[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, BROOKHAVEN NATIONAL LABORATORY]

Low Temperature Mobility of Hydrogen in Uranium Hydride. Exchange Equilibrium of Deuterium between Hydrogen and Uranium Hydride[1]

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It is shown that $UH_3(s)$ and D_2 undergo rapid isotopic exchange at and below room temperature. The reaction is diffusion controlled in the solid. The equilibrium constant for the reaction $UH_3(s) + HD(g) = UH_2D(s) + H_2(g)$ has been measured between 195 and 433°K. The difference in enthalpies between UH_3 and UH_2D is found to be 1186 cal. mole^{-1} at 200°K. The calculated entropy change for the reaction at 200°K. is in good agreement with experiment. A discussion is presented to show why the ratio of the dissociation pressures of UH_3 and UD_3 is independent of temperature between 530 and 700°K.

In the course of the development of the uranium reactor for the conversion of hydrogenic materials to hydrogen for isotopic analysis,[2] we were led to postulate a rapid isotopic interchange between uranium hydride and hydrogen at room temperature. This exchange reaction would be expected to be rapid at elevated temperatures, say above 250°, where the dissociation equilibrium of the hydride into hydrogen is readily established. This process provides a simple mechanism for the exchange. Some preliminary kinetic runs, performed at room temperature by circulating hydrogen enriched in deuterium through a 2-cm. bed of uranium hydride, confirmed our postulate concerning the rapid exchange. Furthermore it was established that the exchange was not limited to the surface of the solid particles, but was complete throughout. The rate of exchange did not follow the simple McKay law observed in homogeneous systems but fell off as the reaction progressed. A typical rate curve is shown in Fig. 1.

The observed kinetic behavior can be explained by the assumption that the rate of exchange is determined by some diffusion process, possibly hydrogen as the diffusing species, in the solid. Such a process is not expected to obey the McKay law even for particles of uniform size.[3,4] The observed rate, as shown in Fig. 1, can be represented by the rate law derived for diffusion controlled reactions.[4] A detailed study of the rate of the reaction has not been undertaken because of the inherent difficulty in determining the particle size distribution of the uranium hydride powder. However, the experiments have been carried sufficiently far to indicate that the diffusion constant of the diffusate is not abnormally large, but rather that the rapid exchange is primarily due to the small particle size of the uranium hydride. The activation energy for the diffusion process is less than 10 kcal. mole^{-1}.

Isotopic analyses of samples of the hydrogen gas in exchange equilibrium with the uranium hydride at room temperature indicated a small fractionation of deuterium between the two phases. A series of experiments was designed to measure this fractionation as a function of temperature.

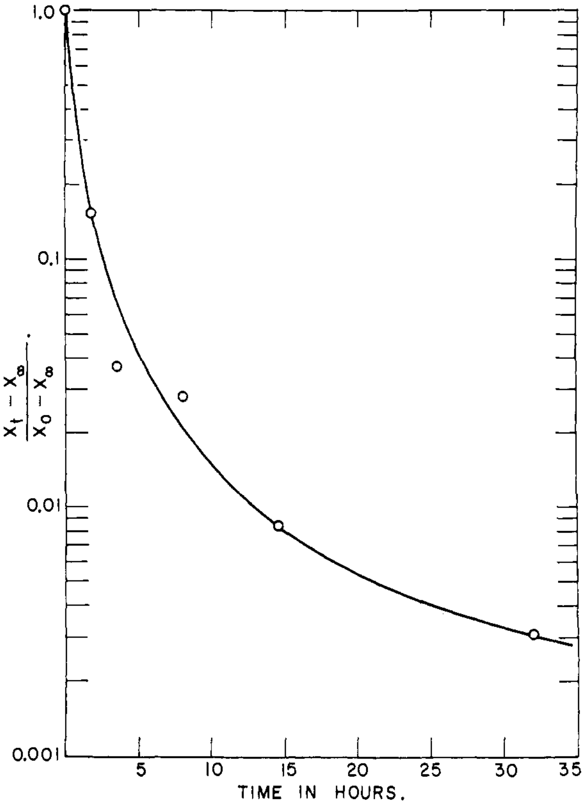

Fig. 1.—Plot of log (1 − fraction exchange) *vs.* time for the exchange between $UH_3(s)$ and $D_2(g)$ at 22° (X is the atom fraction of deuterium in the gas phase).

Equilibrium Experiments

The experiments were designed so as to facilitate the measurement of a fractionation factor close to unity. A tank of hydrogen containing approximately 0.7 atom per cent. deuterium in the form of HD was prepared by the dilution of dry HD with normal hydrogen. The HD was prepared by the deuterolysis of lithium aluminum hydride.[5] An aliquot of the enriched hydrogen was then used to prepare uranium hydride of the same isotopic composition. About ten grams of uranium turnings, cleaned with nitric acid, distilled water and finally acetone was contained in a Pyrex tube between two fine sintered glass discs. The system was then pumped with a mercury diffusion pump overnight while the metal was maintained at a temperature of 250°. The metal was then powdered by a hydriding-dehydriding cycle. A stoichiometric quantity of hydrogen 2.97 moles of hydrogen per mole of uranium, enriched in HD was then added in small batches to convert the uranium to uranium hydride. This conversion was carried out at room temperature. To avoid isotopic fractionation care was exercised near the end of the reaction to avoid having any appreciable amount of hydrogen in the gas phase. The uranium hydride thus prepared has the isotopic composition of the "tank gas."

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[1] Research carried out at the Brookhaven National Laboratory under the auspices of the U. S. Atomic Energy Commission.

[2] J. Bigeleisen, M. L. Perlman and H. C. Prosser, *Anal. Chem*, **24**, 1356 (1952).

[3] K. E. Zimens, *Arkiv Chem. Mineral.*, 20 (1945).

[4] A. Kant, unpublished.

[5] I. Wender, R. A. Friedel and M. Orchin, THIS JOURNAL, **71**, 1140 (1949).

The vessel containing the uranium hydride was immersed in a thermostat and then about 70 cc. (N.T.P.) of "tank gas" was continuously circulated over the uranium hydride by means of an automatic Toepler pump. Small samples of hydrogen were removed from time to time for isotopic analysis. Since both phases have the same initial isotopic composition, and the uranium hydride phase is in considerable excess, and since the isotopic fractionation factor is close to unity, the isotopic composition of the uranium hydride at equilibrium can be taken as the same as its initial composition, or that of "tank gas." The hydrogen samples were analyzed for deuterium mass spectrometrically by intercomparison with samples of "tank gas" and standards.[6] The final analyses were made on samples which were within 1% of the equilibrium composition. In some cases equilibrium was approached from both directions. At −80° the "half-time" for exchange was about one day. After circulation for seven days at this temperature the hydrogen was deemed to be in equilibrium and no changes in isotopic composition could be detected. In another experiment at −80° it was found that the rate of exchange of H_2 and D_2 catalyzed by UH_3 was many fold more rapid than the exchange with the solid. This observation is in agreement with the diffusion controlled mechanism. At 77°K. there is no measurable exchange between solid and gas in a week.

Results and Discussion

The results of the equilibrium experiments are given in Table I. The method of calculation of the equilibrium constant for the reaction

$$HD(g) + UH_3(s) = H_2(g) + UH_2D(s) \qquad (1)$$

from the isotopic composition is entirely analogous to that for the NH_3–HD exchange.[7] Figure 2 shows a plot of log K_1 vs. $1/T$ from the present equilibrium measurements together with calculations based on the dissociation pressures of UH_3 and UD_3.[8]

TABLE I

EQUILIBRIUM IN THE REACTION $HD(g) + UH_3(s) = H_2(g) + UH_2D(s)$

T, °K.	$D_s \times 10^{3\,a}$	$D_g \times 10^{3\,b}$	$K \pm 0.01$
195	7.73	5.69	2.04
301	7.73	7.70	1.51
381	7.73	8.42	1.38
433	7.73	8.64	1.34

[a] D_s—atom fraction of D in UH_3. [b] D_g—atom fraction of D in H_2.

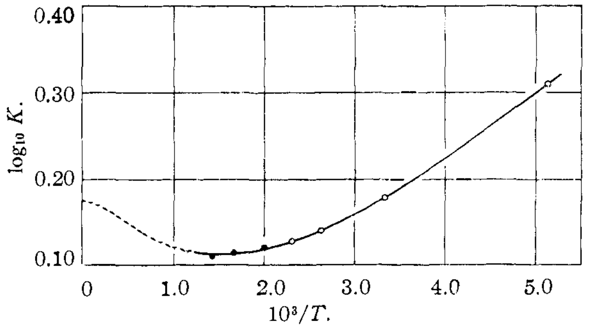

Fig. 2.—Equilibrium plot of log K vs. $1/T$ for the reaction $UH_3(s) + HD(g) = UH_2D(s) + H_2(g)$; ○, this research; ●, calculated from the dissociation pressures of UH_3 and UD_3.

The dissociation equilibria, which have been measured in the temperature interval between 530 and 700°K. by Spedding, *et al.*,[8] are related to the exchange equilibrium by the equations

$$UH_3(s) = U(s) + 3/2H_2(g) \qquad (2)$$

$$U(s) + 3/2D_2 = UD_3(s) \qquad (3)$$

$$UD_3(s) + 2UH_3(s) = 3UH_2D(s) \qquad (4)$$

$$HD(g) = 1/2H_2(g) + 1/2D_2(g) \qquad (5)$$

These lead to

$$K_1^3 = K_2K_3K_4K_5^3 \qquad (6)$$

The equilibrium constant K_4 is expected, by the rule of the geometric mean, to be the statistical one, 27. This is confirmed, in the present case, by the dissociation pressures of UH_3–UT_3 mixtures,[9] which have been studied as a function of the mole fraction of tritium. K_5 is the well known disproportionation equilibrium constant of HD.[10] Thus $K_1 = 3(P_{H_2}/P_{D_2})^{1/2}K_5$. Spedding, *et al.*,[8] give $P_{H_2}/P_{D_2} = 0.720$ at 630°K. and find the ratio of the dissociation pressures independent of temperature in the range 530–700°K. Flotow and Abraham[9] find, similarly, that the ratio of the dissociation pressures of UH_3 and UT_3 is independent of temperature. The value of $(P_{H_2}/P_{D_2}) = 0.720$ leads to a value of K_1 which is about 1.6% higher than that extrapolated from our equilibrium measurements. A small, 1–2%, contamination of protium in the deuterium in the dissociation measurements would lead to just such a discrepancy. For the calculation of K_1 from the dissociation measurements we have, therefore, used a value of $P_{H_2}/P_{D_2} = 0.698$.

We may note that both the exchange experiments and the measurements of the dissociation pressures were carried out without regard to the existence of two forms of UH_3.[11,12] In the exchange experiments measurements were made on samples which should have contained varying amounts of the α form. No effect of sample preparation or method of approach to equilibrium was found on K_1. We assume, therefore, that the effect of crystal structure on K_1 is probably less than 1%.

The behavior of K_1 as a function of temperature is a rather interesting one. At low temperatures we find from Fig. 2 that

$$K_1 = 0.815e^{179/T} \qquad (7)$$

Equation 7 when combined with the enthalpy difference $(H^\circ_{e-H_2} - H^\circ_{HD})_{200°K.}$ for hydrogen[13] leads to $(H^\circ_{UH_3} - H^\circ_{UH_2D})_{200°K.} = 1186$ cal. mole^{-1}. In calculating the enthalpy difference of the hydrogen isotopes it is significant to note that the rotational correction[14] based on the Euler–Maclaurin summation is inadequate below room temperature. At room temperature and above, eq. 10 given by Bigeleisen[14] is applicable. Just above room temperature K_1 falls below the statistical value of 3/2, passes through a minimum at about 650°K., and

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(6) *Cf.* R. E. Weston, Jr., and J. Bigeleisen, *J. Chem. Phys.*, **20**, 1400 (1952).

(7) M. L. Perlman, J. Bigeleisen and N. Elliott, *J. Chem. Phys.*, **21**, 70 (1953).

(8) F. H. Spedding, A. S. Newton, J. C. Warf, O. Johnson, R. W. Nottorf, I. B Johns and A. H. Daane, *Nucleonics*, **4**, 4 (1949).

(9) H. Flotow and B. M. Abraham, AECD-3074, Jan. 5, 1951.

(10) H. C. Urey, *J. Chem. Soc.*, 562 (1947).

(11) R. N. R. Mulford, F. H. Ellinger and W. H. Zachariasen, AECU 2700.

(12) R. Caillat, H. Coriou and P. Pério, *Compt. rend.*, **237**, 812 (1953).

(13) H. W. Woolley, R. B. Scott and F. G. Brickwedde, *J. Research Natl. Bur. Standards*, **41**, 379 (1948).

(14) J. Bigeleisen, *J. Chem. Phys.*, **21**, 1333 (1953).

then of course must approach the statistical value of 3/2 at high temperatures.

This temperature dependence is readily understood in terms of the structures and molecular parameters of UH_3 and H_2. The vibrational frequency of HD is approximately $\sqrt{3/2}$ that of H_2, whereas the frequencies in UH_3 which are affected by the replacement of one hydrogen by deuterium are reduced roughly by a factor of $\sqrt{2}$. Thus in spite of the large zero point energy of hydrogen, $(H^\circ_{0\,\mathrm{UH_3}} - H^\circ_{0\,\mathrm{UH_2D}})$ is greater than $(H^\circ_{0\,\mathrm{H_2}} - H^\circ_{0\,\mathrm{HD}})$. By the same argument however

$$\prod^{12N} \frac{\omega_{i\mathrm{UH_2D}}}{\omega_{i\mathrm{UH_3}}} < \left(\frac{\omega_{i\mathrm{HD}}}{\omega_{i\mathrm{H_2}}}\right)^N$$

Since the temperature independent factor in equation 7, defined as A, can be expressed in terms of the frequencies of UH_3, UH_2D, H_2 and HD by the relation

$$A = \frac{3}{2}\left(\prod_i^{12N} \frac{\omega_{i\mathrm{UH_2D}}}{\omega_{i\mathrm{UH_3}}}\right)^{1/N} \Big/ \left(\frac{\omega_{\mathrm{HD}}}{\omega_{\mathrm{H_2}}}\right) \qquad (8)$$

its value is less than the statistical one. Because of the small heat of reaction, the fact that A is less than 3/2 causes K to drop below the statistical value at room temperature. At high temperatures the excitation of the vibrations in the solid and gas must be taken into consideration and

$$K_1 = \frac{3}{2}\left[\prod_i^{12N} \frac{\omega_{i\mathrm{UH_2D}}}{\omega_{i\mathrm{UH_3}}} \frac{(1 - e^{-U_{i\mathrm{UH_3}}})}{(1 - e^{-U_{i\mathrm{UH_2D}}})}\right]^{1/N} \times \frac{\omega_{\mathrm{H_2}}}{\omega_{\mathrm{HD}}} \frac{(1 - e^{-U_{\mathrm{HD}}})}{(1 - e^{-U_{\mathrm{H_2}}})} \times e[(H^\circ_{0\,\mathrm{UH_3}} - H^\circ_{0\,\mathrm{UH_2D}}) - (H^\circ_{0\,\mathrm{H_2}} - H^\circ_{0\,\mathrm{HD}})]/RT \qquad (9)$$

This equation, which is the ratio of partition function ratios, is readily derived by combination of the partition function ratio of isotopic solids with the ratio for a gas.[15] The partition function ratio for isotopic solids is derived by the method of Bigeleisen and Mayer[15] for a solid consisting of harmonic oscillators with an arbitrary frequency distribution.

The factor

$$\left[\prod_i^{12N} (1 - e^{-U_{i\mathrm{UH_3}}})/(1 - e^{-U_{i\mathrm{UH_2D}}})^{1/N}\right]$$

is unity or greater since the frequencies in UH_2D reach the equipartition distribution at lower temperatures than the corresponding frequencies in UH_3. This accounts for the minimum in log K *vs.* $1/T$. The corresponding inverse factor for the hydrogen molecule contributes less than 1% to K_1 up to 1500°K. The asymptotic approach of K_1 to 3/2 needs no further amplification.

If we assume that those frequencies in solid UH_3 that are shifted by deuterium substitution for hydrogen are lowered by a factor of $\sqrt{2}$, then from the position of the minimum in the plot of log K *vs.* $1/T$ and the experimentally determined value of $\Delta H^\circ_{200°}$ for the reaction, one finds that there must be two or more vibrational frequencies for each UH_3 "molecule" in the lattice between 400 and 1500 cm.$^{-1}$. The minimum at 650°K. cannot be explained by one frequency per UH_3 "molecule," whereas two frequencies suffice. This is not at all an unreasonable frequency range.

The existence of two frequencies in UH_3 in the range of 400–1500 cm.$^{-1}$ together with the fact that the zero point energy difference between UH_3 and UH_2D is only 356 cal. mole^{-1} greater than the difference between H_2 and HD, suffices to explain the somewhat surprising independence of the ratio of the dissociation pressures of UH_3 and UH_2D on temperature. From equation 6 we obtain

$$\frac{\partial \ln (P_{\mathrm{H_2}}/P_{\mathrm{D_2}})}{\partial (1/T)} = 2\left(\frac{\partial \ln K_1}{\partial (1/T)} - \frac{\partial \ln K_5}{\partial (1/T)}\right) \qquad (10)$$

From Fig. 2 and the discussion above we find $\partial \ln K_1/\partial(1/T) \simeq 0$ between 500–1000°K. In this temperature range $\partial \ln K_5/\partial(1/T) = 40.6°$. This leads to an immeasurably small difference in the heats of dissociation of UH_3 and UD_3 between 500–1000°K.

By intercomparison of equations 7 and 8, together with the known ratio of $\omega_{\mathrm{HD}}/\omega_{\mathrm{H_2}}$,[14] we find

$$\left(\prod_i^{12N} \frac{\omega_{i\mathrm{UH_2D}}}{\omega_{i\mathrm{UH_3}}}\right)^{1/N} = 0.471 \qquad (11)$$

An approximate calculation of this product ratio can be made as follows. We consider the hypothetical gaseous UH_3 molecule with structural parameters as determined by Mulford, Ellinger and Zachariasen.[11] From these and the Teller–Redlich product rule[16] one finds

$$\prod_i^{6} \frac{\omega_{i\mathrm{UH_2D}}}{\omega_{i\mathrm{UH_3}}} = 0.454 \qquad (12)$$

If we now assume that the translations and rotations of the hypothetical gaseous UH_3 molecule give rise to vibrations in the acoustical range, then these vibrations will be excited to the full equipartition value at all temperatures above 200°K. Their contribution to K_1 will exactly cancel and

$$\left(\prod_i^{12N} \frac{\omega_{i\mathrm{UH_2D}}}{\omega_{i\mathrm{UH_3}}}\right)^{1/N} \simeq \prod_i^{6} \frac{\omega_{i\mathrm{UH_2D}}}{\omega_{i\mathrm{UH_3}}} \qquad (13)$$

If we draw an analogy with the computations of Sayre and Beaver[17] on the vibrational spectra of NaH(s) and NaD(s), they find no isotope effect in the acoustical branch of the lattice frequency distribution. This would again serve to reduce any effect of the acoustical branch on the ratio of the product of the frequencies. The fact that equation 13 is satisfied within 3%, almost the experimental error, is not too surprising therefore.

From $\Delta H^\circ_{298\cdot16}$ for the exchange reaction between $UH_3(s)$ and HD(g), $(H^\circ_{\mathrm{H_2}} - H^\circ_{\mathrm{HD}})_{298\cdot16}$,[14] $(H^\circ_{\mathrm{H_2}} - H^\circ_{\mathrm{D_2}})_{298\cdot16}$[14] and the rule of the geometric mean, *i.e.*, $(H^\circ_{\mathrm{UH_3}} - H^\circ_{\mathrm{UD_3}})_{298\cdot16} = 3\,(H^\circ_{\mathrm{UH_3}} - H^\circ_{\mathrm{UH_2D}})$, we obtain the heat of the reaction

$$UH_3 + 3/2D_2 = UD_3 + 3/2H_2$$
$$\Delta H^\circ_{298.61} = -641 \pm 50 \text{ cal.} \qquad (14)$$

The uncertainty in $\Delta H^\circ_{298\cdot16}$[14] is an estimate of the error introduced by the use of the rule of the geometric mean. This value may be compared with the calorimetric determinations of Abraham and Flotow.[18] These workers have determined the heats of formation of UH_3 and UD_3 to be −30, 352 ± 30 cal. mole^{-1} and −31, 021 ± 30 cal.

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[15] J. Bigeleisen and M. G. Mayer, *J. Chem. Phys.*, **15**, 261 (1947).

[16] *Cf.* O. Redlich, *Z. physik. Chem.*, **B28**, 371 (1935).

[17] E. V. Sayre and J. J. Beaver, *J. Chem. Phys.*, **18**, 584 (1950).

[18] B. M. Abraham and H. Flotow, unpublished.

mole^{-1}, respectively, at 298.16°K. These heats of formations lead to $\Delta H^{\circ}_{298.16}{}^{14} = -669 \pm 45$ cal. The close agreement between the calorimetric heat and that calculated from $\partial \ln K_1/\partial\, 1/T$ substantiates our conclusion that the free energy difference between UH_3 and UH_2D does not appreciably depend on the relative amounts of α and β forms of UH_3.

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[CONTRIBUTION FROM BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

The Kinetics of the Exchange of Water between $Cr(H_2O)_6{}^{+3}$ and Solvent

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Measurements of the exchange of water between solvent and $Cr(H_2O)_6{}^{+3}$ have been extended to dilute solution. The rate is best expressed as rate $= k_1(Cr(H_2O)_6{}^{+3})$ over a wide range of ionic strength. k_1 increases slightly with ionic strength and has an average value at infinite dilution of 2.07×10^{-4} min.$^{-1}$ at 27° in both nitrate and perchlorate solutions. An activation energy of 27.6 kcal./mole is found at 0.7 molar ionic strength.

Investigation of the rate of substitution of water for water in aquo ions is of fundamental importance in understanding substitution reactions in complex ions. A start has been made by studying the water exchange reaction of $Cr(H_2O)_6{}^{+3}$.[1,2] These studies, limited to concentrated solutions, suggested the rate law: rate $= k_2(Cr(H_2O)_6{}^{+3})$(anion). Values of k_2 were surprisingly independent of ionic environment. The present authors have extended the measurements to more dilute solutions enabling more rigorous testing of rate laws. As has been pointed out,[1] comparisons of rates of water exchange with rates of complex ion formation reactions can give information regarding mechanisms and the present data should be more useful in this connection.

Experimental

The general procedure and methods have been described previously.[2] H_2O^{18} again was used as the tracer.

The significant innovation in experimental procedure involved sampling by precipitation and ignition of $CrPO_4 \cdot 6H_2O$. The basic process used was as follows. To 10 ml. of solution at room temperature and 0.1 *M* in Cr^{+3}, 0.1 *M* in H^+ was added solid $NaH_2PO_4 \cdot H_2O$ in 10% excess with vigorous stirring. After solution occurred (*ca.* 1 min.) solid $NaC_2H_3O_2$ was added until the *p*H was 5. The resulting slurry was stirred 5 min., the lavender solid filtered on a Hirsch funnel, washed 5 times with ordinary distilled water, and dried 20 min. by sucking air through the filter. The powder was further dried over $CaSO_4$ in a vacuum desiccator for 40 min.

Modification of the precipitation was necessary when Cr^{+3} was < 0.1 *M* or $H^+ > 0.1$ *M* or total anion concentration > 1.0 *M*. For some samples dilution with ordinary distilled water was sufficient to obtain the basic conditions. If Cr^{+3} was < 0.1 *M*, Na_2HPO_4 replaced $NaH_2PO_4 \cdot H_2O$. With $H^+ > 0.1$ *M* or anion concentration > 1.0 *M* after dilution to 0.1 *M* Cr^{+3}, Na_2HPO_4 again replaced $NaH_2PO_4 \cdot H_2O$.

Chemical analyses of the dry solids showed that they were indeed $CrPO_4 \cdot 6H_2O$.

Tracer experiments showed that *ca.* 1% "induced exchange" occurred during precipitation, the amount of exchange being reproducible with constant conditions of precipitation, varying slightly from run to run as these conditions changed.

The ignition of $CrPO_4 \cdot 6H_2O$ to $CrPO_4 + 6H_2O$ was carried out as follows: 0.25 g. in a small Pt boat was placed in a horizontal Pt crucible. The latter was inserted in a horizontal Vycor tube which was then attached to a vacuum line. The Vycor tube could be heated by means of a tube furnace. Next, the solid was outgassed for 20 min. by pumping at 10^{-5} mm. Dry, oxygen-free, N_2 was then admitted to 1 atm. pressure (this was necessary to prevent loss of sample from the boat during the initial heating). The temperature of the sample was raised to 160° in 15 min. following a time schedule, then held constant at 160° for 20 min. *Ca.* $4H_2O/Cr$ had been evolved at this stage and collected in a cool portion of the Vycor tube. The N_2 and H_2O were pumped off through a $-180°$ trap, collecting the H_2O. Ignition was continued at 10^{-5} mm., raising the temperature to 750° in 30 min. according to a fixed time schedule. This temperature was maintained for 10 min. The final $2H_2O/Cr$ were trapped out continuously during this 40-min. period. Total H_2O was transferred to a sample tube and equilibrated with CO_2 for mass spectrometer analysis.[2]

Tracer studies showed that exchange of oxygen between phosphate and H_2O occurred above 160°. Because of this, $15.2 \pm 0.4\%$ of the oxygen in the final sample was derived from phosphate.

Materials.—Chromic perchlorate was made by reducing CrO_3 in $HClO_4$ with 30% H_2O_2. Excess H_2O_2 was destroyed by heating in the presence of platinized Pt. The solution was evaporated to crystals and these were recrystallized from H_2O. Another source of the chromic salt was commerical reagent recrystallized from H_2O. Results were independent of the source of the salt. Sodium perchlorate was made from NaOH and $HClO_4$.[3] $(C_2H_5)_4NBr$ was recrystallized from absolute C_2H_5OH. All water was redistilled from alkaline permanganate and then from Pyrex. The 1.5% H_2O^{18} used was purchased from the Stuart Oxygen Company through the A. E. C. Starting materials were the best commercial grades available used without further purification unless noted above.

Treatment of Data.—The rate of the chemical reaction producing the isotope exchange was calculated from the mass spectrometer data by methods described previously.[2] All calculations ignore isotope effects on the rate.

Values of k_1 reported are based on the expression: rate $= k_1(Cr(H_2O)_6{}^{+3})$, and those of k_2 on the expression: rate $= k_2(Cr(H_2O)_6{}^{+3})$ (anion). The concentration of H_2O could not be varied sufficiently or independently enough to justify inclusion in rate laws. The *k*'s as calculated refer to the exchange of all $6H_2O$.

All concentrations are expressed in molar units. μ refers to molar ionic strength.

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(1) J. P. Hunt and H. Taube, *J. Chem. Phys.*, **19**, 602 (1951).

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(3) H. F. Walton, "Inorganic Preparations," Prentice-Hall, Inc., New York, N. Y., 1948, p. 72.