[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA, LOS ANGELES]

Decomposition of Hexachloro-μ-trichloroditungstate(III) Ion and Exchange of Radiochlorine between this Ion and Chloride Ion in Aqueous Solution[1]

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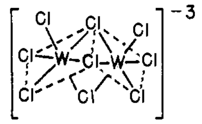
In HCl and HCl–H_2SO_4 solutions of essentially constant acidity and constant chloride ion concentration, the rate of conversion of $W_2Cl_9^{-3}$ to other forms of W(III) and to higher oxidation states appears to be first order in $W_2Cl_9^{-3}$ with a rate constant of *ca.* 3×10^{-6} sec.$^{-1}$ at 25° over a range 0.01–0.26 *f* initial concentration of $W_2Cl_9^{-3}$. The rate apparently does not depend strongly on the concentration of HCl in the range 0.8–12.6 *f* and of H_2SO_4 in the range 0–6 *f*. Up to 10% of the $W_2Cl_9^{-3}$ is converted to other forms of W(III) under some of these conditions. Catalytic effects may have influenced the results. Rates of exchange of radiochlorine between $W_2Cl_9^{-3}$ and Cl^- were measured in HCl solutions under conditions where the decomposition was much slower. All nine chlorine atoms of $W_2Cl_9^{-3}$ were shown to be kinetically equivalent in the exchange despite their structural non-equivalence. The data do not permit selection between the rate laws $R = k_1 \cdot (W_2Cl_9^{-3})$ and $R = k_2(W_2Cl_9^{-3})(Cl^-)$ because of the high concentrations of HCl used to minimize decomposition rates and because the data are not sufficiently accurate. At 25° $k_1 \sim 2 \times 10^{-4}$ sec.$^{-1}$ and $k_2 \sim 2 \times 10^{-5}$ l. mole^{-1} sec.$^{-1}$ over the range 0.11–0.26 *f* $H_3W_2Cl_9$ and 9.9–12.6 *f* HCl. Methods were developed for separating $W_2Cl_9^{-3}$ and Cl^-.

Substitution reactions of the hexachloro-μ-trichloroditungstate(III) ion,[2] $W_2Cl_9^{-3}$, are known[3] to be slow. Accordingly, the exchange of radiochlorine between this complex and free chloride ion in aqueous solution should be slow and under favorable conditions may be accessible to a kinetic study. Moreover, consideration of the double-fused-octahedral geometry[4] of $W_2Cl_9^{-3}$ suggests that



there may exist a difference in exchange lability of the three bridge chlorine atoms from the remaining six non-bridge chlorine atoms.

Hence, we have investigated the rate of conversion of the hexachloro-μ-trichloroditungstate(III) ion into other species of tungsten(III) and into higher oxidation states in various aqueous solutions in an effort to find conditions which would permit kinetic measurements and examination of the relative exchange labilities of the bridge and non-bridge chlorine atoms in this complex ion. The rate of exchange of radiochlorine between this complex ion and free chloride ion has been studied for several aqueous solutions in which the decomposition of the complex ion is relatively slow.

Experimental

Radiochlorine Tracer.—Radiochlorine-36 (310,000-year half-life), produced by (n,γ) reaction on potassium chloride, was obtained in a radiochemically purified form as a 1.6 *f* hydrochloric acid solution from the Oak Ridge National Laboratory. Tests showed that all the radioactivity was present as chloride ion of long half-life.

Potassium Hexachloro-μ-trichloroditungstate(III).—This substance was prepared by the electrolytic method of Collenberg (*alias* Olsson), *et al.*,[5,6] as modified by Goodenow and Garner.[7] The crude product was recrystallized twice from 80% ethanol and the resulting olive-green crystals washed twice with 95% ethanol, three times with absolute ethanol, then with ether, all under a nitrogen atmosphere. The compound was dried at 110° in a vacuum oven which was preflushed with nitrogen, then stored over magnesium perchlorate in an evacuated desiccator kept in the dark. Several lots were prepared during the course of the research.

Purity of the several lots was checked by titration of weighed samples with standardized potassium permanganate, using Zimmermann–Reinhardt "preventative" solution, by the method of Olsson[8] and by determination of total chlorine in weighed samples by the method of Bernhardi-Grisson,[9] the values falling in the range 98–100% purity. Some decomposition of the dried compound was sometimes noted after about one month; repurification was then undertaken before use of such lots.

Other Reagents.—Tetramethylammonium and tetraethylammonium sulfates were prepared by metathesis of the commercial chlorides with silver sulfate and recrystallized from water by evaporation of most of the water with an air stream, followed by drying the crystals over magnesium perchlorate in a vacuum desiccator. Tests with silver nitrate showed these compounds were free of chloride ion. All other chemicals were C.P. or reagent grade. All distilled water and all aqueous acid solutions employed were freed from dissolved oxygen shortly before use by gentle boiling and cooling in a nitrogen atmosphere.

Decomposition Studies.—Solutions of the complex in various acids were prepared and the rate of conversion of $W_2Cl_9^{-3}$ into other forms studied, using a nitrogen atmosphere to protect the complex against oxidation by oxygen. Conversion into tungsten oxidation states greater than +3 was followed by titrations with standardized potassium permanganate, using Zimmermann–Reinhardt solution.[8] Conversion into other forms of tungsten(III) as well as into higher oxidation states was followed by scanning the absorption spectra of the solutions over the range 350–700 mμ with a Cary Model 11 recording spectrophotometer and by determining the absorbancies of the absorption peaks at 452 mμ (green $W_2Cl_9^{-3}$) and 515 mμ (red W(III), possibly $W_3Cl_{14}^{-5}$) with a Beckman Model B spectrophotometer. The spectrum of $W_2Cl_9^{-3}$ was found to agree with that reported for "green tungsten(III)" by Lingane and Small,[10] who also reported a spectrum for "red tungsten(III)" which has almost no absorption at the 452-mμ peak of $W_2Cl_9^{-3}$. We found that Beer's law was obeyed over the range of interest, 0.07–0.5 millimolar in $W_2Cl_9^{-3}$, at the 452-mμ peak. Decomposition rates were also followed for exchange solutions during some of the exchange runs.

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[1] Presented in part at the 133rd National Meeting of A.C.S., San Francisco, California, April 1958. This investigation partly supported by U. S. Atomic Energy Commission under Contract AT(11-1)-34, Project No. 12.

[2] Most authors have referred to this ion as the "enneachloroditungstate(III) ion." The name used in this article follows the nomenclature rules of the Committee on Inorganic Nomenclature of the International Union of Chemistry as supplemented by the more recent proposals of Fernelius, Larsen, Marchi and Rollinson, *Chem. Eng. News*, **26**, 520 (1948), Rule VI, for "bridge" coördination compounds.

[3] O. Collenberg and K. Sandved, *Z. anorg. allgem. Chem.*, **130**, 1 (1923).

[4] C. Brosset, *Arkiv Kemi, Mineral. Geol.*, **12A**, No. 4 (1936); L. Pauling, *Chem. Eng. News*, **25**, 2970 (1947).

[5] O. Olsson, *Z. anorg. Chem.*, **88**, 49 (1914).

[6] O. Collenberg and A. Guthe, *Z. anorg. allgem. Chem.*, **134**, 317 (1924); O. Collenberg and J. Backer, *Z. Elektrochem.*, **30**, 230 (1924).

[7] E. L. Goodenow and C. S. Garner, THIS JOURNAL, **77**, 5268 (1955).

[8] O. Olsson, *Ber.*, **46**, 566 (1913).

[9] Bernhardi-Grisson, "Dissertation," Berlin, 1910, p. 36; see also O. Olsson, "Inaugural-dissertation," Uppsala, 1914, p. 30.

[10] J. J. Lingane and L. A. Small, THIS JOURNAL, **71**, 973 (1949).

Exchange Runs.—The more carefully made exchange runs were carried out with solutions 8–13 *f* in hydrochloric acid since these were found from the decomposition studies to give relatively little decomposition of the complex during the times required for the exchange runs. Potassium hexachloro-μ-trichloroditungstate(III) is only slightly soluble in such solutions (*e.g.*, 0.01 *f* in 12 *f* hydrochloric acid at 25°). Hence, in the process of preparing the exchange solutions, the potassium compound was converted into the free acid by passage through a cation-exchange resin in the hydrogen form. For each run 15 ml. of a saturated solution (*ca.* 0.1 *f*) of the potassium compound in air-free distilled water at 0° was added to the top of a 50-ml. buret packed with 50–100-mesh Dowex-50 cation-exchange resin (hydrogen form) which had been dried by drawing air through the column for several hours. The dry resin absorbed water from the solution (ice-water was circulated through a jacket on the column to prevent the heat liberated from raising the temperature appreciably and increasing decomposition of the complex), thus enabling the concentration of the complex to be increased to as much as 0.3 *f*. About 8 ml. of deep-green solution was drawn from the column in several minutes into a cooled receiver and immediately saturated with hydrogen chloride gas under conditions where the temperature was maintained below 15°. A 0.1-ml. aliquot was removed at this point for titration with standardized sodium hydroxide utilizing a Beckman *p*H meter with glass and calomel electrodes; calculation of the hydrochloric acid concentration was made by subtracting the three equivalents of hydrogen ion per complex ion from the total hydrogen ion concentration and the hydrochloric acid concentration adjusted by admixture with hydrochloric acid. The solution was transferred to a reaction vessel, 0.25 ml. of stock radiochlorine-labeled hydrochloric acid added, the mixture shaken (time taken as zero time for the exchange run) and then placed in a bath thermostated at 0 or 25°. In some of the early runs the potassium complex was used at low concentrations in place of the free acid complex at higher concentrations.

Aliquots of 0.5 ml. each were removed immediately and at later known times for separation of $W_2Cl_9^{-3}$ from Cl^- by one of the methods outlined below and for determination of the specific activity of the $W_2Cl_9^{-3}$. A 0.25-ml. aliquot of the unseparated exchange solution was taken for determination of total radioactivity. Initially and at later times approximately concurrently with samples taken for the separation and radioassay purposes, aliquots of 0.1 ml. each were withdrawn from the unseparated exchange solution to follow the extent of decomposition of $W_2Cl_9^{-3}$ by both the permanganate titration method and the spectrophotometric method mentioned in the section on decomposition studies. The 0.1-ml. aliquot taken for spectrophotometric assay was diluted to 5.00 ml. with 12 *f* hydrochloric acid and the absorbancy of the 452-mμ absorption peak determined with a Beckman Model B spectrophotometer using a 1-cm. Pyrex cell fitted with a spacer to give a 0.1-cm. light path; a rubber bulb was fitted over the cell to prevent escape of hydrogen chloride into the spectrophotometer. An experimentally determined graph of absorbancy *versus* molar concentration of $W_2Cl_9^{-3}$ was used to convert the absorbancies to concentrations.

All solutions of the complex were handled in a nitrogen atmosphere. No effort was made to exclude light from the solutions.

Separation of $W_2Cl_9^{-3}$ from Cl^-.—Two different methods for separating $W_2Cl_9^{-3}$ from Cl^- in the exchange runs were investigated:

(1) **Adsorption of $W_2Cl_9^{-3}$ on Anion-exchange Resins.**—Experiments with 50–100-mesh Dowex-2-X8 anion-exchange resin (nitrate form) showed that $W_2Cl_9^{-3}$ could be 99–100% adsorbed on the resin from hydrochloric or sulfuric acid solutions and about 70% of the Cl^- eluted with 4 *f* sulfuric acid. A 0.5-ml. aliquot of exchange solution was passed through the column (0.7-cm. diameter, 40-cm. length) in one minute, followed by 9 ml. of 4 *f* sulfuric acid at 0°. Use of this separation in trial exchange runs gave erratic exchange rates, shown to arise from decomposition of a small fraction of the complex on the resin, and the method was abandoned for exchange-run purposes.

(2) **Precipitation of $W_2Cl_9^{-3}$ with Ammonium Ion or Tetralkylammonium Ions.**—Tetramethylammonium and tetraethylammonium sulfates were demonstrated to be efficient precipitating agents and were used satisfactorily in early exchange runs. Most of the runs, however, were made with ammonium hydrosulfate as a precipitant, inasmuch as this compound was readily available and it was easier to redissolve the precipitate for purification purposes. Reprecipitation and efficient washing were required to free the precipitated ammonium hexachloro-μ-trichloroditungstate(III) from coprecipitated chloride ion; small amounts of other tungsten(III) chloro complexes could conceivably be coprecipitated, but reasonably close agreement between spectrophotometric and titration values for the $W_2Cl_9^{-3}$ content of the precipitates suggests that little such coprecipitation occurred. The procedure was as follows. Each 0.5-ml. aliquot of exchange solution was delivered into 3 ml. of saturated ammonium hydrosulfate solution at 0°, stirred, then centrifuged. The supernatant liquid was discarded and the centrifuge cone given one wash with water and at least seven washes with 2 ml. each of absolute ethanol without disturbing most of the precipitate in the cone. The precipitate was then suspended in 3 ml. of absolute ethanol, centrifuged, washed several times with absolute ethanol, then dissolved in the minimum volume of air-free distilled water at 0°. This solution was mixed with 10 ml. of absolute ethanol at 0° to reprecipitate the ammonium compound, which was centrifuged, washed seven times with absolute ethanol, dispersed in absolute ethanol, centrifuged and finally washed seven times with absolute ethanol. About 70–75% of the original complex was recovered, with less than 0.01% of the free chloride ion remaining with the complex as shown by experiments with removal of radiochlorine-labeled chloride ion. All operations were carried out in a nitrogen atmosphere.

Specific Radioactivity Determinations.—For all runs reported in Table II the separated and purified ammonium hexachloro-μ-trichloroditungstate(III) fraction was dissolved and made up to a 5.00-ml. volume with air-free 2 *f* sulfuric acid at 0°. After removal of a 0.25-ml. aliquot which was made up to 10.0 ml. with a 4 *f* sulfuric acid–6 *f* hydrochloric acid mixture for spectrophotometric assay at 452 mμ, the remaining 4.75 ml. was titrated by the permanganate method outlined earlier, thus giving an independent determination of the amount of complex as well as converting the complex to forms of tungsten(VI) which could be counted without the gradual formation of a precipitate. The titrated solution was made up to 10 ml. with 2 *f* sulfuric acid in a Desicote-treated volumetric flask and the solution transferred quantitatively into a cell used with the above dip-type G-M tube. A 0.25-ml. aliquot from the unseparated exchange solution was similarly titrated and dip-counted to obtain the average specific activity of the chlorine in the exchange solution. The statistical counting error was kept below 1% standard deviation. Background corrections of *ca.* 23 counts per minute (c.p.m.) were made. The recovery time of the counter was found electronically to be 40–50 microseconds, for which the corresponding coincidence error was less than 1% even at the highest counting rates (*ca.* 7800 c.p.m.).

Results and Discussion

Decomposition of $W_2Cl_9^{-3}$.—For solutions of essentially constant acidity and constant chloride ion concentration, plots of the logarithm of $W_2Cl_9^{-3}$ concentration *versus* time were made for each run. The experimental points (usually five to nine per run) fell closely on a straight-line graph for each run, suggesting that the decomposition is first order in $W_2Cl_9^{-3}$. Because the total extent of decomposition followed was less than 25% and accuracy was not great, the data can be fit nearly as well to a zero-order or second-order plot of $W_2Cl_9^{-3}$ concentration or its reciprocal, respectively, *versus* time. The latter graphs exhibit systematic although small curvature, whereas the data fit the first-order graphs well. Values of the first-order decomposition rate constant, k_d, are given in Table I. There appears to be no strong dependence of the rate on the formal concentration of hydrochloric acid (ionic strength was not held constant). For rates based on the titration method, the rate in

6 *f* sulfuric acid is apparently comparable to the rates in the hydrochloric acid solutions. There is sufficient variation in rate constants found for different solutions of essentially the same concentration conditions to suggest that catalytic effects may be present. Rate constants based on the titration method generally are somewhat smaller than those based on the spectrophotometric method.

TABLE I

FIRST-ORDER RATE CONSTANTS FOR $W_2Cl_9^{-3}$ DECOMPOSITION AT 25°

(T, titration method; S, spectrophotometric method)

Reaction mixture, initial concn., *f* HCl	H_2SO_4	$W_2Cl_9^{-3}$	$10^7 k_d$, sec.$^{-1}$ T	S
..	6.0	0.10	27	
0.8	5.4	.10	38	
5.0	4.0	.012		130
6.0	3.0	.012		500
8.0	..	.010	38	
8.0	..	.136	50	
9.9	..	.109	24	53
10.0	..	.010	19	
10.0	..	.209	26	38
10.2	..	.114	22	
12.0	..	.010	13	
12.3	..	.186	11	33
12.6	..	.262	21	

The reaction products and stoichiometry of the decomposition are not known. The fact that the solutions often turned red, then blue, on prolonged standing (sometimes developing dark-colored precipitates) and the fact that the values of $W_2Cl_9^{-3}$ concentrations determined by titration (which measures the total reducing equivalents of the system) and by spectrophotometry (which measures conversion of $W_2Cl_9^{-3}$ to other forms of tungsten (III) in addition to higher oxidation states) sometimes differed by as much as 10% suggest that some conversion of $W_2Cl_9^{-3}$ to other forms of tungsten(III) is occurring, as well as oxidation to higher oxidation states. For those solutions for which the spectra were scanned from 350 to 700 mμ at various times during the decomposition, the only change observed was a reduction in absorbancy at the 452-mμ peak (associated with the green $W_2Cl_9^{-3}$ ion) and a broadening of the base of this peak. The broadening may arise from conversion of $W_2Cl_9^{-3}$ into one or more red forms of tungsten (III). Lingane and Small[10] reported an absorption peak at 525 mμ and high absorbancy below *ca.* 375 mμ for a red tungsten(III) solution; Laudise and Young[11] gave 515 mμ for the absorption maximum in the visible spectrum of a red tungsten(III) solution which they reported contained the $W_3Cl_{14}^{-5}$ ion. Using the molar absorbancies of the 452-mμ peak of $W_2Cl_9^{-3}$ and the 525-mμ peak of "red tungsten(III)" given by Lingane and Small, we estimate that more than 20% of the $W_2Cl_9^{-3}$ in our solutions would have had to be converted to the red form in order for an observable peak to appear in the vicinity of 525 mμ in the spectra we took. Total decomposition by all paths was less than 20% in all of the solutions for which we scanned the spectra.

Qualitative observations made at 0, 25 and 50° showed that the rate of decomposition increased with increasing temperature. At 0° the decomposition rate of a solution initially 0.03 *f* in $K_3W_2Cl_9$, 0.5 *f* in hydrochloric acid and 4 *f* in sulfuric acid was the same in the dark as in laboratory fluorescent lighting up to at least 46 hr. (~ 4% decomposition), suggesting that the decomposition is not photosensitive.

Exchange between $W_2Cl_9^{-3}$ and Cl^{*-}.—For the exchange reactions

$$W_2Cl_9^{-3} + Cl^{*-} \rightleftarrows W_2Cl_8Cl^{*-3} + Cl^-,$$

$$W_2Cl_8Cl^{*-3} + Cl^{*-} \rightleftarrows W_2Cl_7Cl^*{}_2^{-3} + Cl^-, \text{ etc.}$$

the fraction exchange *F* may be defined by the relationship

$$F = S_c/S_\infty = (9a + b)x/(9ay_0) \qquad (1)$$

where S_c and S_∞ are the specific activities of the tungsten complex at time *t* and at infinite time, respectively, *a* and *b* are, respectively, the volume formal concentrations of the initially inactive tungsten complex and free chloride ion, and *x* and y_0 are the net radioactivities (c.p.m.) of the complex at time *t* and of the free chloride ion at zero time, respectively. If all nine chlorine atoms of the $W_2Cl_9^{-3}$ ion are kinetically equivalent, the McKay plot[12,13] of log(1 − *F*) *versus t* will be linear unless there be variable catalytic effects or appreciable net decomposition of the tungsten complex during the time interval involved; the straight-line plot extrapolates to unity on the (1 − *F*) ordinate at zero time unless there is separation-induced exchange or incomplete separation for which a correction is not made. If the nine chlorines are not kinetically equivalent, the McKay plot may be more complex. Three pertinent cases are examined here: (1) 9 − *p* of the nine ligand chlorines exchange with Cl^- so rapidly they are included in the zero-time exchange and the other *p* chlorines exchange with Cl^- at a mutually equivalent measurable rate; (2) *p* ligand chlorines are kinetically equivalent and exchange with Cl^- at a measurable rate, the remaining 9 − *p* chlorines exchanging with Cl^- at a mutually equivalent and measurable but slower rate; and (3) same as case 2 except that the remaining 9 − *p* chlorines exchange with Cl^- so slowly that no significant exchange involving them is observed during the experiments. In the first case the McKay plot will be linear but will have a zero-time (1 − *F*)-intercept of *p*/9, *F* being calculated by equation 1 to include all nine chlorines per $W_2Cl_9^{-3}$ ion. From the geometry of this ion *p* would be expected to be 9 (for which case 2 reduces to case 1), 6 or 3; the corresponding (1 − *F*)-intercepts are 1.00, 0.67 and 0.33, respectively, which are readily distinguishable experimentally. For case 2 the McKay plot will give a complex curve *convex* toward the origin. For case 3 the McKay plot will also give a complex curve *convex* toward the origin if *F* is calculated in the conventional way to include all nine chlorines per $W_2Cl_9^{-3}$ ion; the McKay plot will be linear if *F* is cal-

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[11] R. A. Laudise and R. C. Young, THIS JOURNAL, **77**, 5288 (1955).

[12] H. A. C. McKay, *Nature*, **142**, 997 (1938).

[13] O. E. Myers and R. J. Prestwood, "Radioactivity Applied to Chemistry," A. C. Wahl and N. A. Bonner, editors, John Wiley and Sons, Inc., New York, N. Y., 1951, Chap. 1.

culated on the basis of only p chlorines exchanging

$$F = (pa + b)x/(pay_0) \qquad (2)$$

Moreover, if F is calculated by equation 2 assuming p to be 3 or 6, and actually all nine chlorines enter into exchange on an equivalent basis, the McKay plot will be a complex curve *concave* toward the origin and values of $(1 - F)$ will ultimately become negative (thus demonstrating the falseness of the assumption).

McKay plots prepared from our exchange data using equation 1 to calculate F gave good straight-line graphs up to at least one reaction half-time with no zero-time exchange. Decomposition of the complex was less than 10% (usually much less) during one exchange half-time, and no correction was made for the decomposition nor for the negligible isotope effect. If equation 2 was used, with $p = 3$ or $p = 6$, the McKay plots were concave toward the origin, and $(1 - F)$ values became negative ultimately; *e.g.*, for a typical run the 9-chlorine assumption gave a value of 77% exchange at 13 hr., whereas the 6-chlorine and 3-chlorine assumptions gave, respectively, 112 and 212% exchange for the same exchange time. A typical McKay plot is shown in Fig. 1. Thus, it is clear that no chlorines *in* the $W_2Cl_9^{-3}$ ion *undergo* exchange with Cl^- within the short separation time and that all nine chlorines are equivalent in an exchange sense although they are not structurally equivalent.

The equivalent exchange lability of all of the nine chlorines in the $W_2Cl_9^{-3}$ ion may arise as a result of intramolecular exchange among the chlorines of the complex at a rate fast compared to exchange with free chloride ion. This does not appear probable inasmuch as two of the bridge chlorine bonds probably would have to break in order to permit the necessary internal rearrangement. More probably the kinetic equivalence of the nine chlorines is achieved through a dynamic equilibrium with an intermediate. *E.g.*, the red complex, $W_3Cl_{14}^{-5}$, postulated by Laudise and Young,[11] or the red complex, WCl_5^{-2}, reported by Collenberg and Backer,[6] might function as exchange intermediates through the reversible reactions without having to be present in concentrations which we would have detected.

$$3W_2Cl_9^{-3} + Cl^- \rightleftharpoons 2W_3Cl_{14}^{-5}$$

$$W_2Cl_9^{-3} + Cl^- \rightleftharpoons 2WCl_5^{-2}$$

Support for the presence of species of tungsten(III) other than $W_2Cl_9^{-3}$ in the exchange solutions is found in the concurrently made decomposition studies, in which total loss of green $W_2Cl_9^{-3}$, indicated by spectral absorbancy decrease, was not usually paralleled by equivalent loss in reducing strength of the solution.

Table II presents a summary of all exchange runs made with $H_3W_2Cl_9$ at a controlled temperature (earlier runs made with $K_3W_2Cl_9$ at lower concentrations and in sulfuric acid–hydrochloric acid mixtures gave comparable but less accurate results), calculated on the basis of all nine chlorines of the complex kinetically equivalent. The exchange half-times, $t_{1/2}$, were obtained graphically from analysis of the McKay plots. If the exchange reaction is assumed to be first order in concentration of the complex and either zero order or first order in formal concentration of hydrochloric acid, the corresponding first-order and second-order rate constants, k_1 and k_2, respectively, may be calculated from the exchange half-time by the relationships

$$R = k_1a = k_2ab = 9ab\,(\ln 2)/(9a + b)t_{1/2} \qquad (3)$$

where R is the constant rate of exchange of Cl atoms between $W_2Cl_9^{-3}$ and Cl^- in gram-atoms l.$^{-1}$ sec.$^{-1}$ in a given exchange run. The values of k_1 and k_2 given in Table II do not permit distinguishing between the two rate laws, partly because the effect of varying $W_2Cl_9^{-3}$ concentration is fairly small relative to the high concentrations of hydrochloric acid employed to give low decomposition rates and partly because accurate reproducibility was not achieved.

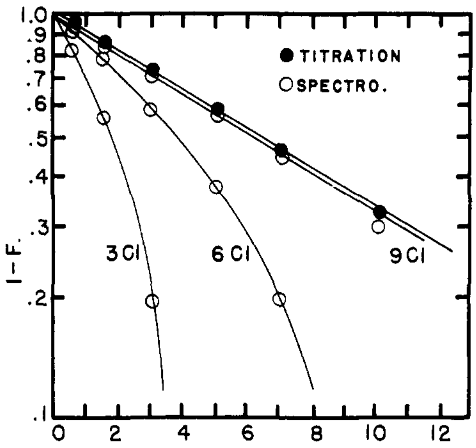

Fig. 1.—Rate of exchange of radiochlorine between $W_2Cl_9^{-3}$ and Cl^- in 0.186 f $H_3W_2Cl_9$ and 12.3 f HCl at 25° as a function of number of chlorines assumed exchangeable in $W_2Cl_9^{-3}$ ion ("titration" and "spectro." refer to method used for determining amount of complex taken for radioassay; see Experimental, section on specific radioactivity determinations).

TABLE II

EXCHANGE BETWEEN $W_2Cl_9^{-3}$ AND Cl^{*-} AT 25°

(T, titration method; S, spectrophotometric method)[a]

Exchange mixture, initial concn., f $H_3 \cdot W_2Cl_9$	HCl*	Exchange half-time, hr. T	S	10^5k_1, sec.$^{-1}$ T	S	10^6k_2, l. mole^{-1} sec.$^{-1}$ T	S
0.215	9.86	7.9	7.9	18	18	19	19
.109	9.89	9.0	8.0	18	20	18	20
.209	9.95	7.0	7.0	21	21	21	21
.114	10.2	6.0	6.0	26	26	26	26
.136	11.4	6.9	4.3	23	37	20	32
.137	12 ± 1	8.3	8.0	19	20	16	17
.186	12.3	6.3	6.3	24	24	20	20
.262	12.6	5.4	4.8	27	31	21	24

[a] Refers to method used for determining amount of complex taken for radioassay; see Experimental (specific radioactivity determinations).

Several exchange runs were carried out at 0° in sulfuric acid–hydrochloric acid solutions. Essentially no exchange was observed over a several-day period. For example, less than 0.2% exchange was found at three days in a solution 0.073 *f* in the potassium salt of the complex, 4 *f* in sulfuric acid and 0.5 *f* in hydrochloric acid.

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LOS ANGELES 24, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN]

Vapor Pressure of Liquid Tellurium

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The vapor pressure of liquid tellurium was measured with a silica Bourdon gage and can be represented by $\log_{10}P_{\text{mm}} = -10{,}663.14/T + 64.73140 - 18.61687 \log_{10}T + 0.00341783T$ from the triple point to 855°C. The magnitudes of these parameters indicate that the van der Waals constants of tellurium vapor must be unusually large. The extrapolated boiling point is 994 ± 3° and the heat of vaporization is $33.8 - 0.009t$(°C.) kcal. mole^{-1}.

Introduction

The vapor pressure of liquid tellurium has been reported by four investigators. The two earliest sets of measurements[1,2] were by dynamic methods and were discordant and apparently quite inaccurate. A static method, involving a Bourdon gage, was employed in the third.[3] The fourth,[4] also static, was based on measurement of vapor density by means of tracer quantities of radioactive tellurium and calculation of the pressure. In addition, measurements of the sublimation pressure of solid tellurium over the temperature range 320 to 410°[5] permit extrapolation to 449.7°, the triple point,[6] to obtain one additional datum. The present measurements utilize a vitreous silica Bourdon gage similar to that of Brooks,[3] with certain refinements which are described elsewhere.[7]

Experimental

Two series of measurements were made. For the first, tellurium (semiconductor grade, 99.999+% pure) procured from American Smelting and Refining Company was used. For the second, tellurium which had been zone refined and repeatedly sublimed to an impurity content less than one part per hundred million was used (this impurity content was determined electrically and does not take account of possible surface contamination by tellurium dioxide). This tellurium was further purified by distilling it out of the silica vapor pressure apparatus into a narrow vertical silica tube where it refluxed repeatedly. After the apparatus had been degassed for 24 hr. at 800° and 10^{-6} mm. pressure, the lower portion of the tellurium was melted gently at a temperature below that at which TeO_2 is volatile[8] and allowed to run back into the apparatus, which was then sealed off. The two series of measurements used different gages and different thermocouples.

Both sets of thermocouples (Pt–Pt–10% Rh) were repeatedly calibrated *in situ*[7] at the melting points of zinc (419.50°), aluminum (660.15°) and copper–silver eutectic (779.2°). The temperatures are considered to accord with the international temperature scale within 0.2° on the second series of measurements and 0.3° on the first series. The pressure measurements are believed accurate within 0.1 mm., except at the highest temperatures where the probable temperature error is equivalent to a larger pressure error.

The first series consisted of 30 measurements, from 484 to 782°; five of the measurements were at temperatures below 600° and were of little significance because the 0.1 mm. error was a large fraction of the total pressure. The second series consisted of 17 measurements, from 507 to 855°, of which four were below 600°. Each "measurement" consisted of the average of two to five observations, spaced by several minutes, at a single temperature.

Results and Discussion

The vapor pressure data are presented in chronological sequence in Table I. The observations are represented by the formula

$$\log_{10}P = -10{,}663.14/T + 64.73140 - 18.61687 \log_{10} T + 0.00341783T \quad (1)$$

where P is pressure in mm. at 0° and standard gravity, T is temperature in degrees Kelvin. For the triple point this expression predicts 0.17 mm. Linear extrapolation of Niwa's data[5] yields 0.187 mm.; however, as noted below, the extrapolation should not be linear, and 0.17 mm. is the best estimate from the reported observations. The validity of this expression in representing the observations may be judged from Fig. 1. The deviations of literature data also are shown.

A Clausius–Clapeyron-like equation for the vaporization process can be rigorously derived[9] in the form

$$d \log_e P/d(1/T) = -C_1C_2\Delta H/R \quad (2)$$

where ΔH is the molar heat of vaporization, R is the gas constant and C_1 and C_2 are correction factors for the non-zero volume of the liquid and the non ideal behavior of the gas, respectively. These correction factors are given by

$$C_1 = 1/(1 - V_1/V_g) \text{ and } C_2 = 1/(1 + B/V_g)$$

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