

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Exchange and Transfer Equilibria of Acids, Bases, and Salts in Deuterium-Protium Oxide Mixtures. The Ion Product Constant of Deuterium Oxide

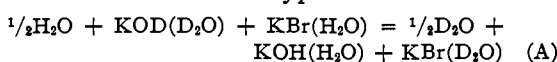
BY RICHARD W. KINGERLEY AND VICTOR K. LAMER

It has been pointed out previously¹ that quantitative data on equilibria in mixtures of deuterium and protium oxides are necessary for the interpretation of the kinetics of acid-base catalyzed reactions,¹ the dissociation constants of deuterio acids,^{2,3} and the conductance of salts in H₂O-D₂O mixtures.⁴

Several of these equilibrium reactions have been measured directly,^{2,5,6} and many have been calculated indirectly by a combination of processes.⁷ Much information has been accumulated on the hydrogen-deuterium exchanges for a number of different compounds^{8,9} as well as for the solubilities of salts in deuterium and protium oxides.¹⁰

Since few investigators have clearly defined the exact thermodynamic processes involved in their work, apparent anomalies and contradictions appear in the literature. It is proposed in this work to examine the experimental procedures and analyze the processes involved.

For a reaction of the type



there exists a free energy of exchange when potassium hydroxide is converted into potassium deuterioxide and in addition a free energy of transfer of potassium hydroxide and potassium bromide from one solvent to the other. The latter process has been carelessly handled or neglected by most investigators.

Electromotive force data obtained from galvanic cells without liquid junction frequently involve both types of free energy contributions. For example, the conversion of NaOD to NaOH, first investigated by Abel, Bratu and Redlich¹¹ using H₂-D₂ gas and silver-silver chloride electrodes, involves both exchange and transfer.

(1) LaMer, *Chem. Rev.*, **19**, 363 (1936).

(2) Rule and LaMer, *THIS JOURNAL*, **60**, 1974 (1938).

(3) Brescia, *ibid.*, **60**, 2811 (1938).

(4) LaMer and Chittum, *ibid.*, **58**, 1642 (1936).

(5) Brescia, *J. Chem. Phys.*, **7**, 310 (1939).

(6) Noonan and LaMer, *J. Phys. Chem.*, **43**, 247 (1939).

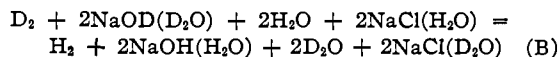
(7) Korman and LaMer, *THIS JOURNAL*, **58**, 1396 (1936).

(8) Brodsky, *Trans. Faraday Soc.*, **33**, 1180 (1937).

(9) Hamill and Freudenberg, *THIS JOURNAL*, **57**, 1427 (1935); Orr, *Trans. Faraday Soc.*, **32**, 1633 (1936).

(10) Eddy and Menzies, *J. Phys. Chem.*, **44**, 207 (1940).

(11) Abel, Bratu and Redlich, *Z. physik Chem.*, **A173**, 353 (1935).



Although the transfer of sodium chloride was not treated explicitly by these authors,¹¹ the validity of their calculations is not affected since a second transfer arising from the corresponding acid cell compensated the transfer involved in the first. Their excellent work, however, has been erroneously criticized by others (see ref. 2, footnote 12, and ref. 6, p. 256, for a refutation of some of these misunderstandings).

The free energy contribution arising from transfer alone may be determined in the case of a salt from the solubilities of the salt in the respective solvents. The unequal solubility at saturation requires an activity coefficient correction arising from the difference in the ionic strength. Most of the solubility studies in D₂O¹⁰ have involved salts which are quite soluble and consequently require uncertain interionic activity coefficient corrections in normalizing to standard states. The difficultly soluble salt thallic chloride has accordingly been chosen for determining the free energy of transfer from H₂O to D₂O. For a compound exhibiting both exchange and transfer we have chosen calcium hydroxide.

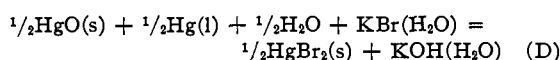
When H₂O-D₂O mixtures are treated with compounds containing replaceable hydrogen atoms a mutual exchange of hydrogen and deuterium often takes place. The change in the deuterium content of the solvent measures the direction and extent of the equilibrium. Such processes are free from transfer since the solvent remains sensibly constant.

Brodsky⁸ defined an exchange factor $\alpha = (\text{D}/\text{H})_{\text{solvent}}/(\text{D}/\text{H})_{\text{solute}}$ and determined its value for a series of compounds by analyzing for the decrease in deuterium content with an interferometer. Most compounds studied have exchange factors close to unity. He is disturbed, however, by the fact that his value of $\alpha = 1.05$ for NaOH is not consistent with the value of the equilibrium constant, $K = 1.56$, for the process $\frac{1}{2}\text{H}_2\text{O} + \text{NaOD}(\text{D}_2\text{O}) = \frac{1}{2}\text{D}_2\text{O} + \text{NaOH}(\text{H}_2\text{O}) \quad (\text{C})$

obtained by Korman and LaMer⁷ from a combination of accurate e. m. f. measurements. He

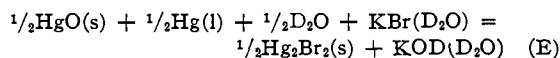
suggested (p. 1184) that the discrepancy arose from experimental error in the measurements of Abel, Bratu and Redlich,¹¹ which were involved in the calculations. We shall demonstrate that the correct reason for the discrepancy is that the e. m. f. calculations involve both transfer and exchange processes, and that Brodsky is not justified in equating α and K .

It is proposed to measure directly process (A) which has been calculated indirectly⁷ from e. m. f. measurements and to calculate the ion product constant of deuterium oxide. These measurements will involve the equilibrium state of the reaction:

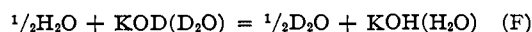


which Newton and Bolinger¹² found could be studied by analytical methods.

In deuterium oxide the reaction becomes



Subtracting (E) from (D) gives (A). In some cases it may be desirable to eliminate the transfer free energy of KBr to obtain



The thermodynamic constant, K_a , for reaction (D) is:

$$K_a(\text{H}_2\text{O}) = \frac{(\text{KOH})_{\text{H}_2\text{O}} f_{\text{KOH}}(\text{H}_2\text{O})}{(\text{KBr})_{\text{H}_2\text{O}} f_{\text{KBr}}(\text{H}_2\text{O})} \quad (1)$$

For reaction (E)

$$K_a(\text{D}_2\text{O}) = \frac{(\text{KOD})_{\text{D}_2\text{O}} f_{\text{KOD}}(\text{D}_2\text{O})}{(\text{KBr})_{\text{D}_2\text{O}} f_{\text{KBr}}(\text{D}_2\text{O})} \quad (2)$$

where the activity in each expression has been separated into its stoichiometric concentration and activity coefficient (f) factors. The former of these two quantities was obtained from the experimental data. The latter ratio, $(f_{\text{KOH}}/f_{\text{KBr}})_{\text{H}_2\text{O}} = 0.772/0.765$ at 25° ¹³ and at the ionic strength investigated ($\mu = 0.1$) is 1.01. It has been assumed to be the same at the several temperatures studied and in the H_2O - D_2O mixtures. The latter assumption is justifiable since the dielectric constants of H_2O and of D_2O are sensibly identical in the pure state and in their mixtures.¹⁴

The increase in free energy of a reaction in any given state, ΔF , is related to the increase in free energy in its standard state ΔF^0 , by the expression

$$\Delta F = \Delta F^0 + RT \ln K_a \quad (3)$$

(12) Newton and Bolinger, *THIS JOURNAL*, **52**, 921 (1930).

(13) Taylor, "Treatise on Physical Chem.," D. Van Nostrand Co., New York, N. Y., 1931, Vol. 1, p. 772.

(14) Wyman and Ingalls, *THIS JOURNAL*, **60**, 1182 (1938).

At equilibrium, $\Delta F = 0$ and therefore in H_2O

$$\Delta F^0_{\text{H}_2\text{O}} = -RT \ln K_a(\text{H}_2\text{O}) \quad (4)$$

and in D_2O

$$\Delta F^0_{\text{D}_2\text{O}} = -RT \ln K_a(\text{D}_2\text{O}) \quad (5)$$

Dividing (1) by (2)

$$\frac{K_a(\text{H}_2\text{O})}{K_a(\text{D}_2\text{O})} = \frac{(\text{KOH})_{\text{H}_2\text{O}}(\text{KBr})_{\text{D}_2\text{O}} f_{\text{KOH}}(\text{H}_2\text{O}) f_{\text{KBr}}(\text{D}_2\text{O})}{(\text{KOD})_{\text{D}_2\text{O}}(\text{KBr})_{\text{H}_2\text{O}} f_{\text{KOD}}(\text{D}_2\text{O}) f_{\text{KBr}}(\text{H}_2\text{O})} \quad (6)$$

The activity coefficient ratio may be set equal to unity if the standard state is properly chosen. This may be done by assigning the value unity to the activity coefficient of the electrolytes at infinite dilution in H_2O , and similarly the activity coefficient of the electrolytes as unity at infinite dilution in D_2O . This ratio at any finite concentration of electrolyte will also be unity at the same ionic strength in the two solvents. Any small specific interaction differences of KOH and KBr will cancel. The ratio of the thermodynamic constants for expression (6) becomes equal to the quotient of the ratio of (KOH) to (KBr) in the two solvents.

From (4) and (5) we obtain for equation (A)

$$\Delta F^0 = \Delta F^0(\text{H}_2\text{O}) - \Delta F^0(\text{D}_2\text{O}) = -RT \ln K_a(\text{H}_2\text{O})/K_a(\text{D}_2\text{O}) = -RT \ln K_a(\text{H}_2\text{O})/K_a(\text{D}_2\text{O})$$

where ΔF^0 represents the free energy of transfer and of exchange of reaction (A), and the ratio $K_a(\text{H}_2\text{O})/K_a(\text{D}_2\text{O})$ represents the equilibrium constant for the reaction.

The increase in entropy for the reaction in the standard state ΔS^0 was calculated from the temperature coefficient of the free energy, $\delta \Delta F^0/\delta T = -\Delta S^0$. The increase in heat content ΔH^0 between the products and the reactants of the reaction was obtained from the thermodynamic expression $\Delta F^0 = \Delta H^0 - T\Delta S^0$.

Experimental Procedure

For the mercuric oxide-mercurous bromide equilibrium in H_2O approximately 2 g. each of red mercuric oxide, mercurous bromide, and mercury was added to 100 cc. of a 0.1 *N* solution of potassium bromide. When H_2O - D_2O mixtures were used as solvents, 1 g. each of the solid constituents was added to 40 cc. of solution. The mixtures were placed in Pyrex glass stoppered bottles, sealed with paraffin, and rotated in a thermostat. At six constant intervals of from twelve to twenty-four hours the solid phase was allowed to settle and an aliquot of supernatant liquid added directly to potassium acid phthalate.

If the solvent contained D_2O it was recovered at this point by distillation under reduced pressure, and the excess of phthalate determined by titration with base. Unsatisfactory results were obtained by direct distillation

from alkaline solution. All aliquots were analyzed for bromide ion concentration by the Volhard method.

The constancy of the anion ratio OH^-/Br^- over the period from twenty to eighty hours (see Fig. 1) shows that the equilibrium for reaction D is stable for that length of time. On rotating the system for longer periods of time, an abrupt increase in the anion ratio occurred with the simultaneous appearance of a brilliant red compound in the cream colored mixture of finely divided solids. Newton and Bolinger mention that a red compound appeared after a lapse of several months.

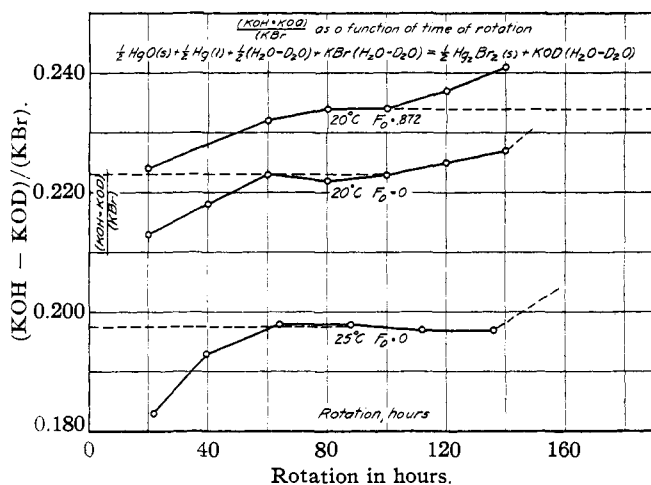
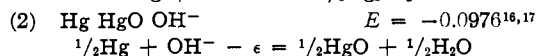
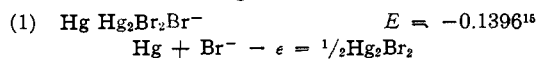
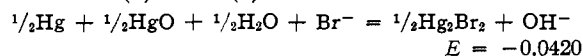


Fig. 1.— $(\text{KOH} - \text{KOD})/(\text{KBr})$ as a function of time of rotation.

That we are studying the equilibrium of a definite process (D) uncomplicated by side reactions over the stable period is established by the reproducibility of the data. Thermodynamics defines absolute equilibrium as a state from which no spontaneous change can occur, but it does not forbid the study of systems in metastable equilibrium for a given process if the behavior and results are reproducible as in the present case. As a final proof that we are measuring the equilibrium state of reaction D is evident from the following calculation from existing electromotive force data.



Subtract (2) from (1)



This potential corresponds to an equilibrium

(15) Gerke and Geddes, *J. Phys. Chem.*, **31**, 886 (1927).

(16) Kobayashi and Wang, *J. Sci. Hiroshima Univ.*, **5A**, 71 (1934).

(17) Fried, *Z. physik. Chem.*, **123A**, 406 (1928).

constant of 0.195, which is in satisfactory agreement with the value (0.200) obtained in this investigation at 25° in H_2O .

The solubility of thallos chloride was determined by rotating in a thermostat for several days an excess of the solid in 40 cc. of the $\text{H}_2\text{O}-\text{D}_2\text{O}$ solvent, and analyzing for thallos ion by titration with potassium iodate using the iodine monochloride method.¹⁸ Calcium hydroxide was determined in the saturated solution by adding the aliquot directly to acid phthalate and back titrating with standard base.

The exchange between hydrogen and deuterium in calcium hydroxide was determined by adding a weighed quantity of pure, dry, calcium oxide to a known weight of deuterium oxide, $F_D = 0.1900$. The exchange equilibrium was calculated from the change in density of the solvent.

Purification of Materials.—The protium oxide–deuterium oxide mixtures were recovered and purified in all experiments by distilling from alkaline potassium permanganate followed by a distillation from a neutral solution. The fraction of deuterium in the samples was determined with a 10-cc. pycnometer.

Mercurous bromide was prepared by treating in the cold an excess of redistilled mercury with dilute nitric acid (8 *N*). Potassium bromide was added to the mercurous nitrate solution,

the precipitated mercurous bromide washed fifteen times with distilled water, filtered on a sintered glass funnel, and dried at 105°.

Thallos chloride was prepared by adding thallos sulfate solution and hydrochloric acid slowly to hot water as described by Hogge and Garrett.¹⁹ The preparation was dried for two hours at 115° and stored in an amber bottle.

Commercial red mercuric oxide was treated with twelve washings of distilled water and dried. This preparation gave results identical with that of a sample of the compound made in this Laboratory.

Calcium oxide was prepared by dissolving an equivalent amount of c. p. calcium carbonate in hydrochloric acid and making the clear filtered liquid slightly basic with ammonia. Carbon dioxide gas was slowly bubbled into the hot solution to precipitate calcium carbonate. The compound was washed and ignited to the oxide at a bright red heat in an electric furnace.

C. p. potassium bromide was recrystallized twice before use. Mercury was distilled twice at low pressure in an all glass apparatus.

Results and Discussion

The equilibrium measurements for reactions (D) and (E) are recorded in Table I. The third

(18) Swift and Garner, *THIS JOURNAL*, **58**, 113 (1936).

(19) Hogge and Garrett, *ibid.*, **63**, 1089 (1941).

column gives the fraction of deuterium in the solvent, $^{20} F_D = \Delta s / 0.176$ where $\Delta s = (d_{25}^{25} - 1)$.

TABLE I
EQUILIBRIUM CONCENTRATIONS OF (KOH) AND (KBr)
FOR THE REACTIONS (c) AND (d)

Run	°C.	F_D	(KOH- KOD), m./l.	(KBr), m./l.	KOH-KOD/(KBr)
			$\frac{1}{2}\text{HgO}(s) + \frac{1}{2}\text{Hg}(l) + \frac{1}{2}(\text{H}_2\text{O}-\text{D}_2\text{O}) + \text{KBr}(\text{H}_2\text{O}-\text{D}_2\text{O}) = \frac{1}{2}\text{Hg}_2\text{Br}_2(s) + \text{KOD}(\text{H}_2\text{O}-\text{D}_2\text{O})$		
44	20	0	0.01803	0.0809	0.223 \approx 0.001
49	0		.01834	.0823	.223
59	0		.01697	.0760	.223
53	0.422		.01579	.0830	.190
54	.478		.01534	.0825	.186
55	.528		.01513	.0833	.182
56	.720		.01537	.0919	.167
57	.834		.01347	.0851	.158
61	.872		.01323	.0860	.154
		(1.000)	(.145)
27	25	0	0.01606	0.0811	0.198 \approx 0.001
28	0		.01650	.0833	.198
29	0.522		.01399	.0857	.163
33	.718		.01236	.0827	.149
30	.875		.01206	.0876	.138
32	.949		.01180	.0878	.134
34	.950		.01112	.0836	.133
		(1.000)	(.129)
25	30	0	0.01486	0.0843	0.176 \approx 0.001
18	0		.01481	.0844	.175
22	0		.01486	.0847	.175
65	0.478		.01243	.0860	.145
62	.527		.01209	.0857	.141
68	.575		.01231	.0886	.139
64	.870		.01038	.0876	.119
70	.924		.01050	.0888	.118
36	.950		.00956	.0818	.117
		(1.000)	(.113)
7	35	0	0.01351	0.0859	0.157 \approx 0.001
16	0		.01341	.0861	.156

The fourth and fifth columns contain the hydroxide and bromide ion concentration on the volume molar basis at equilibrium. The last column is the concentration ratio (KOH-KOD/KBr) at the F_D indicated. In Fig. 2, F_D of the solvent is plotted against the concentration ratio and extrapolated to 100% deuterium. The results of this linear extrapolation and the thermodynamic constants for both equilibria are recorded in Table II. Combination of these two equilibria yields the value for reaction (A) as given in Table III. For this reaction ΔH° is about 200 cal. Within experimental error there is no heat capacity effect.

A series of exchange equilibria calculated directly and indirectly is compiled in Table IV. The

(20) Stokland, Ronaess and Tronstad, *Trans. Faraday Soc.*, **35**, 312 (1939).

TABLE II
EQUILIBRIUM CONSTANTS AND THERMODYNAMIC DATA
FOR THE REACTIONS

	°C.	K_a	$-\log_{10} K_a$	ΔF°	$-\Delta S^\circ$	$-\Delta H^\circ$
		$\frac{1}{2}\text{HgO}(s) + \frac{1}{2}\text{Hg}(l) + \frac{1}{2}\text{H}_2\text{O} + \text{KBr}(\text{H}_2\text{O}) = \frac{1}{2}\text{Hg}_2\text{Br}_2(s) + \text{KOH}(\text{H}_2\text{O})$				
		$\frac{1}{2}\text{HgO}(s) + \frac{1}{2}\text{Hg}(l) + \frac{1}{2}\text{D}_2\text{O} + \text{KBr}(\text{D}_2\text{O}) = \frac{1}{2}\text{Hg}_2\text{Br}_2(s) + \text{KOD}(\text{D}_2\text{O})$				
H ₂ O	20	0.225	0.6478	869	17.0	4114
	25	.200	.6990	954	17.8	4352
	30	.177	.7520	1043	17.2	4170
	35	.158	.8013	1129	Av.	17.3 4200
D ₂ O	20	.147	.8327	1118	18.2	4217
	25	.130	.8861	1209	19.6	4634
	30	.114	.9431	1307	Av.	18.9 4400

TABLE III
EXCHANGE AND TRANSFER EQUILIBRIUM OF THE REACTION
(A)

	°C.	$K_a(\text{H}_2\text{O})/K_a(\text{D}_2\text{O})$	
		$\frac{1}{2}\text{H}_2\text{O} + \text{KOH}(\text{D}_2\text{O}) + \text{KBr}(\text{H}_2\text{O}) = \frac{1}{2}\text{D}_2\text{O} + \text{KOH}(\text{H}_2\text{O}) + \text{KBr}(\text{D}_2\text{O})$	
	20	1.53 \approx 0.01	
	25	1.54	
	30	1.55	

purpose of this table is to develop indirectly the constant for reaction (A) and compare with the value measured directly in this investigation. By further combinations the ion product constant of deuterium oxide is obtained.

Process I was calculated from the e. m. f. data of Rule and LaMer.² Their results are reported on a weight molal basis and have been converted to a volume molar scale to be consistent with the subsequent constants. This process does not include the transfer $\text{QH}_2(\text{H}_2\text{O}) = \text{QH}_2(\text{D}_2\text{O})$ since there is a solid phase of quinhydrone present. Any difference in the solubility of QH_2 in the two waters will not change the e. m. f. of the cell since the solid phase in the saturated solution is in equilibrium with its solid phase whose activity is constant. Process II is an exchange process obtained by Hamill and LaMer²¹ by the distillation method and may be used with confidence to obtain Process III. Process VI was determined from e. m. f. measurements at 21° and is assumed to have the same value at 25°.

Process VII was determined indirectly as indicated and compares well with the value (VIII) obtained directly in this investigation. Process X was written from the preceding equilibria with the assumption that the transfer free energy for potassium bromide and for potassium chloride

(21) Hamill and LaMer, unpublished data.

TABLE IV
 EXCHANGE AND TRANSFER EQUILIBRIA IN SOLUTION AT 25°

Process	K	Ref.
I $2\text{DCl}(\text{D}_2\text{O}) + \text{QH}_2(\text{s}) = 2\text{HCl}(\text{H}_2\text{O}) + \text{QD}_2(\text{s})$	17.30	(2)
II $\text{QH}_2 + \text{D}_2\text{O} = \text{QD}_2 + \text{H}_2\text{O}^*$	0.96	(21)
III $2\text{DCl}(\text{D}_2\text{O}) + \text{H}_2\text{O} = 2\text{HCl}(\text{H}_2\text{O}) + \text{D}_2\text{O}$	18.02	I-II
IV $2\text{DCl}(\text{D}_2\text{O}) + \text{H}_2(\text{g}) = 2\text{HCl}(\text{H}_2\text{O}) + \text{D}_2(\text{g})$	1.42	(6)
V $\text{H}_2\text{O} + \text{D}_2(\text{g}) = \text{D}_2\text{O} + \text{H}_2(\text{g})$	12.69	III-IV
VI $\text{D}_2(\text{g}) + 2\text{NaOD}(\text{D}_2\text{O}) + 2\text{H}_2\text{O} + 2\text{NaCl}(\text{H}_2\text{O}) = \text{H}_2(\text{g}) + 2\text{NaOH}(\text{H}_2\text{O}) + 2\text{D}_2\text{O} + 2\text{NaCl}(\text{D}_2\text{O})$	29.90	(11)
VII $\frac{1}{2}\text{H}_2\text{O} + \text{NaOD}(\text{D}_2\text{O}) + \text{NaCl}(\text{H}_2\text{O}) = \frac{1}{2}\text{D}_2\text{O} + \text{NaOH}(\text{H}_2\text{O}) + \text{NaCl}(\text{D}_2\text{O})$	1.53	$\frac{1}{2}(\text{VI-V})$
VIII $\frac{1}{2}\text{H}_2\text{O} + \text{KOD}(\text{D}_2\text{O}) + \text{KBr}(\text{H}_2\text{O}) = \frac{1}{2}\text{D}_2\text{O} + \text{KOH}(\text{H}_2\text{O}) + \text{KBr}(\text{D}_2\text{O})$	1.54	R. K. and V. K. L.
IX $\text{DCl}(\text{D}_2\text{O}) + \text{KOD}(\text{D}_2\text{O}) + \text{H}_2\text{O} + \text{KBr}(\text{H}_2\text{O}) = \text{HCl}(\text{H}_2\text{O}) + \text{KOH}(\text{H}_2\text{O}) + \text{D}_2\text{O} + \text{KBr}(\text{D}_2\text{O})$	6.54	VIII- $\frac{1}{2}$ III
X $\text{D}^+(\text{D}_2\text{O}) + \text{OD}^-(\text{D}_2\text{O}) + \text{H}_2\text{O} = \text{H}^+(\text{H}_2\text{O}) + \text{OH}^-(\text{H}_2\text{O}) + \text{D}_2\text{O}$	6.54	IX
XI $\text{H}_2\text{O} = \text{H}^+ + \text{OH}^-$	1.06×10^{-14}	R. K. and V. L.
	1.008×10^{-14}	(22)
XII $\text{D}_2\text{O} = \text{D}^+ + \text{OD}^-$	0.154×10^{-14}	R. K. and V. L.

* Conditions of experiment are such that the process involves exchange only uncomplicated by any transfer processes.

is the same in passing from deuterium oxide to protium oxide.

Our value for the ion product constant at 25° agrees well with the value of 1.6×10^{-15} , reported by Abel, Bratu and Redlich,¹¹ but differs

H_2O to pure D_2O when corrected for the density of $\text{H}_2\text{O}-\text{D}_2\text{O}$ mixtures.

To determine the transfer equilibrium constant for reaction $x(\text{D}_2\text{O}) = x(\text{H}_2\text{O})$ the solubilities of thallos chloride and calcium hydroxide were determined in $\text{H}_2\text{O}-\text{D}_2\text{O}$ mixtures. Thallos chloride was chosen since the metal, thallium, exhibits a marked similarity to the alkali group and has a chloride of low solubility.

Calcium hydroxide is the only sparingly soluble base that does not form a solid phase containing water of crystallization which would complicate the interpretation of the solubility measurements. The results are shown in Table V with the extrapolated value in 100% deuterium. The solubility of thallos chloride in ordinary water agrees exactly with the recent value reported by Hogge and Garrett¹⁹ when their value is corrected to a volume molar scale. Eddy and Menzies¹⁰ have determined the solubility of a series of relatively soluble salts in the two solvents. Since the solubilities of the salts differ in the two solvents it is necessary to correct the solubilities of the salts in D_2O to the hypothetical value they would have in a solution of D_2O at the same ionic strength as the saturated salt in H_2O . This may be done by applying the necessary but small activity coefficient correction to the data in columns 2 and 3 to yield column 4 of Table VI, which is a thermodynamic equilibrium constant of transfer.

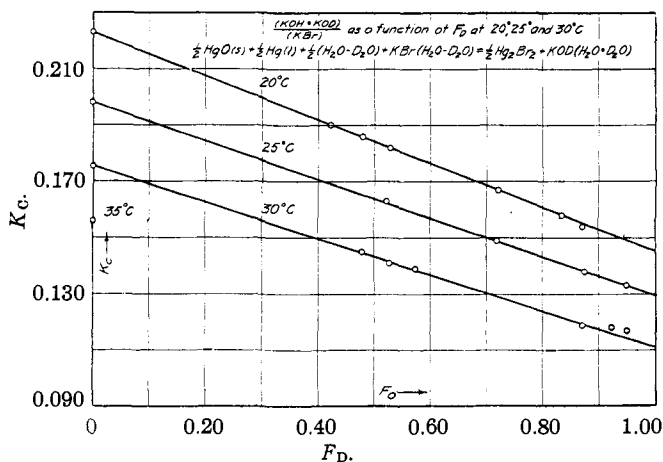


Fig. 2.— $(\text{KOH}-\text{KOD})/(\text{KBr})$ as a function of F_D at 20, 25 and 30°.

by 20% from the value 1.95×10^{-15} of Wynne-Jones.²³ The latter investigator has erroneously applied a correction to the former work to change it from a molal scale to a volume molar scale. The former¹¹ have reported their concentrations as moles in 55.51 moles of water ($\text{H}_2\text{O}-\text{D}_2\text{O}$) which is a molal scale in H_2O , but becomes a constant volume function in passing from pure

(22) Harned and Hamer, *THIS JOURNAL*, **55**, 2194 (1933).

(23) Wynne-Jones, *Trans. Faraday Soc.*, **32**, 1397 (1936).

TABLE V
SOLUBILITY OF TlCl AND Ca(OH)₂ IN H₂O-D₂O MIXTURES AT 25°

F _D	TlCl, m./l.	Ca(OH) ₂ -Ca(OD) ₂ , m./l.
0	0.01617	0.0215-Ca(OH) ₂
0.868	.01267	.0126
.925	.01241	.0120
(1.00)	(.01213)	(.0112)-Ca(OD) ₂

TABLE VI
TRANSFER EQUILIBRIUM CONSTANTS $K = a_x(\text{H}_2\text{O})/a_x(\text{D}_2\text{O})$ AT 25°; $X(\text{D}_2\text{O}) = X(\text{H}_2\text{O})$

X	Solubility, moles/l.		$a_x(\text{H}_2\text{O})/$ $a_x(\text{D}_2\text{O})$	Investigator
	H ₂ O	D ₂ O		
KBr	5.71	5.10	1.15	Eddy and Menzies
KCl	4.80	4.38	1.12	Shearman and Menzies
Ca(OH) ₂	0.0215	0.0112	1.63	Kingerley and LaMer
TlCl	.01617	.01213	1.30	Kingerley and LaMer

The activity ratio for Ca(OH)₂ is corrected for the exchange process, see Table VII.

TABLE VII
EXCHANGE CONSTANT FOR CALCIUM HYDROXIDE AT 25°
 $\text{D}_2\text{O} + \text{Ca}(\text{OH})_2 (x\text{D}_2\text{O}) = \text{H}_2\text{O} + \text{Ca}(\text{OD})_2 (x\text{D}_2\text{O})$
(0.07445 moles CaO).

Initial		Final		Reaction with CaO		K _e
F _D = 0.1900	F _D = 0.1909	H ₂ O	D ₂ O	H ₂ O	D ₂ O	
H ₂ O	D ₂ O	H ₂ O	D ₂ O	H ₂ O	D ₂ O	$(\text{H}_2\text{O})/(\text{Ca}(\text{OD})_2)$ $(\text{D}_2\text{O})/(\text{Ca}(\text{OH})_2)$
1.8359	0.3874	1.7725	0.3763	0.0634	0.0111	0.83

The value of the coefficient for potassium chloride was obtained by extrapolating the data of Shedlovsky and MacInnes²⁴ to saturation. The same procedure was used for potassium bromide for the data of Harned.²⁵ Hogge and Garrett¹⁹ have reported the activity coefficients of thallos chloride in a saturated solution of salt. For calcium hydroxide it was necessary to use the Debye-Hückel limiting law $f(0.0112 m)/f(0.0215 m) = 0.555/0.653 = 0.847$. In all cases the activity coefficients were assumed to be identical in D₂O as in H₂O at equal concentrations.¹⁵

The use of data from the solubility of relatively soluble salts to obtain transfer constants in dilute solutions would involve the difference in dilution effects in the two waters. This accounts for the higher value ($K = 1.21$) obtained for potassium chloride (0.1 M) from e. m. f. measurements⁶ than that from solubility measurements ($K = 1.12$).

The transfer of HCl was calculated indirectly from the kinetic data of Brescia²⁶ as follows:

Process	K	Reference
I H ₂ O + D ₂ O = 2HDO	3.27	(27)
II 2DCI(D ₂ O) + H ₂ O = 2HCl(H ₂ O) + D ₂ O	18.02	III (Table IV)

(24) Shedlovsky and MacInnes, THIS JOURNAL, 59, 503 (1937).

(25) Harned, *ibid.*, 48, 3095 (1926).

(26) Brescia, *ibid.*, 60, 2811 (1938).

(27) Topley and Eyring, J. Chem. Phys., 2, 217 (1934).

III DCI(D ₂ O) + H ₂ O = HDO + HCl(H ₂ O)	7.69	1/2(I + 11)
IV D ⁺ (D ₂ O) + H ₂ O = H ⁺ (D ₂ O) + HDO	3.76	(26)
V HCl(D ₂ O) = HCl(H ₂ O)	2.04	III-IV

It can be seen that hydrochloric acid and calcium hydroxide have a larger free energy of transfer than salts, with no atoms in common with the solvent.

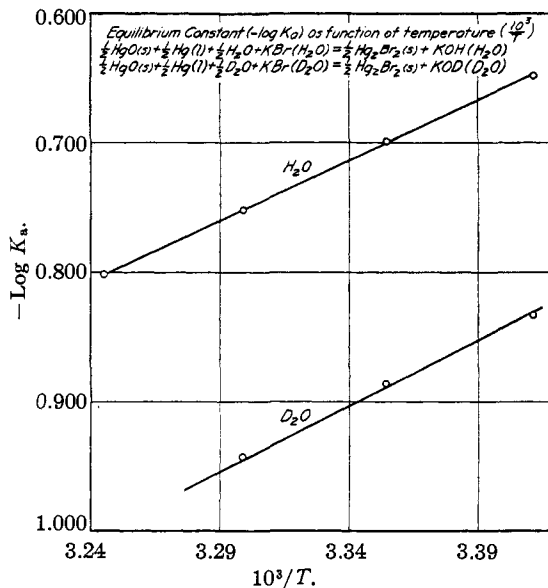
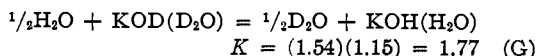
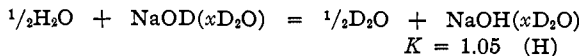


Fig. 3.—Equilibrium constant ($-\log K_a$) as a function of temperature ($10^3/T$).

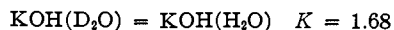
By using the value for the transfer of potassium bromide we may eliminate this process from equation (A) and obtain



Brodsky⁸ has measured the exchange associated with this process by measuring the change in deuterium oxide content of a mixed water sample of composition $x\text{D}_2\text{O}$ upon treatment with sodium hydroxide followed by distillation at an indefinite temperature



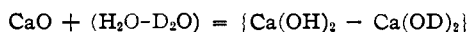
These processes should differ by the transfer of sodium hydroxide or potassium hydroxide. From the constants of the above reactions the transfer of the base becomes



Experimental difficulties prevent this reaction from being studied by solubility, but a large value of transfer would be expected by comparison with calcium hydroxide ($K = 1.63$).

Brodsky⁸ has reported the value of α to be 1.04

for twenty-two substances investigated by seven authors. This value is the general average from data where the deviations from unity do not exceed the experimental errors. It should be emphasized that other investigators⁹ have reported exchange constants that differ from unity by as much as 50%. For this reason calcium hydroxide was investigated. A sample of D₂O ($F_D = 0.1900$) was treated with calcium oxide and the density of the solvent showed a slight increase ($F_D = 0.1909$). The reaction involved is



and the equilibrium is

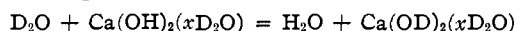


Table VII shows the results of the determination and the calculated value of the exchange constant, $K = 0.83$. This corresponds to a value of $\alpha = 0.91$.

Summary

The equilibrium process $\frac{1}{2}\text{H}_2\text{O} + \text{KOD} (\text{D}_2\text{O}) + \text{KBr}(\text{H}_2\text{O}) = \frac{1}{2}\text{D}_2\text{O} + \text{KOH}(\text{H}_2\text{O}) + \text{KBr}(\text{D}_2\text{O})$ has been determined from analytical measurements of the process $\frac{1}{2}\text{HgO}(\text{s}) + \frac{1}{2}\text{Hg}(\text{l}) + \frac{1}{2}\text{H}_2\text{O} + \text{KBr}(\text{H}_2\text{O}) = \frac{1}{2}\text{Hg}_2\text{Br}_2(\text{s}) + \text{KOH}(\text{H}_2\text{O})$ in H₂O-D₂O mixtures and found to compare favorably with the value calculated by indirect means. Four temperatures, 20, 25, 30

and 35°, have been investigated using protium oxide and three temperatures, 20, 25, 30° using deuterium oxide. From the temperature coefficients the several thermodynamic functions were calculated.

The importance of the difference between exchange and transfer free energy has been emphasized for the purpose of clarifying statements appearing in the literature.

The solubilities of thallos chloride and calcium hydroxide have been determined in the two waters at 25° and the exchange coefficient of the base measured in a sample of mixed solvent.

A series of transfer equilibrium constants have been obtained from solubility measurements in this investigation and others calculated from existing data.

An indirect means has been developed for calculating the ion product constant of deuterium oxide. The value obtained was 1.54×10^{-15} , in good agreement with the value reported by Abel, Bratu and Redlich.

Finally it has been shown that in equilibria in mixtures of H₂O-D₂O both the free energy of transfer and the free energy of exchange are contributing factors but in many cases the latter is of minor importance.

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[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Surface Tension of Solutions of Electrolytes as a Function of the Concentration. III. Sodium Chloride

BY GRINNELL JONES AND WENDELL A. RAY

Prior measurements of the relative surface tensions of solutions of some eleven salts have in each case shown the existence of a minimum in the surface tension-concentration curve at extreme dilution.¹ Similar measurements have now been carried out with sodium chloride at 25° over a concentration range of 0.0001 up to 2 molar.

The sodium chloride (Mallinckrodt analytical reagent grade) was purified by twice precipitating with hydrogen chloride, washing and drying the crystals by centrifugation and, finally, by drying and fusing in a platinum dish. The resulting salt was not hygroscopic. A saturated solution

(1) Grinnell Jones and Wendell A. Ray, *THIS JOURNAL*, **59**, 187 (1937); **63**, 288 (1941); Grinnell Jones and L. D. Frizzell, *J. Chem. Phys.*, **8**, 986 (1940).

showed no red coloration with phenolphthalein. The density measurements, made by means of two 50-ml. Ostwald type pycnometers, gave duplicate results, differing by no more than a few parts per million. The measurements, which were made by the differential capillary rise method, give the "apparent relative surface tension" as defined on page 291 of the second paper of this series, and are the mean of at least two independent determinations which usually differed by no more than a few thousandths of a per cent.

These results are given in Table I and are shown graphically in Figs. 1 and 2.

Interpretation of the Data.—The densities of sodium chloride can be expressed over the range