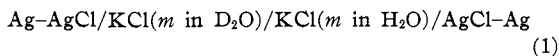


[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Thermodynamics of Strong Electrolytes in Protium-Deuterium Oxide Mixtures II. Potassium Chloride¹

BY VICTOR K. LA MER AND EVAN NOONAN

In this paper we shall report measurements of the temperature coefficient of the cell



containing potassium chloride at equal molal concentrations in H_2O and D_2O to determine the various thermodynamic properties of the transfer process



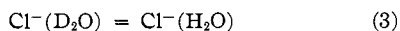
These properties will be interpreted in terms of the difference of solvation energies of the ions in the two solvents.

The interpretation of the measurements of cells of type (1) employing D_2O are so confused and conflicting that it is desirable to develop in detail the cell process involved to avoid misunderstanding and to clarify the interpretation.

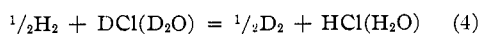
Contrary to repeated statements in the recent literature,²⁻⁴ the solubility difference of silver chloride in light and heavy water cannot contribute to the e. m. f. of a cell reversible to the silver chloride electrode because the silver chloride in saturated solution is in equilibrium with the solid phase whose activity is fixed.⁵

The molal potential of the silver chloride half cell in heavy water, however, may differ from that in light water because the standard reference state of the electrolyte is changed due to a difference in the free energy of solvation of chloride ions and of cations in the isotopic solvents.

Drucker⁴ measured cell (1) using calomel electrodes instead of silver chloride electrodes. His treatment implies that the cell process is



for when the e. m. f. of cell (1) is subtracted from the result of Abel, Bratu and Redlich⁶ for the reaction



(1) For Paper I of this series, Hydrochloric Acid, see Noonan and La Mer, *J. Phys. Chem.*, **43**, 247 (1939).

(2) Brodskii, *Trans. Faraday Soc.*, **33**, 1180 (1937).

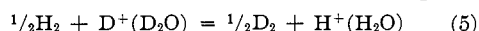
(3) Schwarzenbach, Epprecht and Erlenmeyer, *Helv. Chim. Acta*, **19**, 1292 (1936).

(4) Drucker, *Trans. Faraday Soc.*, **33**, 660 (1937).

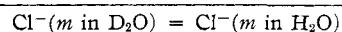
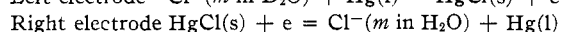
(5) (a) Rule and La Mer, *THIS JOURNAL*, **60**, 1974 (1938); (b) p. 1976; (c) see also, Abel and Redlich, *Z. Elektrochem.*, **44**, 204 (1938).

(6) Abel, Bratu and Redlich, *Z. physik. Chem.*, **A173**, 353 (1935); for further measurements on this process see paper I of this series.¹

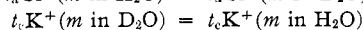
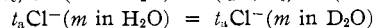
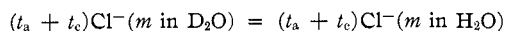
a zero potential is obtained. Drucker⁴ (p. 665) concludes that this supports his contention that the "solution tensions of hydrogen and deuterium are equal," corresponding to $E = 0$ for the process



The actual process in Drucker's cell, however, is quite different from (3). At the electrodes the following reactions take place



In addition a fraction, t_a , of a Faraday of current will be carried by t_a equivalents of chloride ion migrating from H_2O across the boundary to D_2O . At the same time t_c equivalents of potassium ion will be transported from D_2O to H_2O . The observed potential is generated by the sum of these electrode and transport processes. Thus



yielding the net reaction



It should be noted that, even in the case of potassium chloride, where t_c is almost exactly equal to 0.5, eq. (6) does not become equivalent to eq. (3) since the free energy change in the process $\text{K}^+(\text{D}_2\text{O}) = \text{K}^+(\text{H}_2\text{O})$ is not necessarily equal to that for eq. (3).

The net process in cell (1) then is the transference of t_c equivalents of potassium chloride from light to heavy water. This treatment assumes that the free energy contributions arising from the transport of H_2O into D_2O and of D_2O into H_2O cancel. Hittorf transference numbers are used ordinarily in transfer problems and automatically take care of the transport of solvent across the boundary when *the solvent is the same on both sides*. In the case of cell (1) true transference numbers should be used and in addition *the transference numbers of light and heavy water should be considered in the total cell process*. At the present time these quantities are unknown. Measurements of process (2) by means of cells without transference are now in progress. A comparison of the data

from both types of cells should answer the question of the importance of the free energy contribution arising from the differential transfer of solvents, which is neglected in the treatment given above.

It must also be emphasized at this point that it is impossible to measure the difference in free energy of solvation of any single ion in D_2O and H_2O by exact thermodynamic methods. Essentially this is the problem of single ion activity. It has been generally accepted since the initial work of P. B. Taylor,⁷ Guggenheim⁸ and others that this problem is insoluble and meaningless. The failure of most investigators, in the field of heavy water research, to recognize this principle is a major source of confusion in interpreting cell processes. From measurements of cells with transference only information on electrically equivalent amounts of cations and anions can be obtained, as represented in eq. (6). Dividing the observed e. m. f. of cell (1) by the average transference number of potassium ion gives the partial molal free energy change associated with the transfer of potassium chloride from D_2O to H_2O at a concentration m . In D_2O , $t_{K^+} = 0.4939$ and in H_2O , $t_{K^+} = 0.4898$ for 0.1 M potassium chloride at 25°.⁹

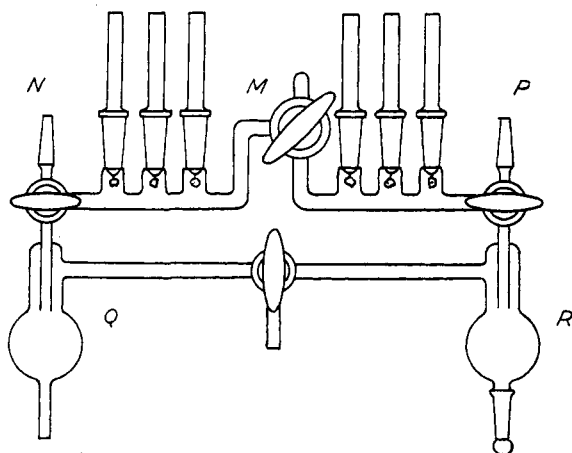


Fig. 1.

Experimental

Solutions were made up by weight with recrystallized potassium chloride. D_2O was purified as previously described.¹ After boiling the solution *in vacuo* to remove oxygen, purified nitrogen was admitted to the flasks. The H_2O solutions were

prepared identically, their concentration being adjusted finally by adding water from a calibrated 0.25-ml. hypodermic syringe. The cell is shown in Fig. 1. Stopcock M where the junction was formed had a 3-mm. bore. Three thermal type silver chloride electrodes were used on each side. The flask containing heavy water solution was attached at P, the one containing light water at N. After evacuating the cell and flushing with nitrogen, the electrodes were soaked for one hour in wash portions of the respective solutions; these were drawn off into bulbs Q and R. Sixteen ml. of each solution was sufficient to wash the electrodes once and fill the cell. Stopcock M was opened and readings were taken after the cell had remained for two hours at the specified temperature. Readings were continued at intervals for an hour; with properly made cells no drift in e. m. f. occurred over a two-hour period. The potential at 25° was reproduced to within 0.02 mv. in most cases after the 5° and again after the 45° measurements.

The e. m. f. of a concentration cell reversible to the anion in which the solvent is the same throughout the cell is given by the equation

$$-FE = \int_{m_1}^{m_2} t_c d\mu \quad (7)$$

where t_c is the transference number of the cation, μ is the chemical potential of the salt and m_1 and m_2 are the molalities of the concentrated and dilute solutions, respectively. Now

$$\mu = \mu_0^K + RT/F \ln m_K \gamma_K + \mu_0^{Cl} + RT/F \ln m_{Cl} \gamma_{Cl} \quad (8)$$

where subscript 0 refers to an arbitrary standard state for the particular solvent involved.

If $m_K = m_{Cl} = \text{constant}$, then the change in chemical potential of potassium chloride on passing from light to heavy water becomes

$$d\mu = d\mu_0^K + RT/F d \ln \gamma_K + d\mu_0^{Cl} + RT/F d \ln \gamma_{Cl} \quad (9)$$

The almost identical dielectric constants¹⁰ of D_2O and H_2O predict at most only a small difference in the activity coefficients arising from differences in the ion atmospheres in the solvents H_2O and D_2O as given by the Debye-Hückel equations. $d \ln \gamma_K$ and $d \ln \gamma_{Cl}$ in eq. (9) may therefore be neglected in dilute solutions and become equal to zero for $m = 0$, (subscript zero), yielding

$$-FE_0 = \int_{H_2O}^{D_2O} t_c (d\mu_0^K + d\mu_0^{Cl}) \quad (10)$$

(7) P. B. Taylor, *J. Phys. Chem.*, **31**, 1478 (1927).

(8) Guggenheim, *ibid.*, **33**, 842 (1929); **34**, 1540 (1930).

(9) Longworth and MacInnes, *THIS JOURNAL*, **59**, 1666 (1937).

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

TABLE I
ELECTROMOTIVE FORCE OF THE CELL
Ag-AgCl/KCl(*m* in D₂O)/KCl(*m* in H₂O)/AgCl-Ag
IN PROTIUM-DEUTERIUM OXIDE MIXTURES. THERMODYNAMIC DATA FOR THE PROCESS
KCl(*m* in D₂O) = KCl(*m* in H₂O)

$\Delta s/$ 0.1076	<i>m</i> in D ₂ O	<i>m</i> in H ₂ O	<i>T</i> °C.	<i>t</i> _c	E. m. f. obsd., v.	<i>E/t</i> _c v.	$-\Delta\bar{F}$ cal.	$-\Delta\bar{S}$ cal. deg.	$-\Delta\bar{H}$ cal.	$\Delta\bar{C}_p$ cal. deg.	$\gamma_{\text{KCl(H}_2\text{O)}}$	$\gamma'_{\text{KCl(D}_2\text{O)}}$
0.978	0.10203	0.10201	5	0.4909	0.00560	0.01141	263.1					
			25	.4918	.00475	.00966	222.7	1.72	736	8.8	0.768	0.927
			45	.4927	.00415	.00842	194.2					
.898	.47390	.47381	5	.4905	.00436	.00889	205.0					
			25	.4914	.00339	.00690	159.1	2.08	779	6.6	.656	.750
			45	.4923	.00260	.00528	121.8					
.886	.03443	.03442	5	.4903	.00512	.01044	240.7					
			25	.4912	.00437	.00890	205.2	1.49	649	8.5	.840	.999
			45	.4917	.00386	.00785	181.0					
.886	.10172	.10169	5	.4907	.00503	.01025	236.4					
			25	.4916	.00427	.00869	200.4	1.54	659	7.6	.769	.910
			45	.4925	.00373	.00757	174.6					
.738	.10456	.10454	5	.4904	.00406	.00828	190.9					
			25	.4913	.00346	.00704	162.3	1.21	523	6.6	.767	.879
			45	.4922	.00304	.00618	142.5					
.424	.10661	.10652	5	.4898	.00232 ^a	.00470	108.4					
			25	.4907	.00199 ^a	.00401	92.5	0.69	298	3.1	.763	.824
			45	.4916	.00174 ^a	.00350	80.7					

^a Subtract concentration correction of 0.00002 v.

which, on integration, takes the form

$$-E_0/t_c = \Delta E_0^{\text{KCl}} \quad (11)$$

ΔE_0^{KCl} relates to a change in the standard state, *i. e.*, it is a measure of the Gibbs free energy of transfer of potassium chloride from H₂O to D₂O at infinite dilution. At higher concentrations the contributions to the activity coefficient arising from all types of intermolecular and interionic action will be different in each isotopic solvent.¹¹

We have therefore combined the change in standard state on passing from light to heavy water and the activity coefficient in heavy water into an absolute activity coefficient γ' , whose value is unity in H₂O at infinite dilution. Values of γ' are given in the last column of Table I. They were calculated from the integrated form of equation (7)

$$E = \frac{2t_c RT}{F} \ln \frac{m_{\text{D}_2\text{O}} \gamma'_{\text{D}_2\text{O}}}{m_{\text{H}_2\text{O}} \gamma_{\text{H}_2\text{O}}} \quad (12)$$

Concentrations are expressed on a modified molal scale; moles of potassium chloride per 55.51 gram atoms of oxygen in the solvent. Transference numbers at 25° were taken from the measurements of Longworth and MacInnes.⁹ Estimated values

(11) Shearman and Menzies, *THIS JOURNAL.*, **59**, 185 (1937), report that the solubility of potassium chloride is 8% lower in D₂O than in H₂O at 25°.

of *t*_c at 5 and 45° were based on the results of Samis.¹² Activity coefficients of potassium chloride in H₂O were taken from the data of Shedlov-

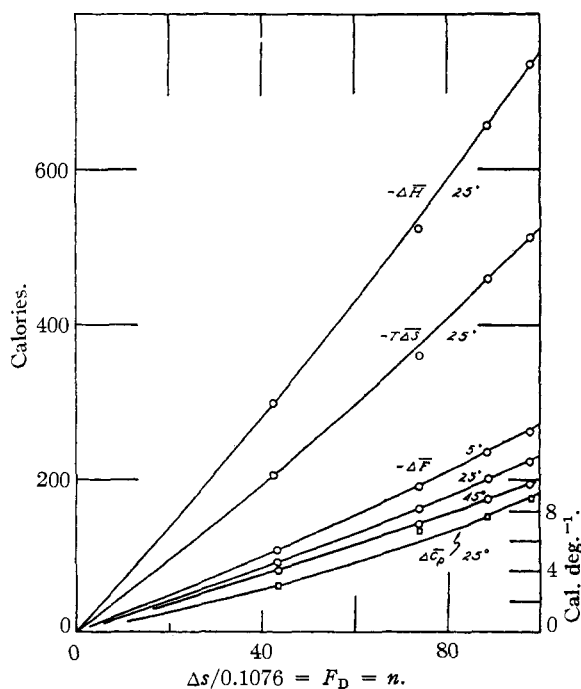


Fig. 2.

(12) Samis, *Trans. Faraday Soc.*, **33**, 469 (1937).

sky and MacInnes¹³ and are recorded in column 12 of Table I.

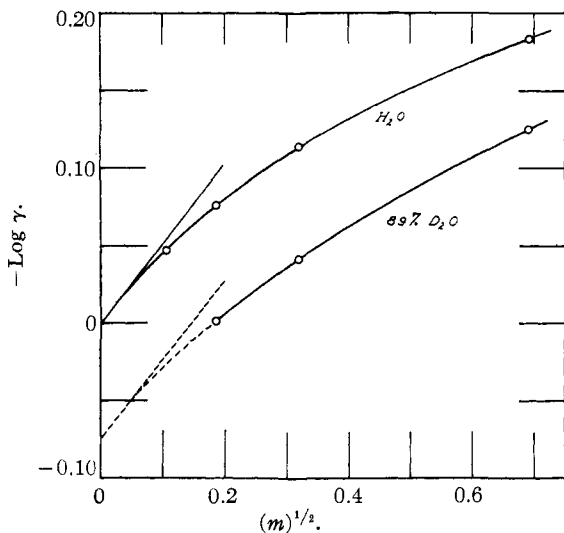


Fig. 3.

Figure 3 is a plot of $-\log \gamma$ for potassium chloride in light water and of $-\log \gamma'$ for 89% D_2O against the square root of the concentration.

The partial molal free energy, heat content, heat capacity and entropy changes for the process $KCl(0.1 m \text{ in } D_2O) = KCl(0.1 m \text{ in } H_2O)$ are plotted in Fig. 2 against $\Delta s/0.1076$, as a measure of the deuterium content of the solvent.¹⁴ It will be noticed that the partial molal quantities show a small deviation from linearity. Lange and Martin¹⁵ report that the integral heat of solution of sodium chloride in isotopic water mixtures is a linear function of the deuterium content. The calorimetric value of these authors for the difference in the integral heat of solution of potassium chloride in D_2O and H_2O is -615 cal. at 25° and a final concentration of $0.13 m$. Our value for the partial molal heat change at $0.1 m$ is -753 cal.

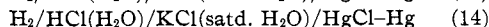
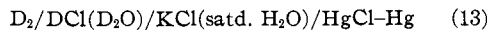
From Wyman and Ingalls¹⁰ accurate measurements of the dielectric constants of H_2O and D_2O it is now certain that the difference in D is too small to explain the solvation energy effects of strong electrolytes on the basis of the Born theory. The answer is to be sought in other directions, such as the difference in vibration frequencies, the work of orienting the molecules in the field of the ions, and related phenomena.

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

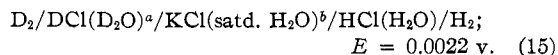
(14) Stokland, Ronaess and Tronstad, *Trans. Faraday Soc.*, **35**, 312 (1939).

(15) Lange and Martin, *Z. physik. Chem.*, **A178**, 214 (1936); **A180**, 233 (1937).

Schwarzenbach, Epprecht and Erlenmeyer³ have measured the following cells



Subtracting (14) from (13) yields

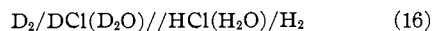


The liquid junction potentials due to differences in ionic mobilities at a and b although oppositely directed are not necessarily equal and consequently cannot be ignored safely as is assumed in Schwarzenbach's treatment.³ MacInnes and Longworth¹⁶ give the following values for the potential of the cell: $KCl(\text{satd.})/HCl(0.1 m)$, on the basis of their transference data using various theoretical treatments for the calculation. Thus

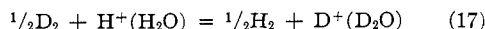
-2.0 mv.	(Guggenheim)
-2.9	(MacInnes)
-4.13	(Henderson)
-5.50	(Planck)

The substitution of D_2O for H_2O on one side of this boundary introduces complications which are well recognized when one employs alcohol instead of D_2O .

When cell (15) is written as

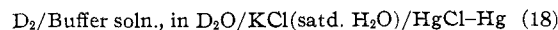


the double bars express only the pious hope that the use of a saturated potassium chloride bridge has eliminated the liquid-liquid potentials at a and b in (15), so that this cell measures the free energy of the process



In a recent paper by Abel and Redlich^{5c} it is emphasized clearly that eq. (17) does not yield the "normal potential" of deuterium since different solvents, H_2O and D_2O , are employed.

Drucker,⁴ as well as Schwarzenbach, Epprecht and Erlenmeyer,³ have attempted to measure the dissociation constants of deuterio acids using cells of the type



Again the difficulty of liquid junction potential due to a difference in the solvation energy of ions in H_2O and D_2O emerges. Since relatively small differences in strength between the proto and deuterio acids are the primary point of interest this complication is of sufficient magnitude to weaken the interpretation of data from cell (18) for this purpose. Dissociation constants obtained by

(16) "Cold Spring Harbor Symposium on Quantitative Biology," Vol. IV, 18 (1936).

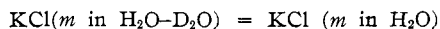
these authors do not align well with those determined in this Laboratory¹⁷ by conductance and by the use of thermodynamically exact cells. It seems certain that the data obtained with cell (18) will require some revision.

Summary

1. Measurements of the cell with transference Ag-AgCl/KCl(*m* in H₂O-D₂O)/KCl(*m* in H₂O)/AgCl-Ag have been made at 0.1 *m* over a wide range of deu-

(17) La Mer and Chittum, *THIS JOURNAL*, **58**, 1642 (1936); ref. 5a; Yates, unpublished conductance measurements.

terium content and at 5, 25 and 45°. The partial molal free energy, entropy and heat content changes have been evaluated for the process



which corresponds to the process occurring in the cell when the differential transport of the waters is neglected.

2. The absolute activity coefficients of potassium chloride in isotopic mixtures have been calculated referred to potassium chloride at infinite dilution in H₂O as unity.

NEW YORK, N. Y.

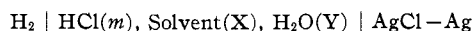
RECEIVED NOVEMBER 14, 1938

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Properties of Electrolytes in Mixtures of Water and Organic Solvents. I. Hydrochloric Acid in Ethanol- and Isopropanol-Water Mixtures of High Dielectric Constant

BY HERBERT S. HARNED AND CALVIN CALMON

In order to investigate further the effects of different solvent mixtures on the thermodynamic properties of a strong electrolyte, we have measured the electromotive forces of the cells



in mixtures containing 10 and 20% ethyl alcohol and 10% isopropyl alcohol at 25°. In these media of high dielectric constant, hydrochloric acid is completely ionized so that considerations regarding the results will not be complicated by the effects of ionic association to be found in media of lower dielectric constant ($D < 50$). These results along with similar data in dioxane-, methanol- and glycerol-water mixtures will serve as an introduction to this complicated subject.

Electromotive Force and Density Data

The electromotive forces were obtained in the usual manner with silver-silver chloride electrodes made by heating silver oxide, and subsequently electrolyzing in hydrochloric acid solutions. The density determinations were made with pycnometers of about 30-cc. capacity. The alcohols were purified by fractional crystallization. Density determinations of the alcohol-water mixtures agreed to within less than 0.005% with those in the "International Critical Tables." Table I contains the electromotive force, density data, and the vapor pressures employed for correcting cell

electromotive forces to one atmosphere hydrogen pressure.

The densities have been expressed by the equation

$$d = d^0 + a'm - b'm^2 + e'm^3 \dots \quad (1)$$

the constants of which are contained in Table II. The ratio of concentration in moles per liter solution, *c*, to molality, *m*, may be expressed to within $\pm 0.05\%$ by the useful equation

$$c/m = d^0 - A'm \quad (2)$$

The constant *A'* is also included in the table.

Standard Potentials

The standard potentials of the cells were obtained by the use of the function *E'*, defined by the equation

$$E' = E + 0.1183 \log m - \frac{0.1183 u \sqrt{c}}{1 + A \sqrt{2c}} -$$

$$0.1183 \log (1 + 0.002 m M_{xy}) = E_m^0 + f(m) \quad (3)$$

where *E* is observed electromotive force, *u* the Debye and Hückel constant, *A* the parameter which involves the mean distance of approach of the ions, *a*, and *M_{xy}* the mean molecular weight of solvent. ($A = Ka$ and $M_{xy} = 100/(X/M_1 + Y/M_2)$ where *a* is in Ångströms and *M₁* and *M₂* are the molecular weights of organic solvent and water, respectively.) These quantities are given in Table II. The value of "a" employed was 4.3 Å. as found by Harned and Ehlers¹ for aqueous solu-

(1) Harned and Ehlers, *THIS JOURNAL*, **55**, 2179 (1933).