Topic 3200

Water; Hydrogen Ions

Chemists are often faced with the situation where on adding salt MX to water ($\ell$) experimental evidence shows that the cation exists as a hydrate $\text{M(H}_2\text{O)}\text{)_n}$. For example, adding $\text{CuSO}_4$(s), a white powder, to water produces a blue solution containing $[\text{Cu(H}_2\text{O)}\text{)_4}]^{2+}$. If solute molecules bind solvent molecules to produce new solute molecules, one can imagine a limiting situation where, as the depletion of solvent continues, there is little ‘solvent’ as such left in the system.

An important example of the problems linked to description concerns hydrogen ions in aqueous solution [1]. Two common descriptions are (a) $\text{H}^+$(aq), and (b) $\text{H}_3\text{O}^+$(aq). As a starting point, we assume that the system comprises $n_j$ moles of solute $\text{HX}$ and $n_1$ moles of water.

A simple description of hydrogen ions is in terms of $\text{H}^+$(aq) although intuitively the idea of protons as ions in aqueous solutions is not attractive. Arguably a more satisfactory description of hydrogen ions in solution is in terms of $\text{H}_3\text{O}^+$ ions. Description of hydrogen ions in aqueous solution as $\text{H}_3\text{O}^+$ finds general support. Adam recalls [2] the experiment conducted by Bagster and Cooling [3]. The latter authors observed that the electrical conductivity of a solution of $\text{HC}_\ell$ in $\text{SO}_2(\ell)$ is low but increases dramatically when 1 mole of water $(\ell)$ is added for each mole of $\text{HC}_\ell$.

Moreover on electrolysis, hydrogen ions and water are liberated at the cathode; water $(\ell)$ drips from this electrode.

In the chemistry of aqueous solutions, two ions $\text{H}^+$ and $\text{OH}^-$ command interest. Hydrogen ions are also called [1] hydronium ions when written as $\text{H}_3\text{O}^+$. The latter ion is a flat pyramid with $d(\text{O-H}) = 96.3$ pm; the HOH angle $= 110-112^0$ [4]. A case for writing the formula $\text{H}_3\text{O}^+$ is based on the existence of isomorphous solids, $\text{NH}_4\text{ClO}_4^-$ and $\text{H}_3\text{O}^+\text{ClO}_4^-$. The mass spectra of $\text{H}^+(\text{H}_2\text{O})_n$ have been observed for $1 \leq n \leq 8$ [5]. Neutron-scattering and X-ray scattering data show that for $\text{D}_3\text{O}^+$ ions in solution, $d(\text{O}–\text{D}) = 101.7$ pm [6]. In an ‘isolated’ $\text{H}_3\text{O}^+$ ion the O-H bond length is 97 pm and the HOH angle is 110 - 112 $^0$. 
In aqueous solution, $\text{H}_3\text{O}^+$ ions do not exist as solutes comparable to $\text{Na}^+$ ions in $\text{NaCl(aq)}$. Instead a given $\text{H}_3\text{O}^+$ ion transfers a proton to a neighbouring water molecule. The time taken for the transfer is very short, approx. $10^{-13}$ seconds granted that the receiving water molecule has the correct orientation. But a given $\text{H}_3\text{O}^+$ ion has a finite lifetime, sufficient to be characterised by thermodynamic and spectroscopic properties. The rate determining step in proton migration involves reorientation of neighbouring water molecules, thereby accounting for the increase in molar conductance $\lambda_\infty(\text{H}^+;\text{aq})$ with increase in $T$ and $p$ [7-10]. [In ice, proton transfer is rate determining and so the mobilities of $\text{H}^+$ and $\text{OH}^-$ ions are higher in ice than in water ($\ell$).] The high mobility of protons in aqueous solution involves a series of isomerizations between $\text{H}_2\text{O}_4^+$ and $\text{H}_3\text{O}_2^+$, the first triggered by hydrogen bond cleavage of a second shell water molecule and the second by the reverse, hydrogen bond formation [11]. An iconoclastic approach, expressed by Hertz and co-workers, argues against the existence of $\text{H}^+$ ions as such except in so far as this symbol describes as dynamical property of a solution [12,13]. In their view $\text{H}_3\text{O}^+$ is ephemeral. Among other interesting ions discussed in this context are $\text{H}_5\text{O}_3^+$ [14].

Comparisons are often drawn between $\text{NH}_4^+(\text{aq})$ and $\text{H}_3\text{O}^+(\text{aq})$ ions but they are not really related. For example the electrical mobility of $\text{NH}_4^+(\text{aq})$ is not exceptional.

The chemical potential of $\text{H}^+(\text{aq})$ describes the change in Gibbs energy when $\delta n(\text{H}^+)$ moles are added at constant $n(\text{H}_2\text{O})$, $n(X)$, $T$ and $p$. The chemical potential of $\text{H}^+(\text{aq})$ is related to the molality $m(\text{H}^+) = n(\text{H}^+)/n_1M_1$ and the single activity coefficient $\gamma(\text{H}^+)$. The Gibbs energy of an aqueous solution $G(\text{aq})$ prepared using $n_1$ moles of water and $n_j$ moles of acid $\text{H}^+X^-$ is given by the equation (a) (for the solution at defined $T$ and $p$, which we assume is close to the standard pressure $p^0$).

$$G(\text{aq}) = n_1 \cdot \mu_1(\text{H}_2\text{O};\text{aq}) + n(\text{H}^+) \cdot \mu(\text{H}^+;\text{aq}) + n(X^-) \cdot \mu(X^-;\text{aq})$$ (a)

where

$$\mu(\text{H}^+) = [\partial G/\partial n(\text{H}^+)]_{n(\text{H}_2\text{O}),n(X^-)}$$ (b)

and

$$\mu(\text{H}^+;\text{aq}) = \mu^0(\text{H}^+;\text{aq}) + R \cdot T \cdot \ln[m(\text{H}^+) \cdot \gamma(\text{H}^+)/m^0]$$ (c)
For the electrolyte $H^+ X^-$ with $\nu = 2$,

\[
\mu(H^+ X^-;aq) = \mu^0(H^+ X^-;aq) + 2 \cdot R \cdot T \cdot \ln[m(H^+ X^-) \cdot \gamma_\pm(H^+ X^-)/m^0]
\]

and, all $T$ and $p$,

\[
\lim[m(H^+ X^-) \to 0] \gamma_\pm = 1.0
\]

In a similar fashion, we define the partial molar volume, enthalpy and isobaric heat capacity for $H^+$ in aqueous solution.

\[
V(H^+;aq;T;p) = [\partial V / \partial n(H^+)]_{T,p,n(H_2O),n(X^-)}
\]

\[
H(H^+;aq;T;p) = [\partial H / \partial n(H^+)]_{T,p,n(H_2O),n(X^-)}
\]

For electrolyte $H^+ X^-$,

\[
V^\infty(H^+X^-;aq;T;p) = V^\infty(H^+;aq;T;p) + V^\infty(X^-;aq;T;p)
\]

\[
H^\infty(H^+X^-;aq;T;p) = H^\infty(H^+;aq;T;p) + H^\infty(X^-;aq;T;p)
\]

and

\[
C_p^\infty(H^+X^-;aq;T;p) = C_p^\infty(H^+;aq;T;p) + C_p^\infty(X^-;aq;T;p)
\]

The chemical potential of $H_3O^+$ ions in aqueous solution describes the change in Gibbs energy when $\delta n(H_3O^+)$ ions are added at constant $n(H_2O)$, $n(X^-$), $T$ and $p$. At defined $T$ and $p$,

\[
\mu(H_3O^+;aq) = [\partial G / \partial n(H_3O^+)]_{n(H_2O),n(X^-)}
\]

The chemical potential of the electrolyte $H_3O^+X^-$ in aqueous solution is described by the following equation.

\[
\mu(H_3O^+X^-;aq) = \mu^0(H_3O^+X^-;aq) + 2 \cdot R \cdot T \cdot \ln[m(H_3O^+X^-) \cdot \gamma_\pm(H_3O^+X^-)/m^0]
\]

where $m(H_3O^+X^-) = n(H_3O^+X^-)/n(H_2O)M_1$

\[
n(H_2O) = n_1 - n(H_3O^+)
\]

and where limit$[m(H_3O^+X^-) \to 0] \gamma_\pm (H_3O^+X^-) = 1.0$ at all $T$ and $p$. Thus the chemical potential $\mu(H_3O^+X^-;aq;T;p)$ of the electrolyte $H_3O^+X^-$ is related to the molality $m(H_3O^+X^-)$ and the mean ionic activity coefficient $\gamma_\pm (H_3O^+X^-)$. We compare two descriptions of the same system. In description I, the system is an aqueous solution containing $H^+$ and $X^-$ ions whereas in description II the system is an aqueous solution containing $H_3O^+$ and $X^-$ ions.

Description I; $n_j$ moles of $H^+ X^-$

\[
G(aq;I) = n_1 \cdot \mu_1(aq;I) + n_j \cdot \mu(H^+;aq;I) + n_j \cdot \mu(X^-;aq;I)
\]
Description II

\[ G(\text{aq}; \text{II}) = (n_i - n_j) \cdot \mu_1(\text{aq}; \text{II}) + n_j \cdot \mu(\text{H}_2\text{O}^+; \text{aq}) + n_j \cdot \mu(\text{X}^-; \text{aq}; \text{II}) \]  

At equilibrium, 

(a) \[ G(\text{I}; \text{aq}) = G(\text{II}; \text{aq}) \]  

(b) \[ \mu_1(\text{aq}; \text{I}) = \mu_1(\text{aq}; \text{II}) \]  

and  

(c) \[ \mu(\text{X}^-; \text{aq}; \text{I}) = \mu(\text{X}^-; \text{aq}; \text{II}) \]  

At equilibrium (at defined \( T \) and \( p \)) \[ \mu(\text{H}^+; \text{aq}) + \mu_1(\text{aq}) = \mu(\text{H}_2\text{O}^+; \text{aq}) \]  

In effect we shifted a mole of water for each mole of \( \text{H}^+ \) ions from consideration as part of the solvent in description I to part of the solute in description II forming \( \text{H}_2\text{O}^+ \) ions. The link between these descriptions is achieved through two formulations of \( G^{eq}(\text{aq}) \) which is identical for both systems (as are \( V^{eq}, S^{eq} \) and \( H^{eq} \)). The equality of the total Gibbs function and equilibrium chemical potentials of substances common to both descriptions leads to equation (u) relating \( \mu(\text{H}^+; \text{aq}) \) and \( \mu(\text{H}_2\text{O}^+; \text{aq}) \). We take the analysis a stage further and use the equations relating chemical potential and composition for the two ions \( \text{H}^+ \) and \( \text{H}_2\text{O}^+ \) in aqueous solution at defined \( T \) and \( p \).

Description I  

\[ m(\text{H}^+) = n(\text{H}^+) / n_1. M_1 \]  

\[ m(\text{X}^-) = n(\text{X}^-) / n_1. M_1 \]  

Description II  

\[ m(\text{H}_2\text{O}^+) = n(\text{H}_2\text{O}^+)/(n_1 - n_j). M_1 \]  

and \[ m(\text{X}^-; \text{II}) = n(\text{X}^-)/(n_1 - n_j). M_1 \]  

Also, \[ \mu^{eq}(\text{H}_2\text{O}^+; \text{aq}) = \mu^{eq}(\text{H}^+; \text{aq}) + \mu^{eq}_1(\text{aq}) \]  

Hence, \[ \mu^{0}(\text{H}_2\text{O}^+ \text{ X}^{-}; \text{aq}) + 2. R. T. \ln[m(\text{H}_2\text{O}^+ \text{ X}^{-})/m^0] \]  

\[ = \mu^{0}(\text{H}^+ \text{ X}^{-}; \text{aq}) + 2. R. T. \ln[m(\text{H}^+ \text{ X}^{-})/m^0] \]  

\[ + \mu^{1}_1(\ell; T; p) - 2. \phi(\text{I}) . R. T. m(\text{H}^+ \text{ X}^{-}) . M_1 \]  

But  

\[ \lim(n_j \to 0)m(\text{H}^+ \text{ X}^{-}) / m(\text{H}_2\text{O}^+) = 1.0 \]  

\[ \gamma^0(\text{H}^+ \text{ X}^{-}) / \gamma^0(\text{H}_2\text{O}^+ \text{ X}^{-}) = 1 \]  

\[ \phi(\text{I}) = 1.0 \]  

Hence, \[ \mu^0(\text{H}_2\text{O}^+; \text{aq}) = \mu^0(\text{H}^+; \text{aq}) + \mu^0_1(\text{H}_2\text{O}; \ell) \]  

Also, \[ V^0(\text{H}_2\text{O}^+; \text{aq}) = V^0(\text{H}^+; \text{aq}) + V^0_1(\text{H}_2\text{O}; \ell) \]  

And \[ C^0(\text{H}_2\text{O}^+; \text{aq}) = C^0(\text{H}^+; \text{aq}) + C^0_1(\text{H}_2\text{O}; \ell) \]  

Interestingly the difference in reference chemical potentials of \( \text{H}^+(\text{aq}) \) and \( \text{H}_2\text{O}^+(\text{aq}) \) equals the chemical potential of water (\( \ell \)) at the same \( T \) and \( p \). We combine equations (z) and (za) to obtain an equation relating the mean
ionic activity coefficients $\gamma_\pm(H^+X^-)$ and $\gamma_\pm(H_3O^+X^-)$. Thus (at defined T and p )

$$\ln[\gamma_\pm(H_3O^+X^-)] = \ln[\gamma_\pm(H^+X^-)] + \ln[\frac{m(H^+X^-)}{m(H_3O^+X^-)}]$$

$$-\phi(I) \cdot \frac{m(H^+X^-)}{M} \cdot M_1$$  \hspace{1cm} (ze)

$$+ \left[ \frac{1/2 \cdot R \cdot T}{\mu} \right] \cdot \left[ \mu^0(H^+X^-;aq) + \mu^0(H_3O^+X^-;aq) \right]$$

Then

$$\ln[\gamma_\pm(H_3O^+X^-)] = \ln[\gamma_\pm(H^+X^-)] + \ln[\frac{m(H^+X^-)}{m(H_3O^+X^-)}]$$

$$-\phi(I) \cdot \frac{m(H^+X^-)}{M} \cdot M_1$$  \hspace{1cm} (zf)

Also from equations (v) and (w),

$$\ln[\frac{m(H^+X^-)}{m(H_3O^+X^-)}] = \ln[1 - M_1 \cdot \frac{m(H^+X^-)}{M}]$$  \hspace{1cm} (zg)

Clearly in dilute aqueous solutions where $\{\frac{m(H^+X^-)}{m(H_3O^+X^-)}\}$ is approximately unity and $\phi(I) \cdot \frac{m(H^+X^-)}{M} \cdot M_1$ is negligibly small, the two mean ionic activity coefficients are equal but this approximation becomes less acceptable with increase in the ratio $n(H^+X^-)/n(H_2O)$.

Footnotes


[13] H. G. Hertz, B. M. Braun, K. J. Muller and R. Maurer,