

[CONTRIBUTION FROM THE OAK RIDGE NATIONAL LABORATORY CHEMISTRY DIVISION]

Chemistry of Aqueous Uranium(V) Solutions. III. The Uranium(IV)-(V)-(VI) Equilibrium in Perchlorate and Chloride Solutions¹

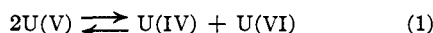
BY FREDERICK NELSON AND KURT A. KRAUS

(1) The equilibrium constant K_{eq} for the reaction $2UO_2^{+} + 4H_3O^{+} \rightleftharpoons UO_2^{++} + U^{+4} + 6H_2O$ was obtained as a function of ionic strength for perchlorate and chloride solutions using polarographic, spectrophotometric and potentiometric methods. (2) A Debye-Hückel expression was found to represent the data up to $\mu = ca. 1.0$ and the activity constant $K_{eq}^0 = K_{eq}(\gamma_{UO_2^{++}}\gamma_{U^{+4}})/(\gamma_{UO_2^{+}}^2\gamma_{H_3O^{+}}^4) = (1.7 \pm 0.3) \times 10^6$ was evaluated. (3) The stability constant of the uranyl chloride complex UO_2Cl^{+}

$$K^0(VI_0) = (UO_2Cl^{+})\gamma_{UO_2Cl^{+}}/[(UO_2^{++})(Cl^{-})\gamma_{UO_2^{++}}\gamma_{Cl^{-}}] = 2.4$$

was estimated from a comparison of K_{eq} for chloride and perchlorate solutions. (4) Some observations on the polarography of uranium(V) and uranium(VI) have been included. The diffusion current constants of uranium(VI) and the ratio of the diffusion current constants of uranium(V) and (VI) were evaluated as a function of ionic strength.

In previous papers^{2a,b} it was shown that uranium (IV), uranium(V) and uranium(VI) form equilibrium mixtures—at times metastable—according to the equation



The corresponding equilibrium constant

$$K'_{eq} = (U(IV))(U(VI))/(U(V))^2 \quad (2)$$

(parentheses indicate molar concentrations) is strongly pH dependent. At low acidities K'_{eq} is of the order of unity and preparation of equilibrium mixtures containing a large fraction of uranium(V) is feasible.

In the work here reported, equilibrium (1) was studied as a function of acidity and ionic strength μ , in perchlorate and chloride solutions. The equilibrium constant

$$K_{eq} = (UO_2^{++})(U^{+4})/(UO_2^{+})^2(H_3O^{+})^4 \quad (3)$$

for the reaction



was evaluated using estimates of the stability constants of the chloride complexes and the previously determined³ values of the acid constant of U^{+4}

$$K(IV)_a = (H_3O^{+})(UOH^{+3})/(U^{+4}) \quad (5)$$

for the reaction



Through the use of a Debye-Hückel expression³ it was possible to extrapolate the values of K_{eq} to $\mu = 0$ and to obtain the activity constant

$$K_{eq}^0 = K_{eq}\gamma_{UO_2^{++}}\gamma_{U^{+4}}/\gamma_{UO_2^{+}}^2\gamma_{H_3O^{+}}^4 \quad (7)$$

Experimental—Techniques and Materials

Equilibrium mixtures of uranium in the various oxidation states were prepared (a) by mixing stock solutions of uranium (IV) and uranium(VI), (b) by dissolving anhydrous uranium tetrachloride in uranium(VI) solutions, (c) by dissolving anhydrous uranium pentachloride in the supporting electrolyte⁴ and (d) by addition of acid to uranium(V) solutions causing (limited) disproportionation into uranium (IV) and (VI). The uranium(V) solutions used in the last method were prepared by electrolytic reduction of uranium(VI) solutions of low acidity (*ca.* $10^{-3}M H_3O^{+}$).^{2a}

(1) This document is based on work performed for the Atomic Energy Commission at the Oak Ridge National Laboratory.

(2) K. A. Kraus and F. Nelson, *THIS JOURNAL*, (a) **71**, 2510 (1949); (b) **71**, 2517 (1949).

(3) K. A. Kraus and F. Nelson, *ibid.*, **72**, 3901 (1950).

(4) Uranium pentachloride reacts instantaneously with water to form equimolar amounts of uranium(IV) and uranium(VI) which then react to attain equilibrium.^{2b}

In the experiments with uranium pentachloride this salt was sometimes added to uranium(VI) solutions to vary the uranium(IV)-uranium(VI) ratio from unity. Preparation of solutions and purity of materials were discussed earlier.^{2a,b,3} The experiments were carried out in a thermostated room at $25 \pm 1^{\circ}$. The temperature of most solutions was maintained at $25.0 \pm 0.2^{\circ}$.

Analysis for the relative amounts of uranium in each oxidation state at equilibrium was carried out primarily polarographically and spectrophotometrically. The polarographic equipment and method of determining the concentrations in the various oxidation states from the diffusion currents of uranium(V) and (VI) were described earlier.^{2a} Additional diffusion current data are given below. Spectrophotometric measurements were used to determine the concentration of uranium(IV). The equipment and "calibration" data are described elsewhere.³ Acidity of the solutions was measured potentiometrically with a glass-calomel (saturated KCl or NaCl) electrode assembly and the vibrating reed recorder for which performance data have been given.⁵

General Discussion of Analytical Methods

To obtain the equilibrium constant K'_{eq} (equation 2) the concentrations of uranium in the various oxidation states at equilibrium must be obtained. This can be done from a knowledge of the initial concentrations and determination of the equilibrium concentration of one oxidation state. The determination of the equilibrium concentrations of more than one oxidation state thus usually affords a check on the precision of the method.

Polarography of Uranium(VI) and Uranium(V).—The uranium(VI) and uranium(V) concentrations were usually determined polarographically. The diffusion current constants K_6 of uranium (VI)⁶ and the ratio $R = K_5/K_6$ of the diffusion current constants of uranium(V) and (VI) were obtained as a function of ionic strength, acid concentration and uranium concentration. At a given ionic strength and $T = 25 \pm 0.2^{\circ}$ K_6 was found to be essentially constant in the acid range 0.001 to *ca.* 0.1 *M* and in the uranium(VI) concentration range 0.0005 to 0.005 using a capillary with $m^{3/4}t^{1/6} = 2.465 \text{ mg.}^{3/4} \text{ sec.}^{-1/2}$ at $-0.4 \text{ v. vs. S.C.E.}$ (see Table I). At acidities considerably above 0.1 *M*, K_6 increases probably because of appreciable disproportionation of uranium(V) during the life of a mercury drop as suggested by Harris and Koltzoff.⁷ If no pronounced maxima appeared, addi-

(5) K. A. Kraus, R. A. Holmberg and C. J. Borkowski, *Anal. Chem.*, **32**, 341 (1950).

(6) The diffusion current constant K (with subscript to indicate the oxidation state) is given by the Ilkovic equation $K = i_d/Cm^{3/4}t^{1/6}$. For methods of measurement see ref. 2a.

(7) W. E. Harris and I. M. Koltzoff, *THIS JOURNAL*, **67**, 1484 (1945).

tion of $2 \times 10^{-4}\%$ thymol did not materially affect K_6 ; otherwise, addition of the suppressor brought the values of K_6 in line with those observed in the absence of maxima. Below $\mu = 0.5$, K_6 is approximately the same for chloride and perchlorate solutions and does not change appreciably with μ .⁸ The slightly lower values of K_6 at $\mu < 0.05$ are of questionable significance because of the lower precision of the experiments in this range. An increase in K at $\mu < ca. 0.1$ was avoided by using proportionately lower uranium concentrations, thus keeping the concentration of supporting electrolyte at least fifty times that of the uranium(VI).⁹

TABLE I

EFFECT OF VISCOSITY ON DIFFUSION CURRENT CONSTANTS

μ	Sodium perchlorate solutions			Potassium chloride solutions		
	K_6	η^a	$K_{6\eta^{1/2}}$	K_6	η^b	$K_{6\eta^{1/2}}$
0.011			1.48	1.48	(1.00) ^c	1.48
.025	1.48	(1.00)	1.48	1.52	(1.00)	1.52
.055	1.51	(1.00)	1.52	1.52	(1.00)	1.51
.10	1.52	(1.01)	1.52	1.52	(1.00)	1.52
.25	1.52	1.02	1.53			
.50	1.52	1.02	1.53	1.53	0.997	1.53
1.00	1.49	1.034	1.52	1.55	0.995	1.55
2.00	1.46	1.160	1.57	1.57	1.002	1.57
3.51				1.60	1.034	1.63
3.73	1.33	1.506	1.63			

^a Viscosities of sodium perchlorate solutions by J. H. Edgerton, Chemistry Division, Oak Ridge National Laboratory. ^b Viscosities of potassium chloride solutions from International Critical Tables, Vol. V, p. 17. ^c Values in parentheses are assumed.

Above $\mu = 0.5$, K_6 decreases appreciably in perchlorate solutions and increases slightly in chloride solutions. The capillary constant ($m^{2/3}t^{1/6}$) was found to be independent of ionic strength (within ca. 1%) for sodium perchlorate solutions of ionic strength $\mu = 0.1, 2.0, 3.8$ and 8.4 . At first glance the difference in K_6 for chloride and perchlorate solutions might be attributed to chloride complexing of uranium(VI). This interpretation, however, appears unlikely since the product $K_{6\eta^{1/2}}$ (where η is the viscosity of the solutions) is approximately the same for the two media at the same ionic strength as shown in Table I.¹⁰ It is of interest that the observed increase of $K_{6\eta^{1/2}}$ is paralleled by similar increases of diffusion coefficients of some electrolytes and uncharged molecules.¹¹

The values of the ratios R of the diffusion current constants of uranium(V) and (VI) as a first approximation, appear to be only slightly larger than

(8) It had previously been shown^{2a} that the diffusion coefficients D_6 calculated from this and the earlier work are in agreement with those calculated by Harris and Kolthoff⁷ for chloride solutions, but not with those of Kern and Orlemann (THIS JOURNAL, 71, 2103 (1949)) for perchlorate solutions. Since our new measurements show little difference between chloride and perchlorate solutions, this disagreement thus persists. Kritchovsky and Hindman recently re-evaluated D_6 in perchlorate solutions (*ibid.*, 71, 2096 (1949)) and found agreement with the value of Kern and Orlemann. However, since they do not give the capillary constant on which the value of D_6 depends^{2a} no further comparison can be made.

(9) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., revised reprint, 1946, p. 83.

(10) According to the Ilkovič equation K_6 is proportional to the square root of the diffusion coefficient. If Stokes' law holds, the latter is proportional to the viscosity and hence one might expect $K_{6\eta^{1/2}}$ to be a constant.

(11) See ref. 9, pp. 50 and 52.

unity and the same for chloride and perchlorate solutions and independent of ionic strength (Table II). The slight decrease of R in the concentrated chloride solutions is of questionable significance.

TABLE II

RATIO R OF DIFFUSION CURRENT CONSTANTS OF URANIUM (V) AND URANIUM(VI) IN CHLORIDE AND PERCHLORATE SOLUTIONS

$T = 25 \pm 0.2^\circ$; $pH = 2-3$; 1 to $5 \times 10^{-8} M U$; $m^{2/3}t^{1/6} = 2.465 \text{ mg.}^{2/3}\text{sec.}^{-1/2}$ at -0.4 vs. S.C.E.

$M \text{ NaClO}_4$	R	$M \text{ KCl}$	R
0.08	1.02	0.026	1.03
.11	1.04	0.097	1.01
.25	1.05	0.10	1.02 ± 0.01^a
.31	1.05		
.53	1.01		
1.02	1.04	0.50	$1.04 \pm .03^b$
2.00	$1.04 \pm .02^c$	1.00	$1.02 \pm .01^c$
3.73	$1.04 \pm .02^c$	2.00	$0.98 \pm .01^c$

^a Data from ref. 2a. Average of 3 determinations with maximum deviation given. ^b Average of 6 determinations with standard deviation given. ^c Average of 2 determinations with maximum deviation given. Actual experimental error is probably larger.

Spectrophotometry.—For some solutions the concentration of uranium(IV) was determined by this method using the spectral data previously described.⁸ Advantage was taken of the facts that U^{+4} and UOH^{+3} have the same extinction coefficient near $625 \text{ m}\mu$, that they have equal and practically negligible extinction coefficients near $695 \text{ m}\mu$ and that uranium(V) and uranium(VI) have only negligible absorption in this wave length range. The uranium(IV) concentration could thus readily be calculated from the difference of the observed extinction coefficients at 625 and $695 \text{ m}\mu$. Use of differences in extinction coefficients rather than "absolute" extinction coefficients at one wave length (e.g., $625 \text{ m}\mu$) appears preferable since small variations in "background" absorption become less important.

Potentiometry.—During the reaction of uranium(IV) with uranium(VI) as well as during disproportionation of uranium(V) to yield uranium(IV) and (VI) a change in acidity occurs which is principally determined by reactions (4) and (6). Thus knowing the initial concentrations of the various oxidation states, the change in acidity, and $K(\text{IV})_a$, the equilibrium constant K'_{eq} can be calculated. Although with the solutions used here the potential changes of a glass-electrode assembly usually were only a few millivolts, the values of K'_{eq} calculated by this method were in satisfactory agreement with those calculated by other methods.

Results and Discussion

Calculations.—The equilibrium constant K'_{eq} represents a formal relationship between the concentrations of the various oxidation states irrespective of ionic species present. It is thus dependent on the acidity of the solutions, on the concentration of complexing agents (chloride ions) as well as on the ionic strength.

The equilibrium constant K_{eq} (equation 2) can be calculated from K'_{eq} by evaluating the concentrations of the species UO_2^{++} , UO_2^+ and U^{+4}

TABLE III
URANIUM(IV)-(V)-(VI) EQUILIBRIUM CONSTANTS IN CHLORIDE AND PERCHLORATE SOLUTIONS ($T = 25 \pm 0.2^\circ$)

A. Reproducibility of Methods

Solutions	$(H_2O^+) \times 10^3$ initial	$(H_2O^+) \times 10^3$ final	Method ^f	U(IV)	Equil. concn. $\times 10^4$ U(V)	U(VI)	K'_{eq}	$K_{eq} \times 10^{-7}$
$1.477 \times 10^{-3} M UCl_5$ $\mu = 0.029 (Cl^-)$	2.50	7.13	S	4.19	6.39	4.19	0.430	1.21
			A	4.12	6.53	4.12	0.398	1.12
$2.058 \times 10^{-3} M U(VI)$ $\mu = 0.27 (ClO_4^-)$	0.77	5.52	P	2.91	9.04	23.5	0.835	10.6
			S	2.93	9.00	23.5	0.850	10.8
$1.485 \times 10^{-3} M UCl_5$ $\mu = 0.27 (ClO_4^-)$			A	2.68	8.70	23.2	0.824 ^g	10.4
$1.372 \times 10^{-3} M UCl_5$ $\mu = 0.5 (Cl^-)$	3.50	7.80	P	3.84	6.01	49.2	5.24	21.3
			A	3.78	6.16	49.0	4.91 ^g	20.0

B. Dependence on Acidity

$(H_2O^+) \times 10^3$	$M U(IV) \times 10^4$	$M U(V) \times 10^4$	$M U(VI) \times 10^4$	K'_{eq}	$K_{eq} \times 10^{-7}$	Method of analysis	Method of preparation
$\mu = 0.10-0.11 (Cl^-) = ca. 0.105$							
7.2	8.80	7.25	8.80	1.48	5.7	P	b
9.9	14.10	7.56	14.10	3.46	4.9	P	b
10.4	6.84	7.98	41.6	4.43	5.4	P	d
11.2	7.07	7.90	41.7	4.72	4.5	P	d
(Av. = 5.1)							
$\mu = 0.49-0.51 (Cl^-) = ca. 0.50$							
4.65	4.72	4.44	47.2	1.13	24.2	P	b
5.20	5.35	4.35	5.35	1.51	21.2	P	b
3.60	2.95	5.18	14.2	1.56	18.6	P	a
5.60	2.74	8.13	48.1	1.99	23.4	P	c
5.84	3.12	8.58	48.5	2.06	21.5	P	c
7.10	11.0	12.03	40.7	3.09	17.2	P	e
7.30	2.75	5.38	42.7	4.06	20.7	P	d
7.80	3.84	6.10	49.2	5.08	20.8	P	c
8.38	11.05	9.29	40.9	5.24	17.0	P	d
10.2	8.10	5.44	42.9	11.6	20.0	P	d
12.8	11.10	2.42	11.5	21.7	19.6	P	b
13.5	6.30	1.42	7.28	22.7	17.5	P	b
(Av. = 20.1)							

C. Ionic Strength Dependence

μ	$(H_2O^+) \times 10^3$	(Cl^-)	$M U(IV) \times 10^3$	$M U(V) \times 10^4$	$M U(VI) \times 10^4$	K'_{eq}	$K_{eq} \times 10^{-7}$	Method of analysis	Method of preparation
Chloride solutions (KCl-HCl)									
0.0085	5.82	0.0076	0.231	5.57	0.231	0.772	0.68	S	b
.0131	8.83	.0114	.403	4.74	0.403	.721	0.87	S	b
.0133	8.98	.0114	.403	4.78	0.403	.711	0.82	S	b
.0260	7.75	.024	.417	11.9	2.571	.757	1.54	P	c
.0297	7.13	.0299		See Table IIIa			1.16	S, A	b
.0389	8.25	.0323	.495	15.74	4.952	.990	1.90	S	c
.10-0.11	7.2-11.2	.105		See Table IIIb			5.10	P	
.49-.51	4.65-13.5	.50		See Table IIIb			20.1	P	
.99	5.45	.99	.302	6.42	4.84	3.55	48	P	c
1.97	3.87	1.97	.218	4.59	3.08	3.06	108	P	c
1.97	6.00	1.97	.667	4.25	3.52	13.0	120	P	c
Perchlorate solutions (NaClO ₄ -HClO ₄)									
0.115	5.00	0.018	0.241	8.44	2.60	0.33	4.4	P	c
.27	5.52	.018		See Table IIIa			10.6	P, S, A	c
.53	6.49	.009	.484	8.17	2.54	1.84	17.1	P	c
1.02	4.36	.016	.264	7.26	2.30	1.15	41.0	P	c
1.97	4.15	.015	.255	5.32	2.32	2.09	118	P	c
1.97	4.95	.015	.361	5.36	2.41	3.02	91.6	P	b

^a Disproportionation of electrolytically prepared U(V) solution. ^b Addition of UCl₅ (solid) to chloride or perchlorate solutions. ^c Addition of UCl₅ (solid) to U(VI) chloride or perchlorate solutions. ^d Addition of U(IV) solutions to U(VI) chloride or perchlorate solutions. ^e Addition of UCl₅ (solid) to U(VI) chloride or perchlorate solutions. ^f (S) Spectrophotometric method. (P) Polarographic method. (A) Acid-change method. ^g In calculation considered small amount of hydrolysis of U(VI) in the initial solution using the value of $K(VI)_2 = 6.0 \times 10^{-6}$ ($\mu = 0.1 Cl^-$) given by MacInnes and Longworth¹² for the reaction $UO_2^{++} + 2H_2O \rightleftharpoons UO_2OH^+ + H_3O^+$.

This may be done from the stoichiometric concentrations of uranium(IV), (V) and (VI) using the appropriate acid constants and chloride complex constants. Of the possible acid constants only that of uranium(IV) need be considered since uranium(V) and (VI) do not appreciably hydrolyze^{2,12-14} at acidities where equilibrium measurements were made. Since uranium(V) ($\text{UO}_2(\text{H}_2\text{O})_5^+$) appears to have a structure similar to that of uranium(VI) ($\text{UO}_2(\text{H}_2\text{O})_6^{2+}$) but a smaller positive charge, and since furthermore uranium(VI) only forms a weak chloride complex, it appears reasonable to assume that uranium(V) is only negligibly complexed by chloride ions. Assuming also that uranium(IV) and (VI) form only the monochloride complexes UCl^{+3} and UO_2Cl^+ at the chloride concentrations used, one can set

$$\left. \begin{aligned} (\text{U(VI)}) &= (\text{UO}_2^{2+}) + (\text{UO}_2\text{Cl}^+) \\ (\text{U(V)}) &= (\text{UO}_2^+) \\ \text{and } (\text{U(IV)}) &= (\text{U}^{4+}) + (\text{UOH}^{+3}) + (\text{UCl}^{+3}) \end{aligned} \right\} \quad (8)$$

Using equations (2), (3), (5) and (8), letting

$$K(\text{IV})_c = (\text{UCl}^{+3})/(\text{U}^{4+})(\text{Cl}^-) \quad (9)$$

and

$$K(\text{VI})_c = (\text{UO}_2\text{Cl}^+)/(\text{UO}_2^{2+})(\text{Cl}^-) \quad (10)$$

and defining $c = (\text{Cl}^-)$ and $h = (\text{H}_3\text{O}^+)$ one obtains

$$K_{\text{eq}} = K'_{\text{eq}} \frac{1}{h^4(1 + cK(\text{VI})_c)(1 + cK(\text{IV})_c + K(\text{IV})_a/h)} \quad (11)$$

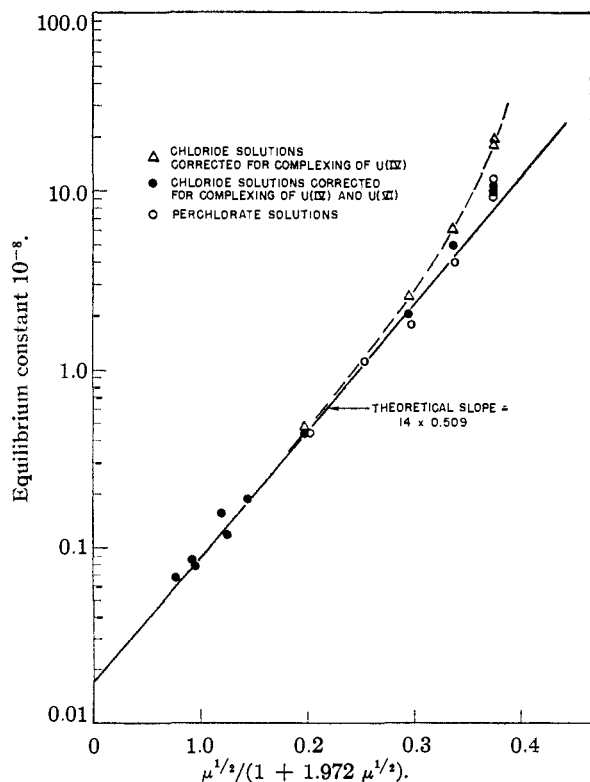


Fig. 1.—Equilibrium constants in chloride and perchlorate solutions ($25.0 \pm 0.2^\circ$).

(12) D. A. MacInnes and L. G. Longworth, Report A-360, Nat. Defense Res. Committee, Office of Sci. Res. and Dev., Nov., 1942.

(13) J. Sutton, J. National Res. Council of Canada No. 1612, Ontario, 1947.

(14) S. Ahrland, *Acta Chem. Scand.*, **3**, 374 (1949).

For perchlorate solutions, where $c = 0$, equation (11) simplifies to

$$K_{\text{eq}} = K'_{\text{eq}} \frac{1}{h^4(1 + K(\text{IV})_a/h)} \quad (12)$$

The constants $K(\text{IV})_a$ and $K(\text{IV})_c$ were calculated as a function of ionic strength μ from the Debye-Hückel equation

$$\log K = \log K^0 + 0.509 \Delta(Z_i^2) \frac{\mu^{1/2}}{1 + 0.3286 \hat{a} \mu^{1/2}} \quad (13)$$

where K and K^0 represent the various molarity and activity constants, where \hat{a} is a parameter (distance of closest approach) and where $\Delta(Z_i^2)$ represents the arithmetical sum of the squares of the charges of the ions involved in the equilibrium (with the product ions positive and the reagent ions negative). The following numerical values of the constants were found³ earlier to be satisfactory

for $K(\text{IV})_a$: $K^0(\text{IV})_a = 0.21$, $\Delta(Z_i^2) = -6$ and $\hat{a} = 7.5 \text{ \AA}$.
for $K(\text{IV})_c$: $K^0(\text{IV})_c = 7.0$, $\Delta(Z_i^2) = -8$ and $\hat{a} = 7.5 \text{ \AA}$.

The corresponding constants for $K(\text{VI})_c$ are evaluated below.

Evaluation of the Activity Constant.—The results of the experiments are summarized in Tables IIIa, b and c. The three methods (polarographic, spectrophotometric and potentiometric) apparently yield within the experimental error the same equilibrium constants K_{eq} (Table IIIa) indicating that there are no systematic errors in the various experimental methods. The acid dependence of K'_{eq} at constant μ is as predicted from equations 4 and 11 (see Table IIIb). This furnishes further proof that the assignment of the species U^{4+} , UOH^{+3} , UO_2^+ and UO_2^{2+} and the value of the acid constant $K(\text{IV})_a$ are correct. The ionic strength dependence of the equilibrium constant is given in Table IIIc. It was found that K_{eq} increases by a factor of *ca.* 200 as the ionic strength increases from 0.0085 to 2.

In view of the fact that it was possible to represent the ionic strength dependence of $K(\text{IV})_a$ satisfactorily by the Debye-Hückel equation³ (equation 13) the same equation was applied to the ionic strength dependence of K_{eq} . For this equilibrium $\Delta(Z_i^2)$ is 14, and a plot of $\log K_{\text{eq}}$ vs. $\mu^{1/2}/(1 + 0.3286 \hat{a} \mu^{1/2})$ should have a slope of $14 \times 0.509 = 7.126$. By trial and error it was found that, using $\hat{a} = 6.0 \text{ \AA}$, the data (particularly for perchlorate solutions) fell along a straight line of the theoretical slope and by extrapolation to $\mu = 0$ the activity constant $K_{\text{eq}}^0 = (1.7 \pm 0.3) \times 10^6$ was found (see Fig. 1).

The data for chloride solutions, corrected for chloride complexing of uranium(IV), tended to be higher than those for perchlorate solutions. From the deviations the stability constant of the uranium(VI) chloride complex was estimated. Assuming again that equation 13 is applicable, $K(\text{VI})_c^0 = 2.4$ was found using $\hat{a} = 6.0 \text{ \AA}$. and $\Delta(Z_i^2) = -4$. In view of the limited precision of the data, the arbitrary limitation of the complexing reactions, and the large uncertainty in the value $K(\text{IV})_c$ on which $K(\text{VI})_c$ is directly dependent (equation 11), this stability constant can only be considered a rough approximation, showing that uranium(VI) is only weakly complexed by chloride ions.

The agreement of the data with the Debye-Hückel expression (equation 13) is surprisingly good considering that $\Delta(Z_i^2)$ is extremely large, that the ionic strength range covered is large, that highly charged ions are involved, and only one parameter (\bar{a}) is used. Furthermore, the numerical value of the parameter $\bar{a} = 6.0 \text{ \AA}$. is quite reasonable if compared with those used to represent activity coef-

ficients of simple electrolytes and if compared with the parameter $\bar{a} = 7.5 \text{ \AA}$. used to represent $K(\text{IV})_a$ where the average charge of the ions was higher. It thus appears that considerable confidence can be placed in the use of the Debye-Hückel expression (equation 13) for estimation of activity constants for equilibria involving highly charged ions.

OAK RIDGE, TENNESSEE

RECEIVED JULY 28, 1950

[CONTRIBUTION FROM THE RESEARCH LABORATORY, GODFREY L. CABOT, INC.]

Heats of Adsorption on Carbon Black. III

BY M. H. POLLEY, W. D. SCHAEFFER AND W. R. SMITH

The heats of adsorption of *n*-decane and dihydromyrcene have been measured at 100° on a series of furnace and channel carbon blacks. With one exception, the results obtained are in line with those previously determined with lower molecular weight hydrocarbons at 0°. The adsorption appears to be physical in nature and initial values between 2 and 3 kcal. per CH₂ group in the adsorbate were obtained for the heat of adsorption. Dihydromyrcene appears to undergo some degree of reaction with the chemisorbed oxygen complex present on the surface of channel blacks. Since this reaction was not observed when other reinforcing carbon blacks were used as adsorbents, it may be concluded that this is not of primary significance in reinforcement.

The differential heats of adsorption of a number of adsorbates on several carbon blacks have been determined calorimetrically in an attempt to correlate the surface activity of these blacks and their varying efficiency in rubber reinforcement. Previous publications have described the adsorption of elementary gases at -195°,¹ and of C₂ to C₅ paraffinic and olefinic hydrocarbons at 0°. In each case the adsorption proved to be van der Waals in nature, and the surface activities revealed by the calorimetric measurements approximated the rubber reinforcing ability of the carbon black adsorbents.

None of the adsorbates studied possessed the two alpha methylene groups characteristic of the unsaturation pattern of natural rubber. These groups have been designated as active in such chemical reactions of rubber as oxidation and vulcanization.⁴ Consequently, if chemical bonds between elastomer and carbon black were a factor in reinforcement, such reaction should become apparent when a hydrocarbon possessing these active methylene groups is adsorbed on carbon black at 100°. Dihydromyrcene (2,6-dimethyl-2,6-octadiene) is the simplest hydrocarbon possessing a structure and unsaturation pattern analogous to natural rubber; consequently, it was selected as the adsorbate in the present study. *n*-Decane was used concurrently to provide a reference adsorbate which would isolate the effect of the dihydromyrcene unsaturation.

Preliminary results with a fully reinforcing channel black, Spheron 6, as the adsorbent have been recently reported.⁵ In the present paper,

measurements have been extended to include additional carbon blacks of varying rubber reinforcing ability.

Experimental

Research grade *n*-decane was obtained from Eastman Kodak Company and was used without further purification. The dihydromyrcene was prepared by the reduction of geraniol with sodium and ethyl alcohol in liquid ammonia.⁶

The following commercial grades of carbon black were employed as adsorbents: Spheron 6, a medium processing channel black; Vulcan 3, a high abrasion furnace black; and Sterling S, a semi-reinforcing furnace black. In addition three modifications of Spheron 6 were prepared for this work. A Spheron 6 sample was "devolatilized" by heating to 925° in a vacuum for a period of 3.5 hours to free the surface of the chemisorbed oxygen complexes which constitute "volatile" matter.⁷ This treatment raised the water sludge pH⁸ of Spheron 6 from 4.1 to 8.7. The second modification was Graphon, *i.e.*, Spheron 6, which had been partially graphitized at 3200°. The third was a sample of Spheron 6 on which the surface acidic complexes⁷ were neutralized by titrating a slurry of Spheron 6 in 1 *N* KCl with 0.1 *N* KOH to a pH of 10.0. After titration, the black was washed with boiling distilled water, to reduce the chloride ion contamination, until the pH was reduced to 6.0. The titration was then repeated in a water slurry to a pH of 8.5 to assure complete neutralization of the surface groups. The black was finally oven dried at 110°. Prior to each adsorption run the carbon black was outgassed in the calorimeter for two hours at room temperature and then for three hours at 250°.

The calorimeters used in this study have been previously described.^{3,5} The reference junction was a solid copper cylinder, 7 mm. × 10 mm., to which one junction of the copper-constantan couple was silver soldered. This junction was sealed in a Pyrex bulb connected to the vacuum line and helium supply so that rapid thermal equilibrium with the bath at the beginning of each run could be attained.

The adsorption apparatus was designed for use with hydrocarbon vapors at 100°. The vapor supply bulb, buret, calorimeter, and reference junction were completely immersed in a circulating oil-bath thermostatically controlled to 100 ± 0.015° by a mercury-xylene type thermoregulator in conjunction with a cold-cathode tube relay.⁹ All por-

(1) R. A. Beebe, J. Biscoe, W. R. Smith and C. B. Wendell, Jr., *THIS JOURNAL*, **69**, 95 (1947).

(2) R. A. Beebe, M. H. Polley, W. R. Smith and C. B. Wendell, Jr., *ibid.*, **69**, 2294 (1947).

(3) R. A. Beebe, G. L. Kington, M. H. Polley and W. R. Smith, *ibid.*, **72**, 40 (1950).

(4) E. H. Farmer, "Advances in Colloid Science," edited by H. Mark and G. Whitby, Vol. II, Interscience Publishers, Inc., New York, N. Y., 1946.

(5) W. D. Schaeffer, M. H. Polley and W. R. Smith, *J. Phys. Colloid Chem.*, **54**, 227 (1950).

(6) E. Chablay, *Ann. Chim.*, **3**, 145 (1917).

(7) W. R. Smith and W. D. Schaeffer, "Proceedings of the Second Rubber Technology Conference," edited by T. R. Dawson, W. Heffer & Sons, Ltd., Cambridge, England, 1948, p. 410.

(8) W. B. Wiegand, *Ind. Eng. Chem.*, **29**, 953 (1937).

(9) C. E. Rudy, Jr., and P. Fugassi, *Ind. Eng. Chem., Anal. Ed.*, **12**, 757 (1940).