the instantaneous moles of minor component in the solid and liquid phases and the total moles of sample, respectively. In the region of partial melting, the identity shown by equation 3 is applicable.

$$K \equiv \frac{X_2'}{X_2} = \left(\frac{n_2'}{n_0(1-\gamma)}\right)\left(\frac{n_0\gamma}{n_2}\right) \qquad (3)$$

Since the total moles of minor component, n_2'', is constant and $n_2'' = n_2 + n_2'$, equation 4 follows from equation 3.

$$K = \frac{(n_2'' - n_2)\gamma}{n_2(1-\gamma)} \qquad (4)$$

Solving for n_2 equation 5 is obtained

$$N_2 = \frac{n_2''\gamma}{K + \gamma(1-K)} \qquad (5)$$

The instantaneous concentration of minor component in the liquid phase is given by equation 6.

$$X_2 = \frac{n_2}{n_0\gamma} = \frac{n_2''}{n_0}\frac{1}{K + \gamma(1-K)} \qquad (6)$$

where $n_2''/n_0 = X_2''$, and γ is the fraction melted at the corresponding equilibrium temperature T_γ. This form is then substituted in equation 2 with a rearrangement of terms to yield equation 7, the form of the melting point equation suitable for plotting calorimetric data when solid solutions occur.

$$T_\gamma = T_0 - \frac{RT_0^2}{\Delta H_F} X_2'' \frac{1}{\frac{K}{1-K} + \gamma} \qquad (7)$$

Equation 7 may be compared with equation 8, the ordinary equation used for plotting calorimetric data in the absence of solid solutions.

$$T_\gamma = T_0 - \frac{RT_0^2}{\Delta H_F}\frac{X_2''}{\gamma} \qquad (8)$$

The $K/(1 - K)$ term in equation 7 corrects the upward curvature of the ordinary plot of T_γ *vs.* $1/\gamma$ and yields a straight line for the case, $0 < K < 1$. For the determination of K, values of $T_{1.00}$, $T_{0.50}$, and $T_{0.25}$ are read off the ordinary curve at reciprocal fractions melted of 1.00, 2.00 and 4.00, respectively. These values are then substituted in equation 9 (derived from equation 7 by solving for K at the indicated values of T_γ).

$$K = \left(\frac{2}{3}\right)\left\{\frac{T_{1.00} - T_{0.50}}{T_{0.50} - T_{0.25}} - \frac{1}{2}\right\} \qquad (9)$$

after determining K, equation 7 is used to replot the data for better extrapolation and interpolation of values of $T_{1.00}$, $T_{0.50}$, and $T_{0.25}$, and for recalculation of K by equation 9. Equations 10 and 11 are then used for calculating T_0 and X_2.

$$T_0 = T_{1.00} + (T_{1.00} - T_{0.50})\frac{1+K}{1-K} \qquad (10)$$

$$X_2 = \frac{\Delta H_F}{RT_0^2}(T_{1.00} - T_{0.50})\frac{(1+K)}{(1-K)^2} \qquad (11)$$

This treatment was applied to data taken from a curve of equilibrium temperature *vs.* reciprocal fraction melted given by Aston and Fink[5] for a mixture of 95.4% 2,2-dimethylbutane and 4.6% 2,3-dimethylbutane, known definitely to form solid solutions.[7,8] The purity, estimated from the T_γ *vs.* $1/\gamma$ plot, calculated by Aston and Fink, was 99.78 mole %, and T_0, estimated from this plot in the usual way, was about −104.85° instead of −98.86°.[7] By applying the treatment outlined above, K was found to be 0.675, T_0 was calculated as −98.86° and X_2'' as 4.6 mole %, in excellent agreement with the theoretical values.

As an independent check on this treatment, equation 7 was used to calculate the solidus temperature of this mixture by setting $\gamma = 0$ and allowing $K = 0.675$, $T_0 = -98.86°$ and $X_2 = 0.046$ as calculated from our treatment of the melting data. The calculated solidus temperature was −109.2°; the observed value[6] for this mixture was −109.4°. Agreement to a few tenths of a degree for this calculation is good.

NOTE ADDED IN PROOF.—The treatment outlined above is for one minor component. A general treatment for two or more minor components does not exist because of the uncertainty in the number of unknown parameters (distribution coefficients and concentrations), and the variability of their relative magnitudes. However, the probability of having more than one minor component in a calorimetric sample which has undergone extensive fractional distillations or crystallizations is relatively rare. Also, replotting the data as suggested above assures the absence of more than one minor component (with different distribution coefficients), when a straight line is obtained for T_γ *versus* $1/[K/(1 - K)] + \gamma$ over the entire range of the experiment. More than one minor component whose distribution coefficients are the same is, of course, allowable.

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[7] H. L. Fink, M. R. Cines, F. E. Frey and J. G. Aston, THIS JOURNAL, **69**, 1501 (1947).

[8] J. W. Tooke and J. G. Aston, *ibid.*, **67**, 2275 (1945).

Deuterium Exchange between Trichloroethylene and Water. Infrared Spectral Data for Trichloroethylene-*d*

BY THOMAS J. HOUSER, RICHARD B. BERNSTEIN, RICHARD G. MIEKKA AND JOHN C. ANGUS

RECEIVED AUGUST 30, 1955

Base-catalyzed deuterium exchange reactions between water and CCl_3H,[1-3] CCl_2BrH,[4] $CClBr_2H$,[4] $CClBrH_2$[5] and C_2Cl_3H[6] have been noted.

The study[3] of the CCl_3H–water exchange offers support for the halocarbanion mechanism; the base-catalyzed exchange of CCl_3D with CBr_3H[7] is a related example. The only datum reported[6] in the trichloroethylene exchange is that some deuteration resulted when C_2Cl_3H was heated with $Ca(OD)_2$ in D_2O. Measurements on the exchange rate of C_2Cl_3H with NaOD in D_2O and on the reverse exchange of C_2Cl_3D with NaOH are reported here.

Purified C_2Cl_3H (n^{25}D 1.4741) was refluxed with sodium deuteroxide (*ca.* 6 *N* NaOD) at 81–84°. The phases were separated and the trichloroethylene weighed, washed, distilled and analyzed for deu-

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[1] Y. Sakamoto, *Bull. Chem. Soc. Japan*, **11**, 627 (1936).

[2] T. W. Newton and G. K. Rollefson, *J. Chem. Phys.*, **17**, 718 (1949).

[3] J. Hine, R. Peek and B. Oakes, THIS JOURNAL, **76**, 827 (1954).

[4] R. H. Sherman and R. B. Bernstein, *ibid.*, **73**, 1376 (1951).

[5] R. B. Bernstein, unpublished data.

[6] L. C. Leitch and H. J. Bernstein, *Can. J. Research*, **28B**, 35 (1950).

[7] G. P. Semeluk and R. B. Bernstein, THIS JOURNAL, **72**, 4830 (1950).

terium.[8] The exchange was repeated with a new charge of NaOD using the same procedures; four exchanges resulted in the preparation of 91% C_2Cl_3D. The NaOD solutions were distilled to dryness; analysis of the recovered water for deuterium (by density) checked the values (±1%) computed by material balance from the deuterium assay of the trichloroethylene samples. Assuming[9] a classical equilibrium constant, the fraction exchanged could be calculated

$$f = \frac{\beta_n - \beta_{n-1}}{\alpha_n - \beta_{n-1}}$$

where β_n = atom fraction D in the trichloroethylene after nth exchange; α_n = atom fraction D in total reaction mixture (nth exchange).

During refluxing, mild explosions occurred with increasing frequency; after several days, reflux was stopped and the trichloroethylene repurified (exchange equilibrium was never attained). The decomposition reaction is probably: $C_2Cl_3H + OH^- \rightarrow C_2Cl_2 + Cl^- + H_2O$. The rate of decomposition (based on weight loss of trichloroethylene and appearance of chloride ion in the aqueous phase), was 0.12%/hour.

Table I summarizes the exchange data, which appear to be first order.

The half-time for exchange was found to be 50 hr.; for the reverse exchange (C_2Cl_3D + NaOH; smaller quantities were used under similar conditions) it was 60 hr. During a typical run the alkali concentration (in the aqueous phase) diminished from 6 to 3 N, so kinetic treatment was not warranted.

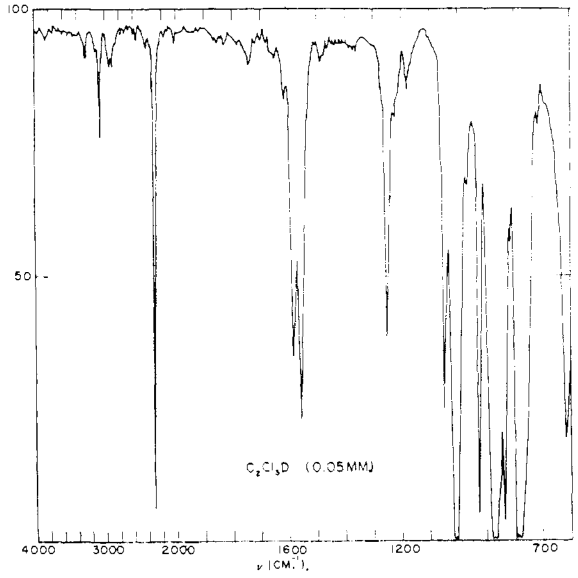

Fig. 1.

TABLE I

EXCHANGE OF TRICHLOROETHYLENE WITH NaOD AND D_2O

Exchange no.	Time of exchange (hr.)	Input trichloroethylene (moles)	Input D_2O (g. atom D)	Input Na (g. atom)	β	α	
1	96	1.12	1.36	0.14	0.378	0.548	0.690
2	48	0.91	2.27	.13	.597	.822	.493
3	72	.80	2.27	.13	.792	.897	.650
4	96	.71	2.27	.13	.906	.950	.722

Figure 1 shows the infrared spectrum[10] of liquid C_2Cl_3D (91% D). The previous infrared[11] and Raman[12] studies did not report overtones or com-

TABLE II

SUMMARY OF INFRARED SPECTRAL DATA AND ASSIGNMENTS

v (cm.⁻¹)	Assignment	v (cm.⁻¹)	Assignment
C_2Cl_3H		C_2Cl_3D	
172[a]	v_9 (a')	172[a]	v_9 (a')
211[a]	v_{12} (a'')	213[a]	v_{12} (a'')
274[a]	v_8 (a')	274[a]	v_8 (a')
381[a]	v_7 (a')	381[a]	v_7 (a')
450[a]	v_{11} (a'')	427[a]	v_{11} (a'')
628[a]	v_6 (a')	618[a]	v_6 (a')
780[a]	v_{10} (a'')	630[a]	v_{10} (a'')
802[b]	$v_3 - v_{11}$		
840[b]	v_5 (a')	797[b]	v_5 (a')
905[b]	$2v_{11}$; $v_6 + v_8$	856	$2v_{11}$
930[b]	v_4 (a')	873[b]	v_4 (a')
988	$v_{10} + v_{12}$	1013[b]	v_3 (a')
1015	$v_6 + v_7$	1053[b]	$v_{10} + v_{11}$
1106	$v_5 + v_8$	1185	$v_2 - v_7$
1141	$v_4 + v_{12}$	1254[b]	$2v_{10}$; $v_4 + v_7$
1227[b]	$v_{10} + v_{11}$	1493	$v_4 + v_{10}$
1245[b]	v_3 (a')	1563	v_2 (a')
1313	$v_4 + v_7$; $v_2 - v_8$	1586	$2v_5$
1366	$(v_{10} + v_{12}) + v_7$	1623	$v_3 + v_6$
1375	$v_4 + v_{11}$; $v_2 - v_{12}$	1657	$(v_4 + v_{10}) + v_9$
1565[c]	$2v_{10}$	1666	$v_4 + v_5$
1587[c]	v_2 (a')	1748	$2v_4$
1676	$2v_5$	1830	$v_2 + v_8$
1758	$v_4 + v_5$	2033	$v_1 - v_8$
1794	$v_2 + v_{12}$	2177	$v_2 + v_6$
1857	$2v_4$; $v_2 + v_8$	2302[d]	v_1 (a')
1981	$(v_4 + v_5) + v_{12}$	2387	$(v_2 + v_6) + v_{12}$
2040	$v_2 + v_{11}$	2437	$v_2 + v_4$
2091	$v_3 + v_5$	2917	$v_1 + v_6$
2172	$(v_2 + v_{12}) + v_7$	2950	$v_1 + v_7 + v_8$ (?)
2211	$v_2 + v_6$	3305	$v_1 + v_3$
2417	$v_2 + v_5$	3821	$v_1 + v_2$
2469	$2v_3$	3942	$(v_1 + v_3) + v_{10}$
2822	$v_2 + v_3$		
2950	$(v_2 + v_{11}) + v_4$		
3085	v_1 (a')		
3144	$2v_2$		
3718	$v_1 + v_6$		
3857	$v_1 + v_{10}$		
3924	$v_1 + v_5$		

[a] Raman data (ref. 12). [b] CS_2 solution (1:20). [c] CCl_4 solution (1:10). [d] Rechecked on Perkin–Elmer Model 12C Spectrometer with LiF prism.

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(8) A Perkin–Elmer Model 21 Infrared Spectrophotometer (0.11 mm. cell) was used. A calibration curve for C_2Cl_3H in CCl_4 was prepared (3085 cm.⁻¹ band). The absorbancy index was 0.021 per mole %. The uncertainty in the analysis was ±1% D.

(9) Using frequencies for C_2Cl_3H and C_2Cl_3D as tabulated below, the equilibrium constant at 350°K. was calculated; methods outlined by Urey, *J. Chem. Soc.*, 562 (1947); Bigeleisen and Mayer, *J. Chem. Phys.*, **15**, 261 (1947). Results were sensitive to the choice of frequencies for the isotopic water molecules. Using observed gaseous frequencies, K = 1.82; using liquid frequencies, K = 1.96. Since these calculations are considered unreliable in any case for liquid phase exchanges, the classical value (K = 2) was assumed for the reaction $C_2Cl_3H + D_2O \rightleftarrows C_2Cl_3D + HOD$.

(10) Perkin–Elmer Model 21 Spectrophotometer (NaCl optics, 0.05 mm. cell).

(11) H. J. Bernstein, *Can. J. Research*, **28B**, 132 (1950).

(12) G. Allen and H. J. Bernstein, *Can. J. Chem.*, **32**, 1044 (1954).

binations above 1250 cm.$^{-1}$. The present data (summarized in Table II) are in good agreement with ref. 11, except for the $\nu_1(a')$ fundamental for C_2Cl_3D. The present value is considered reliable to ±2 cm.$^{-1}$ and is identical with the Raman value.[12]

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The Behavior of Uranyl and Neptunyl Ions with Dowex-50 Cation-exchange Resin[1]

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During the course of an investigation of the kinetics of an oxidation–reduction reaction in a mixed sulfuric acid–perchloric acid media it became desirable to attempt to ascertain the degree of association between Np(VI) and bisulfate ion. The distribution of a metal ion between an aqueous phase and a solid phase composed of a synthetic cation exchanger has been demonstrated to yield quantitative data on the composition of complex ion systems.[2]

In order to demonstrate that the method was indeed applicable under the conditions of this investigation it was deemed advisable to first determine the association constant for some system that had been previously studied by other means. Accordingly we have determined the complexity constants for uranyl sulfate.

Experimental

The ion exchanger used in this study was Analytical Grade AG 50-X12 processed from Dowex-50 by Bio Rad Laboratories. The hydrogen form of the resin was 200–400 mesh. In addition to the intensive purification by the processor the resin was treated with molar perchloric acid followed by exhaustive water washes. The resin was then oven dried at 80° for three hours.

The U^{233} was purified by an ether extraction just prior to use. The Np^{237} was from a pure stock and the oxidation states prepared as previously described.[3]

Known masses of the resin (usually about 0.2 g.) were introduced into 10-ml. erlenmeyer flasks. Measured volumes of solution containing the metal ions in concentrations of the order of magnitude 10^{-4}–10^{-6} molar were then introduced into the flasks which were then agitated in a constant temperature water-bath for timed intervals.

After equilibration the phases were separated. Aliquots of the aqueous phase mounted on tantalum plates were assayed using a methane proportional α-counter.

Results and Discussion

Defining the distribution coefficient in the absence of a complexing agent we have

$$K = [MR]/[M] \qquad (1)$$

where [MR] is the concentration of the metal in the resin phase per gram of air dried resin and [M] is the concentration of the metal ion in solution per ml. of solution at equilibrium. Upon the introduction of a complexing agent (1) becomes

$$K_1 = \frac{[MR]}{[M] + [MA] + \cdots} \qquad (2)$$

Then any of the standard techniques for the calculation of association constants can be employed.[4] This approach ignores the change in composition of the solution and the resin caused by the exchange reaction as well as assuming constancy of metal ion activities. At the metal ion concentrations used the loading of the resin is negligible. Thus the equilibrium constants are concentration ratios for solutions of the given composition.

Included in Table I are the results of the distribution of uranyl ion between 0.955 M $HClO_4$ and the resin as a function of time. Figure 1 graphically demonstrates the variation of the distribution coefficient as a function of bisulfate concentration at constant ionic strength. The solid line is a theoretical curve with the values of the constants k_1 and k_2 given in the defining equations below

TABLE I

DISTRIBUTION COEFFICIENTS OF UO_2^{+2}, NpO_2^{+2} AND NpO_2^+ BETWEEN DOWEX-50 AND 1 M $HClO_4$ AT 25°, μ = 1.0

Time, min.	K		
	UO_2^{+2}	NpO_2^{+2}	NpO_2^+
60	72.6 ± 1.0	5.43 ± 0.04	5.40 ± 1.3
120	74.6 ± 0.1	8.65 ± .98	8.61 + 0.50
180	74.3 ± 1.3	9.13 ± .11	9.72 ± 1.15
240	74.6 ± 1.4	12.12 ± 1.0	14.03 ± .01

$$\frac{[UO_2SO_4]}{[UO_2^{+2}][HSO_4^-]} = \frac{k_1}{[H^+]} = 6.25 \pm 0.75 \qquad (3)$$

$$\frac{[UO_2(SO_4)_2]^{-2}}{[UO_2SO_4][HSO_4^-]} = \frac{k_2}{[H^+]} = 1.22 \pm 0.30 \qquad (4)$$

Comparison with the previous values for the constants reported by other investigators[5] indicates that the method yields the desired quantitative information.

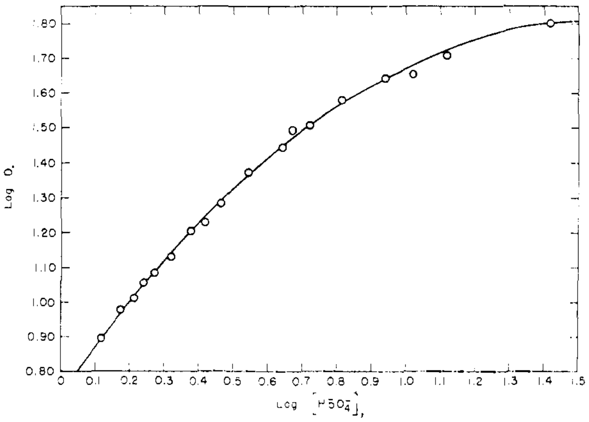

Fig. 1.—Variation of the distribution coefficient of uranyl ion as a function of bisulfate ion at 25.0° and μ = 1.0.

In an effort to extend the technique to a new system the distribution of NpO_2^{+2} between the perchloric acid and the resin was measured as a function of time. The data for this set of experiments are

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[1] Work performed under the auspices of the U. S. Atomic Energy Commission.

[2] See, for example, S. Fronaeus, *Acta Chem. Scand.*, **5**, 859 (1951).

[3] D. Cohen and J. C. Hindman, THIS JOURNAL, **74**, 4679 (1952).

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[5] R. A. Day, Jr., and R. M. Powers, *ibid.*, **76**, 3895 (1954); S. Ahrland, *Acta Chem. Scand.*, **5**, 1151 (1951); R. H. Betts and R. K. Michels, *J. Chem. Soc.*, Supp. Issue #2, S286 (1949).