values of Λ_0 for potassium *n*-octadecylsulfate (83.04) and *n*-octadecyltrimethylammonium picrate (82.13). Thus, Λ_0^+ for potassium (50.2) plus that for the picrate ion (49.2) gave 99.4, as compared with the experimental value of 99.31.

TABLE III

IONIC CONDUCTANCE IN METHANOL

Cation	Λ_0^+	Anion	Λ_0^-
Octd. Me_3N	32.9	Octd. SO_4	32.9
K	50.2	Pi	49.2
Na	42.5	Cl	54.7
Me_4N	66.7		
Et_4N	58.2		
n-Pr_4N	43.9		
n-Bu_4N	36.9		
i-Am_4N	33.3		
n-Bu_3NH	39.9		

Of the values in Table III those for potassium chloride can be best compared with Hartley's results, since his value of Λ_0 for potassium chloride is exactly the same as that obtained in this investigation. Consequently, any differences in the ionic conductances of the potassium ion can be attributed solely to differences in the two methods. Hartley obtained 53.8 for the potassium ion as compared with 50.2 by Kraus' method, a difference of 3.6 units or 7%. Since hydrogen is a fast ion, any errors in determining its mobility would be magnified percentage-wise in calculating the conductance of slower ions. Thus, if the conductance of the hydrogen ion were 2.5% lower, the same value would be obtained for potassium as given here. Furthermore, if Thompson's observations[19] extend to methanol, the results with the long chain salt are apt to be somewhat low. In view of these factors it may be concluded that the Kraus method cannot be greatly in error and is particularly useful for comparing results in several solvents. In this connection it may be pointed out that calculation of the Walden product, $\Lambda_0^+\eta$, for the tetra-*n*-butylammonium ion in acetone, ethylene dichloride, pyridine and nitrobenzene has yielded the values, 0.204, 0.206, 0.212 and 0.212, respectively (based on tetra-*n*-butylammonium triphenylborofluoride). In methanol, using Hartley's ionic conductances, we obtained 0.222, whereas with the long chain salt as standard we obtain 0.202. This suggests that Hartley's value may be slightly high.

As yet we do not have data on enough substituted ammonium ions to gain much information regarding the effect of structure on their relative mobilities. However, in the series of quaternary ammonium salts here reported the tetramethylammonium ion shows a proportionately greater resistance per carbon atom than do the larger members of the series; as the size increases the resistance per carbon atom decreases slightly. On the same basis, the resistance of the tri-*n*-butylammonium ion is too high; its resistance lies between that of the tetra-*n*-propyl- and tetra-*n*-butylammonium ions. These results closely parallel those found in other solvents.[3]

Acknowledgment.—We wish to thank the Rohm and Haas Company for a grant supporting this research.

PHILADELPHIA 4, PENNA. RECEIVED OCTOBER 12, 1950

[CONTRIBUTION FROM THE CHEMISTRY DIVISION OF THE ARGONNE NATIONAL LABORATORY]

Spectrophotometry of Neptunium in Perchloric Acid Solutions[1]

BY R. SJOBLOM AND J. C. HINDMAN

As a preliminary to the investigation of various problems in the solution chemistry of neptunium, details of the absorption spectra of the neptunium(III), (IV), (V) and (VI) ions in various perchloric acid concentrations have been investigated. The analytical usefulness of the various absorption bands has been tested in one molar perchloric acid solution. The spectrum of neptunium(VI) has been found to contain a vibrational fine structure similar to that found for the U(VI) and Pu(VI) ions. As in the case of the plutonium and uranium ions this fine structure is interpreted as arising from symmetrical metal-oxygen vibrations in ions of the type NpO_2^{++}. The vibrational frequency of the Np(VI) ion is 715 cm.$^{-1}$ in one molar perchloric acid, 709 cm.$^{-1}$ in ten molar perchloric acid and 704 cm.$^{-1}$ at *p*H 2.7 (in one molar sodium perchlorate). Evidence is also cited for a vibrational fine structure in the spectrum of Np(V). In this case a vibrational frequency of 753 cm.$^{-1}$ is found in one molar perchloric acid. No evidence has been obtained that would indicate any extensive degree of complex formation between Np^{+3} (hydrated) or Np^{+4} (hydrated) and perchlorate at total perchloric acid concentrations up to ten molar. On the basis of the spectral observations and the data on the disproportionation reaction $2Np(V) \rightleftarrows Np(IV) + Np(VI)$, which occurs at perchloric acid concentration above five molar it is concluded that the ions NpO_2^{++} and NpO_2^+ probably exist even in eight to ten molar acid although the possible existence of ions such as $NpOOH^{++}$ and $NpOOH^{+++}$ cannot be excluded.

Several publications have emphasized the application of absorption spectrum measurements in studies involving the solution behavior of the actinide elements, particularly of uranium[2] and plutonium.[3] Preliminary data on the characteristics of the absorption spectra of the different oxidation states of neptunium have appeared.[4] The purpose of the present investigation was three-

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(1) Presented in part before the Division of Physical and Inorganic Chemistry of the American Chemical Society, Chicago Meeting, Sept. 1950.

(2) J. Sutton, Canadian Research Council Document, CRC-325, "Ionic Species in Uranyl Solutions," March 21, 1947.

(3) (a) G. E. Moore and K. A. Kraus, Paper No. 4.22, "The Transuranium Elements," Vol. 14B of the Plutonium Project Record of the National Nuclear Energy Series, McGraw-Hill Book Co., Inc., New York, 1949. (b) R. E. Connick, M. Kasha, W. H. McVey and G. E. Sheline, Paper No. 4.20, "The Transuranium Elements," Vol. 14B of the National Nuclear Energy Series, McGraw-Hill, New York, 1949. (c) J. C. Hindman, Papers 4.2, 4.4, 4.5 and 4.7, "The Transuranium Elements," Vol. 14B of the Plutonium Project Record of the National Nuclear Energy Series, McGraw-Hill, New York, 1949.

(4) J. C. Hindman, L. B. Magnusson and T. J. LaChapelle, THIS JOURNAL, **71**, 687 (1949), paper No. 15.2, "The Transuranium Elements," Vol. 14B of the Plutonium Project Record of the National Nuclear Energy Series, McGraw-Hill, New York, 1949.

fold: first, to obtain better data on the general features of the absorption spectra, including the ultraviolet region not previously investigated: second, to ascertain the usefulness of the principal neptunium absorption bands in quantitatively analyzing for the various oxidation states; and third, to examine the spectra in perchlorate solutions for changes that might be correlated either with complex formation involving perchlorate or with hydrolysis of the neptunium ions. With respect to hydrolysis phenomena particular attention has been paid to examining evidence that would place limits on the range of acid concentration in which oxygenated ions such as NpO_2^+ and NpO_2^{++} are stable.

In the first part of this paper details of the absorption spectra of the different oxidation states are discussed. The second portion of the paper deals with the effect of perchloric acid concentration on the spectra and includes data on the previously unreported disproportionation reaction

$$2Np(V) \rightleftharpoons Np(IV) + Np(VI)$$

which occurs in neptunium(V) solutions in concentrated acid.

I. **The Absorption Spectra of Np(III), Np(IV), Np(V) and Np(VI) in 1.0 *M* $HClO_4$**—Measurements of details of the absorption spectra of carefully prepared solutions of the oxidation states of neptunium in 1.0 *M* $HClO_4$ have been made. Aliquots of these solutions have been used for examination of the behavior of the principal absorption bands with respect to the Beer–Lambert law

$$E = \log_{10} \frac{I^0}{I} \times \frac{1}{cl} = \frac{d}{cl} \qquad (1)$$

where E is the molar extinction coefficient, c the concentration in moles/liter, l the cell length in cm., and d the optical density.

Experimental

The absorption spectrum measurements from 215 to 400 mμ were made with a Cary recording spectrophotometer model 12 (marketed by the Applied Physics Corporation, Pasadena, California) using silica 2 cm. cylindrical cells. The slit width on the Cary spectrophotometer is automatically controlled. The measurements from 350 to 1050 mμ were made with a Beckman (Model DU) quartz spectrophotometer using matched 1.000 ± 0.001 cm. and 1.003 ± 0.001 cm. silica cells. Silica cells of 0.500 ± 0.002 cm. were also used. Readings on the Beckman spectrophotometer were made at 2-mμ intervals in the region 350–600 mμ and at 2.5-mμ intervals from 600–1050 mμ except in the vicinity of the absorption bands where the region was carefully scanned to locate the exact peak position. The wave length scales of the spectrophotometers were checked using mercury and hydrogen arcs. The density scales were checked by means of Bureau of Standards Corning HT yellow D13 and Jena Bg 14–38 filters.[5]

The stock solution of pure neptunium(V) in 1.0 *M* $HClO_4$ was prepared as follows: Neptunium(IV) hydroxide was precipitated from a sulfuric acid solution with sodium hydroxide, washed thoroughly, then dissolved in 1.0 *M* HCl. Nitric acid was added to make the solution 0.15 *M* in NO_3^- and the solution heated for several hours at 80° to oxidize the neptunium(IV). The course of the oxidation was followed spectrophotometrically. After complete oxidation of the neptunium(IV), the solution was made approximately 0.1 *M* in $N_2H_4{\cdot}HCl$ to reduce any neptunium(VI) that might have been formed to neptunium(V). The neptunium(V) hydroxide was then precipitated with sodium hydroxide, washed carefully, and dissolved in 1.0 *M* $HClO_4$ to give a solution 0.0430 *M* in neptunium(V). Aliquots of this solution were then diluted to give the desired concentrations.

Both neptunium(III) and neptunium(IV) solutions were prepared from the neptunium(V) stock in perchloric acid by hydrogen reduction. Since neptunium(III) is rapidly oxidized in the presence of air to neptunium(IV), precautions had to be taken to exclude air from the solutions. To serve as a means of introducing hydrogen into the solutions a 1-cm. silica cell was fitted with a ground glass stopper through which was sealed a tube having an attached stopcock. A platinum coil was wound around that portion of the tube extending into the solution but so placed as not to obstruct the beam of light. The coil was platinized. A hole was drilled in the side of the cell and the side of the stopper was notched to allow the gas to escape. The cell was made air tight by rotating the stopper and turning the stopcock. A solution 0.015 *M* in neptunium(V) and 1.0 *M* in $HClO_4$ was completely reduced to neptunium(III) in one-half hour. After one week in the stoppered cell the solution showed no signs of oxidation. For the Beer–Lambert law studies portions of this solution were diluted with 1.0 *M* $HClO_4$ to the desired neptunium concentration and these solutions again reduced to neptunium(III).

Neptunium(IV) solutions were also prepared by hydrogen reduction of a neptunium(V) solution. The neptunium(III) produced was reoxidized by blowing air through the solutions. This reaction is very rapid. On standing a very slow oxidation to neptunium(V) occurred. Spectral observations on the solution after standing one week showed the presence of 0.85% neptunium(V). All optical density values have been corrected for the presence of this oxidation state. For the Beer–Lambert law studies solutions prepared in the above manner were diluted with 1.0 *M* $HClO_4$.

Neptunium(VI) was prepared by electrolytic oxidation of a neptunium(V) solution in 1.0 *M* $HClO_4$. The completeness of oxidation was checked spectrophotometrically. There was no evidence that either neptunium(IV) or neptunium(V) was present in the final solution.

All measurements were made at 25 ± 1.0°. Merck and Co., Inc., 70% reagent grade perchloric acid was used for preparing the perchloric acid solutions. The neptunium concentrations of all dilutions were determined by radiometric assay of the Np^{237} isotope used in this work. The specific activity used was 790 counts per minute per microgram in "50 per cent." geometry counter.

Results

Details of the absorption spectra of the various oxidation states are summarized in Figs. 1, 2 and 3.

Neptunium(III) is the only oxidation state whose spectrum shows any marked structure in the ultraviolet region. The Beer law data for the principal Np(III) absorption bands are shown in Fig. 4. The Beer law data for the principal Np(IV) bands at 723 and 964 mμ are summarized in Fig. 5B and C. The spectrum from 350–1050 mμ for neptunium(V) in 1.0 *M* $HClO_4$ shows only two peaks of any consequence, one at 617 mμ and the other at 983 mμ (Fig. 2). Molar extinction coefficients for other characteristic bands of these states are given in Table I. The behavior of the band at 617 mμ conforms to the Beer–Lambert law. As in the case of the 964 mμ band of neptunium(IV), the extinction coefficient of the 983 mμ band of neptunium(V) decreases with increasing neptunium concentration (Fig. 5A). However, for both the 964 mμ neptunium(IV) band and the 983 mμ Np(V) peak the optical density is constant at a constant product of $c \times l$ (Tables II and III). Presumably the failure of the 964 and 983 mμ bands of neptunium(IV) and (V) to obey the Beer–Lambert law is due to the fact that the spectral band width isolated by the

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[5] K. S. Gibson, G. K. Walker and M. E. Brown, *J. Opt. Soc. Am.*, **24**, 58 (1934).

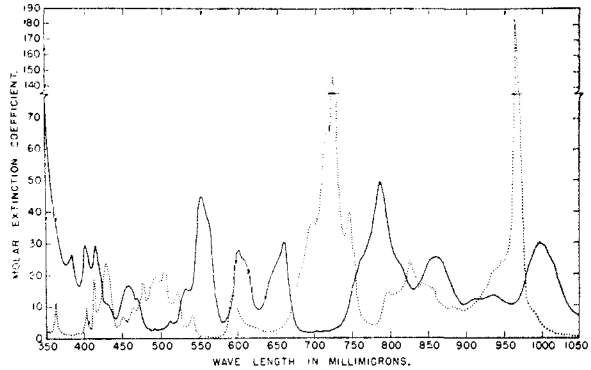

Fig. 1.—Absorption spectra of the neptunium(III) and -(IV) ions in 1.0 *M* $HClO_4$: —, Np(III); - - - - -, Np-(IV).

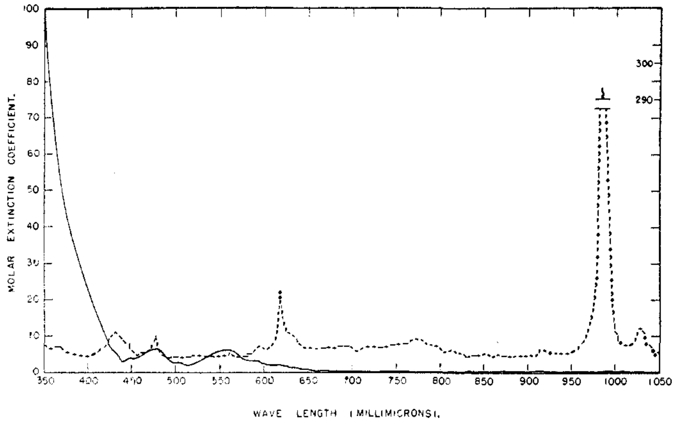

Fig. 2.—Absorption spectra of the neptunium(V) and -(VI) ions in 1.0 *M* $HClO_4$: —, Np(VI); - - - - -, Np(V).

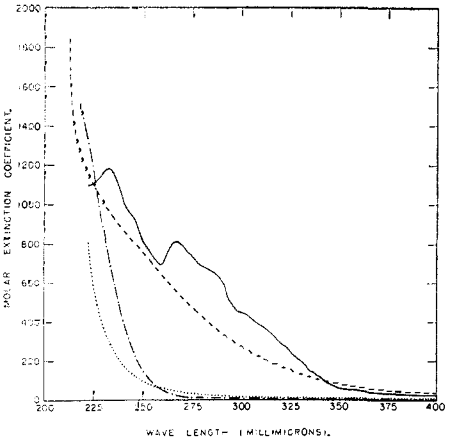

Fig. 3.—Ultraviolet absorption spectra of neptunium ions in 1.0 *M* $HClO_4$: —, Np(III); -·-·, Np(IV); ...., Np(V); - - - - - - -, Np(VI).

slits is not sufficiently narrow with respect to the band width at the peaks of the absorption bands. As would be expected in this case these bands show a variation in optical density with change in slit width (see Fig. 5). Although the data on the effect of slit width in Fig. 5 show a similar effect for the 723 mμ Np(IV) band no deviation from the Beer–Lambert law is observed in this case, therefore, at this wave length the actual spectral band isolated by the slits is not much less than the band width of the absorption band head. Presumably the 964 and 983 mμ bands are more affected because of the decreased dispersion of the spectrophotometer with increasing wave length. The Np(III) bands are unaffected by change in slit width.

It may be concluded from these experiments that the principal neptunium(IV) and neptunium(V) bands can be used for accurate work if a suitable calibration data are obtained and care is taken to duplicate the settings of the slit width. Comparison of values obtained for the neptunium(IV) peaks on two different Beckman spectrophotometers showed that there is an appreciable variation between the different instruments and calibration curves are not interchangeable from one instrument to another.

The absorption spectrum of neptunium(VI) in the visible region shows no absorption bands as suitable for analytical use as those of the other oxidation states. The distinguishable bands of neptunium(VI) are listed in Table I.

The Vibrational Fine Structure in the Spectra of Neptunium(V) and (VI).—Probably the most distinctive feature of the neptunium(VI) absorption spectrum is the existence of a number of weak regularly spaced bands occurring in the blue-violet and near ultraviolet region of the spectrum. Similar bands are observed in the absorption spectra of both the uranyl ion, UO_2^{++}, and the plutonyl ion, PuO_2^{++}. They are attributable to the symmetrical vibrations in the metal–oxygen bonds.[6,7] In the spectrum of neptunium (VI) in 1.0 *M* $HClO_4$ there are eight of these vibrational bands in the 370–475 mμ region having an average frequency difference of 715 cm.$^{-1}$. The positions and character of these bands are illustrated in Fig. 6. In solutions of the uranyl ion, UO_2^{++}, there are eleven regularly spaced bands for which Kasha[7] gives a value of 724 cm.$^{-1}$ for the frequency interval in 0.1 *M* $HClO_4$. Similar measurements by us for 1.0 *M* $HClO_4$ solutions

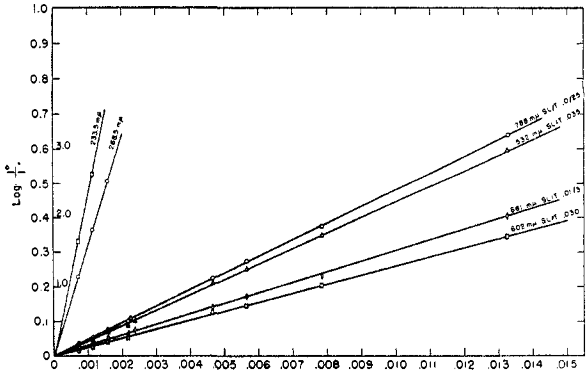

Fig. 4.—Beer law behavior of neptunium(III) absorption bands.

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[6] G. H. Dieke and A. B. F. Duncan, "Spectroscopic Properties of Uranium Compounds," The National Nuclear Energy Series, McGraw-Hill Book Co., Inc., New York, N. Y., 1949.

[7] M. Kasha, *J. Chem. Phys.*, **17**, 349 (1949).

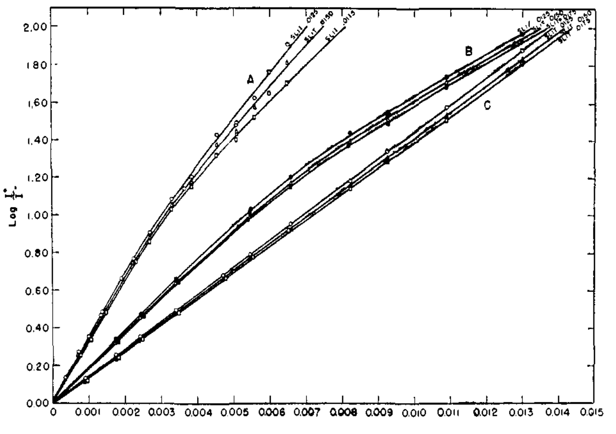

Fig. 5.—Variation of optical density with molarity and slit width for Np(IV) and Np(V) absorption bands: (A), Np(V) peak at 983 mμ; (B), Np(IV) peak at 964 mμ; (C), Np(IV) peak at 723 mμ.

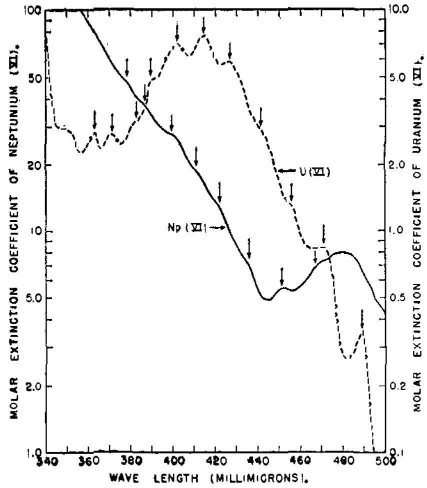

Fig. 6.—Absorption spectra of uranium(VI) and neptunium(VI) in 1.0 M $HClO_4$ showing vibrational fine structure.

gave a frequency interval of 712 cm.$^{-1}$. For comparison, the spectrum of uranium(VI) in 1.0 M $HClO_4$ is shown in Fig. 6. For plutonium(VI) Kasha also reported for the series of four regularly spaced bands in the region 390–430 mμ, a frequency difference of 708 cm.$^{-1}$. Betts and Harvey[8] reported an average value of 657 cm.$^{-1}$ for the frequency interval of the plutonyl vibrational bands in 0.9 M HNO_3.

A similar vibrational fine structure in the absorption spectrum would also be expected for the ion NpO_2^+. Examination of a neptunium(V) spectrum in 1.0 M $HClO_4$ shows eight bands in the 430–600 mμ region having an average frequency interval of 753 cm.$^{-1}$. Figure 7 illustrates the location of these bands. Pending further investigation these bands are presumed to arise from the symmetrical vibrations in the metal–oxygen bonds of the NpO_2^+ ion.

It should be pointed out the existence of the vibrational structure in the solution absorption spectra of these oxygenated ions is probably the best available evidence that these ions are of the type XO_2^+ or XO_2^{++} and are not $X(OH_4)^+$ or $X(OH)_4^{++}$.

TABLE I

DATA ON MOLAR EXTINCTION COEFFICIENTS OF CHARACTERISTIC BANDS OF NEPTUNIUM IONS IN 1.0 M $HClO_4$[a]

λ (mμ)	E	λ (mμ)	E	λ (mμ)	E
		Np(III)			
233.5	2295[b]	462	17.0	661[b]	30.5
267.0	1593[b]	470	12.7	787.5[b]	48.2
384	26.6	532	15.8	858	25.4
402	29.7	552[b]	44.5	910	12.4
416	29.3	602[b]	25.8	998	30.2
		Np(IV)			
363[b]	11.9	476	17.3	697.5	37.2
402	9.4	492	19.4	715	67.0
412	18.5	504[b]	22.9	743[b]	43.0
428[b]	23.9	521	14.7	792.5	14.3
450	6.9	540	7.2	825[b]	24.5
463	9.6	590.5[b]	16.1	840	17.6
				877.5	10.0
		Np(V)			
366	7.5	476	10.3	617[b]	23.7
428	11.1	594	7.1	1030	12.1
		Np(VI)			
448	3.9	504	2.7	590	3.2
476	6.4	557	6.8	620	2.1

[a] Extinction coefficients determined at slit widths of 0.0125 mm. except where sensitivity of instruments required wider slits. [b] Band checked and found to obey Beer's law.

TABLE II

NEPTUNIUM(IV) IN 1.0 M $HClO_4$ OBSERVATIONS AT CONSTANT VALUES OF $c \times l$

[Np] moles/liter	$c \times l \times 10^4$	d at 723 mμ	E at 723 mμ	d at 964 mμ	E at 964 mμ
0.01300	130.0	1.88	144.6	1.91	146.9
.02576	129.1	1.86	144.1	1.88	145.6
.01091	109.1	1.58	144.8	1.74	159.5
.02144	107.4	1.54	143.4	1.73	161.1
.006576	65.76	0.948	144.2	1.20	182.5
.01295	64.88	.939	144.7	1.19	183.4
.003409	34.09	.493	144.6	0.656	192.4
.006507	32.65	.474	145.2	0.634	194.2
.002425	24.25	.349	143.9	0.469	193.4
.004843	24.36	.351	144.1	0.479	196.6
.001775	8.893	.125	140.6	0.170	191.2
.0009006	9.006	.129	143.2	0.174	193.7

TABLE III

Np(V) IN 1 M $HClO_4$ 983 mμ PEAK OBSERVATIONS AT CONSTANT PRODUCT $c \times l$

[Np] mole/liter concn.	$c \times l \times 10^4$	d	E
0.005084	51.00	1.49	292.2
.01012	50.90	1.48	290.8
.003622	36.33	1.14	313.8
.007030	35.36	1.12	316.7
.001903	19.09	.657	344.2
.003728	18.75	.647	345.1
.0007161	7.18	.266	370.4
.001341	6.74	.250	370.6

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[8] R. H. Betts and B. G. Harvey, *J. Chem. Phys.*, **16**, 1089 (1948).

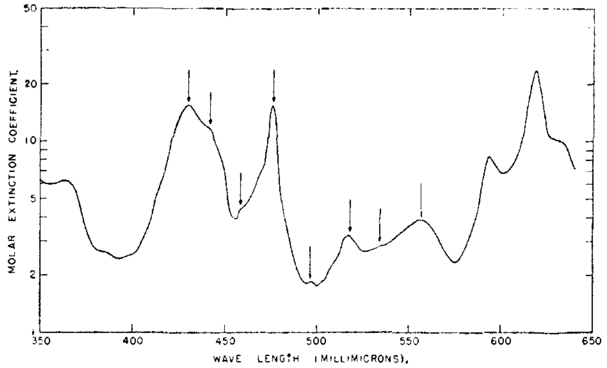

Fig. 7.—The absorption spectrum of neptunium(V) in 1.0 *M* $HClO_4$ showing vibrational fine structure.

II. Influence of Perchloric Acid Concentration on the Absorption Spectra of Neptunium Ions. The Disproportionation of Neptunium(V).—In studying the effect of perchloric acid concentration on the neptunium absorption spectra, the measurements have, except in the case of neptunium(III) solution, been made over a range of acid concentration ranging from those sufficiently low to show the effect of hydrolysis of the ions on the spectra of concentrated acid solutions. This was not possible in the case of neptunium(III) since the insolubility of the neptunium(IV) hydroxide would make the neptunium(III) ion unstable with respect to oxidation by water at acidities sufficiently low for hydrolysis to occur.

Experimental

For the studies on neptunium(V) solution in concentrated acid four solutions of varying perchloric acid concentration were prepared by diluting Merck and Co., Inc., reagent grade 70% perchloric acid with redistilled water. Np(V) in 1.0 *M* $HClO_4$ was added to each of the acids and a portion of the resulting solutions titrated with standardized sodium hydroxide solution to the methyl orange end-point. The acid molarities of the solutions were determined to be 5.34, 7.11, 8.45 and 8.67 *M*, respectively. Np(V), in each of these solutions, was found to disproportionate. The optical densities of the main Np(IV) and Np(V) peaks were followed from the time of mixing until equilibrium was reached, using a Beckman (Model DU) quartz spectrophotometer with quartz cells of 1.003 ± 0.001 cm. length. The slit width used was 0.0125 mm.

In order to find the concentrations of Np(IV) and Np(V) present at equilibrium, the values of the main peaks of the equilibrium mixtures were corrected for the contributions from the other oxidation states Data on the peak heights of the pure Np(IV) and Np(VI) states were obtained by reducing each equilibrium mixture to pure Np(IV), recording the spectrum, and then oxidizing the resultant Np(IV) solutions to Np(VI). The background readings at the peak positions of the pure Np(V) spectra were derived by extrapolation of density–time plots. The concentrations of the Np(IV) and Np(V) states present at equilibrium found by the above method are listed in Table IV. Since Np(VI) has no peaks suitable for analytical use, the concentration of Np(VI) was determined as the difference between the neptunium(IV) and -(V) concentrations as determined spectrophotometrically and the total neptunium concentration obtained from radiometric assay or taken to be equal to the neptunium(IV) concentration. The last column of the table lists the constant *K* for the reaction

$$2\text{Np(V)} \rightleftharpoons \text{Np(IV)} + \text{Np(VI)} \qquad (2)$$

Also given in the table are the observed times for 50% reaction. The kinetics of the disproportionation reaction will be discussed in detail in a subsequent publication.

The spectrum of a neptunium(V) solution at *p*H 5.7 was obtained from a solution prepared by addition of sodium hydroxide to a 1 *M* $HClO_4$ stock solution. The *p*H was measured with a Beckman Model G laboratory *p*H meter.

TABLE IV

THE DISPROPORTIONATION REACTION OF NEPTUNIUM(V). EFFECT OF PERCHLORIC ACID CONCENTRATION

Acid concn., m./l.	Eq. concn. [Np(IV)] m./l. × 10^3	Eq. concn. [Np(V)] from E_{983} m./l. × 10^3	Total concn. m./l. × 10^3	Diff., %	$t^{1/2}$ hr.	$K = [IV][VI]/[V]^2$
5.34	1.24[a]	3.30	5.66[c]	−0.83	52.0	−0.127
	1.18[b]		5.61[d]			
7.11	2.23[a]	0.926	5.38[c]	3.4	12.5	5.78
	2.23[b]		5.57[d]			
8.45	3.48[a]	0.260	7.26[c]	−0.2	0.78	169
	3.50[b]		7.25[d]			
8.67	2.97[a]	0.207	6.06[c]	−10.1	1.42	200
	2.92[b]		5.50[d]			

[a] From E_{723}. [b] From E_{964}. [c] From peak heights. [d] From radio assay. [e] *K* estimated from potential measurements[4] to be 4×10^{-7} for 1 *M* $HClO_4$.

The absorption spectra of the neptunium(IV) solutions in concentrated acid were obtained by reducing the equilibrium mixtures with hydrogen to Np(IV). The reduced solution was checked spectrophotometrically and found to contain no Np(V) or Np(III). To obtain the spectrum of neptunium(IV) at a *p*H of 2.0, neptunium(V) from the stock solution was added to 1.0 *M* perchloric acid and the *p*H adjusted by adding sodium hydroxide solution. The solution was then reduced by hydrogen.

Solutions of neptunium(III) in 5 *M* and 10 *M* perchloric acid were similarly prepared by hydrogen reduction of neptunium(V) solutions in these concentrations of perchloric acid.

Solutions of Np(VI) for spectrophotometric examination were prepared by electrolytic oxidation of a concentrated neptunium(V) solution in 1 *M* perchloric acid. Portions of this latter solution were then added to the proper perchloric acid solution. The spectra at *p*H 2.7, *p*H 4.0 and *p*H 4.9 were of solutions prepared by adding sodium hydroxide solution to an electrolytically prepared Np(VI) solution in 1 *M* $HClO_4$. The solutions of U(VI) in perchloric acid used as a comparison for the Np(VI) solutions were prepared by dissolving a weighed quantity of pure UO_3 in perchloric acid to give a stock solution of 0.9506 *M* in U(VI) and 1.0 *M* in $HClO_4$. Aliquots of this stock solution were added to the proper perchloric acid concentration for the absorption spectra studies. The uranium content was checked by gravimetric analysis.

The neptunium concentrations were determined radiometrically for each sample.

Results

Neptunium(III) resembles plutonium (III)[9] in that change of perchloric acid concentration from 1 to 10 *M* does not significantly affect the absorption spectrum.

Decreasing the hydrogen ion concentration sufficiently causes the occurrence of very definite changes in the spectrum of neptunium(IV). This is illustrated in Fig. 8, which shows the spectrum observed at a *p*H 2.00. The type of changes associated with the hydrolysis reaction are very similar to those observed in the hydrolysis of the Pu^{+4} ion to give $PuOH^{+3}$.[10] That the solution initially formed at this *p*H is not stable is shown by the observation that there is a decrease in the extinction

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(9) J. C. Hindman and D. P. Ames, Paper No. 4.2, "The Transuranium Elements," Vol. 14B of Plutonium Project Record of National Nuclear Energy Series, McGraw-Hill Book Co., Inc., New York, N. Y., 1949.

(10) J. C. Hindman, Paper No. 4.4, "The Transuranium Elements," Vol. 14B of the Plutonium Project Record of the National Nuclear Energy Series, McGraw-Hill Book Co., Inc., New York, N. Y., 1949.

of the principal absorption bands on standing. This optical phenomenon appears similar to that observed during formation of the polymers of plutonium(IV).[11] The further investigation of the spectrophotometric phenomena associated with the hydrolysis of neptunium(IV) will be discussed in a subsequent paper. It is sufficient at this time to note that the spectral changes caused by hydrolysis are very marked.

Increase of the perchloric acid concentration from 1 to 7.11 molar does not appreciably affect the absorption spectrum. However, both the 723 and 964 mμ peaks show a diminution in height of approximately 5% in 8.67 *M* $HClO_4$ and of about 8% in 10 *M* $HClO_4$. Since considerable evidence has been accumulated to show that the tripositive and tetrapositive ions of uranium,[12] neptunium[13] and plutonium[10,12b,14] are X^{+3} (hydrated) and X^{+4} (hydrated) in acid solution, these changes must be ascribed either to complex formation with the perchlorate or to a secondary effect ascribable to the change in the medium caused by the high acid concentration.

In arriving at an interpretation of the results, it is perhaps worthwhile to consider the nature of the absorption spectra of these ions. At the present time, the preponderance of evidence favors the hypothesis that these elements are part of a series in which the 5f shell is being filled. The data leading to this conclusion have been summarized by Seaborg.[15] Presumably, therefore, the characteristic sharp bands in the absorption spectra arise as in the case of the rare earths[16] from forbidden transitions in the f shell. According to this hypothesis the ground and upper states belong to the same configuration, $4f^x$ or for the new series, $5f^x$, the upper state differing only in the value of the collective azimuthal quantum member L or in the spin S, the individual l's remaining the same. With respect to the appearance of forbidden lines various explanations have been advanced[16] which include (1) quadrupole radiation, (2) magnetic dipole radiation, (3) electric dipole radiation due to an asymmetric field and (4) electric dipole radiation in which the field is symmetrical but the symmetry is removed by vibration from the equilibrium position. As a result of extensive researches on the absorption spectra of solutions of the rare earth ions, Broer, Gorter and Hoogschagen[17] have concluded that, with certain exceptions, the intensities of the sharp absorption lines can be accounted for if they arise from electric dipole radiation resulting from a perturbing electric field having no center of symmetry (hemihedric field). The splitting of the lines into several component levels in crystals or the broadening of the bands in solution is presumably due to an internal Stark effect induced by the symmetrical (holohedric) field of the surrounding anions. Transitions of the type $4f^x5d$ are presumably responsible for the diffuse ultraviolet bands such as observed in the absorption spectrum of cerium(III). It would appear quite possible that the relatively intense diffuse ultraviolet absorption bands of neptunium(III) also result from such transitions. That similar transitions for the ions of neptunium(IV), (V) and (VI) may exist are suggested by the marked increase in absorption in the ultraviolet indicating the presence of intense absorption bands in the far ultraviolet beyond the range of the spectrophotometers used in this investigation.

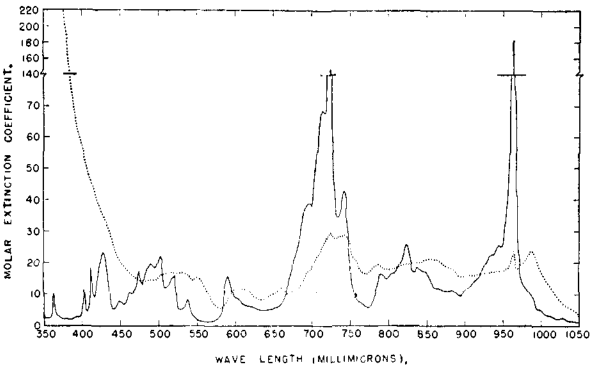

Fig. 8.—Effect of decrease in hydrogen ion concentration on the absorption spectrum of neptunium(IV): —, 1.00 *M* $HClO_4$; ....., *p*H 2.00.

Although the absorption spectra of the transuranium elements in solution resemble those of the analogous rare earths in general complexity of structure and sharpness of bands, there are certain points of difference. In the first place, the relative intensity of absorption is much greater for the principal bands of the transuranium elements than for the equivalent bands of the rare earths. In the case of the tripositive ions the intensity of absorption for the sharp characteristic bands is as much as ten times as great for the transuranium elements as for the rare earths. The transuranium element ions of higher charge show even more intense absorption, as much as a hundred times as great as for the tripositive rare earths. These observations suggest a much greater interaction between the external field and the electrons in the 5f shell of the transuranium elements, an interaction that is intensified in the stronger field of the ions of higher oxidation number. One might expect this to have two results: (1) the effect of change in the environment should be more readily detected in solutions of ions of the transuranium elements and (2) sufficient distortion of the transuranium element ion by an anion might actually result in a change in electronic configuration.

If it is assumed on the basis of the above discussion that the absorption spectra of these ions would be reasonably sensitive to a change in the external field, it would appear that the absence of

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(11) K. A. Kraus, Paper No. 3.16, "The Transuranium Elements," Vol. 14B of the Plutonium Project Record of the National Nuclear Energy Series, McGraw-Hill Book Co, Inc., New York, N. Y., 1949.

(12) (a) E. S. Kritchevsky and J. C. Hindman, THIS JOURNAL, **71**, 2096 (1949), also unpublished results on hydrolysis measurements of UCl_4 in perchlorate solution; (b) K. A. Kraus and F. Nelson, *ibid.*, **72**, 3901 (1950).

(13) J. C. Hindman and E. S. Kritchevsky, *ibid.*, **72**, 953 (1950).

(14) K. A. Kraus and J. R. Dam, Paper No. 4.14, "The Transuranium Elements," Vol. 14B of the Plutonium Project Record of the National Nuclear Energy Series, McGraw-Hill Book Co., Inc., New York, N. Y., 1949.

(15) G. T. Seaborg, Paper No. 21.1, "The Transuranium Elements," Vol. 14B of the Plutonium Project Record of the National Nuclear Energy Series, McGraw-Hill Book Co., Inc., New York, N. Y., 1949.

(16) J. H. Van Vleck, *J. Phys. Chem.*, **41**, 67 (1947).

(17) L. J. F. Broer, C. J. Gorter and J. Hoogschagen, *Physica*, **11**, 231 (1945).

any effect caused by increasing perchloric acid concentration on the absorption spectrum of neptunium(III) can reasonably be interpreted as indicating the absence of any complex formation. With respect to neptunium(IV) consideration of the relatively slight changes observed as compared with the marked effects found on hydrolysis or the changes found in other cases for the transuranium elements where complex formation is known to occur[4,18] suggests that at the most only a slight amount of complex formation has taken place. It is possible, although it is considered less likely, that the replacement of water molecules in the hydration sphere by perchlorate ions does not markedly affect the field. Another possible interpretation is that the spectral changes represent only a secondary effect. Since the observed spectral change is a decrease in absorption intensity it is perhaps due to a decrease in the asymmetric field caused by the disruption of the solution structure by the high perchloric acid concentration and the surrounding of the hydrated ion by a cloud of perchlorate ions.

In the case of neptunium(V) decreasing the acid concentration to *p*H 5.7 does not affect the spectrum. Further decrease in acid is only accompanied by precipitation of the neptunium(V) hydroxide. This behavior is consistent with the present view that Np(V) in acid solution exists as NpO_2^+[19] and that no intermediate ions exist between NpO_2^+ and NpO_2OH. It is more difficult to assess the effect of increasing acid concentration on the spectrum of neptunium(V) because of the disproportionation reaction occurring at high acid concentration. The only observed change in the spectrum was a decrease of approximately 10% in the peak height of the 983 mμ band in concentrated acid solutions.

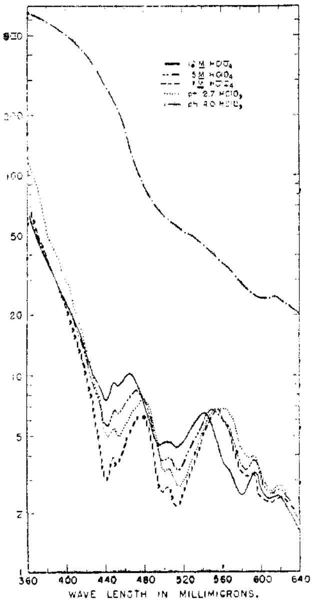

Fig. 9.—Influence of hydrogen ion concentration on the absorption spectra of neptunium(VI): —, Np(VI) in 10.0 *M* $HClO_4$; – – — – –, Np(VI) in 5.0 *M* $HClO_4$; – – – – – –, Np(VI) in 1 *M* $HClO_4$; .... Np(VI) in $HClO_4$ *p*H 2.7; ·—, Np(VI) in $HClO_4$ *p*H 4.0.

Figure 9 illustrates the effect of changing perchloric acid concentration on the spectrum of neptunium(VI). As in the case of uranium[1] and plutonium[20] decreasing the acid concentration sufficiently to cause hydrolysis causes marked changes in the absorption spectrum. These changes include the disappearance of the vibrational bands. Since the hydrolysis to form ions such as NpO_2OH^+ involves the formation of additional metal oxygen bonds with a consequent disruption of the symmetry of the neptunyl ion the disappearance of the vibrational structure is not unexpected.

The effect of increasing acid concentration on the neptunium(VI) spectrum is much less marked. The vibrational bands are not appreciably affected. The frequency interval found for the vibrational bands was 715 cm.$^{-1}$ in 1.0 *M* $HClO_4$, 709 cm.$^{-1}$ in 10 *M* $HClO_4$ and 704 cm.$^{-1}$ at *p*H 2.7 (in 1 *M* $NaClO_4$). In solutions of the uranyl ion, the effect of increasing the perchloric acid concentration is less marked than for neptunium(VI). There is a general decrease in absorption together with a general shift of all the absorption bands to the red without, however, affecting the frequency interval between the vibrational bands.

It is apparent from these observations that even at high perchloric acid concentrations ions of the type NpO^{+4} and UO^{+4} are not formed since the vibrational structure characteristic of the symmetrical vibrations in the $O{=}X^{++}{=}O$ ions persists. It is less easy to rule out the possibility that ions of the type $X(OH)_2^{+4}$ are formed. In this case, the situation might be considered as somewhat analogous to that existing in crystals of such salts as the double nitrates of uranium(VI). Depending on the strength of the hydrogen bonds we might then expect a shift in vibrational frequency similar to that found in going from one double nitrate to another. Since this would probably not exceed 10–25 cm.$^{-1}$, it might easily be undetected in the solution measurements. To elaborate this point other methods of investigation than the measurement of solution absorption spectra will have to be used.

Before concluding the discussion the deductions that can be made from the fact that the neptunium(V) ion disproportionates at high acid concentrations should be considered. In Table V various possible ions of neptunium(V) and (VI) are listed, together with the hydrogen ion functions that would be observed in each case for the reaction

$$2Np(V) + XH^+ \rightleftharpoons Np(IV) + Np(VI) + yH_2O \quad (3)$$

It can be seen by examination of Table V, that the maximum number of hydrogen ions involved in the disproportionation reaction could exceed four only if it were postulated that the neptunium(VI)

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(18) J. C. Hindman, Chap. IV, Vol. 14A of the Plutonium Project Record of the National Nuclear Energy Series, in preparation.

(19) L. B. Magnusson, J. C. Hindman and T. J. LaChapelle, "The Transuranium Elements," Paper No. 15.4 of Vol. 14B of the Plutonium Project Record of the National Nuclear Energy Series, McGraw-Hill Book Co., Inc., New York, N. Y., 1949.

(20) G. E. Moore and K. A. Kraus, Paper No. 4.22, "The Transuranium Elements," Vol. 14B of the Plutonium Project Record of the National Nuclear Energy Series McGraw-Hill Book Co., Inc., New York, N. Y., 1949.

TABLE V

POSSIBLE NEPTUNIUM ION SPECIES TAKING PART IN DISPROPORTIONATION REACTION

Possible ions of Neptunium			H^+ power	H_2O power
Np^{+4}	$NpO_2{}^+$	$NpO_2{}^{++}$	4	−2
Np^{+4}	$NpOOH^{+2}$	$NpO_2{}^{++}$	2	−2
Np^{+4}	NpO^{+3}, $Np(OH)_2{}^{+3}$	$NpO_2{}^{++}$	0	0, −2
Np^{+4}	$NpOH^{+4}$	$NpO_2{}^{++}$	−2	0
Np^{+4}	$NpO_2{}^+$	$NpOOH^{+3}$	5	−2
Np^{+4}	$NpOOH^{+2}$	$NpOOH^{+3}$	3	−2
Np^{+4}	$Np(OH)_2{}^{+3}$, NpO^{+3}	$NpOOH^{+3}$	1	0
Np^{+4}	$NpOH^{+4}$	$NpOOH^{+3}$	−1	0
Np^{+4}	$Np(OH)_2{}^{+3}$	$Np(OH)_2{}^{+4}$	2	−2
Np^{+4}	$Np(OH)^{+4}$	$Np(OH)_2{}^{+4}$	0	0

ion was more susceptible to reaction with hydrogen ion than the neptunium(V) ion. This would appear unlikely in view of the greater formal charge on the neptunium(VI) atom. Furthermore, from the previous discussion, the possibility of ions having fewer than two OH^- groups can also be excluded insofar as both neptunium(V) and neptunium(VI) are concerned. The fact that the disproportionation reaction occurs also eliminates those ion species giving a zero or inverse hydrogen ion function for the reaction. With these restrictions in mind reference can be made to the data on the disproportionation reaction summarized in Table IV. The constant for the reaction can be written in the form

$$K_1' = \frac{[\mathrm{Np(IV)}][\mathrm{Np(VI)}]}{[\mathrm{Np(V)}]^2[\mathrm{H}^+]^x} = K_1 \frac{\gamma^x_{\mathrm{H}^+}\gamma^2_{\mathrm{Np(V)}}}{\gamma_{\mathrm{Np(VI)}}\,\gamma_{\mathrm{Np(IV)}}\,[a_{\mathrm{H_2O}}]^y} \quad (4)$$

In the absence of any quantitative data on the activity coefficients of any of the neptunium ions, an approximate calculation of the hydrogen ion power on the assumption that the activity coefficient ratio $\gamma^2_{\mathrm{Np(V)}}/(\gamma_{\mathrm{Np(VI)}}\gamma_{\mathrm{Np(IV)}})$ is unity, neglecting the water activity term, and using the mean activity coefficients of perchloric acid from the data of Robinson and Baker[21] for the hydrogen ion activity gives an approximately third power hydrogen ion dependence between the 1.0 *M* and 5.34 *M* acid solutions. Although this might be interpreted as indicating the formulas $NpOOH^{+2}$ and $NpOOH^{+3}$ for the neptunium(V) and (VI) ions, respectively, in view of the rather drastic assumptions involved this cannot be taken as conclusive. Further investigations of the disproportionation reaction at constant ionic strength are contemplated to settle the question.

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[21] R. A. Robinson and O. J. Baker, *Trans. Royal Soc. New Zealand*, **76**, 250 (1946).

CHICAGO, ILL. RECEIVED SEPTEMBER 14, 1950

[CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORY, METAL HYDRIDES, INC.]

The Titanium–Hydrogen System and Titanium Hydride. II. Studies at High Pressure

BY THOMAS R. P. GIBB, JR., JAMES J. MCSHARRY AND ROBERT W. BRAGDON

The equilibrium pressure of hydrogen over the metallic titanium–hydrogen system has been measured as a function of the hydrogen content of the solid phase. Measurements have been made over the range 175 to 1000° at pressures ranging up to 5,000 cm. and the results plotted as log *P* *vs.* reciprocal of absolute temperature. A series of straight lines is obtained whose slope increases with decreasing hydrogen content. From these slopes the differential heats of dissociation are calculated. A family of isotherms shows plateaus at compositions approaching TiH_2 indicating presence of a novel phase.

In the first paper of this series[1] it was shown that titanium hydride has an unexpectedly high dissociation pressure. Moreover, the equilibrium pressures above various hydrogen-rich compositions in the Ti–H system were found to exceed the feasible limits of conventional equipment at temperatures of the order of a few hundred degrees. Accordingly a special apparatus was constructed and a technique devised for study of the system over a wide range of conditions. The work reported in this paper includes (1) the design of a special apparatus for investigation up to 1000 p.s.i. at temperatures up to 1000°, (2) a presentation of the results obtained, (3) a discussion of the theoretical implications thereof, and (4) calculation of the heat of dissociation and allied thermodynamic quantities.

Method.—The procedure employed for measurement of dissociation pressure is relatively simple: Titanium hydride, either formed *in situ* or previously, is contained in three bombs D (Fig. 1) attached by capillary tubing to a manifold consisting of recording pressure gages B, B′, B″, C, a calibrated reservoir J, and a hydrogen-purifying train GG′. All volumes are measured by a pressure-drop method employing a manometer–reservoir system A.

Measurement of dissociation pressure is made as follows: a quantity of purified hydrogen at moderately high pressure is admitted to the evacuated and previously purged system. The bombs of hydride are then heated slowly and the pressure developed plotted as a function of temperature as in Fig. 2. The lower left-hand portions of each curve represent thermal expansion. These portions are close to linear except in the vicinity of 140° where there is a barely perceptible dip of unknown origin. The time required at any temperature or pressure for attainment of equilibrium varies from a few minutes to an hour or more depending on these variables and also on the composition and previous thermal history of the sample. The intersection of the nearly linear thermal expansion curve with the steeper portion is taken as the point at which the solid phase just starts to dissociate. This point is assumed to represent the dissociation pressure of TiH_2. From the curved portions of the plots shown in Fig. 2, the equilibrium pressure for various compositions may be ascertained. The exact composition represented by any point on this curve is calculated from the known volume and pressure, *i.e.*, the amount of gaseous hydrogen present in excess of that introduced originally is calculated and subtracted from the amount of hydrogen originally present in the stoichiometric hydride to give the composition of the solid phase at the temperature and pressure in question. Since any point on the curved portions of Fig. 2 represents an equilibrium state, the result of the above calculation gives a composition of the Ti–H_2 system at equilibrium with the hydrogen above it at the temperature and pressure chosen.

In the higher pressure and temperature regions, one

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[1] Thomas R. P. Gibb, Jr., and Henry W. Kruschwitz, Jr., THIS JOURNAL, **72**, 5365 (1950).