$$G_{\rm m}^{\rm ideal} = \mu_+^{\rm ideal} + \mu_-^{\rm ideal}$$

Total ideal molar Gibbs free energy is written as the sum of ideal chemical potentials for cations and anions

 $G_{\rm m}^{\rm ideal} = \mu_+^{\rm ideal} + \mu_-^{\rm ideal}$

$$\mu_{\rm J}^{\rm ideal} = \mu_{\rm J}^{\oplus} + RT \ln x_{\rm J}$$

ideal chemical potential for a species j

Solute activity in real solutes	
$\mu_{\rm B} = \mu_{\rm B}^{\rm o} + RT \ln x_{\rm B}$	In ideal-dilute solutions

 $G_{\rm m}^{\rm ideal} = \mu_{+}^{\rm ideal} + \mu_{-}^{\rm ideal}$ $\mu_{\rm J}^{\rm ideal} = \mu_{\rm J}^{\oplus} + RT \ln x_{\rm J}$ $\mu_{\rm B} = \mu_{\rm B}^{\oplus} + RT \ln x_{\rm B}$ In ideal-dilute solutions $\mu_{\rm J} = \mu_{\rm J}^{\oplus} + RT \ln a_{\rm J}$ for a *real* solution $a_{\rm I} = \gamma_{\rm I} x_{\rm I}$

 $G_{\rm m}^{\rm ideal} = \mu_{\rm +}^{\rm ideal} + \mu_{\rm -}^{\rm ideal}$ $\mu_{\rm J}^{\rm ideal} = \mu_{\rm J}^{\oplus} + RT \ln x_{\rm J}$ $\mu_{\rm J} = \mu_{\rm J}^{\oplus} + RT \ln a_{\rm J} \qquad \text{for a real solution}$ $\mu_{\rm J} = \gamma_{\rm J} x_{\rm J}$ $\mu_{\rm J} = \mu_{\rm J}^{\rm ideal} + RT \ln \gamma_{\rm J} \qquad \text{for a real solution}$

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$$G_{\rm m} = \mu_{+} + \mu_{-} = \mu_{+}^{\rm ideal} + \mu_{-}^{\rm ideal} + RT \ln \gamma_{+} + RT \ln \gamma_{-}$$

real Gibbs energy is the sum of the chemical potentials of both ions

 $G_{\rm m}^{\rm ideal} = \mu_{\rm +}^{\rm ideal} + \mu_{\rm -}^{\rm ideal}$ $\mu_{\rm J}^{\rm ideal} = \mu_{\rm J}^{\oplus} + RT\ln x_{\rm J}$ $\mu_{\rm J} = \mu_{\rm J}^{\oplus} + RT\ln a_{\rm J} \qquad \text{for a real solution}$ $\mu_{\rm J} = \gamma_{\rm J} x_{\rm J}$ $\mu_{\rm J} = \mu_{\rm J}^{\rm ideal} + RT\ln \gamma_{\rm J}$

 $G_{\rm m} = \mu_{+} + \mu_{-} = \mu_{+}^{\rm ideal} + \mu_{-}^{\rm ideal} + RT \ln \gamma_{+} + RT \ln \gamma_{-}$

 $= G_{\rm m}^{\rm ideal} + RT \ln \gamma_+ \gamma_-$

All the deviations from ideality are contained in the last term

$$G_{\rm m}^{\rm ideal} = \mu_+^{\rm ideal} + \mu_-^{\rm ideal}$$

$$\mu_{J}^{ideal} = \mu_{J}^{\oplus} + RT\ln x_{J}$$
$$\mu_{J} = \mu_{J}^{\oplus} + RT\ln a_{J}$$
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Mean activity coefficients $\begin{tabular}{l} \hline \\ \gamma_{\pm} \end{tabular}$

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 γ_{\pm} defined via the geometric mean

Mean activity coefficients

 γ_{\pm}

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 γ_{\pm} defined via the geometric mean

for n numbers x_1, x_2, \ldots, x_n ,

geometric mean $= \sqrt[n]{x_1 \cdot x_2 \cdot \ldots \cdot x_n}$

Mean activity coefficients

 γ_{\pm}

 $G_{\rm m}^{\rm ideal} = \mu_+^{\rm ideal} + \mu_-^{\rm ideal}$ for n numbers x_1, x_2, \ldots, x_n , geometric mean $= \sqrt[n]{x_1 \cdot x_2 \cdot \ldots \cdot x_n}$ $\mu_{\rm I}^{\rm ideal} = \mu_{\rm I}^{\oplus} + RT \ln x_{\rm I}$ Mean activity coefficients $\mu_{\rm J} = \mu_{\rm J}^{\rm e} + RT \ln a_{\rm J}$ we assume, $\mu_{+} = \mu_{+}^{\text{ideal}} + RT \ln \gamma_{+}$ $a_{\rm I} = \gamma_{\rm I} x_{\rm I}$ $\mu_{-} = \mu_{-}^{\text{ideal}} + RT \ln \gamma_{+}$ $\mu_{\rm I} = \mu_{\rm I}^{\rm ideal} + RT \ln \gamma_{\rm I}$ $G_{\rm m} = \mu_{+} + \mu_{-} = \mu_{+}^{\rm ideal} + \mu_{-}^{\rm ideal} + RT \ln \gamma_{+} + RT \ln \gamma_{-}$ $=G_{m}^{ideal} + RT \ln \gamma_{+} \gamma_{-}$

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$$Mean activity coefficients$$

$$\mu_{+} = \mu_{+}^{\rm ideal} + RT\ln \gamma_{\pm}$$

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$$= G_{\rm m}^{\rm ideal} + RT\ln \gamma_{+} \gamma_{-}$$

$$(compound M_{p}X_{q} - p cations and q anions)$$

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$$= G_{m}^{ideal} + RT \ln \gamma_{+} \gamma_{-}$$

$$Compound M_{p}X_{q} - p \text{ cations and q anions}$$

$$\gamma_{\pm} = (\gamma_{+}^{p} \gamma_{-}^{q})^{1/s} \quad s = p + q$$





$$\log \gamma_{\pm} = -A |z_{+}z_{-}| I^{1/2}$$

A = 0.509 for an aqueous solution at 25 °C (depends on temperature and solvent) $\log \gamma_{\pm} = -A |z_{+}z_{-}| I^{1/2}$

A = 0.509 for an aqueous solution at $25 \,^{\circ}\text{C}$ $\log \gamma_{\pm} = -A |z_{+}z_{-}| I^{1/2}$ charge number of an ion *i* positive for cations and negative for anions









Question

Estimate mean activity coefficient of 5.0 mmol kg⁻¹ KCl_(aq) at 25 °C using Debye– Hückel limiting law.

$$\log \gamma_{\pm} = -A |z_{+}z_{-}| I^{1/2}$$

$$I = \frac{1}{2} \sum_{i} z_{i}^{2} (b_{i}/b^{\oplus})$$

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$$= 5.0 \times 10^{-3}$$

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 $\log \gamma_{\pm} = -0.509 \times (5.0 \times 10^{-3})^{1/2} = -0.03...$

 γ_{\pm} = 0.92. The experimental value is 0.927.

For higher ionic strengths

$$\log \gamma_{\pm} = -A |z_+ z_-| I^{1/2}$$

$$\log \gamma_{\pm} = -\frac{A |z_{+} z_{-}| I^{1/2}}{1 + B I^{1/2}}$$

Extended Debye– Hückel law

Valid over a wider ionic strength range (up to ~0.1 mol/kg).

B is an empirical parameter (Ion-size effects)

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Extended Debye-Hückel law

Valid over a wider ionic strength range (up to ~0.1 mol/kg).

B is an empirical parameter (Ion-size effects)

$$\log \gamma_{\pm} = -\frac{A|z_{+}z_{-}|I^{1/2}}{1+BI^{1/2}} + CI$$

Davies equation

Useful up to moderate ionic strengths (~0.5 mol/kg).

B (ion-size effect) and C (a linear correction; CI) are dimensionless empirical parameters

CHEM 3520

Focus 1: Properties of gases

Focus 2: The First Law

Focus 3: The Second and Third Laws

Focus 4: Physical transformation of pure substances

Focus 5: Simple mixtures

Focus 6: Chemical equilibrium

Focus 17: Chemical kinetics Focus 18: Reaction dynamics Focus 6: Chemical equilibrium

The equilibrium constant

The response of equilibria to the conditions

Electrochemical cells

Electrode potentials

 $A \rightleftharpoons B.$

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 $dn_A = -d\xi$

 $dn_{\rm B} = +d\xi.$

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 $dn_A = -d\xi$

 $dn_{\rm B} = +d\xi.$

 ξ extent of reaction:

 $A \rightleftharpoons B.$

 $dn_{\rm A} = -d\xi$ $dn_{\rm B} = +d\xi.$

extent of reaction



If $\Delta_r G < 0$, the forward reaction is spontaneous.exergonicIf $\Delta_r G > 0$, the reverse reaction is spontaneous.endergonicIf $\Delta_r G = 0$, the reaction is at equilibrium.

 $\Delta_{\rm r}G = \mu_{\rm B} - \mu_{\rm A}$

$$\Delta_{\rm r}G = \mu_{\rm B} - \mu_{\rm A} = (\mu_{\rm B}^{\odot} + RT\ln\frac{p_{\rm B}}{p^{\odot}}) - (\mu_{\rm A}^{\odot} + RT\ln\frac{p_{\rm A}}{p^{\odot}})$$

$$\Delta_{\mathrm{r}}G = \mu_{\mathrm{B}} - \mu_{\mathrm{A}} = (\mu_{\mathrm{B}}^{\ominus} + RT\ln\frac{p_{\mathrm{B}}}{p^{\ominus}}) - (\mu_{\mathrm{A}}^{\ominus} + RT\ln\frac{p_{\mathrm{A}}}{p^{\ominus}})$$

Standard Gibbs energy change:

$$\Delta_r G^\circ = \mu_B^\circ - \mu_A^\circ$$

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$$=\Delta_{\rm r}G^{\oplus} + RT\ln\frac{p_{\rm B}}{p_{\rm A}}$$

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'reaction quotient'

$$\Delta_{\mathrm{r}}G = \mu_{\mathrm{B}} - \mu_{\mathrm{A}} = (\mu_{\mathrm{B}}^{\oplus} + RT\ln\frac{p_{\mathrm{B}}}{p^{\oplus}}) - (\mu_{\mathrm{A}}^{\oplus} + RT\ln\frac{p_{\mathrm{A}}}{p^{\oplus}})$$

$$=\Delta_{\rm r}G^{\oplus} + RT\ln\frac{p_{\rm B}}{p_{\rm A}}$$

$$=\Delta_{\rm r}G^{\oplus}+RT\ln Q$$

$$Q = \frac{p_{\rm B}}{p_{\rm A}}$$

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At equilibrium $\Delta_{\rm r}G = 0$

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At equilibrium $\Delta_{\rm r}G = 0$

 $0 = \Delta_{\rm r} G^{\rm e} + RT \ln K$

$$Q = \frac{p_{\rm B}}{p_{\rm A}}$$

'reaction quotient'

$$K = \left(\frac{p_{\rm B}}{p_{\rm A}}\right)_{\rm equilibrium}$$

$$\Delta_{\mathrm{r}}G = \mu_{\mathrm{B}} - \mu_{\mathrm{A}} = (\mu_{\mathrm{B}}^{\oplus} + RT\ln\frac{p_{\mathrm{B}}}{p^{\oplus}}) - (\mu_{\mathrm{A}}^{\oplus} + RT\ln\frac{p_{\mathrm{A}}}{p^{\oplus}})$$

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$$Q = \frac{p_{\rm B}}{p_{\rm A}}$$
 'rea

'reaction quotient'

Ratio of product to reactant pressures at any point in time

$$K = \left(\frac{p_{\rm B}}{p_{\rm A}}\right)_{\rm equilibrium}$$

 $\Delta_{\mathbf{r}}G^{\oplus} = -RT\ln K$

$$Q = \prod_{J} a_{J}^{v_{J}}$$

 $Q = \frac{\text{activities of products}}{\text{activities of reactants}}$

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$2A + 3B \rightarrow C + 2D,$

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$$Q = a_{\rm A}^{-2} a_{\rm B}^{-3} a_{\rm C} a_{\rm D}^{2} = \frac{a_{\rm C}^{2} a_{\rm D}^{2}}{a_{\rm A}^{2} a_{\rm B}^{3}}$$

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$$\Delta_{\mathbf{r}}G = \Delta_{\mathbf{r}}G^{\ominus} + RT \ln Q$$
$$\Box_{\mathbf{r}}G^{\ominus} = \sum_{\text{Products}} v\Delta_{\mathbf{f}}G^{\ominus} - \sum_{\text{Reactants}} v\Delta_{\mathbf{f}}G^{\ominus}$$

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$$Q = \frac{\text{activities of products}}{\text{activities of reactants}}$$

At equilibrium,

$$K = \left(\prod_{J} a_{J}^{v_{J}}\right)_{\text{equilibrium}}$$

thermodynamic equilibrium constant.

$$\Delta_{\rm r}G = \Delta_{\rm r}G^{\oplus} + RT \ln Q$$
$$\Box_{\rm r}G^{\oplus} = \sum_{\rm Products} v\Delta_{\rm f}G^{\oplus} - \sum_{\rm Reactants} v\Delta_{\rm f}G^{\oplus}$$