somewhat time-consuming,[10] and alizarin and alizarin S give lake suspensions which settle out with time.[11,12] The use of the latter two reagents requires some care in *p*H adjustment for sensitivities comparable to those obtained with chloranilic acid. Chloranilic acid in 2 *M* perchloric acid gives roughly the same $ZrCh^{+2}$ color with tetrapositive hafnium, uranium, thorium and stannic tin but only a weak pink color with tetravalent titanium. Ferric ion gives a violet-black color and saturated boric acid gives a light pink color. No visible reaction is observed at this acidity with ferrous, chromic, aluminum, copper, cobalt, manganese, barium or potassium ions. Many of these ions interfere in the use of alizarin or alizarin S, although their effect may be reduced by using higher acidities with consequent loss of sensitivity.[11,13,14]

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[10] F. J. Welcher, "Organic Analytical Reagents," Vol. 4, D. Van Nostrand Company, Inc., New York, N. Y., 1948, pp. 62–63.

[11] Reference 10, Ch. XV.

[12] J. F. Flagg, H. A. Liebhafsky and E. H. Winslow, THIS JOURNAL, **71**, 3630 (1949).

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AMES, IOWA RECEIVED JANUARY 8, 1951

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[CONTRIBUTION FROM THE ARGONNE NATIONAL LABORATORY]

# Oxidation–Reduction Reactions of Neptunium(IV) and -(V)[1]

BY JOHN R. HUIZENGA AND LAWRENCE B. MAGNUSSON

The rate law for the reaction Np(IV) + Fe(III) ⇄ Np(V) + Fe(II) may be expressed as $d[Np(IV)]/dt = k_2[Np(V)][Fe(II)][H^+] - k_1[Np(IV)][Fe(III)]/[H^+]^3$. The reactions involve a hydrolytic mechanism. The forward rate constant, $k_1$, is 3.4 moles$^2$ liters$^{-2}$ min.$^{-1}$ and the reverse rate constant, $k_2$, is 4.7 moles$^{-2}$ liters$^2$ min.$^{-1}$ at 25° in 1.0 *M* perchlorate solutions. The apparent activation energy of the forward reaction is 35 kcal. mole$^{-1}$. The forward rate constant is smaller in nitrate solutions as would be expected from spectral evidence for nitrate complexing of Np(IV).

## Introduction

The aqueous ions of the +5 and +6 oxidation states of uranium, neptunium and plutonium are oxygenated cations, $MO_2^+$ and $MO_2^{+2}$, in non-complexing acidic solutions. The metal to oxygen bonding is strong so that the oxygen is not easily, if at all, removable by reaction with hydrogen ion.[2,3] The oxygenated structure of the +5 and +6 states has a marked influence on the oxidation–reduction kinetics of these elements. The transitions between $MO_2^+$ and $MO_2^{+2}$, with the exception of change in hydration, should require only the transfer of an electron between the heavy metal ion and a reducing or oxidizing agent. As might be expected these transitions are rapid with oxidation–reduction couples which do not inherently involve slow processes. The stable ions of the lower oxidation states, +3 and +4, are of the types $M^{+3}$ and $M^{+4}$ in non-complexing acidic solutions. The transitions between $M^{+3}$ and $M^{+4}$ also require only electron transfer as far as the heavy metal ion is concerned and the reactions are usually rapid. Transitions between the lower oxidation states and the +5 or +6 states, however, have been observed to be slow in general.[4,5,6] The relative slowness of these reactions indicates that the rate of electron transfer is dependent on the mechanism for the addition or removal of oxygen.

Neptunium is particularly suited for studies of the $M^{+4}$–$MO_2^+$ transition since the +5 oxidation state is stable under a wide range of conditions with respect to disproportionation (self oxidation–reduction to higher and lower states). Oxidizing and reducing agents for reaction with the neptunium may be selected with the aid of the fact that the oxidation potential of the Np(IV)–Np(V) couple is *ca.* −0.7 volt in 1 molar hydrogen ion solution.[7,3] Iron is of interest since the oxidation potential of the ferrous–ferric couple is near the potential of the Np(IV)–Np(V) couple so that oxidation–reduction equilibrium constants can be directly determined. Ferrous and ferric ions, furthermore, react at relatively high, yet measurable, rates with the neptunium ions. A preliminary study of this system in hydrochloric acid has been reported.[5] The rate of reduction of Np(V) by ferrous ion was found to be proportional to about the first power of the hydrogen ion concentration.

Precise measurements of the iron–neptunium system have now been made in perchlorate and nitrate solutions. Forward and reverse rate constants, temperature dependence, hydrogen ion dependence and nitrate effect have been determined. Equilibrium measurements will appear in a subsequent publication.

## Experimental

The neptunium stock solutions were prepared by dissolving pure Np(IV) or Np(V) hydroxides, reprecipitated with ammonia from perchlorate solutions and washed free of ammonia, in weighed portions of standardized 8 *M* perchloric acid. Weighed aliquots of the neptunium solutions were dried on platinum plates for alpha-particle counting. Neptunium concentrations were calculated on the basis of 790 alpha-counts-minute$^{-1}$-microgram$^{-1}$ specific counting yield for a 50% geometry counting chamber.[8]

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[1] Presented in part before the Physical–Inorganic Division of the American Chemical Society at the Chicago Meeting in September, 1950.

[2] R. Sjoblom and J. C. Hindman, paper presented at the Meeting of the American Chemical Society at Chicago, September, 1950.

[3] L. B. Magnusson and J. R. Huizenga, results to be published.

[4] E. L. King, "National Nuclear Energy Series," Div. VIII, Vol. 6, to be published.

[5] L. B. Magnusson, J. C. Hindman and T. J. LaChapelle, "National Nuclear Energy Series," Div. IV, Vol. 14B, Transuranium Elements, Pt. II, 1134 (1949).

[6] R. E. Connick, THIS JOURNAL, **71**, 1528 (1949); "National Nuclear Energy Series," Div. IV, Vol. 14B, Transuranium Elements, Pt. I, 268 (1949).

[7] J. C. Hindman, L. B. Magnusson and T. J. LaChapelle, THIS JOURNAL, **71**, 687 (1949); "National Nuclear Energy Series," Div. IV, Vol. 14B, Transuranium Elements, Pt. II, 1059 (1949).

[8] L. B. Magnusson and T. J. LaChapelle, THIS JOURNAL, **70**, 3534 (1948); "National Nuclear Energy Series," Div. IV, Vol. 14B, Transuranium Elements, Pt. I, 39 (1949).

All solution samples for a series of runs testing a reaction variable, such as hydrogen ion concentration, were prepared by dilution of one stock solution of neptunium in about 2.5 *M* perchloric acid solution. The neptunium stock aliquots were measured with a weight buret into calibrated volumetric flasks. Neutral salt solutions of sodium perchlorate or sodium nitrate were added with volumetric pipets to adjust ionic strength.

Equal portions of the diluted neptunium solutions were weighed into 1.00 cm. absorption cells with ground stoppers for spectrophotometric observation of the course of the reactions. The cell compartment of the Beckman spectrophotometer was an air chamber enclosed by brass tanks through which water was circulated from an exterior bath. Air chamber temperatures, measured with a thermometer calibrated by the Bureau of Standards, were constant to ±0.1° during runs. The neptunium solutions were brought to temperature in the cell compartment before the reactions were started. In many of the runs 0.020–0.025 ml. of 2 *M* sodium nitrite solution was added to the neptunium solutions. The spectrum was examined again to see that no appreciable oxidation was occurring. The cells were then removed for not more than two minutes to pipet into each cell ferric or ferrous perchlorate solution, the total added volume never exceeding 2% of the original volume (*ca.* 2.5 ml.) weighed into the cell. After a thorough stirring of the solutions the cells were replaced in the cell compartment for optical density readings of the 723 millimicron absorption band of Np(IV).

Ferric perchlorate reagent was prepared by dissolving ferric hydroxide in a slight excess of standard 8 *M* perchloric acid followed by dilution to a convenient concentration. For determination of Fe(III) content, aliquots were reduced with hydrogen gas and a platinum black catalyst to Fe(II) which was titrated potentiometrically with standard potassium dichromate solution. Ferrous perchlorate reagent was prepared by hydrogen reduction of the ferric perchlorate reagent. Completeness of reduction was measured potentiometrically. Iron ion concentrations in the absorption cells are estimated to be accurate to within about 3%.

## Reaction Rate Laws

As with many types of cations, no evidence has been found of any perchlorate complexing of Np(IV) or Np(V) so the ions are assumed to be $Np^{+4}$ and $NpO_2^+$ in perchlorate solutions. The over-all reaction

$$Np^{+4} + Fe^{+3} + 2H_2O \rightleftharpoons NpO_2^+ + Fe^{+2} + 4H^+ \quad (1)$$

has been established by equilibrium measurements.[3] The dependence of the forward rate on the Np(IV) and Fe(III) concentrations was determined by a method of maintaining one of the variables, the Fe(III) concentration, constant during a reaction. Adding a large excess of Fe(III) is not practical since the reaction would be too rapid for measurement. The method chosen eliminated for the most part the complication introduced by the back reaction which soon becomes appreciable if the Fe(II) concentration is allowed to build up.

**Nitrous Acid as Indirect Oxidant.**—For the purpose of a kinetic study of reaction (1), Fe(III) may be maintained at constant concentrations with an oxidizing agent which reacts rapidly with Fe(II) but very slowly with Np(IV). The rate of oxidation of Fe(II) must be much more rapid than the rate of reduction of Fe(III) by Np(IV). Nitrous acid proved to be a satisfactory oxidant for Fe(II) and, indirectly, Np(IV). The addition of sodium nitrite to 0.02 molar was equivalent to adding nitrous acid over the range of acid concentration of these experiments (0.25–1.0 molar) since the dissociation constant of nitrous acid is $4.5 \times 10^{-4}$.[9] The kinetics of the oxidation of Fe(II) in solutions containing nitrous acid are well known.[10] With nitrous acid in the system the Fe(II) is rapidly oxidized back to Fe(III) maintaining a constant Fe(III) concentration. The rate of oxidation of Np(IV) in solutions containing nitrous acid but no Fe(III) was found to be negligibly low. As confirmation of the catalytic role of the iron, the initial rates of reaction with and without nitrite in solutions containing equal concentrations of iron were identical (Fig. 1).

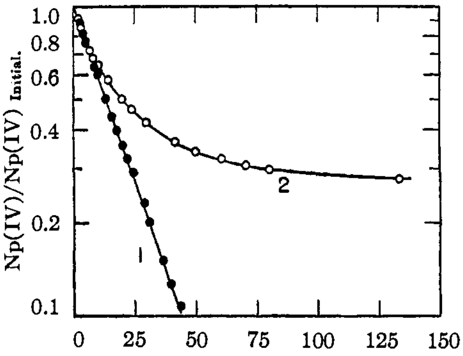

Fig. 1.—Effect of nitrite concentration on the rate of the reaction, $Np^{+4} + Fe^{+3} + 2H_2O \rightarrow NpO_2^+ + Fe^{+2} + 4H^+$, in 1.0 molar perchlorate solution: temperature 24°, 0.48 *M* hydrogen ion, 0.0021 *M* initial Fe(III), 0.00256 *M* initial Np(IV); curve 1, 0.02 *M* $NaNO_2$; curve 2, no nitrite added.

**Fe(III) Dependence.**—The data of Fig. 2 are from preliminary work in nitrate solution. The Np(IV) absorption band at 723 millimicrons follows Beers law so the optical density is proportional to the Np(IV) concentration.[2,11] The observed densities were normalized to unity at zero time for comparative purposes. The observed rate constants were calculated from the reaction half-lives given by the semilog plots of the relative Np(IV) concentrations against time. Since the rate constants vary directly with the Fe(III) con-

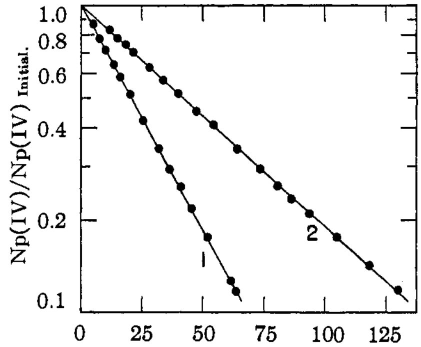

Fig. 2.—Effect of ferric ion concentration on the rate of the reaction, Np(IV) + Fe(III) → Np(V) + Fe(II), in 0.5 *M* nitrate, 0.5 *M* perchlorate solution: temperature 25°, 0.5 *M* hydrogen ion, 0.0042 *M* initial Np(IV); curve 1, 0.0020 *M* Fe(III), $k_{obs.} = 0.0330$ min.$^{-1}$; curve 2, 0.0010 *M* Fe(III), $k_{obsd.} = 0.0165$ min.$^{-1}$.

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[9] M. Schumann, *Ber.*, **33**, 527 (1900).

[10] E. Abel, H. Schmid and F. Pollak, *Monatsh.*, **69**, 125 (1936).

[11] J. C. Hindman, L. B. Magnusson and T. J. LaChapelle, "National Nuclear Energy Series," Div. IV, Vol. 14B, Transuranium Elements, Pt. II, 1039 (1949).

centration and the semilog plots are linear, the rate of reaction is proportional to the Np(IV) and Fe(III) concentrations.

**Temperature Effect.**—The last two rows of Table I give comparable data for two runs at different temperatures. The rate constant at 35.4° after correcting for small hydrogen ion and Fe(III) concentration differences was found to be larger than the rate constant at 24.3° by a factor of 8.54. The temperature effect was assumed to be given by the Arrhenius relation

$$d \ln k/dT = \Delta E/RT^2 \qquad (2)$$

from which an apparent heat of activation, $\Delta E$, of 35 kcal. mole$^{-1}$ was calculated. Eq. (2) was used to correct observed rate constants to 25°.

**Hydrogen Ion Dependence.**—Hydrogen ion concentrations in the forward reaction runs were calculated from the known acid concentrations of the neptunium stock solutions and Fe(III) reagent with allowance for the formation of a small amount of nitrous acid. Change in hydrogen ion concentration during reaction was negligible.

Hydrogen ion dependence was investigated with solutions of constant ionic strength differing in hydrogen ion concentration. Preliminary runs indicated that the rate of reaction is inversely dependent on some power of the hydrogen ion concentration. The rate law including hydrogen ion as a variable may be postulated as

$$dx/dt = -k_1ax/b^r = -k_3ax \qquad (3)$$

where $a$, $b$ and $x$ are the concentrations of Fe(III), hydrogen ion and Np(IV). Hence

$$\log k_3 = -r \log b + \log k_1 \qquad (4)$$

A plot of the logarithm of the rate constants at 25°, $k_3$, against the logarithm of hydrogen ion concentration should give a straight line of slope $-r$ (Fig. 3). Table I summarizes the data obtained for runs over the range 0.5–1 molar hydrogen ion concentration at an ionic strength of 1.0. The observed rate constant, $k_{obsd.}$, is equal to $k_3a$ of equation (3). Three lines of slope $-2$, $-3$ and $-4$ are included in Fig. 3. The rate constants fit closely the line of slope $-3$, indicating that the rate of reaction is inversely dependent on the third power of the hydrogen ion concentration. The last column of Table I gives the calculated values of $k_1$ at 25° with $r$ equal to 3. The best value of $k_1$ with an estimated uncertainty is 3.4 ± 0.2 moles$^2$ liters$^{-2}$ min.$^{-1}$ at 25°, $\mu$ = 1.0.

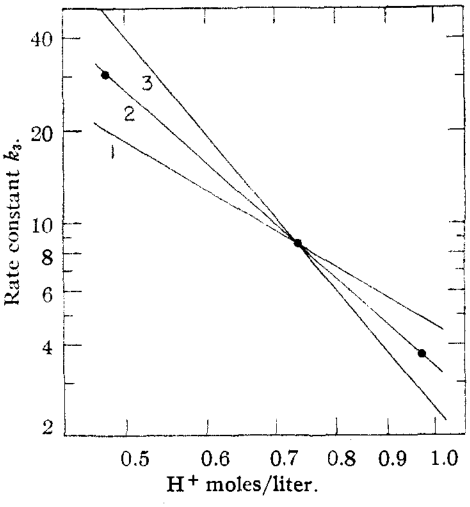

Fig. 3.—Hydrogen ion dependence of the forward reaction rate in perchlorate solutions. Data from Table I: lines 1, 2 and 3 have slopes $-2$, $-3$ and $-4$, respectively.

TABLE I

EFFECT OF HYDROGEN ION CONCENTRATION AND TEMPERATURE ON RATE CONSTANT IN PERCHLORATE SOLUTIONS (0.0026–0.0052 $M$ initialNp(IV), $\mu$ = 1.0)

| H$^+$ mole/liter | Fe$^{+++}$ moles/liter × 10$^3$ | Temp., °C. | $k_{obsd.}$ × 10$^3$ | $k_3$ | $k_1$ |
|---|---|---|---|---|---|
| 0.482 | 2.08 | 24.2 | 53.3 | 30.1 | 3.37 |
| .736 | 2.13 | 23.8 | 14.4 | 8.59 | 3.43 |
| .972 | 2.12 | 24.9 | 8.06 | 3.81 | 3.50 |
| .950 | 2.05 | 24.3 | 7.29 | 4.09 | 3.51 |
| .945 | 2.04 | 35.4 | 63.0 | ... | .. |

**Ionic Strength Effect.**—The direction of the effect of changing ionic strength, $\mu$, was noted by including a run at $\mu$ = 2.0. All other runs in perchlorate solutions were at an ionic strength of 1.0. Increasing ionic strength decreases the reaction rate constant in this region (Table II).

TABLE II

EFFECT OF IONIC STRENGTH ON RATE CONSTANT IN SODIUM PERCHLORATE SOLUTIONS

| $\mu$ | H$^+$ mole/liter | Fe$^{+++}$ moles/liter × 10$^3$ | Temp., °C. | $k_{obsd.}$ × 10$^3$ | $k_1$ |
|---|---|---|---|---|---|
| 1.0 | 0.972 | 2.12 | 24.9 | 8.06 | 3.50 |
| 2.0 | .942 | 2.05 | 24.8 | 6.30 | 2.68 |

**Rates in Nitrate Solutions.**—The rates of oxidation of Np(IV) by Fe(III) were also examined in nitrate solutions. Preliminary observations by the authors of spectral changes in nitrate solutions have indicated appreciable concentrations of at least one nitrate complex species of Np(IV) in the range 0–1 molar nitrate concentration. The rate of Np(IV) oxidation in nitrate solution was consequently expected to be lower in general than in perchlorate solution. Np(IV) can be maintained for long periods of time in pure nitrate solutions. A very low rate of oxidation observed could be attributed to the iron impurity in the reagents.

The reaction rate data for the nitrate solutions are summarized in Tables III and IV. The reac-

TABLE III

EFFECT OF HYDROGEN ION CONCENTRATION ON RATE CONSTANTS IN NITRATE SOLUTIONS (*ca.* 10$^{-3}$ $M$ Np)

| $NO_3^-$ mole/liter | H$^+$ mole/liter | $\mu$ | Fe$^{+++}$ moles/liter × 10$^3$ | Temp., °C. | $k_{obsd.}$ × 10$^3$ | $k_4$ |
|---|---|---|---|---|---|---|
| 0.50 | 0.25 | 1.0 | 0.82 | 24.0 | 87 | 2.0 |
| 0.50 | .51 | 1.0 | 0.82 | 24.0 | 10.8 | 2.1 |
| 1.0 | .459 | 2.0 | 2.00 | 24.8 | 24.3 | 1.22 |
| 1.0 | .943 | 2.0 | 2.04 | 24.8 | 2.91 | 1.24 |

TABLE IV

EFFECT OF NITRATE ON RATE CONSTANTS (*ca.* 10$^{-3}$ $M$ Np)

| $NO_3^-$ mole/liter | H$^+$ mole/liter | $\mu$ | Fe$^{+++}$ moles/liter × 10$^3$ | Temp., °C. | $k_{obsd.}$ × 10$^3$ | $k_1$ | $k_4$ |
|---|---|---|---|---|---|---|---|
| .. | 0.482 | 1.0 | 2.08 | 24.2 | 53.3 | 3.37 | .. |
| 0.50 | .485 | 1.0 | 2.08 | 24.8 | 39.8 | .. | 2.25 |
| .. | .942 | 2.0 | 2.05 | 24.8 | 6.30 | 2.68 | .. |
| 1.0 | .943 | 2.0 | 2.04 | 24.8 | 2.91 | .. | 1.24 |

tion rate is lower in nitrate solutions than in perchlorate solutions of the same ionic strength and hydrogen ion concentration. The last column of the tables lists values of the rate constants, $k_4$, calculated for 1.0 molar hydrogen ion concentration based on the assumption that the rate of reaction is inversely dependent on the third power of the hydrogen ion concentration. The agreement in the calculated constants for solutions of the same ionic strength (Table III) indicates that the inverse third power of the hydrogen ion concentration applies to the rate law in the nitrate solutions. From the experimental evidence the rate law in nitrate solution is similar to (3)

$$\mathrm{d}x/\mathrm{d}t = -k_4ax/b^3 \qquad (5)$$

where the rate constant, $k_4$, however, is an unknown function of the nitrate concentration. The available data do not permit formulating as general a rate law as was possible for the reaction in perchlorate solution. The kinetic data and spectral observations indicate partial complexing of Np(IV) by nitrate so that the rate constant of (5) does not have a simple power dependence on the nitrate concentration.

**Back Reaction in Perchlorate Solution.**—The equilibrium constant of reaction (1)

$$K = (\mathrm{NpO_2}^+)(\mathrm{Fe}^{+2})(\mathrm{H}^+)^4/(\mathrm{Np}^{+4})(\mathrm{Fe}^{+3}) \qquad (6)$$

is equal to 0.72 at 25° in terms of ion concentrations in moles liter$^{-1}$ in 1.0 molar perchlorate solutions.[3] The preliminary study of the reverse reaction of Np(V) and Fe(II) in hydrochloric acid solution indicated that the rate was proportional to the first power of the hydrogen ion.[5] The reverse rate law may be postulated as

$$\mathrm{d}(\mathrm{NpO_2}^+)/\mathrm{d}t = -k_2(\mathrm{NpO_2}^+)(\mathrm{Fe}^{+2})(\mathrm{H}^+) \qquad (7)$$

At equilibrium the forward and reverse rates must be equal

$$k_1(\mathrm{Np}^{+4})(\mathrm{Fe}^{+3})/(\mathrm{H}^+)^3 = k_2(\mathrm{NpO_2}^+)(\mathrm{Fe}^{+2})(\mathrm{H}^+) \qquad (8)$$

$$K = k_1/k_2 \qquad (9)$$

The value of the reverse rate constant, $k_2$, should be equal to 4.7 ± 0.3 moles$^{-2}$ liters$^2$ min.$^{-1}$ in 1.0 molar perchlorate solution at 25°. The consistency of the raw laws and constants was checked by an experimental determination of the rate of reduction of Np(V) by Fe(II). The course of the reaction was followed by noting the growth of the 723 millimicron absorption band of Np(IV). No method was available for maintaining a constant concentration of Fe(II) as was done with Fe(III). Since the reaction is not complete, the postulated rate law should have the general form

$$\mathrm{d}x/\mathrm{d}t = k_2(c_1 - x)(c_2 - x) - k_1(c_3 + x)(c_4 + x) \qquad (10)$$

where $x$ is the concentration increment of Np(IV) produced by reduction of Np(V) and $c_1$, $c_2$, $c_3$ and $c_4$ are the initial concentrations of Np(V), Fe(II), Np(IV) and Fe(III). A relatively small but not negligible concentration of Fe(III) was present in the Fe(II) reagent. No Np(IV) was detectable before the start of the reaction. The second term on the right-hand side of the equation is the rate of reoxidation of Np(IV) by Fe(III). By arrangement of terms in (10) one obtains an integrable expression of the type

$$\int \frac{\mathrm{d}x}{ax^2 + bx + c} \qquad (11)$$

The reaction data are plotted in Fig. 4. Two theoretical curves calculated from the integrated form of (11) with the rate constants as parameters are included in the figure. The upper curve has the highest values while the lower curve has the lowest values for the rate constants which are within the estimated experimental error and consistent with the equilibrium constant. The agreement between the observed and calculated concentrations within the estimated experimental error is satisfactory and is taken to be supporting evidence for the rate laws.

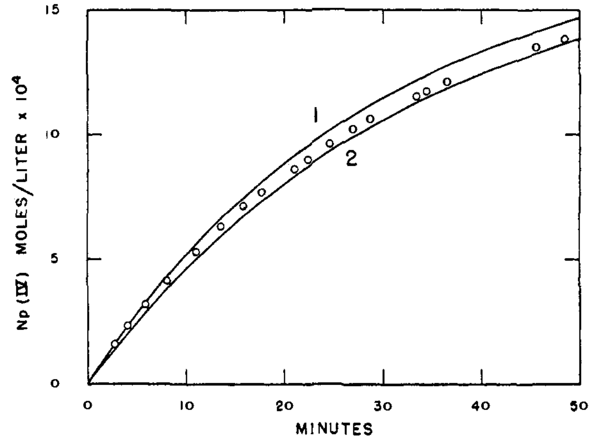

Fig. 4.—Growth of Np(IV) by the backward reaction at 25°. Initial concentrations: 0.986 *M* H$^+$; 0.00329 *M* Np(V); 0.00379 *M* Fe(II); 0.00024 *M* Fe(III); ionic strength = 1.0; ○, experimental points; curve 1, $k_1$ = 3.60, $k_2$ = 5.00; curve 2, $k_1$ = 3.20, $k_2$ = 4.44.

## Discussion of Reaction Mechanisms

The data rule out the direct oxidation of Np$^{+4}$ to Np(V) as in the reaction

$$\mathrm{Np}^{-4} + \mathrm{Fe}^{+3} + 2\mathrm{H_2O} \rightleftharpoons \mathrm{NpOOH}^{+2} + \mathrm{Fe}^{+2} + 3\mathrm{H}^+ \qquad (12)$$

To satisfy the inverse third power hydrogen ion dependence, reaction (12) would necessarily be in rapid equilibrium. The postulate that reaction (12) is in rapid equilibrium would require that the rate of reaction be inversely dependent on the ferrous ion concentration. The data of Fig. 1 show that the rate of reaction must be independent of the ferrous ion concentration. The initial rates of the runs with (curve 1) and without nitrite (curve 2) are identical yet the ferrous ion concentration in the system without nitrite increases continuously from zero.

One may conclude that the rate-determining step of the forward reaction is preceded by the formation in reversible equilibrium of one or more hydrolyzed species. Since the reacting species are unknown, the rate-determining step for the forward and backward reactions can be described only in a generalized manner as in the equation

$$\mathrm{Np(OH)}_x{}^{+4-x} + \mathrm{Fe(OH)}_y{}^{+3-y} \rightleftharpoons \mathrm{NpO}^{+2} + \mathrm{Fe}^{+2} + \mathrm{H}^+ + \mathrm{H_2O} \qquad (13)$$

in which the sum of $x$ and $y$ is 3.

The rate of reduction of Np(V) by Fe(II) is remarkably high compared to the rates with other reducing agents. Hydrazine, hydroxylamine, iodide, oxalate, sulfite and stannous ion react only very slowly, if at all, with Np(V) at room temperature. The observed rates of reduction with these reagents are probably mainly the rates of disproportionation of Np(V) to Np(IV) and Np(VI).

CHICAGO, ILL. RECEIVED DECEMBER 1, 1950

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY]

# Melting and Glassy State Transitions in Cellulose Esters and their Mixtures with Diluents[1,2]

BY LEO MANDELKERN AND PAUL J. FLORY

Specific volume–temperature measurements carried out dilatometrically on cellulose triacetate, cellulose acetate containing 2.3 acetyl groups per glucose unit, cellulose tributyrate, and cellulose butyrate containing 2.6 butyryl groups per unit indicate two second order transitions in each case. For the triacetate these occur at 30 and 105° and for the tributyrate at 40 and 120°. The partial esters exhibit somewhat higher transitions than the corresponding triesters. The change in the expansion coefficient at the lower transition is unusually small, but unmistakable nevertheless. The upper transition is depressed much less by diluents than is the glassy transition of polystyrene. Melting temperatures $T_m$ of mixtures of cellulose tributyrate with diluents have been determined from the volume change observed dilatometrically. Extrapolation of these measurements yields $T_m^0 = 206–207°$ for cellulose tributyrate. The depression of $T_m$ depends on the volume fraction of diluent in the manner predicted by theory; results for six different diluents give 3000 ± 200 cal. for the heat of fusion per mole of repeating unit. Undiluted cellulose (2.6) butyrate melts at 178°, showing a surprisingly large volume change for a copolymeric material. This observation, and the small difference in $T_m$ compared with the tributyrate as well, indicate co-crystallization of dibutyrate and tributyrate units. The entropy of fusion of cellulose tributyrate is compared with values for several synthetic chain polymers. Heats of mixing with amorphous cellulose tributyrate, also calculated from the dependence of $T_m$ on diluent concentration, are zero within experimental error for three of the diluents (tributyrin, benzophenone and ethyl benzoate); for the others (hydroquinone monomethyl ether, dimethyl phthalate and ethyl laurate) they are positive.

## Introduction

Melting and second order transition phenomena in cellulose derivatives have remained remarkably obscure in contrast to the importance attached to these phenomena in other polymers. Ueberreiter[3] measured the specific volumes of two cellulose acetates over rather limited temperature ranges with results which indicate a second order, or glassy state, transition at 49° in one case and at 56° in the other. Clash and Rynkiewicz[4] reported similar measurements on several plasticized cellulose esters of unspecified composition. Although crystallinity has been established by X-ray methods in a number of instances,[5,6] the temperature at which the last traces of crystallinity disappear at equilibrium, *i.e.*, the melting temperature $T_m^0$, has remained virtually unknown for any cellulose derivative. Part of this lack of information on melting temperatures may be attributed to the failure of conventional methods; the cellulose derivatives often melt above their thermal decomposition temperatures, and where this is not the case they "melt" to liquids so viscous that the physical change may not be evident by direct observation.

The dilatometric method has proved highly successful, though tedious, for the study of first order (melting) transition phenomena as well as for the detection of second order (glassy) transitions in polymers.[7,8] A recent statistical thermodynamic theory of crystallinity in polymers and their mixtures with diluents affords several methods for determining the heat of fusion of the crystalline polymer from melting temperature studies.[9] The preferred one of these involves measurement of the depression of $T_m$ by diluents. According to the theory referred to

$$(1/T_m - 1/T_m^0) = (R/h_u(\mathrm{v}_2/\mathrm{v}_1)(v_1 - \kappa_1 v_1^2) \quad (1)$$

where $T_m^0$ is the absolute melting temperature of polymer (of high molecular weight) in the absence of diluent: $h_u$ is the heat of fusion per mole of structural unit; $\mathrm{v}_2$ and $\mathrm{v}_1$ are the molar volumes of the polymer unit and of diluent molecules respectively; $v_1$ is the volume fraction of the diluent, and $\kappa_1$ is the energy of mixing parameter characteristic of a given polymer-diluent pair; $\kappa_1$ is equal to $B\mathrm{v}_1/RT$ where $B$ represents the energy of mixing per cc. at infinite dilution. Thus, the depression of the melting point of the polymer by diluent should depend on the heat of fusion of the crystalline polymer, the molar volume of the diluent and its energy of interaction with the polymer. Equation (1) may be rearranged to the more convenient form

$$(1/T_m - 1/T_m^0)\ /v_1 = (R/h_u)(\mathrm{v}_2/\mathrm{v}_1)(1 - \kappa_1 v_1) \quad (2)$$

A plot of the function on the left, once $T_m^0$ has been established either directly or by extrapolation, against $v_1/T_m$ permits determination of both $h_u$ and $\kappa_1$ from the slope and intercept. Thus, both the heat of fusion of the polymer and the mixing parameter $\kappa_1$ may be deduced from measurements

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