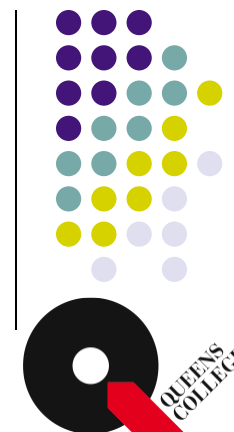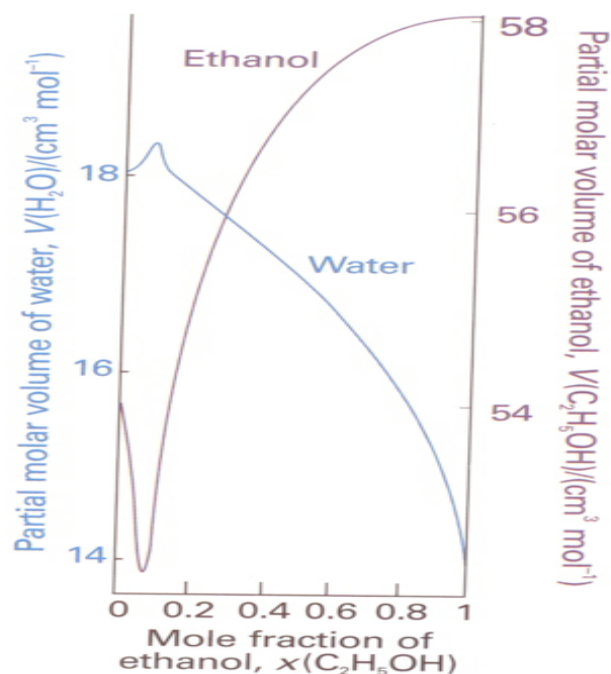# Chap. 5. <u>Simple mixtures</u>

Partial molar volume: $V_J = \left(\dfrac{\partial V}{\partial n_J}\right)_{p,T,n_{J'\neq J}}$

<u>**Change in volume per mole**</u> **of component _J_ to a large volume of mixture**

Ratio of volume change to the amount of mole

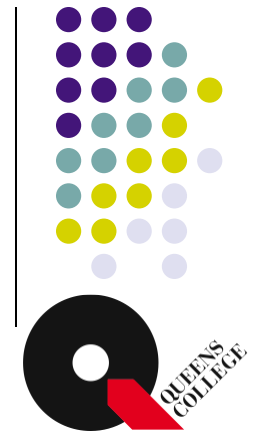**Fig 5.1 Partial molar volumes of water and ethanol at 25°C**

Partial molar volume: $V_J = \left(\dfrac{\partial V}{\partial n_J} \right)_{p,T,n_{J' \neq J}}$

Change in volume per mole of component **J** to a large volume of mixture

Ratio of volume change to the amount of mole

Example for two component system

$$dV = V_A dn_A + V_B dn_B$$

functions of mole fractions

$x_A = n_A / (n_A + n_B)$
$x_B = n_B / (n_A + n_B)$

$$V = \int_0^{n_A} V_A dn_A + \int_0^{n_B} V_B dn_B = V_A \int_0^{n_A} dn_A + V_B \int_0^{n_B} dn_B = V_A n_A + V_B n_B$$

Always true

If x_A and x_B remain constant

Partial molar Gibbs energy (chemical potential)

$$\mu_J = \left(\frac{\partial G}{\partial n_J}\right)_{p,T,n_{J' \neq J}}$$

Two-component system

$$(dG)_{T,p} = \mu_A dn_A + \mu_B dn_B \quad \longrightarrow \quad G = n_A \mu_A + n_B \mu_B$$
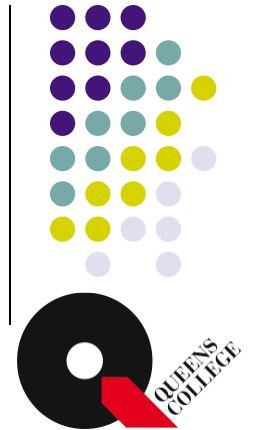
Multi-component system

$$(dG)_{T,p} = \sum_J \mu_J dn_J \quad \longrightarrow \quad G = \sum_J \mu_J n_J$$

Fundamental equation of chemical thermodynamics

$$dG = V dp - S dT + \sum_J \mu_J dn_J$$

Maximum non-expansion work system can do

$$-(dG)_{T,p} = -\sum_J \mu_J dn_J \geq -dw_e$$

Relation of chemical potential to other types of energies

Start from $dG = V\,dp - S\,dT + \sum_J \mu_J\,dn_J$
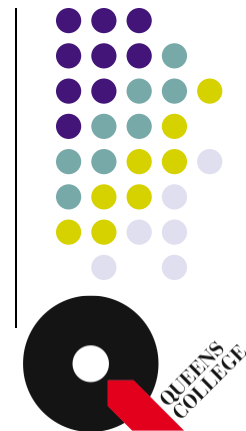
and use
$$U = G - pV + TS$$
$$H = G + TS$$
$$A = G - pV$$

$$dU = dG - p\,dV - V\,dp + T\,dS + S\,dT = T\,dS - p\,dV + \sum_J \mu_J\,dn_J$$

$$dH = dG + T\,dS + S\,dT = T\,dS + V\,dp + \sum_J \mu_J\,dn_J$$

$$dA = dG - p\,dV - V\,dp = -S\,dT - p\,dV + \sum_J \mu_J\,dn_J$$

Alternative

$$\mu_J = \left(\frac{\partial U}{\partial n_J}\right)_{V,S,n_{J'\neq J}} = \left(\frac{\partial H}{\partial n_J}\right)_{p,S,n_{J'\neq J}} = \left(\frac{\partial A}{\partial n_J}\right)_{V,T,n_{J'\neq J}}$$

Gibbs-Duhem equation

Integration of fundamental equation at fixed temperature and pressure

$$G = \int_0^{n_1,\ldots,n_J,\ldots} (dG)_{T,p} = \sum_J \int \mu_J dn_J = \sum_J \mu_J n_J$$

integration at fixed mole fractions

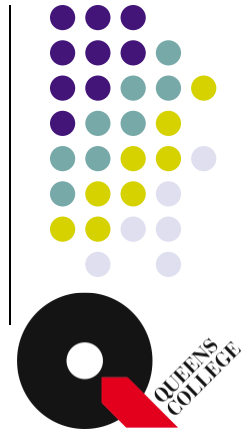**Differentiation of G assuming n_J and μ_J as independent**

$$(dG)_{T,p} = \sum_J \mu_J dn_J + \sum_J n_J d\mu_J \qquad (1)$$

Fundamental equation

$$(dG)_{T,p} = \sum_J \mu_J dn_J \qquad (2)$$

(1)-(2) $\Rightarrow$
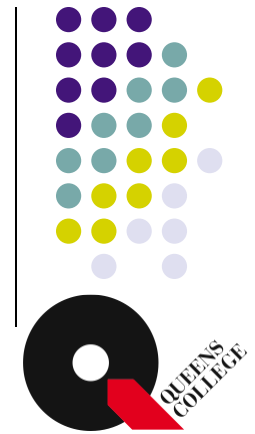
$$0 = \sum_J n_J d\mu_J$$

Change of chemical potentials in multi-component system in equilibrium are interdependent

The thermodynamics of mixing two perfect gases

$$\left(\frac{\partial \mu}{\partial p}\right)_T = V_m = \frac{RT}{p} \qquad \xrightarrow{\text{integration}} \qquad \mu = \mu^\ominus + RT \ln \left(\frac{p}{p^\ominus}\right)$$

↑ Perfect gas

Two separate perfect gases A and B, amounts n_A and n_B, at pressure p

$$G_i = n_A \mu_A^i + n_B \mu_B^i = n_A \mu_A^\ominus + n_B \mu_B^\ominus + n_A RT \ln \left(\frac{p}{p^\ominus}\right) + n_B RT \ln \left(\frac{p}{p^\ominus}\right)$$

Two mixed perfect gases A and B, amounts n_A and n_B, at pressure p

Partial pressure of gas A: $\qquad p_A = x_A p, \ x_A = \dfrac{n_A}{n_A + n_B}$

Partial pressure of gas B: $\qquad p_B = x_B p, \ x_B = \dfrac{n_B}{n_A + n_B}$

$$G_f = n_A \mu_A^i + n_B \mu_B^i = n_A \mu_A^\ominus + n_B \mu_B^\ominus + n_A RT \ln \left(\frac{x_A p}{p^\ominus}\right) + n_B RT \ln \left(\frac{x_B p}{p^\ominus}\right)$$

$$\Delta_{mix} G = G_f - G_i = nRT(x_A \ln x_A + x_B \ln x_B)$$

$$\Delta_{mix} S = -\left(\frac{\partial \Delta_{mix} G}{\partial T}\right)_{p, n_A, n_B} = -nR(x_A \ln x_A + x_B \ln x_B)$$

$$\Delta_{mix} H = \Delta_{mix} G + T \Delta_{mix} S = 0$$

The chemical potentials of liquids

chemical potential of pure liquid A

= chemical potential of the vapor in equilibrium with the liquid

↳ **vapor pressure of A in equilibrium with pure liquid A**

(1) $\mu_A^* = \mu_A^\ominus + RT \ln \left(\dfrac{p_A^*}{p^\ominus} \right)$

chemical potential of liquid A mixed with another substance

↳ **vapor pressure of A in equilibrium with non-pure liquid A**

(2) $\mu_A = \mu_A^\ominus + RT \ln \left(\dfrac{p_A}{p^\ominus} \right)$

(2)-(1) → $\mu_A = \mu_A^* + RT \ln \left(\dfrac{p_A}{p_A^*} \right)$

Rault's law: $p_A = x_A p_A^*$

↳ **mole fraction in the liquid phase**

$\mu_A = \mu_A^* + RT \ln x_A$ **(ideal solution)**
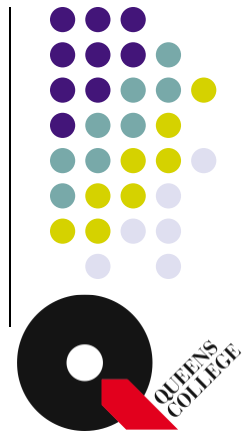
Mixture of two liquids forming an ideal solution

Pure and separate A and B liquids

$$G_i = n_A \mu_A^* + n_B \mu_B^*$$

Mixed ideal solution of A and B

$$G_f = n_A(\mu_A^* + RT \ln x_A) + n_B(\mu_B^* + RT \ln x_B)$$

$$\Delta_{mix}G = G_f - G_i = RT(n_A \ln x_A + n_B \ln x_B) = nRT(x_A \ln x_A + x_B \ln x_B)$$
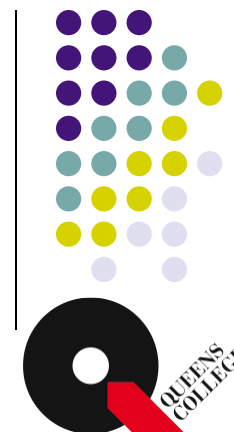
$$\Delta_{mix}S = -\left(\frac{\partial \Delta_{mix}G}{\partial T}\right)_{p,n_A,n_B} = -nR(x_A \ln x_A + x_B \ln x_B)$$

A and B are physically and chemically equivalent

$$\Delta_{mix}V = \left(\frac{\partial \Delta_{mix}G}{\partial p}\right)_{T,n_A,n_B} = 0 \quad \text{no net volume change with mixing}$$

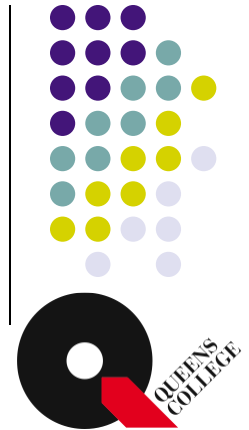$$\Delta_{mix}H = \Delta_{mix}G + T\Delta_{mix}S = 0 \quad \text{no net energy change with mixing}$$

Regular solution: $\Delta_{mix}H \neq 0$ and $\Delta_{mix}S = -nR(x_A \ln x_A + x_B \ln x_B)$
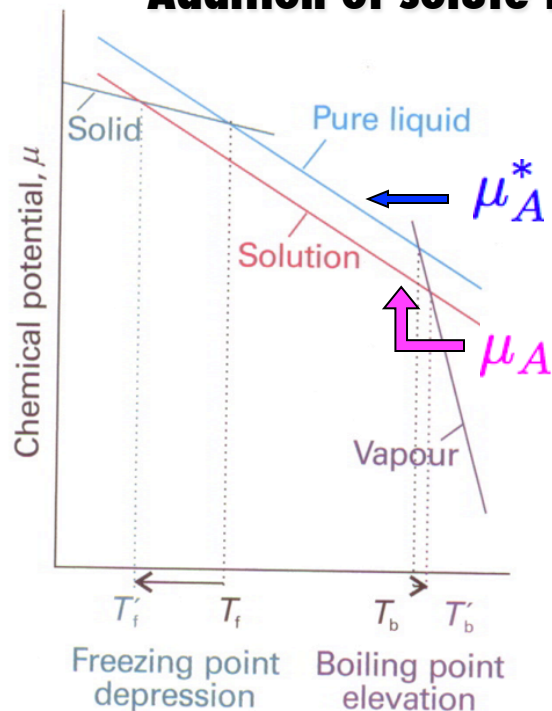
Colligative properties

Properties depending on the number of solute particles present, not their identity

e.g. Elevation of boiling point, Depression of freezing point

Addition of solute B lowers the chemical potential of solvent A

$$x_A = 1 - x_B$$

independent of the identity

$$\mu_A = \mu_A^* + RT \ln x_A$$

Solute is not in either vapor or solid

Ideal solution - dilute solution

Elevation of boiling point

A: solvent, B: solute

(1) $\mu_A(g) = \mu_A^*(g)$ **no solute in gas phase**

(2) $\mu_A(l) = \mu_A^*(l) + RT \ln x_A$ **ideal solution**

(1)=(2) $\implies$ $\mu_A^*(g) = \mu_A^*(l) + RT \ln x_A$

$\implies$ $\ln x_A = \dfrac{\mu_A^*(g) - \mu_A^*(l)}{RT} = \dfrac{\Delta_{vap}G}{RT}$

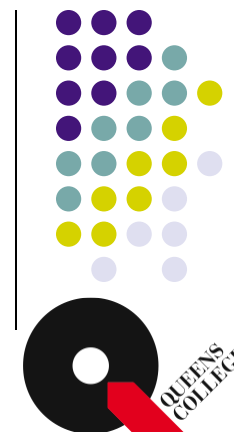$\implies$ $\dfrac{d}{dT} \ln x_A = \dfrac{1}{R} \dfrac{d}{dT} \left(\dfrac{\Delta_{vap}G}{T} \right) = -\dfrac{1}{R} \dfrac{\Delta_{vap}H}{T^2}$ **Gibbs-Helmholtz equation**

$\implies$ $\ln x_A = -\dfrac{1}{R} \displaystyle\int_{T_B^*}^{T_B} \dfrac{\Delta_{vap}H}{T^2} dT \approx \dfrac{\Delta_{vap}H}{R} \left(\dfrac{1}{T_B} - \dfrac{1}{T_B^*} \right)$ **(3)**

Dilute solution, $\ln x_A = \ln(1 - x_B) \approx -x_B$ $\longrightarrow$ **(3)**

$\implies$ $x_B \approx \dfrac{\Delta_{vap}H}{R} \dfrac{T_B - T_B^*}{T_B T_B^*} \approx \dfrac{\Delta_{vap}H}{RT_B^{*2}} \Delta T_B$

$\Delta T_B \approx \dfrac{RT_B^{*2}}{\Delta_{vap}H} x_B = K_b b$ $\Longleftarrow$ **Molality of solute**

Boiling-point constant

Depression of freezing point   A: solvent, B: solute

(1) $\mu_A(s) = \mu_A^*(s)$ **no solute in solid phase**

(2) $\mu_A(l) = \mu_A^*(l) + RT \ln x_A$ **ideal solution**

(1)=(2) $\Longrightarrow$ $\mu_A^*(s) = \mu_A^*(l) + RT \ln x_A$

$\Longrightarrow$ $\ln x_A = \dfrac{\mu_A^*(s) - \mu_A^*(l)}{RT} = -\dfrac{\Delta_{fus}G}{RT}$

$\Longrightarrow$ $\dfrac{d}{dT} \ln x_A = -\dfrac{1}{R}\dfrac{d}{dT}\left(\dfrac{\Delta_{fus}G}{T}\right) = \dfrac{1}{R}\dfrac{\Delta_{fus}H}{T^2}$
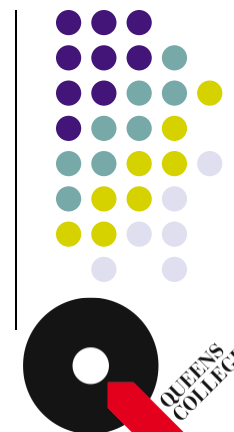
$$\ln x_A = \frac{\Delta_{fus}H}{R}\left(\frac{1}{T_f^*} - \frac{1}{T_f}\right)$$

Dilute solution, $x_B = \dfrac{\Delta_{fus}H}{R}\dfrac{T_f^* - T_f}{T_f^* T_f} \approx \dfrac{\Delta_{fus}H}{RT_f^{*2}}\Delta T_f$
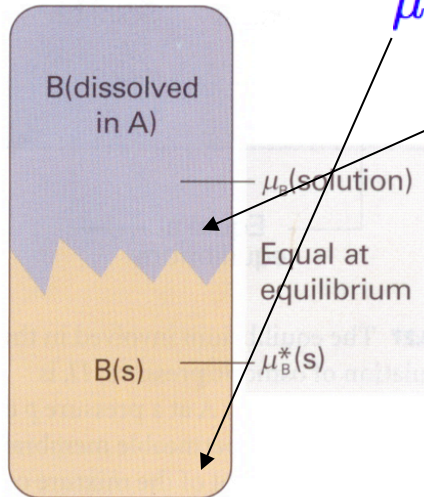
$$\Delta T_f = \frac{RT_f^{*2}}{\Delta_{fus}H}x_B = K_f b \ \Longleftarrow \ \textbf{Molality of solute}$$

$\Uparrow$ **Freezing-point constant**

Solubility

pure solute

$$\mu_B^*(s) = \mu_B(l) = \mu_B^*(l) + RT \ln x_B$$

saturated solution

$$\ln x_B = \frac{\mu_B^*(s) - \mu_B^*(l)}{RT} = -\frac{\Delta_{fus}G}{RT}$$

B(dissolved in A)

μ_B(solution)

Equal at equilibrium

B(s)

$\mu_B^*(s)$

Use Gibbs-Helmholtz equation & assume enthalpy of fusion is independent of temperature
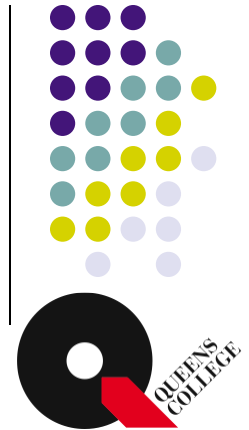
$$\ln x_B \approx \frac{\Delta_{fus}H}{R} \left(\frac{1}{T_f^*} - \frac{1}{T_s} \right)$$

Not reliable. The assumption of ideal solution is not valid because x_B is not close to 1.
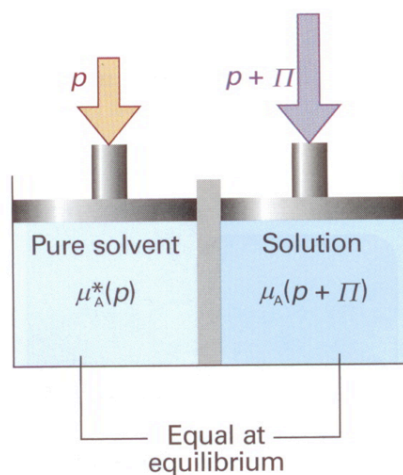

p*(acetone)

p*(chloroform)

Raoult's law

K(CH₃COCH₃)

K(CHCl₃)

Henry's law

Pressure/Torr

Mole fraction of chloroform, x(CHCl₃)
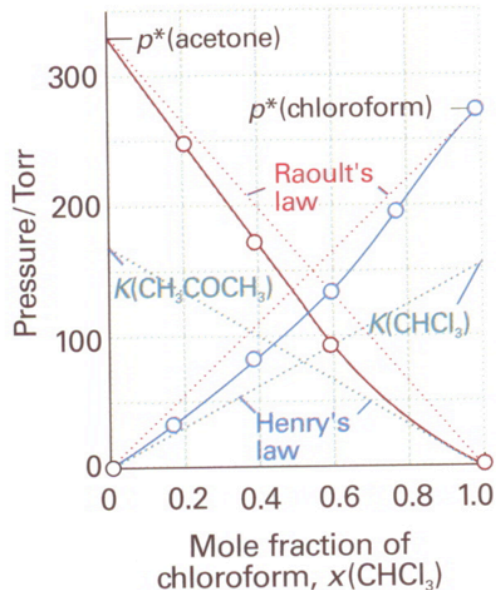
⟵ Examples of non-ideality

Henry's law: $p_B = x_B K_B$

Osmosis (Push)

Spontaneous passage of a pure solvent into a solution separated from it by a semipermeable membrane

Π: **Osmotic pressure**

$$\mu_A^*(p) = \mu_A(x_A, p + \Pi) \qquad \textbf{(1)}$$

$$\mu(x_A, p + \Pi) = \mu_A^*(p + \Pi) + RT \ln x_A \qquad \textbf{(2)}$$

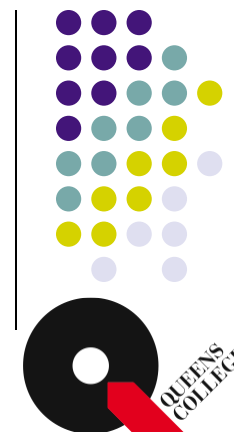$$\mu_A^*(p + \Pi) = \mu_A^*(p) + \int_p^{p+\Pi} V_m dp \qquad \textbf{(3)}$$
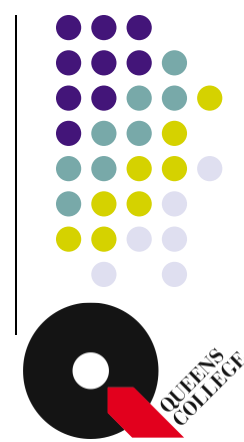
Combine (1)-(3)

$$-RT \ln x_A = \int_p^{p+\Pi} V_m dp$$

$$-\ln x_A = -\ln(1 - x_B) \approx x_B$$

$$RT x_B = \int_p^{p+\Pi} V_m dp \approx \Pi V_m = \Pi \frac{V}{n}$$

$$\longrightarrow \quad \Pi = \frac{RT n x_B}{V} = RT[B] \qquad \textbf{van't Hoff equation}$$

Activity and Activity Coefficient for Solvent

For a solvent, $\qquad \mu_A = \mu_A^* + RT \ln \left(\dfrac{p_A}{p_A^*} \right)$

(Assuming that vapor behaves like a perfect gas)

Activity: $\quad a_A = \dfrac{p_A}{p_A^*} \qquad \longrightarrow \qquad \mu_A = \mu_A^* + RT \ln a_A$

$$a_A = \gamma_A x_A \quad \text{where} \quad \lim_{x_A \to 1} \gamma_A = 1$$

Activity coefficient ⬆

$$\mu_A = \mu_A^* + RT \ln x_A + RT \ln \gamma_A$$

Activity and Activity Coefficient for Solute

For a solute, $\qquad \mu_B = \mu_B^* + RT \ln \left(\dfrac{p_B}{p_B^*} \right) = \mu_B^* + RT \ln \left(\dfrac{K_B}{p_B^*} \right) + RT \ln \left(\dfrac{p_B}{K_B} \right)$

Standard chemical potential of solute: $\mu_B^{\ominus} = \mu_B^* + RT \ln \left(\dfrac{K_B}{p_B^*} \right)$
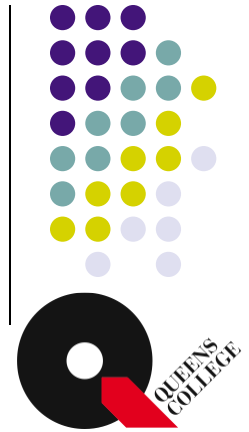
$$a_B = \dfrac{p_B}{K_B} = \gamma_B x_B \quad \text{where} \quad \lim_{x_B \to 0} \gamma_B = 1$$

$$\mu_B = \mu_B^{\ominus} + RT \ln x_B + RT \ln \gamma_B$$

Biological standard state: pH=7, $\quad G^{\oplus}, H^{\oplus}, \mu^{\oplus}, S^{\oplus}$

$$\mu_{H+} = \mu_{H+}^{\ominus} + RT \ln a_{H+} = \mu_{H+}^{\ominus} - (RT \ln 10) \times \text{pH}$$

$$\mu_{H+}^{\oplus} = \mu_{H+}^{\ominus} - 7RT \ln 10$$

Activities of ions in solution of MX (one cation and one anion)

$$\mu_+^{ideal} = \mu_+^{\ominus} + RT \ln x_+ \quad \textbf{and} \quad \mu_-^{ideal} = \mu_-^{\ominus} + RT \ln x_-$$

$$G_m = \mu^{ideal} + \mu^{ideal} + RT \ln \gamma_+ + RT \ln \gamma_- = G_m^{ideal} + RT \ln(\gamma_+ \gamma_-)$$

Mean activity coefficient: $\quad \gamma_{\pm} = (\gamma_+ \gamma_-)^{1/2}$

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

Activities of ions in solution of M_pX_q (p cations and q anions)

Mean activity coefficient: $\quad \gamma_{\pm} = (\gamma_+^p \gamma_-^q)^{1/(p+q)}$

$$G_m = p\mu_+ + q\mu_-$$

Physical meaning of mean activity coefficient

$$w_e = (p\mu_+ + q\mu_-) - (p\mu_+^{ideal} + q\mu_-^{ideal}) = (p+q)RT\ln\gamma_\pm$$

⬑ **electrical work of charging ions**

$$\ln\gamma_\pm = \frac{w_e}{sRT}, \quad s = p+q$$

Debye-Hückel Theory (further information, 5.1)

$$w_e = -\frac{(pz_+^2 + qz_-^2)F^2}{8\pi\epsilon N_A r_D}$$

Debye length: $\quad r_D = \left(\dfrac{\epsilon RT}{2\rho F^2 I b^\ominus}\right)^{1/2}$ **, Ionic strength:** $\quad I = \dfrac{1}{2b^\ominus}(b_+ z_+^2 + b_- z_-^2)$

Faraday constant: $\quad F = N_A e = 9.649 \times 10^4 \text{ C mol}^{-1}$

$$pz_+^2 + qz_-^2 = -(p+q)z_+ z_- = s|z_+ z_-| \quad \textbf{(charge neutrality)}$$

$$\ln\gamma_\pm = -|z_+ z_-|\frac{F^3}{4\pi N_A}\left(\frac{\rho b^\ominus}{2\epsilon^3 R^3 T^3}\right)^{1/2} I^{1/2} = -|z_+ z_-| A I^{1/2} \qquad \textbf{A=0.509 for aquous solution, 25 °C}$$