CATION HYDRATION ENERGY AND THERMODYNAMIC ELECTRODE POTENTIAL

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Calculations where crystal lattice energy and conditional assumptions necessary for dividing the sum of the hydration (solvation) energy into its components are used are being doubted increasingly [1]. In view of this, it is advisable to adopt other methods. As early as 1937 Klein and Lange [2] calculated the real hydration energy of individual ions using metal—solution contact potential difference (Volta potential). Using the same method, after some improvement, Hush [3] calculated afresh the real hydration energies of 49 ions. However, as rightly pointed out in [4], this investigation suffers from certain drawbacks and the results obtained are not beyond doubts. For the real hydration energy of H^+ ion, in particular, Hush found a value of 257.3 kcal/mole which differs by 3 kcal/mole from that calculated in [4] and [5].

Randles' precise study [5] occupies a special place primarily because a reproducibility of ±0.001 V was obtained in this study for experimental determination of metal—solution Volta potential; the reproducibility was ±0.04 V in [2]. Randles' calculation of the hydration energy of alkali metal cations and, what is more important, of H^+ ion is also more rigorous than in [2-4].

The real hydration energy of M^+ ions was calculated by the following equation (Randles' notations have been altered partly):

$$\Delta G^0_{hr}(M^+) = -\Delta H^0_f(M^+_{(g)}) + T[S^0(M^+_{(g)}) - S^0(M_{(c)})] - F\cdot E^0(M, M^+) + F\left[E^0(Hg, Cl^-) - \frac{\alpha_e\text{-}(Hg)}{|q_e|} - \Delta\psi^0(Hg, Cl^-)\right], \quad (1)$$

where $\Delta H^0_f(M^+_{(g)})$ and $\Delta S^0_{M^+(g)}$ are respectively the enthalpy of formation and entropy of M^+ ions in the gas phase, $S^0_{M(c)}$ is the entropy of the metal, α_e-(Hg) is the work of electron release from mercury, $|q_e|$ is the elementary electron charge, and $\Delta\psi^0(Hg, Cl^-)$ is the Volta potential of a given electrode.

As we showed in 1952 [6], the total work of electron release from a metal, referred to an electron charge, and the metal—solution Volta potential are the thermodynamic potentials of the respective electrode (half cell) E_t. Therefore,

$$E^0(Hg, Cl^-) - \left[\frac{\alpha_e\text{-}(Hg)}{|q_e|} + \Delta\psi^0(Hg, Cl^-)\right] = E^0(Hg, Cl^-) - E^0_t(Hg, Cl^-). \quad (2)$$

Apparently, the difference between a thermodynamic and a relative electrode potential of any electrode is the thermodynamic potential of that electrode to which the E^0 value pertains. In the given case it is the standard hydrogen electrode, i.e.,

$$E^0(Hg, Cl^-) - \left[\frac{\alpha_e\text{-}(Hg)}{|q_e|} + \Delta\psi^0(Hg, Cl^-)\right] = -E^0_t(H_2, H^+) \quad (3)$$

and Eq. (1) can be written as

$$\Delta G^0_{hr}(M^+) = -\Delta H^0_f(M^+_{(g)}) + T[S^0(M^+_{(g)}) - S^0(M_{(c)})] - FE^0(M, M^+) - FE^0_t(H_2, H^+). \quad (4)$$

Thus, Randles, like other authors [2-4], actually used in his study the standard thermodynamic electrode potential of a hydrogen electrode. It must be noted that this was not indicated either by Randles or by the authors of [2-4].

In the case studied by Randles, i.e., in the calculation of the hydration energy of alkali metal cations, Eq. (4) does not require rectification but is imprecise for M^{z+} cation in general. As was shown in [7, 8], the thermodynamic electrode potential is

$$E_t(M, M^{z+}) = -\frac{\Delta G_{er}}{zF}, \quad (5)$$

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TABLE 1

Ion	$-\Delta G^0_{hr}(M^{z+})$	$-\Delta G^0_{hc}(M^{z+})$	$-\Delta G_{hc}(M^{z+})$ [14]	Ion	$-\Delta G^0_{hr}(M^{z+})$	$-\Delta G^0_{hc}(M^{z+})$	$-\Delta G_{hc}(M^{z+})$ [14]
Cs^+	68,7	72	66	Cd^{2+}	432	438	425
Rb^+	76,4	79	74	Mn^{2+}	440	446	433
K^+	81,5	85	79	Mg^{2+}	460	466	450
Il^+	82,9	86	80	Zn^{2+}	486	492	479
Na^+	99,1	102	97	Cu^{2+}	499	505	491
Ag^+	115,4	118	113	Ce^{3+}	848	857	836
Zi^+	123,0	126	121	In^{3+}	977	986	965
Cu^+	137	140	139	Al^{3+}	1006	1015	1094
H^+	261,4	264	–	Fe^{3+}	1038	1047	1025
Pb^{2+}	360	366	353	Ga^{3+}	1109	1118	1097
Cu^{2+}	383	389	373	–	–	–	–

where ΔG_{er} is the molar energy of the electrode process consisting, as defined by us [6-8], in ion transfer from a metal to a solution and concurrent release of z electrons to an inert gas. This process may be replaced by an energy-equivalent aggregate of processes, viz., metal vaporization, ionization of the atoms formed, and hydration of M^{z+} ions, i.e.,

$$\Delta G_{er} = \Delta G_f(M^{z+}_{(g)}) + z\Delta G_f(e^-_{(g)}) + \Delta G_{hr}(M^{z+}) = \Delta G_f(M^{z+}_{(aq)}), \quad (6)$$

where $\Delta G_f(M^{z+}_{(aq)})$ is the energy of formation of the hydrated $M^{z+}_{(aq)}$ ions. In fact, under the usually adopted conditions the electrochemical potential of electrons in an inert gas is zero, i.e., the formation energy $\Delta G_f(e^-_{(g)}) = 0$. Since the energy of metal formation is also taken as zero, ΔG_{er} reduces to the energy of hydrated ion formation $\Delta G_f(M^{z+}_{(aq)})$, and in Eq. (4), $FE^0_t(H_2, H^+) = \Delta G^0_f(H^+_{(aq)})$.

In congruence with (5) and (6) the real ion hydration energy is

$$\Delta G^0_{hr}(M^{z+}) = -\Delta G^0_f(M^{z+}_{(g)}) - zF \cdot E^0_t(M, M^{z+}). \quad (7)$$

Substituting $-\Delta G^0_f(M^{z+}_{(g)})$ and $-zF \cdot E^0_t(M, M^{z+})$ by the quantities defining them we get

$$\Delta G^0_{hr}(M^{z+}) = -\Delta H^0_f(M^{z+}_{(g)}) + T(S^0_{M^{z+}(g)} - S^0_{M(c)} + \Delta S_e) - zF \cdot E^0(M, M^{z+}), \quad (8)$$

where ΔS_e is a correction taking into account the different electronic states of atoms and ions. Tarasatti [9] introduces another correction accounting for the electron entropy in the gas phase, but it is redundant as $\Delta G^0_f(e^-_{(g)}) = 0$. Equation (8) reduces to (4) when $S^0(M^{z+}_{(g)}) = S^0(M_{(g)})$.

To determine the quantity $E^0_t(H_2/H^+)$, which is of independent interest, we shall now make use of Randles' data and other quantities used by him: $\Delta\psi^0(Hg, Cl^-) = 0.208$, $E^0(Hg, Cl^-) = 0.2676$, and $\alpha_e\text{-}(HG)/|q_e| = 4.53$ V. Then, from Eq. (3), we get $E^0_t(H_2, H^+) = -4.47$ V. This value differs by 0.06 V from the value 4.41 V obtained by us in 1952 [6] by the use of $\Delta\psi^0(Hg, Hg_2^{2+}) = 0.69$ V [2], a standard electrode potential $E^0(Hg, Hg_2^{2+}) = 0.80$, and $\alpha_e\text{-}(Hg)/|q_e| = 4.52$ V.

Presently the value of $E^0(Hg, Cl^-)$ is known to a precision of ±0.0001 V, while the probable error of $\Delta\psi^0(Hg, Cl^-)$ measurement, as was shown earlier, is ±0.001 V. Thus, the error of the $E^0_t(H_2, H^+)$ calculation depends on the precision of measurement of the work of electron release from mercury. The $\alpha_e\text{-}(Hg)$ value used by Randles was found by photoelectric method as early as 1928. It is reported in [10] as 4.48 ± 0.02 eV (an average of 28 experiments) and in [11] as 4.50 ± 0.03 eV (an average of 37 experiments). Therefore, it can be assumed that in Eq. (3) $\alpha_e\text{-}(Hg)/|q_e| = 4.49 \pm 0.02$ V. Then the thermodynamic electrode potential $E^0_t(HG, H^+) = -4.43 \pm 0.02$ V.

It should be noted that Frumkin and Damaskin [12, 13] calculated the electrode potential, as calculated in [6-8], using the absolute (thermodynamic) hydrogen electrode potential calculated by Tarasatti [9], which they denoted by ε_T with a value of 3.31 V, and a

water surface potential of 0.13 ± 0.02 V taken by Tarasatti.† They denoted the latter entity by ε_K and showed that $\varepsilon_K = -E_t^\circ(H_2, H^+) = 4.44$ V. Convergence of this value and the above referred value of 4.43 V is logical. At the same time, for calculating ε_T, the real ion hydration energy calculated by Randles is used. Hence, in concurrence with Eq. (2), the value to be determined is introduced at one of the calculating stages which Tarasatti overlooked, and the ε_T value obtained is linked with the calculating peculiarities noted by Frumkin and Damaskin.

The fact that $E_t^\circ(H_2, H^+) = 4.43 \pm 0.02$ V shows that the last term in Eq. (8) equals −102.17 ± 0.5 kcal/mole, i.e., in cases where inaccuracies of other quantities can be ignored, the error in $\Delta G_{hr}^\circ(M^{z+})$ calculation is ±0.5 z kcal/mole. The values of $\Delta H_t^\circ(M_{(g)}^{z+})$, $S^\circ(M_{(g)}^{z+})$, $S^\circ(M_{(c)})$, and $E^\circ(M, M^{z+})$ can be obtained from handbooks. Combination of $\Delta G_{hr}^\circ(M^+)$ values calculated thus for five alkali metal cations with their relative hydration energies [14] calculated under the assumption that $\Delta G_{hr}^\circ(H^+)^* = 0$ permits evaluation of $\Delta G_{hr}^\circ(H^+)$. This gives the same value of $\Delta G_{hr}^\circ(H^+) = -261.4$ kcal/mole. Convergence of $\Delta G_{hr}^\circ(H^+)$ values merely reiterates that all the quantities used except $F \cdot E_t^\circ(H_2, H^+)$ do not add much error to the calculation.

The $\Delta G_{hr}^\circ(H^+)$ value obtained was used for calculating the real hydration energy of the cations (Table 1) whose $\Delta G_{hr}(M_{(rel)}^{z+})$ data are available from [14]. Note that the authors of [14] restricted themselves only to those ions for which the term ΔS_e, used also in Eq. (8), is known.

Further, Table 1 contains values of chemical cation hydration energy $\Delta G_{hc}^\circ(M^{z+})$ calculated by using the value of the surface potential of water given above. Assuming the precision of χ calculation evaluated by Tarasatti to be correct, the probable error of $\Delta G_{hc}^\circ(M^{z+})$ should be ±1.0 z kcal/mole for the alkali metal cations Tl^+, Ag^+, and Zn^{2+} and ±1.2 z kcal/mole for other cations due to the effect of probable inaccuracy of electrode potential measurements. However, according to [13], what is known is only that $\chi \approx +0{,}1$ V. The most reliable $\Delta G_{hc}(M^{z+})$ data calculated with the use of the thermochemical data with $\Delta H_{hc}(Cs^+) = \Delta H_{hc}(I^-)$ taken from the monograph [15], are given in Table 1 for comparison.

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*In this case the water molecules are oriented by oxygen atoms inside the phase.