns out to be trivial for samples 1 and 2 since the same E_f values are obtained if the hydrogen ion concentration throughout the cell is taken to be that in the neptunium compartment. The E' values for sample 3 would be 0.2 millivolt smaller by the latter method of calculation. The junction potentials due to the hydrogen ion concentration differences are negligible for all three samples.

From the slope of the plot of E_f/T against $1/T$ in Fig. 2, ΔH for reaction (2) is -35.3 ± 0.3 kcal. in 1 molal $HClO_4$ in the region of 25°. Equation (9) defines the formal potential, E_f, of the Np(V)–Np(IV) couple. The data of Table V yield 0.7423 ± 0.0008 v. for the potential at 25.0° in 1.0 molal $HClO_4$. The entropy change is -61 cal./deg. The $HClO_4$ molarities of samples 1, 2, 3 and the hydrogen electrode solution were 0.985, 0.985, 0.977 and 0.985, resp., at 25.0°. The average value of the formal potential in 1.0 molar $HClO_4$ calculated from eq. (9) and the data of Table V is 0.7459 at 25.0°. Cohen and Hindman have measured the Np(V)–Np(IV) couple by a different technique with nearly the same results.[12] Their value for the formal potential in 1.0 molal $HClO_4$ is 0.7391 v. With no catalytic couple in the system, Cohen and Hindman found that a total Np concentration of at least 0.007 *M* was necessary to establish apparent equilibrium. Their data obtained with a gold electrode, it may be noted, seem to show an approach to a formal potential near 0.742 v. with increasing Np(V)/Np(IV) ratio.

Discussion

Applying the experimental value from this work for the entropy change in a reaction involving a +5 state together with other data we may estimate the effect of temperature on disproportionation equilibria in acid perchlorate solutions. The entropy changes for analogous reactions of ions of uranium, neptunium and plutonium are measures, furthermore, of the similarity of the ions. The disproportionation stabilities of Pu(IV) and Pu(V) are of particular interest since the potentials of the plutonium couples are all in the region of 1 volt in 1 *M* perchloric acid solutions; *i.e.*, all four oxidation states have comparable stabilities.

The entropy change for a disproportionation of Pu(IV) may be calculated from experimental data for the reactions

$$3Pu^{+4} + 2H_2O = 2Pu^{+3} + PuO_2^{+2} + 4H^+ \quad (10)$$

$$Pu^{+3} + 2H_2O = PuO_2^{+2} + 3/2H_2 + H^+ \quad (11)$$

$$Pu^{+3} + H^+ = Pu^{+4} + {}^1/_2H_2 \quad (12)$$

From the results of Connick and McVey,[13] ΔF for reaction (10) is 2.7 kcal. in 1 molal perchloric acid at 25°. For reaction (11) Connick and McVey[7] give a value of ΔH equal to 77.8 kcal., derived in part from heat data obtained by Evans.[14] For reaction (12) Connick and McVey[7] obtained ΔH equal to 13.52 kcal. Combining these data, we calculate 37.2 kcal. and 116 cal./deg. for ΔH and ΔS, respectively, for reaction (10).

The stability of Pu(V) in the equilibria

$$2PuO_2^+ + 4H^+ = PuO_2^{+2} + Pu^{+4} + 2H_2O \quad (13)$$

$$3PuO_2^+ + 4H^+ = 2PuO_2^{+2} + Pu^{+3} + 2H_2O \quad (14)$$

may be estimated by analogy to Np(V). Free energy data on Pu(V) are available from the measurements of Kasha[15] and Kraus and Moore.[16] For the reaction

$$PuO_2^+ + H^+ = PuO_2^{+2} + 1/2H_2 \quad (15)$$

we calculate an average value of 21.4 kcal. for ΔF. From the data for reactions (11), (12) and (15) we obtain

$$Pu^{+4} + 2H_2O = PuO_2^+ + {}^1/_2H_2 + 3H^+;\ \Delta F = 26.6 \text{ kcal.} \quad (16)$$

By analogy to neptunium ΔS is assumed equal to 61 cal./deg., whence ΔH is equal to 44.8 kcal. From the data for reactions (11), (12) and (16) we calculate ΔF, ΔH and ΔS for reaction (13) to be -5.2 kcal., -25.3 kcal. and -67 cal./deg., respectively. Similarly for reaction (14) the values of ΔF, ΔH and ΔS are -6.5 kcal., -19.3 kcal. and -43 cal./deg.

Entropy changes for neptunium disproportionation reactions may be calculated from data on the neptunium couples reported by Cohen and Hindman[12] and in this paper. For the reactions

$$3Np^{+4} + 2H_2O = 2Np^{+3} + NpO_2^{+2} + 4H^+ \quad (17)$$

$$2NpO_2^+ + 4H^+ = NpO_2^{+2} + Np^{+4} + 2H_2O \quad (18)$$

$$3NpO_2^+ + 4H^+ = 2NpO_2^{+2} + Np^{+3} + 2H_2O \quad (19)$$

the entropy changes are 130, -55 and -17 cal./deg. in 1 molal perchloric acid at 25°.

The entropy changes for the disproportionation of U(V) in the reactions

$$2UO_2^+ + 4H^+ = UO_2^{+2} + U^{+4} + 2H_2O \quad (20)$$

$$3UO_2^+ + 4H^+ = 2UO_2^{+2} + U^{+3} + 2H_2O \quad (21)$$

may also be calculated by applying the neptunium analogy. From the equilibrium data of Nelson and Kraus[17] ΔF for reaction (20) is *ca.* -11.6 kcal. in molar perchlorate solution at 25°. Combining (20) with the reaction

$$UO_2^+ + H^+ = UO_2^{+2} + {}^1/_2H_2 \quad (22)$$

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[12] D. Cohen and J. C. Hindman, THIS JOURNAL, **74**, 4679, 4682 (1952).

[13] R. E. Connick and W. H. McVey, University of California Radiation Laboratory report No. 1687, March, 1952. Connick and McVey correct the data of Kasha (ref. 15) for reduction caused by the plutonium α-particles.

[14] M. W. Evans, "Transuranium Elements," NNES, Div. IV, Vol. 14B, McGraw-Hill Book Co., Inc., 1949, p. 282.

[15] M. Kasha, "Transuranium Elements," NNES, Div. IV, Vol. 14B, McGraw-Hill Book Co., Inc., New York, N. Y., 1949, p. 295.

[16] K. A. Kraus and G. E. Moore, *ibid.*, p. 550.

[17] F. Nelson and K. A. Kraus, THIS JOURNAL, **73**, 2157 (1951).

for which ΔF is 1.7 kcal.,[18-20] we find ΔF equal to 15.0 kcal. for the reaction

$$U^{+4} + 2H_2O = UO_2^{+2} + 2H^+ + H_2 \tag{23}$$

Fontana[21] has determined the heat of reaction (23) to be 32.9 kcal.; whence ΔS is 60 cal./deg. Assuming the same entropy change for the reaction

$$2UO_2^+ + H_2 = 6H^+ + 2U^{+4} + 4H_2O \tag{24}$$

as for the analogous neptunium reaction and adding to (23), we obtain ΔS for reaction (20) equal to −62 cal./deg. From the data of Kritchevsky and Hindman[18] and Fontana[21] for the reaction

$$U^{+3} + H^+ = U^{+4} + {}^1/_2H_2 \tag{25}$$

ΔF is −14.5 kcal. and ΔH is −23.7 kcal. Combining these values with the entropy changes for reactions (20) and (24) we obtain ΔS equal to −32 cal./deg. for reaction (21). Combination of (20) and (21) yields 122 cal./deg. for the entropy change of the reaction

$$3U^{+4} + 2H_2O = 2U^{+3} + UO_2^{+2} + 4H^+ \tag{26}$$

The reaction entropies are summarized in Table VI. More recent determinations[7,10,21,22] of some of the heats of reactions measured by Evans[14] suggest that the ΔH of reaction (11) may be larger than 77.8 kcal. A larger value for the heat of the reaction would shift the calculated plutonium entropy changes in the direction of those for the uranium and neptunium reactions. Comparison of results for the disproportionation of the +4 states indicates that the assumption of equal entropy changes for analogous reactions is an approximation. The entropy differences appear to occur mainly in the oxygenated ions of the +6 state. From the relation

TABLE VI

SUMMARY OF ENTROPY CHANGES FOR DISPROPORTIONATION REACTIONS IN 1 MOLAL PERCHLORATE SOLUTIONS AT 25°

Values in parentheses calculated by assuming ΔS equal to −61 cal./deg. for the reaction $XO_2^+ + {}^1/_2H_2 + 3H^+ = X^{+4} + 2H_2O$.

Reaction	ΔS, cal./deg. U	Np	Pu
$3X^{+4} + 2H_2O = 2X^{+3} + XO_2^{+2} + 4H^+$	122	130	116
$2XO_2^+ + 4H^+ = XO_2^{+2} + X^{+4} + 2H_2O$	(−62)	−55	(−67)
$3XO_2^+ + 4H^+ = 2XO_2^{+2} + X^{+3} + 2H_2O$	(−32)	−17	(−43)

$$(\partial \Delta F/\partial T)_{P,N} = -\Delta S \tag{27}$$

and the approximate entropy changes of Table VI, we may predict with respect to disproportionation that the stability of the X^{+4} ion will decrease and the stability of the XO_2^+ ion will increase with increasing temperature. The predicted trends agree with an observation that Pu(V) appeared to be more stable at higher temperature.[23]

Acknowledgment.—The authors are indebted to J. C. Hindman and D. Cohen for e.m.f. and spectrophotometric apparatus used in the measurements and to P. Wehner for providing a pure sodium perchlorate solution.

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Separation of Carrier-free Scandium from a Calcium Target

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RECEIVED DECEMBER 17, 1952

Scandium can be separated carrier-free from calcium by filtration of a solution containing Sc of the order 10^{-9} *M* or less and calcium about 10^{-3} *M*. The effects of a number of variables on the adsorption of Sc by filter paper have been determined. Eighty per cent. of the Sc present can be recovered in one hour.

Introduction

A sample which is to be used in the measurement of the β-spectrum of a positron or negatron emitter must have a high specific activity in order that the results be accurate. The presence of stable atoms produces questionable data because these atoms absorb part of the energy of the β-particle before it emerges from the surface of the sample. If the isotope to be studied is separated with the addition of an isotopic carrier, the sample will necessarily contain many stable atoms and will have a relatively low specific activity, whereas when a carrier-free separation is performed, the specific activity of the sample will be relatively high.

It has been known that when a solution is filtered through filter paper some of the ions present are adsorbed by the paper in considerable quantity. When a solution with a scandium concentration of the order of 10^{-9} gram atom/liter, or less, and calcium about 10^{-3} gram atom/liter is filtered, an appreciable amount of scandium is adsorbed by the paper, while the calcium passes through with the filtrate. Many factors, *e.g.*, *p*H, salt concentration, etc., affect the per cent. scandium adsorbed. The effects of a number of variables on the adsorption have been determined, and a procedure for separating scandium carrier-free in quantities of 10^{-9} gram atom or less from a calcium target has been devised.