**Topic 3170**

**Volume of Reaction; Dependence on Pressure**

Consider a chemical equilibrium between two solute X(aq) and Y(aq) in aqueous solution at fixed T and p. We assume that the thermodynamic properties of the two solutes are ideal. The chemical equilibrium is be expressed as follows.

\[ X(aq) \Leftrightarrow Y(aq) \]  \hspace{1cm} (a)

The (dimensionless intensive) degree of reaction \( \alpha \) is related to the equilibrium constant \( K^0 \) using equation (b) [1].

\[ \alpha = \frac{K^0}{1 + K^0} \]  \hspace{1cm} (b)

At fixed temperature, \( \frac{d\alpha}{dp} = \frac{K^0}{(1 + K^0)^2} \cdot \frac{d \ln(K^0)}{dp} \)  \hspace{1cm} (c)

Or,

\[ \frac{d\alpha}{dp} = - \frac{K^0}{(1 + K^0)^2} \cdot \frac{\Delta V^0(aq)}{R \cdot T} \]  \hspace{1cm} (d)

\( \Delta V^0(aq) \) is the limiting volume of reaction. The (equilibrium) volume of the system at a defined T and p is given by equation (e).

\[ V(aq) = n_X \cdot V_x^a(aq) + n_Y \cdot V_Y^a(aq) + n_1 \cdot V_1^a(\ell) \]  \hspace{1cm} (e)

\( V_1^a(\ell) \) is the molar volume of solvent, water. If \( n_0 \) is total amount of solute, (i.e. X and Y) in the system,

\[ V(aq) = (1 - \alpha) \cdot n_X^0 \cdot V_x^a(aq) + \alpha \cdot n_X^0 \cdot V_Y^a(aq) + n_1 \cdot V_1^a(\ell) \]  \hspace{1cm} (f)

Or,

\[ V(aq) = n_X^0 \cdot V_x^a(aq) + \alpha \cdot n_X^0 \cdot \Delta V^a(aq) + n_1 \cdot V_1^a(\ell) \]  \hspace{1cm} (g)

\( \Delta V^a(aq) \) is the limiting volume of reaction. We assume that at temperature T, the properties \( V_x^a(aq), \Delta V^a(aq) \) and \( V_1^a(\ell) \) are independent of pressure.

Hence using equations (d) and (g) [2,3],

\[ \left( \frac{\partial V(aq)}{\partial p} \right)_T = -n_X^0 \cdot \frac{[\Delta V^a(aq)]^2}{R \cdot T} \cdot \frac{K^0}{[1 + K^0]^2} \]  \hspace{1cm} (h)

We have taken account of the fact that,

\[ \frac{d \ln(K^0)}{dp} = \frac{\Delta V^a(aq)}{R \cdot T} \]  \hspace{1cm} (i)

Similarly [2] \( \left( \frac{\partial V(aq)}{\partial T} \right)_p = n_X^0 \cdot \frac{\Delta V^a(aq) \cdot \Delta H^a(aq)}{R \cdot T^2} \cdot \frac{K^0}{[1 + K^0]^2} \)  \hspace{1cm} (j)
Equation (h) shows that irrespective of the sign of $\Delta V^\infty (aq)$, the contribution to $\left( \frac{\partial V(aq)}{\partial p} \right)_T$ is always negative. No such generalisation emerges with respect to equation (j) [4]. A closely related subject concerns the dependence of rate constants on pressure leading to volumes of activation [5].

**Footnotes**

[1] From equation (a)

\[
X(aq) \rightleftharpoons Y(aq)
\]

At $t = 0$, $n_X^0$ mol

At equilib; $n_X^0 - \xi$ mol

In volume $V$ $\left( n_X^0 - \xi \right)/V$ mol $m^{-3}$

For a system where the thermodynamic properties are ideal,

\[
K^0 = \frac{(\xi/V) / \left[ (n_X^0 - \xi)/V \right]}{}
\]

Or, $K^0 = \frac{(\xi/V) / \left[ (n_X^0 - \xi)/V \right]}{\left[ (n_X^0 - \xi)/V \right]}$. By definition, $\alpha = \frac{\xi}{n_X^0}$.

Then, $K^0 = \frac{(n_X^0 \cdot \alpha/V) / \left[ (n_X^0 - \xi)/V \right]}{\left[ (n_X^0 - \xi)/V \right]}$.

Or, $K^0 = \alpha / (1 - \alpha)$. $K^0 = \alpha \cdot (1 + K^0)$

[2] $dV/dp = \left[ m^3 \right]/\left[ N m^{-2} \right] = [m^5 N^{-1}]$

\[
\frac{n_X^0 \cdot [\Delta V^\infty (aq)]^2}{R \cdot T} \cdot \frac{K^0}{[1 + K^0]^2} = [\text{mol}] \cdot \frac{[m^3 \text{ mol}^{-1}]^2}{[J K^{-1} \text{ mol}^{-1}] \cdot [K]} [1]
\]

\[
= \frac{[m^6]}{[N m]} = [m^5 N^{-1}]
\]

[3] $\frac{dV}{dT} = \frac{[m^3]}{[K]}

\[
\frac{n_X^0 \cdot [\Delta V^\infty (aq) \cdot \Delta H^\infty (aq)]}{R \cdot T^2} \cdot \frac{K^0}{[1 + K^0]^2}
\]

\[
= [\text{mol}] \cdot \frac{[m^3 \text{ mol}^{-1}] \cdot [J \text{ mol}^{-1}]}{[J K^{-1} \text{ mol}^{-1}] \cdot [K]} = [m^4 K^{-1}]
\]


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