CHM202: *Energetics and dynamics of chemical reactions*

Fugacity and activity

Slides for online lectures

Must be followed along with recommended textbook by Atkins (8th or later edition) or any other reference book

(figures/texts taken from *Atkins' Physical Chemistry*, 8th Ed)

$$dU = TdS - PdV \quad + \sum_i \mu_i dn_i$$

Reversible change

$$\boxed{dG = -SdT + VdP + \sum_i \mu_i dn_i}$$

Reversible change

$$G = G^0 + nRTln\left({}^{P}/_{P^0}\right)$$

Reversible change, constant temp, **ideal gas**

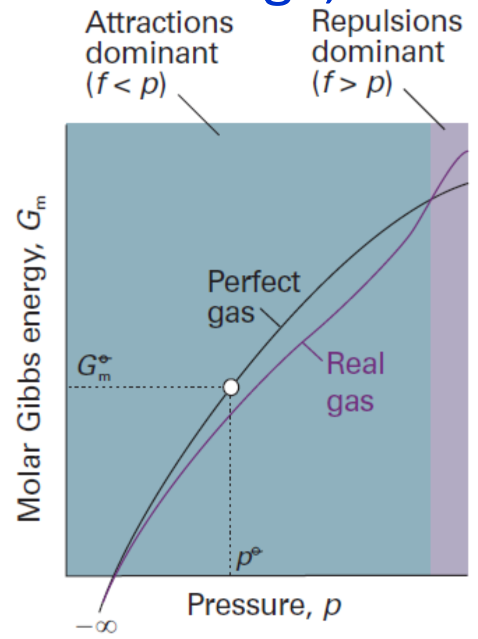
$$G = G^0 + nRTln\left({}^{f}/_{P^0}\right)$$

f: fugacity

Reversible change, constant temp, **ALL gases**

$$f = \varphi \times P$$

$$\boxed{ln\varphi = \int_0^P \frac{Z-1}{P} dP}$$



$$\mu_A = \mu_A^0 + RTln\left({}^{P_A}\!/_{P^0}\right)$$

Reversible change, constant Temp, ideal vapour

$$\mu_A = \mu_A^* + RTln\left({}^{P_A}\!/_{P_A^*}\right)$$

Exact! (no approximation yet other than vapour behaves ideally)

$$P_A \approx x_A \times P_A^*$$

Raoult's Law (Ideal solution)
Solvent in almost pure form

$$\boxed{\mu_A \approx \mu_A^* + RTlnx_A}$$

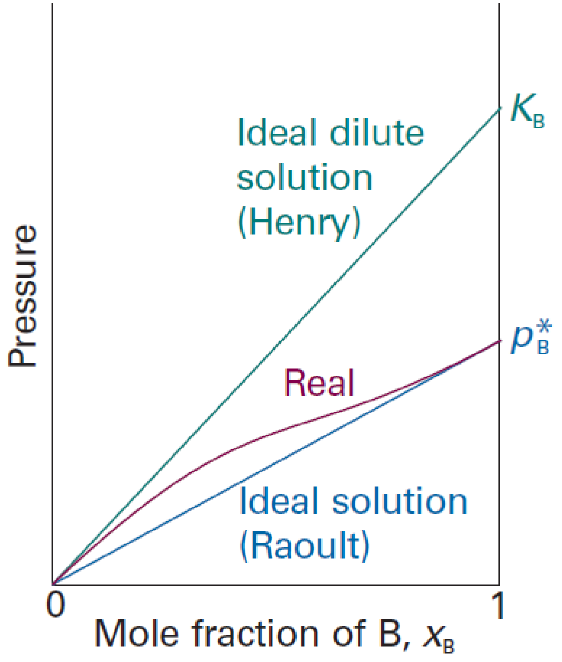
$$y_A \approx \frac{x_A \times P_A^*}{P_B^* + (P_A^* - P_B^*) \times x_A}$$

$$P_B \approx x_B \times K_B$$

Henry's Law
("Ideal" dilute solution)
Solute in low concentration

Vapour
A + B
$y_A + y_B = 1$
P_A & P_B

Liquid
A + B
$x_A + x_B = 1$



Ideal solution

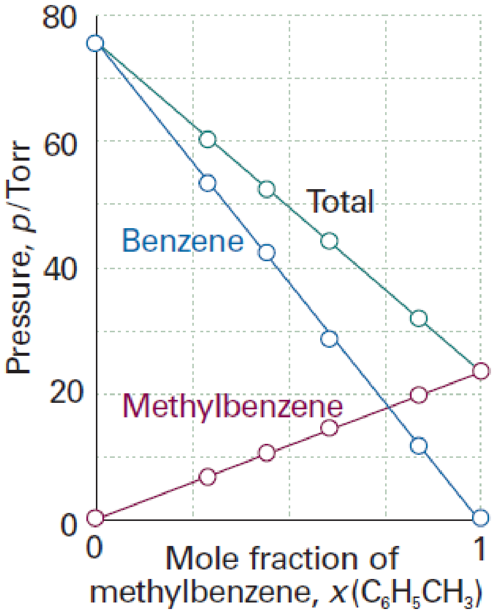
$$P_A \approx x_A \times P_A^*$$

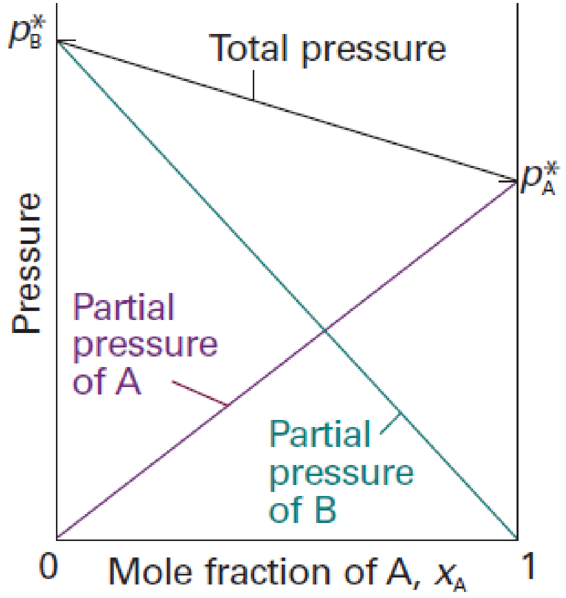
$$\boxed{\mu_A \approx \mu_A^* + RTlnx_A}$$

$$\boxed{\mu_B \approx \mu_B^* + RTlnx_B}$$

Raoult's Law is followed by A **<u>at ALL concentrations</u>**

Raoult's Law is followed by B **<u>at ALL concentrations</u>**





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

$$d\mu_A = 0 + RT \frac{dx_A}{x_A}$$

$$x_A d\mu_A = RT\, dx_A$$

$$-x_B d\mu_B = RT\, dx_A$$

$$d\mu_B = -RT \frac{dx_A}{x_B}$$

$$= -RT \frac{(-dx_B)}{x_B}$$

$$= RT \frac{dx_B}{x_B}$$

$$= RT\, d\ln x_B$$

$$\int_{\mu_B^*}^{\mu_B} d\mu_B = RT \int_0^{x_B} d\ln x_B \Rightarrow \boxed{\mu_B = \mu_B^* + RT\ln x_B}$$

$$\mu_A \longleftrightarrow \mu_B$$

$$\sum_i n_i d\mu_i = 0$$ Gibbs-Duhem eq^n

$$n_A d\mu_A + n_B d\mu_B = 0$$

$$x_A d\mu_A + x_B d\mu_B = 0$$

$$x_A + x_B = \frac{n_A}{n_A+n_B} + \frac{n_B}{n_A+n_B}$$

$$= 1$$

$$dx_A + dx_B = 0$$

$$dx_A = -dx_B$$

Ideal solution

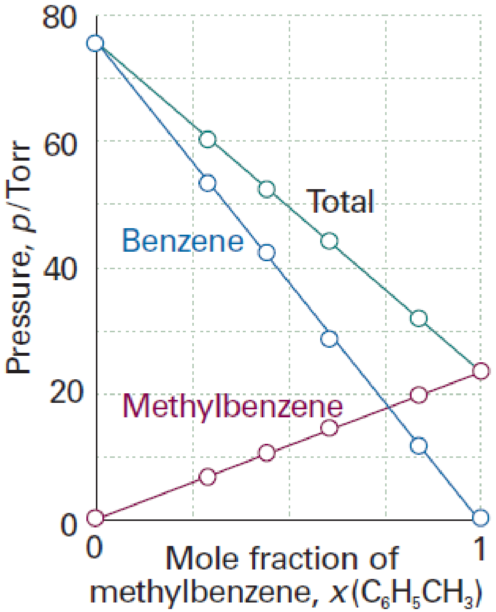
$$P_A \approx x_A \times P_A^*$$

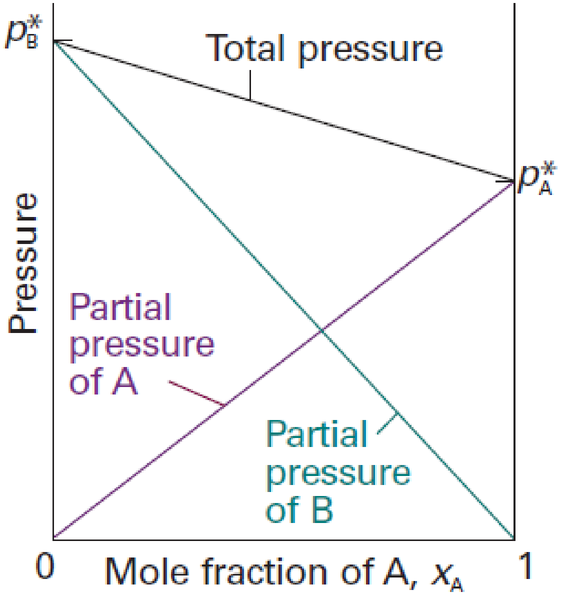
$$\boxed{\mu_A \approx \mu_A^* + RT ln x_A}$$

Raoult's Law is followed by A **at ALL concentrations**

$$\boxed{\mu_B \approx \mu_B^* + RT ln x_B}$$

Raoult's Law is followed by B **at ALL concentrations**





Real solution

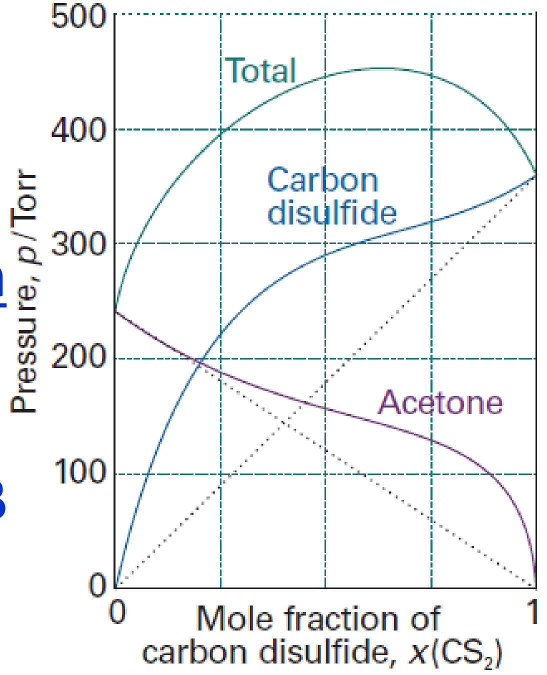
$$\boxed{\mu_A = \mu_A^* + RT ln \left({P_A}/{P_A^*} \right)}$$

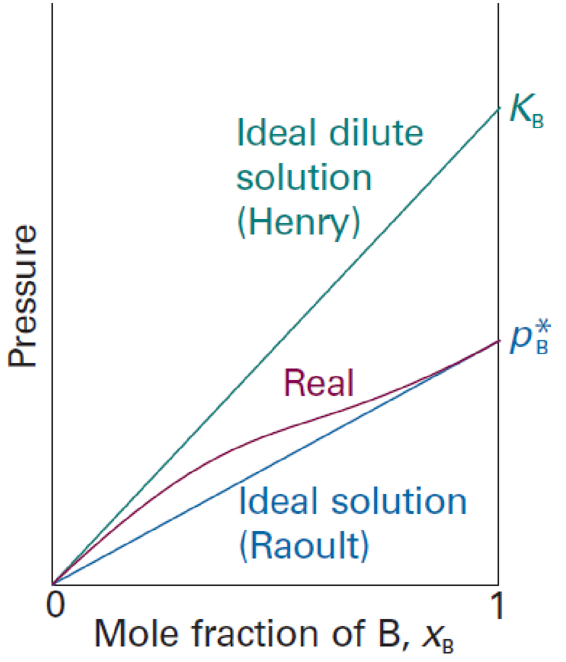
$$\boxed{\mu_B = \mu_B^* + RT ln \left({P_B}/{P_B^*} \right)}$$

Raoult's Law is followed by A or B **in almost pure form (x_A or $x_B \rightarrow 1$)**

$$P_B \approx x_B \times K_B$$

Henry's Law is followed by A or B **in low concentration ($x_B \rightarrow 0$)**



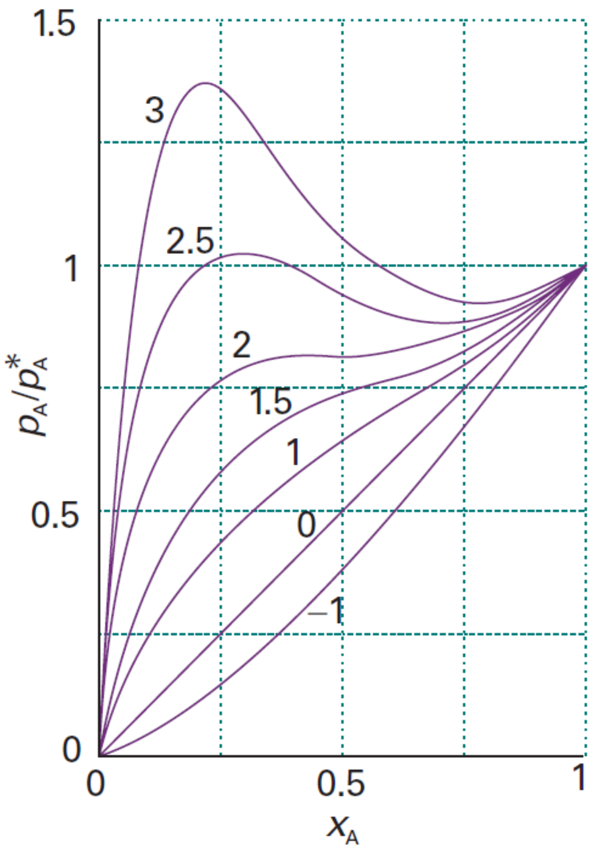


Phase	Approximation	Exact equation
Gas/Vapour	$\mu = \mu^0 + RTln\left({}^{P}/_{P^0}\right)$ when P → 0	$\mu = \mu^0 + RTln\left({}^{f}/_{P^0}\right)$ ***f: fugacity*** $f = \varphi \times P$ f → P or ϕ → 1 when P → 0 $ln\varphi = \int_0^P \frac{Z-1}{P} dP$
Liquid (solution): Solvent	$P_A \approx x_A \times P_A^*$ $\mu_A \approx \mu_A^* + RTlnx_A$ when x_A → 1	$\mu_A = \mu_A^* + RTln\left({}^{P_A}/_{P_A^*}\right)$ $\boxed{\mu_A = \mu_A^* + RTlna_A}$ ***a: activiity*** $a_A = \gamma_A \times x_A$ a_A → x_A or γ_A → 1 when x_A → 1 $\boxed{a_A = {}^{P_A}/_{P_A^*}}$

Phase	Approximation	Exact equation
Liquid (solution): Solute	$P_B \approx x_B \times K_B$ $\mu_B \approx \mu_B^* + RTln\left({K_B}/{P_B^*}\right) + RTlnx_B$ when $x_B \rightarrow 0$	$\mu_B = \mu_B^* + RTln\left({P_B}/{P_B^*}\right)$ $\boxed{\mu_B = \mu_B^* + RTln\left({K_B}/{P_B^*}\right) + RTlna_B}$ ***a: activiity*** $a_B = \gamma_B \times x_B$ $a_B \rightarrow x_B$ or $\gamma_B \rightarrow 1$ when $x_B \rightarrow 0$ $\boxed{a_B = {P_B}/{K_B}}$

Activity of regular solution: Margules equation

$$\ln \gamma_A = \beta x_B^2 \qquad \ln \gamma_B = \beta x_A^2$$



Justification 5.4 *The Margules equations*

The Gibbs energy of mixing to form a nonideal solution is

$$\Delta_{mix}G = nRT\{x_A \ln a_A + x_B \ln a_B\}$$

This relation follows from the derivation of eqn 5.31 with activities in place of mole fractions. If each activity is replaced by γx, this expression becomes

$$\Delta_{mix}G = nRT\{x_A \ln x_A + x_B \ln x_B + x_A \ln \gamma_A + x_B \ln \gamma_B\}$$

Now we introduce the two expressions in eqn 5.57, and use $x_A + x_B = 1$, which gives

$$\begin{aligned}\Delta_{mix}G &= nRT\{x_A \ln x_A + x_B \ln x_B + \beta x_A x_B^2 + \beta x_B x_A^2\}\\ &= nRT\{x_A \ln x_A + x_B \ln x_B + \beta x_A x_B(x_A + x_B)\}\\ &= nRT\{x_A \ln x_A + x_B \ln x_B + \beta x_A x_B\}\end{aligned}$$

as required by eqn 5.31. Note, moreover, that the activity coefficients behave correctly for dilute solutions: $\gamma_A \to 1$ as $x_B \to 0$ and $\gamma_B \to 1$ as $x_A \to 0$.

$$a_A = \gamma_A x_A = x_A e^{\beta x_B^2} = x_A e^{\beta(1-x_A)^2} \qquad p_A = \{x_A e^{\beta(1-x_A)^2}\} p_A^*$$