

## Free Energies of Transfer of Alkali Chlorides from Light to Heavy Water from Cells without Liquid Junction Potentials

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Electrochemical measurements have been made on the cells  $M$  (in Hg)/MCl (in  $D_2O$ )/AgCl, Ag—Ag, AgCl/MCl (in  $H_2O$ )/ $M$  (in Hg), in which  $M$  is Li, Na, or K. From the emf values obtained free energy changes are calculated for the transfer processes: MCl (in  $H_2O$ )  $\rightarrow$  MCl (in  $D_2O$ ). The dilute solution values for the different chlorides are found to be virtually the same, *viz.*  $+ 210 \pm 10$  cal/mole at  $25^\circ C$ , referred to standard states in the molarity units, which for these solutions give the same values as those in the mole fraction or "reduced molality" units (*i.e.*, moles of solute per 55.5 moles of water). The similarity of the emf values suggests that most of the transfer free energies are to be ascribed to the chloride ions.

The results are discussed in terms of the structural differences between liquid  $H_2O$  and  $D_2O$ . Making use of other recent electrochemical and thermodynamic data the experimental values are also applied to derive the equilibrium constant for the isotopic fractionation of hydrogen between water and the aqueous hydronium ion at different temperatures. At  $25^\circ C$ , *e.g.*, a value of  $9.0 \pm 0.3$  is calculated for the equilibrium constant  $L$  of the reaction:

$$2 D_3O^+ + 3 H_2O = 2 H_3O^+ + 3 D_2O.$$

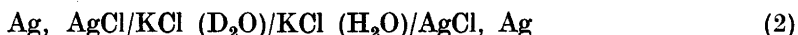
The transfer free energies of electrolytes and nonelectrolytes from light to heavy water are of particular interest for studies of the deuterium solvent isotope effects on acid-base equilibria and on the kinetics of acid-base catalysis.<sup>1</sup> Although it can be inferred that for a number of cases, *e.g.*, for simple hydronium or hydroxide ion-catalyzed organic reactions, the contributions from these transfer effects are small in magnitude and are effectively cancelled out, the situation becomes more complicated when the acid-base reaction in question involves ions or other species that cause significant disturbances in the surrounding water structure.<sup>2</sup> In the latter case, the structural differences between liquid  $H_2O$  and  $D_2O$  are expected to give rise to transfer free energies of considerable magnitudes.

The present paper reports determinations of the free energy changes for the processes: MCl ( $H_2O$ )  $\rightarrow$  MCl ( $D_2O$ ), in which  $M$  is Li, Na, or K, by means

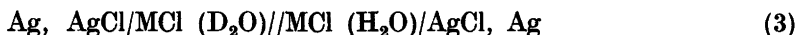
of the amalgam cells (1), which are not complicated by liquid junction potentials of unknown magnitudes and thus lead to exact thermodynamic values.



The transfer free energy from  $\text{H}_2\text{O}$  to  $\text{D}_2\text{O}$  has been previously measured for potassium chloride by La Mer and Noonan<sup>3</sup> from the cell (2), the net process of which was assumed to be the transference



of  $t^+$  equivalents of potassium chloride from light to heavy water,  $t^+$  being the cation transference number. It was recognized that possible emf contributions arising from the transport of  $\text{H}_2\text{O}$  into  $\text{D}_2\text{O}$  and of  $\text{D}_2\text{O}$  into  $\text{H}_2\text{O}$  across the boundary could not be accounted for. More recently, Greyson<sup>4</sup> has made emf measurements on the cell



in which the double bars represent a cation exchange membrane. He also calculated transfer free energies from the voltages observed by making an assumption the validity of which was not experimentally assessed, *viz.* that all the contributions of the transport of ionic species and of the different waters through the membrane could be ignored.

## EXPERIMENTAL

*Materials.* Reagent grade chemicals were used throughout. Deuterium oxide was from Norsk Hydroelektrisk Kvälstofaktieselskab, Norway. It was purified and analyzed as described in connection with an earlier study.<sup>5</sup> The deuterium atom fraction was 0.9932.

The amalgams employed for the electrochemical cells were prepared by electrolysis as described by Smith and Taylor<sup>6</sup> and kept under a nitrogen atmosphere. The concentrations of the dissolved metals in the amalgams were approximately 0.05 % by weight, excepting the case of lithium, where about 0.003 % amalgams were used owing to the high reactivity of these amalgams. As the amalgams showed a tendency to deteriorate with time, even when prepared from carefully purified materials and stored under exclusion of atmospheric oxygen, only freshly prepared amalgams were used for the emf measurements.

All the electrolyte solutions used for the cells were evacuated to remove dissolved air and a nitrogen atmosphere substituted.

*Emf measurements.* The cells used were equipped with a silver-silver chloride electrode (Radiometer, Type P 500) and an amalgam electrode. The total volumes of the cells were approximately 10 ml, and their filling took place in a nitrogen atmosphere. The amalgam electrode was equipped with a vertical capillary tube (length, 6 cm; inside diameter, 0.1 mm), through which fresh amalgam was dropped into the solution at a rate of approximately one drop per 3 to 5 sec. In order to prevent the used amalgam to react further with the cell solution, the bottom compartment of the cell below the amalgam electrode contained a 2 cm thick layer of carbon tetrachloride, which isolated the used amalgam from the cell electrolyte. Nevertheless, as observed from the voltage readings, the electrolyte in the cell deteriorated slowly through the reaction between the amalgam electrode and water. The influence of this could be easily eliminated, however, by extrapolating the readings to the time of inserting the electrode into the solution.

In the measurements, the silver-silver chloride electrode was first equilibrated with the cell electrolyte for several hours before the amalgam electrode was inserted. The voltage readings were then made on a Croydon Type P 10 Precision Potentiometer. The readings were always made at the same phase of the developing new amalgam drop and

continued for 2 to 3 min, which allowed an extrapolation to the time of inserting the electrode. In the equipment used the rate of voltage change through the deterioration was only about 0.15 mV/min.

The measurements were repeated on fresh electrolyte solutions 5 to 10 times. The standard deviation of measurement was approximately 0.25 mV for sodium and potassium chlorides, whereas less precise values with a standard deviation of 0.7 mV were obtained for lithium chloride. The same measurements were made on both protium and deuterium systems at the same molar chloride concentrations and the emf of the cell (1) was then calculated. For 0.1 M alkali chloride solutions and for those of lower concentration (0.02 to 0.08 M) the emf kept constant within the limits of error, whereas for higher concentrations the values were less than those for dilute solutions. This showed that the ionic atmosphere effects on the activity coefficients of the electrolytes investigated were similar in  $H_2O$  and  $D_2O$  and were therefore cancelled out from the emf values of the cells (1) in the concentration range below 0.1 M.

### DISCUSSION

*Interpretation of the emf values.* The average emf values observed for the cells (1) at 25°C are given in Table 1 along with the respective standard deviations of measurements. The table also contains the free energy changes calculated for the transfer of one mole of the electrolyte in question from light water to heavy water to the same concentration. In the values calculated, the concentrations were in moles of solute per one liter of solution. As the molar volumes of the liquid waters are virtually the same <sup>7</sup> the dilute solution values of Table 1 are equivalent to those calculated for the mole fraction units or for the "reduced molality scale" of Noonan and La Mer,<sup>8</sup> that is, for a scale in which the concentrations are expressed in moles of solute per 55.5 moles of solvent.

Table 1. Emf values at 25°C for the cells (1) with the same molar chloride concentrations in light and heavy water (99.3 %).

Cell electrolyte	Concn., moles/l	Emf, mV	$\Delta G$ , cal/mole
LiCl	0.1	-8.8 ± 1.0	+ 202 ± 23
NaCl	0.02-0.1	-9.2 ± 0.4	+ 212 ± 9
»	1.0	-7.3 ± 0.4	+ 168 ± 9
»	4.0	-6.0 ± 0.4	+ 138 ± 9
KCl	0.02-0.1	-9.5 ± 0.4	+ 219 ± 9
»	1.0	-7.6	+ 175
CdCl <sub>2</sub>	0.05	-9.45 ± 0.20	+ 436 ± 10

It can be seen that the value of 223 cal/mole, determined by La Mer and Noonan<sup>3</sup> for the transfer free energy of potassium chloride from light to heavy water at 25°C and at 0.1 M concentration, agrees excellently with the corresponding dilute solution value of Table 1, 219 cal/mole. This demonstrates that the free energy contributions from the transport of the waters across the boundary in the cell (2) are effectively cancelled out, as assumed by La Mer and Noonan. On the other hand, the free energy values calculated by Greyson<sup>4</sup> for alkali chlorides from the cell (3) are significantly different from those of

the present study. The values obtained by him for 0.1 M solutions are considerably lower than those of Table 1, *viz.* 110, 140, and 180 cal/mole for LiCl, NaCl, and KCl, respectively. This invalidates his assumption of cancellation of the potential differences arising from the transport phenomena involved in the passage of current through the membrane used.

The most remarkable feature of the values of Table 1 is that, for dilute solutions, the transfer free energies for the different chlorides are virtually the same, *viz.* about 210 cal. per one mole of the *chloride ion*. A chloride of a rather different type, cadmium chloride, which was investigated to make a comparison, shows also a similar value. Its transfer free energy calculated per one gram equivalent of the chloride is  $218 \pm 5$  cal. Although it must be recognized that, in principle, it is impossible to determine transfer free energies for single ions by exact thermodynamic methods, the above values suggest that the contributions of the cations to the overall free energies measured must be relatively small. Otherwise, one would expect characteristic differences between the different chlorides investigated.

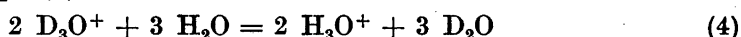
The transfer free energies of electrolytes from light to heavy water are to be ascribed to the structural differences between liquid H<sub>2</sub>O and D<sub>2</sub>O, which give rise to solvent-ion interactions that are not equal. The physical properties and other facts indicate that liquid deuterium oxide is structurally more ordered than liquid protium oxide,<sup>9</sup> that is, that the degree of hydrogen bonding is greater in the former solvent at ordinary temperatures. Therefore, *e.g.*, such solutes that do not properly adapt themselves into the surrounding water structure will shift the structure equilibrium in D<sub>2</sub>O more in the direction of disorder than in H<sub>2</sub>O.

It is evident from recent NMR and other studies of the effects of ions on water structure<sup>10-13</sup> that cations and anions, even when of the same formal charge and of the same size, interact very differently with the surrounding water molecules. Around a cation, the minimum energy results from a configuration in which the O—H bonds of the nearest water molecules point outwards. Consequently, as concluded by Noyes,<sup>14</sup> cations of a wide range of sizes adapt themselves well into the water structure. Considering the free energy of transfer from H<sub>2</sub>O to D<sub>2</sub>O the above suggests that simple inorganic cations behave very similar to other species that are hydrogen-bonded to the solvent through their O—H groups, for which the net effect on the transfer free energy must be relatively small. Furthermore, it may be concluded that the activity coefficients of simple cations do not appreciably depend on the deuterium content of the water because they are attached to the water structure mainly through isotopically similar atoms, *viz.* through the oxygen atoms of the closest water molecules.

On the other hand, the possible configurations of the water molecules around anions are relatively sharply dependent on the nature of the anion,<sup>14</sup> which is expected to lead to characteristic differences in the transfer of these ions from H<sub>2</sub>O to D<sub>2</sub>O. In this connection it is very interesting to note that, differing from other electrolytes thus far investigated, lithium fluoride is more soluble in deuterium oxide than in protium oxide,<sup>15</sup> which indicates that the transfer free energy for the fluoride ion from H<sub>2</sub>O to D<sub>2</sub>O has a negative value.

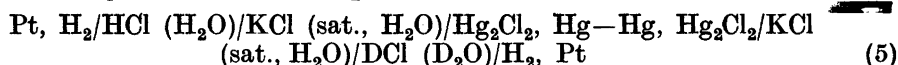
In terms of the Gibbs-Duhem equation, the above conclusions can be contrasted with the observation that cations and anions have very different influences on the relative activities of isotopically different waters. Thus, Googin and Smith,<sup>16</sup> who investigated the effect of dissolved electrolytes on the isotopic fractionation of hydrogen between aqueous electrolyte solutions and their vapors showed that most of the electrolyte effect was to be ascribed to the anions.

*Isotopic fractionation of hydrogen in the hydronium ion.* The above results have a close connection with the problem of isotopic exchange equilibria between water and the dissolved hydronium ion. The principle of the geometric mean<sup>17</sup> makes it possible to relate all these equilibria to a single one, represented by eqn. (4), with an



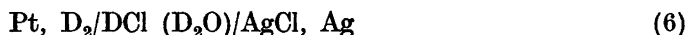
equilibrium constant denoted usually by  $L$ . Of course, when equilibria of the type (4) are applied to various phenomena in acid solutions in  $\text{H}_2\text{O}-\text{D}_2\text{O}$  mixtures of different composition it is assumed that the respective free energies of transfer of the waters and the hydronium ions from a reference water to that under study are cancelled out. This is not an unjustified assumption since the species involved can be inferred to adopt themselves equally well to the surrounding solvent structure.

Purlee<sup>18</sup> attempted to calculate  $L$  from the emf values of certain galvanic cells, but the lack of the free energy value for the transfer of the chloride ion from  $\text{H}_2\text{O}$  to  $\text{D}_2\text{O}$  prevented him doing so. Instead he calculated a value of 11.0 for  $L$  at  $25^\circ\text{C}$  from the cell (5). However, liquid junction potentials of unknown magnitudes were incorporated into the values obtained from this

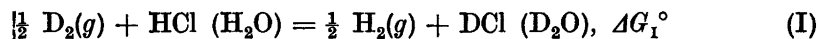


cell (*cf.* Ref. 3).

If the free energy of transfer of chloride ions from a dilute solution in light water to the same molar concentration in deuterium oxide can be assumed to be 210 cal/mole at  $25^\circ\text{C}$ , within an estimated accuracy of  $\pm 10$  cal, it is now possible to calculate the value of  $L$  with the aid of more recent electrochemical data. Gary, Bates and Robinson<sup>19</sup> have extensively studied the cell (6) and compared the results with those for the corresponding protium system. At



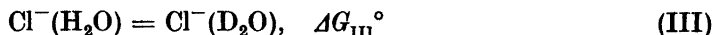
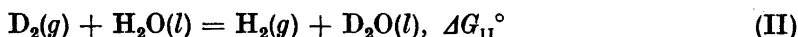
$25^\circ\text{C}$ , the standard emf was lower by 4.31 mV (on the mole fraction scale) for the deuterium system, which corresponds to a value of 99.9 calories for the standard free energy change of the reaction



It is easily seen that the standard free energy change  $\Delta G_L^\circ$  for the reaction (4) is given by

$$\Delta G_L^\circ = - 2 \Delta G_I^\circ + \Delta G_{II}^\circ + 2 \Delta G_{III}^\circ \quad (7)$$

in which the latter free energies are those of the reactions



Here, as in the calculation of  $L$  in general, it has been assumed that the functional form \* of the hydronium ion in water is  $\text{L}_3\text{O}^+$  ( $\text{L} = \text{H}, \text{D}$ ) and that the transfer free energies involved in the reaction (4) are negligible.

Accurate values for the equilibrium (II) in the gas phase are available,<sup>20</sup> from which with the aid of the known vapor pressures of the waters<sup>7</sup>  $\Delta G_{\text{II}}^\circ$  is found to be  $-1515$  cal/mole at  $25^\circ\text{C}$ . Using the value of  $210$  cal/mole for  $\Delta G_{\text{III}}^\circ$ ,  $9.0$  is obtained for  $L$  at  $25^\circ\text{C}$ . It can also be calculated that an uncertainty of  $10$  cal in the value of  $\Delta G_{\text{III}}^\circ$ , which is the least attainable value in the strict thermodynamic sense, makes an uncertainty of  $0.3$  units in the value of  $L$ .

The above value may be contrasted with the results of other recent estimations of  $L$ :  $9.7 \pm 1.5$ <sup>21</sup> ( $31^\circ\text{C}$ ; NMR),  $11.4 \pm 0.7$ <sup>22</sup> (temperature not given; NMR),  $8.9 \pm 1.0$ <sup>23</sup> ( $13.5^\circ\text{C}$ ; isotopic fractionation of hydrogen between acid solutions and their vapors).

*The effect of temperature of  $L$ .* According to Gary, Bates and Robinson<sup>19</sup> the temperature dependence of the standard free energy change of the reaction (I) is given by

$$\Delta G_{\text{I}}^\circ = 852.4 - 5.87 T + 0.01123 T^2 \text{ (cal)} \quad (8)$$

An empirical equation of a similar form can be derived by the method of least squares for the reaction (II), using the known values for the equilibrium constant of the corresponding gas phase reaction at different temperatures<sup>20</sup> and those for the vapor pressures of  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ :<sup>7</sup>

$$\Delta G_{\text{II}}^\circ = -2720.6 + 5.71 T - 0.00566 T^2 \text{ (cal)} \quad (9)$$

An estimation of the temperature influence on the process (III) can be made if it is assumed that the temperature variation of the emf of the cell (1) is effectively due to the chloride ions, in accordance with the fact that the values for the different chlorides were substantially independent of the cations present. This assumption can not lead to a serious error, at least, when applied to a relatively narrow temperature range.

In Table 2 are given emf values for the cell (1) with cadmium chloride solutions, which could be accurately investigated over a wider range of temperatures than the alkali chloride solutions, owing to the low reactivity of cadmium amalgams. By the method of least squares that part of the respective standard free energy change that depends on temperature is found to be  $-7.57 T + 0.01145 T^2$  cal/equiv., from which with the above value of  $210$  cal for  $\Delta G_{\text{III}}^\circ$  at  $25^\circ\text{C}$  the following empirical equation is obtained:

$$\Delta G_{\text{III}}^\circ = 1450.2 - 7.57 T + 0.01145 T^2 \text{ (cal)} \quad (10)$$

\* In the present context this only means that the isotopic fractionation of hydrogen in the hydronium ion occurs in  $\text{L}_3\text{O}^+$ . Therefore, this assumption does not postulate anything about the further hydration of the  $\text{L}_3\text{O}^+$  ion.

Table 2. Emf values for the cells (1) with cadmium chloride solutions at different temperatures. The mole fraction of cadmium chloride in the solutions is 0.0009, which corresponds to about 0.05 M concentration at 25°C.

$T, ^\circ\text{K}$	Emf, mV	$\Delta G, \text{ cal/equiv.}$
283.1	-10.22	+ 236
291.6	- 9.53	+ 220
296.7	- 9.62	+ 222
302.6	- 9.24	+ 213
311.5	- 9.13	+ 211
319.1	- 9.10	+ 210
325.8	- 8.95	+ 206
332.5	- 8.97	+ 207

Finally, by combining eqns. (8), (9), and (10), the following equation is obtained for the temperature dependence of  $\Delta G_L^\circ$ :

$$\Delta G_L^\circ = -1525.0 + 2.31 T - 0.00522 T^2 \text{ (cal)} \quad (11)$$

from which the value of  $L$  can be computed for different temperatures. The results of such calculations are given in Table 3 for a number of selected temperatures.

The most accurate direct measurement of  $L$  earlier made is probably that of Heinzinger and Weston<sup>23</sup> at 13.5°C. Their method involved the determination of the isotopic composition of the water in aqueous perchloric acid solutions by measuring the H/D ratio in the equilibrium vapor, which latter contained only water. In the calculations, which gave a value of 8.9 for  $L$  at 13.5°C, the following assumptions were made: first, the electrolyte effect of the dissolved perchloric acid on the isotopic fractionation of hydrogen between the liquid and vapor phases was the same as that measured for sodium perchlorate; second, perchloric acid itself was not completely dissociated in the solutions studied, for which a correction was made using estimated values for the fractionation of hydrogen in the undissociated acid. The former assumption is in agreement with the results of Googin and Smith,<sup>16</sup> whereas the latter brings about an uncertainty, the influence of which can be eliminated, however, if the results are extrapolated to zero perchloric acid concentration.

Table 3. Values calculated for the standard free energy change of the reaction  $2 \text{ D}_2\text{O}^+ + 3 \text{ H}_2\text{O} = 2 \text{ H}_2\text{O}^+ + 3 \text{ D}_2\text{O}$  at different temperatures and the respective equilibrium constants  $L$ .

$^\circ\text{C}$	$\Delta G_L^\circ, \text{ cal}$	$L$
5	-1286	10.3
15	-1293	9.6
25	-1300	9.0
35	-1309	8.5
45	-1318	8.0

The values calculated for the equilibrium constant of the reaction  $\text{H}_2\text{O} + \text{H}_2\text{DO}^+ = \text{HDO} + \text{H}_3\text{O}^+$  were, when corrected for the electrolyte effect: 0.964, 0.929, and 0.899 at perchloric acid molalities of 0.958, 4.353, and 7.125, respectively. From these a value of 0.974 can be extrapolated for zero perchloric acid concentration. By the rule of the geometric mean<sup>17</sup> this gives  $(1.5 \times 0.974)^6 = 9.7$  for  $L$  at 13.5°C, which is exactly the same value as that calculated from eqn. (11) for this temperature.

Finally, it is to be noted that Lietzke and Stoughton<sup>24</sup> have also studied the cell (6) and reported voltage differences for the protium and deuterium systems that are considerably higher than those given by Gary, Bates and Robinson.<sup>19</sup> For instance, at 25°C, their value is 7.4 mV, which can be contrasted with the value of 4.31 mV of the latter authors. Although the reasons for this discrepancy are not known at the present, it can be noted that the value of Gary, Bates and Robinson agrees with the earlier value of 4.5 mV of Noonan and La Mer<sup>8</sup> and, as shown above, it leads along with the other data to acceptable values of  $L$ , whereas that of Lietzke and Stoughton does not. *E.g.*, at 13.5°C, the value calculated for  $L$  using the data of Lietzke and Stoughton is 13.0, which is considerably higher than those derived from other experimental sources.

## REFERENCES

1. Salomaa, P., Schaleger, L. L. and Long, F. A. *J. Am. Chem. Soc.* **86** (1964) 1; *J. Phys. Chem.* **68** (1964) 410.
2. Salomaa, P. and Vesala, A. *Acta Chem. Scand.* **20** (1966) 1414.
3. La Mer, V. K. and Noonan, E. *J. Am. Chem. Soc.* **61** (1939) 1487.
4. Greyson, J. *J. Phys. Chem.* **66** (1962) 2218.
5. Salomaa, P. *Acta Chem. Scand.* **20** (1966) 1263.
6. Smith, P. L. and Taylor, N. W. *J. Res. Natl. Bur. Std.* **25** (1940) 731.
7. Kirshenbaum, I. *Physical Properties and Analysis of Heavy Water*, McGraw, New York 1951, Chapter 1.
8. Noonan, E. and La Mer, V. K. *J. Phys. Chem.* **43** (1939) 247.
9. Thomas, M. R., Scheraga, H. A. and Schrier, E. E. *J. Phys. Chem.* **69** (1965) 3722, and earlier references therein.
10. Hindman, J. C. *J. Chem. Phys.* **36** (1962) 1000.
11. Buijs, K. and Choppin, G. R. *J. Chem. Phys.* **39** (1963) 2035, 2042.
12. Fabricand, B. P., Goldberg, S. S., Leifer, R. and Ungar, S. G. *Mol. Phys.* **7** (1963-64) 425.
13. Yamatera, H., Fitzpatrick, B. and Gordon, G. *J. Mol. Spectry.* **14** (1964) 268.
14. Noyes, R. M. *J. Am. Chem. Soc.* **84** (1962) 513.
15. Birtbaler, W. and Lange, E. *Z. Elektrochem.* **43** (1937) 649.
16. Googin, J. M. and Smith, H. A. *J. Phys. Chem.* **61** (1957) 345.
17. Bigeleisen, J. *J. Chem. Phys.* **23** (1955) 2264.
18. Purlee, E. L. *J. Am. Chem. Soc.* **81** (1959) 263.
19. Gary, R., Bates, R. G. and Robinson, R. A. *J. Phys. Chem.* **68** (1964) 1186.
20. Kirshenbaum, I. Ref. 7, Chapter 3.
21. Gold, V. *Proc. Chem. Soc.* **1963** 141.
22. Kresge, A. J. and Allred, A. L. *J. Am. Chem. Soc.* **85** (1963) 1541.
23. Heinzinger, K. and Weston, R. E. *J. Phys. Chem.* **68** (1964) 744.
24. Lietzke, M. H. and Stoughton, R. W. *J. Phys. Chem.* **68** (1964) 3043.

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