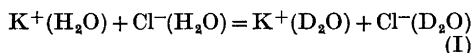


Standard Free Energy of Transfer of Potassium Chloride from Light to Heavy Water from Solubilities of Sparingly Soluble Salts

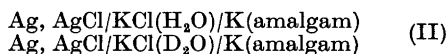
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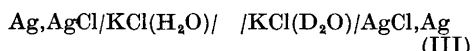
The thermodynamics of transfer of sparingly soluble electrolytes from light to heavy water can be readily studied by solubility measurements.¹ The ionic strength corrections are then small enough to permit reliable extrapolation to zero ionic strength. For more soluble salts, such as potassium chloride, other methods have been devised. However, it is a very disturbing fact that the reported standard free energy values for even such a formally simple process as



are widely divergent. Salomaa and Aalto² measured the difference between the EMF's of the cells



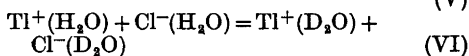
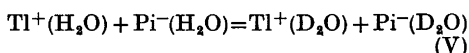
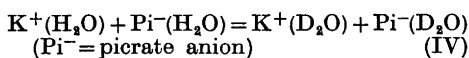
without liquid junction and arrived at a value of 900 ± 40 J/mol at 25°C.* In contrast, Greyson⁴ obtained 525 ± 50 J/mol from the EMF of the cell



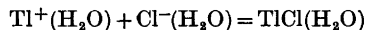
in which the double bars represent a cation exchange membrane.

We report here the results of an independent determination of the transfer free energy in question. Our method involves the measurement of the standard free energy values of the processes (IV), (V), and (VI). All the solutes in question are sparingly soluble and hence the ionic strength corrections can be calculated by means of the Debye-Hückel equation. The standard free energy change for process (I) is simply the sum of those for

(IV) and (VI) minus that for (V). Process (VI) has been previously studied by Kingerley and LaMer.⁵



A possible drawback to the above method which deserves most careful consideration is that the analytical solubility measurements do not distinguish between simple and associated ions. Bearing this in mind, the solubilities of the picrates were also measured in the presence of an added common ion, K⁺ or Tl⁺ ion, but no differences were evident in the calculated values of the solubility products (see below). This showed that complex formation was not significant in the studied solutions. Further, various literature values⁶ for the equilibrium constant of the reaction



and the solubility data indicate that only 2 to 5 % of the dissolved thallium(I) chloride in equilibrium with the solid phase is undissociated. This will cause only a minor error when calculating the solubility product, which, moreover, will largely cancel out from the ratio of the solubility products in H₂O and D₂O. Even if such cancellation were not complete, the free energy change for (VI), and hence that for (I), would be slightly underestimated, not overestimated, as the transfer free energies from H₂O to D₂O are definitely higher for ionic species than for nonionic species composed of similar constituents.¹

Reagent grade chemicals were used throughout. *Potassium* and *thallium(I) picrates* were prepared from picric acid and potassium and thallium(I) nitrates. They were first precipitated from solutions of picric acid in 50 % aqueous ethanol at 60°C. After cooling, the precipitates were collected by filtration and washed several times, first with cold water and subsequently with cold ethanol. The products were purified further by three recrystallizations from 50 % ethanol. The potassium picrate was then dried *in vacuo* during several weeks. The yellow modification of thallium(I) picrate first prepared and

* The standard states are here on the mole fraction scale throughout. Whenever the original values were given in other units, they have been converted to this scale using the relative densities of light and heavy water.³

Table 1. Solubilities of potassium and thallium(I) picrates in light and heavy water at 25°C. I = ionic strength (mol l^{-1}). (Pi) = picrate concentration (mol l^{-1}) at equilibrium. K_s is the uncorrected value of the solubility product ($\text{mol}^3 \text{l}^{-3}$), and K_s° the value at zero ionic strength.

Salt	Solvent	Added electrolyte	(Pi)	I	$10^4 K_s$	$10^4 K_s^\circ$
KPi	H ₂ O	—	0.02321	0.02321	5.39	4.05
»	»	0.00990 M KNO ₃	0.01867	0.02857	5.33	3.95
»	»	0.02085 »	0.01498	0.03583	5.37	3.82
»	»	0.03013 »	0.01305	0.04138	5.64	3.91
»	»	0.03987 »	0.01161	0.05148	5.98	4.05
KPi	D ₂ O	—	0.01886	0.01886	3.56	2.73
»	»	0.01056 M KNO ₃	0.01392	0.02448	3.41	2.55
»	»	0.01992 »	0.01197	0.03189	3.82	2.75
»	»	0.03175 »	0.00944	0.04119	3.89	2.71
TiPi	H ₂ O	—	0.01096	0.01096	1.201	0.974
»	»	—	0.01107	0.01107	1.225	0.993
»	»	—	0.01090	0.01090	1.188	0.963
»	»	—	0.01099	0.01099	1.208	0.979
»	»	—	0.01086	0.01086	1.179	0.956
»	»	—	0.01095	0.01095	1.199	0.972
»	»	0.01023 M TiNO ₃	0.00735	0.01758	1.292	1.000
»	»	0.01521 »	0.00607	0.02128	1.292	0.979
»	»	0.02006 »	0.00521	0.02527	1.317	0.979
TiPi	D ₂ O	—	0.00829	0.00829	0.687	0.571
»	»	—	0.00823	0.00823	0.677	0.562
»	»	—	0.00835	0.00835	0.697	0.570
»	»	—	0.00825	0.00825	0.681	0.566

recrystallized by the above procedures was not the thermodynamically stable modification at 25°C.⁷ It was therefore left in contact with its saturated water solution for several months,⁷ during which its complete conversion to the stable red modification occurred. The salt was then washed with cold anhydrous ethanol and dried *in vacuo*. The purified salts were used not only in the solubility measurements, but also as standard substances in gravimetric analyses (see below).

The purification and analysis of the heavy water employed have been described earlier.⁸ The deuterium atom fraction was 0.9982.

In the solubility measurements, 1.5 to 2 g of each picrate was mechanically agitated in a carefully sealed flask with 50 ml of water (or a water solution containing added electrolyte), first for one day at 35°C and then for at least one week at $25.00 \pm 0.02^\circ\text{C}$. The solid phases were allowed to settle and 40 ml volumes of the supernatant liquid phases were withdrawn and analyzed for picrate.

The analyses were performed by a gravimetric procedure of Spacu and Gafiteanu⁹ with minor modifications. The method is

based on the precipitation of picrate as its silver thiourea complex (VII). The sample solutions were heated to 90°C, and 5 ml



of a silver nitrate solution (0.5 M AgNO₃), 0.05 M HNO₃) was added to each. The thiourea complexes were then precipitated by dropwise addition of 5 ml of 1 M thiourea solution. The precipitates formed were allowed to settle and cool to room temperature in the dark, filtered through fine grade porcelain filter crucibles and washed successively twice with a 5:1 mixture of anhydrous ether and ethanol and thrice with anhydrous ether. The precipitates were then dried *in vacuo* overnight and weighed. Highly consistent values were obtained when the same procedure was carefully followed. When weighed amounts of the purified potassium and thallium(I) picrates were analyzed, the weights of the precipitates were $98.64 \pm 0.27\%$ of those calculated from the weight of picrate taken using formula (VII). In order to eliminate this small systematic error in analysis, an empirical gravimetric

correction factor, based on the above analyses, was applied to the solubility data.

When solutions of picrates in deuterium oxide were analyzed, the reagent solutions were prepared by dissolving the chemicals in heavy water. Protium thiourea was used as it was calculated that it would decrease the deuterium atom fractions in the final solutions by 0.0036 unit only. The procedure was identical to that described above except that only anhydrous ether was used to wash the precipitates. The ratio of the empirical and calculated gravimetric factors was close to that found for the protium system. In order to prevent possible protium-deuterium exchange in the precipitates, care was taken to exclude moisture during the operations.

The results of the solubility measurements are collected in Table 1. The solubility products, expressed in molar units, were converted to their values at zero ionic strength by applying the Debye-Hückel equation

$$-\log \gamma_i = Az_i^2 I^{1/2} / (1 + Ba_i I^{1/2})$$

the values of the parameters A and B of which were calculated using the recently redetermined values of the dielectric constants of light and heavy water.¹⁰ Empirical values for the ion-size parameters a_i ¹¹ were employed (for a recent use of these parameters, see Ref. 12).

From the values in the table, it follows that $K_s^\circ(\text{H}_2\text{O})/K_s^\circ(\text{D}_2\text{O})$ is 1.478 ± 0.031 for potassium picrate, and 1.714 ± 0.015 for thallium(I) picrate. When the standard states are converted to the mole fraction scale, the above values give, respectively, 950 ± 50 J/mol and 1320 ± 25 J/mol, for the standard free energy changes of processes (IV) and (V).

Correspondingly, one obtains from the solubility data reported by Kingerley and LaMer⁵ the value 1280 J/mol for the free energy change of process (VI) at 25°C. A consistent value, 1250 ± 50 J/mol, has been obtained in this laboratory¹³ in connection with a study on a number of thallium salts. Thus, combining the results for (IV), (V), and (VI), a value of 880 ± 75 J/mol is obtained for the free energy of transfer of potassium chloride (eqn. I) when the last-mentioned value for (VI) is used. The value reported by Kingerley and LaMer gives 910 J/mol with a standard error which is probably of the above magnitude. It is seen that the value

900 ± 40 J/mol obtained previously from measurements on cells without liquid junctions² is in excellent agreement with the present value, whereas the value, 525 ± 50 J/mol, derived from the data for the cell (III) is not.

One may question whether cells of type (III) are applicable at all if the solvents, the lyons of which are exchangeable with the cations present are different on both sides of the membrane. It was clearly pointed out by LaMer and Noonan¹⁴ three decades ago that the liquid junction complications are always well recognized when one employs, say, alcohol instead of D_2O in the other half-cell. Liquid junction difficulties of similar nature, though of smaller influence, have been met in some earlier studies of processes in the $\text{H}_2\text{O} - \text{D}_2\text{O}$ system when the glass electrode has been used.¹⁵

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