

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)

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

$$dG = -SdT + VdP + \sum_i \mu_i dn_i$$

$$G = G^0 + nRT \ln(P/P_0)$$

$$G = G^0 + nRT \ln(f/P_0)$$

$$f = \varphi \times P$$

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

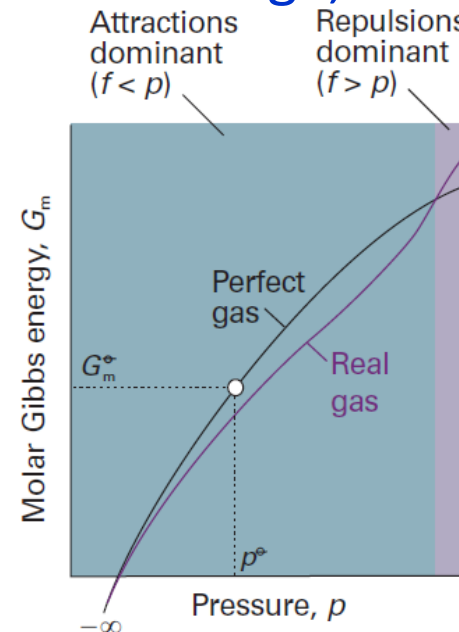
Reversible change

Reversible change

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

***f*: fugacity**

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



$$\mu_A = \mu_A^0 + RT \ln \left(P_A / P^0 \right)$$

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

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

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

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

$$P_B \approx x_B \times K_B$$

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

Reversible change, constant
Temp, ideal vapour

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

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

Vapour
A + B

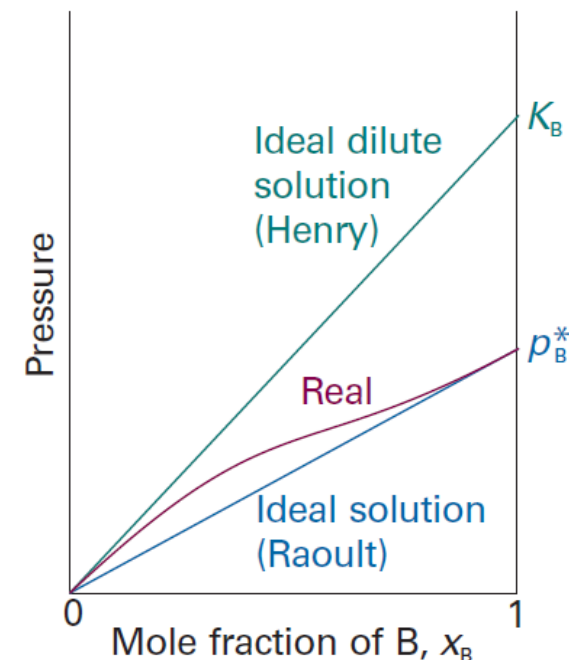
$$y_A + y_B = 1$$

$$P_A \text{ \& } P_B$$

Liquid

A + B

$$x_A + x_B = 1$$



Ideal solution

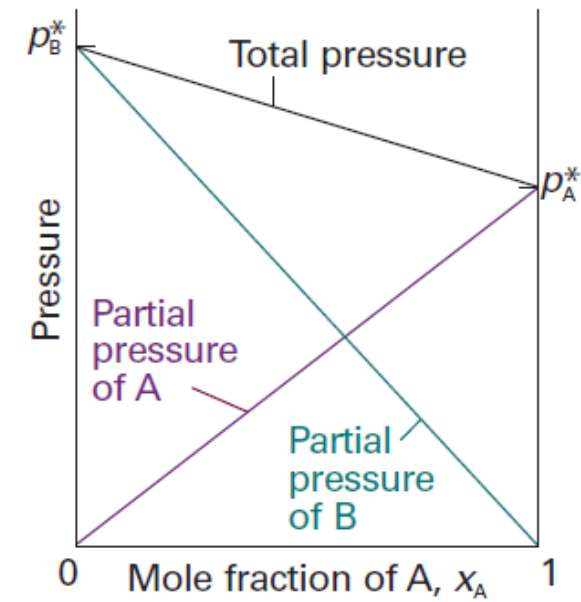
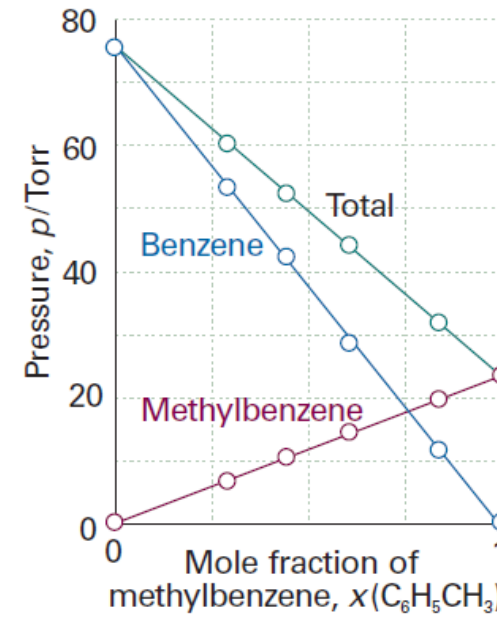
$$P_A \approx x_A \times P_A^*$$

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

$$\mu_B \approx \mu_B^* + RT \ln x_B$$

Raoult's Law is followed
by A at ALL concentrations

Raoult's Law is followed
by B at ALL concentrations



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

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

$$x_A d\mu_A = RT dx_A$$

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

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

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

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

$$= RT d \ln x_B$$

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

$$\mu_A \leftrightarrow \mu_B$$

$$\sum_i n_i d\mu_i = 0 \quad \text{Gibbs-Duhem eqn}$$

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

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

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

$$= 1$$

$$dx_A + dx_B = 0$$

$$dx_A = -dx_B$$

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

Ideal solution

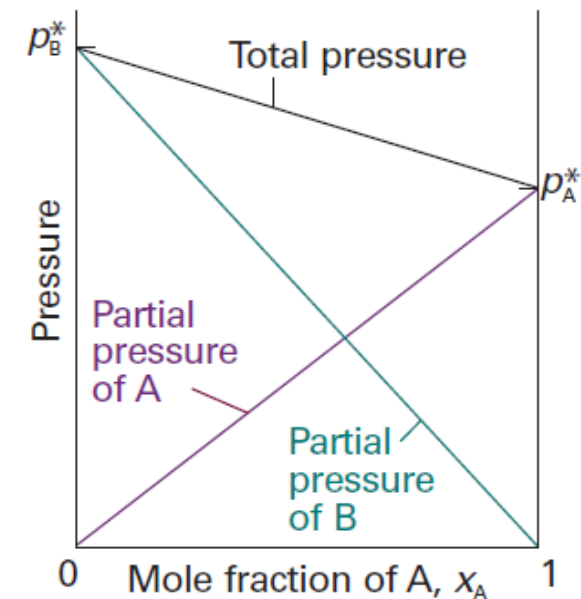
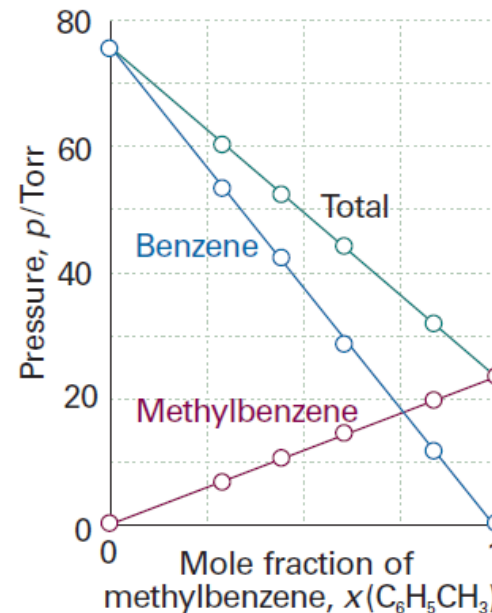
$$P_A \approx x_A \times P_A^*$$

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

$$\mu_B \approx \mu_B^* + RT \ln x_B$$

Raoult's Law is followed
by A at ALL concentrations

Raoult's Law is followed
by B at ALL concentrations



Real solution

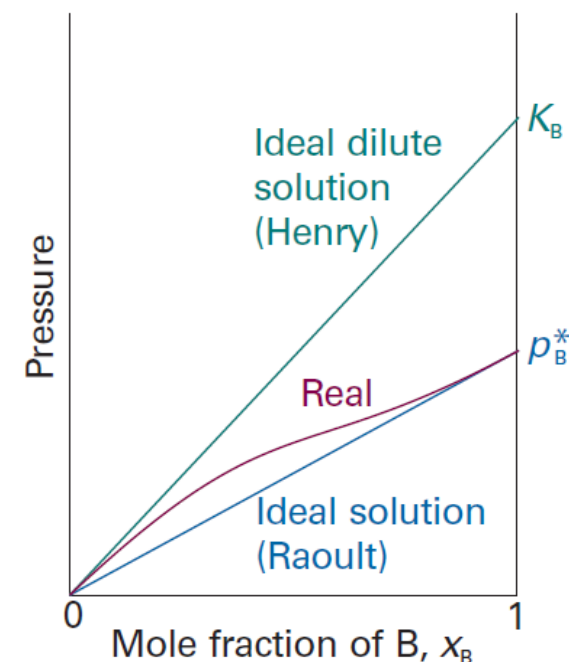
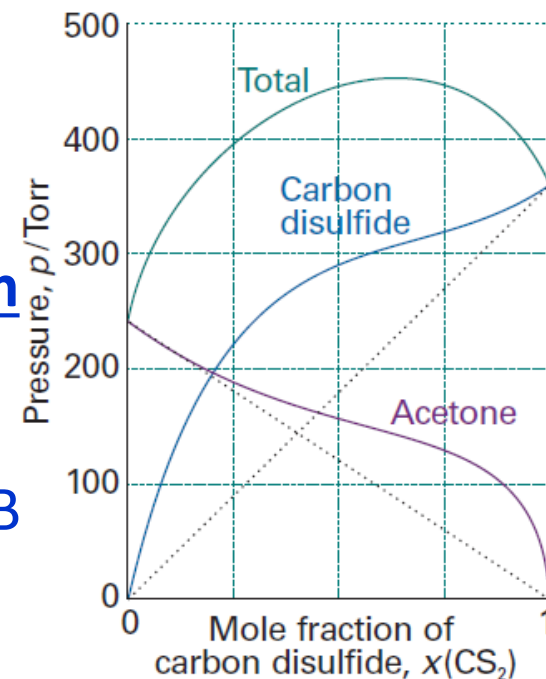
$$\mu_A = \mu_A^* + RT \ln \left(\frac{P_A}{P_A^*} \right)$$

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

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	$\mu = \mu^0 + RT \ln \left(P / P_0 \right)$ <p>when $P \rightarrow 0$</p>	$\mu = \mu^0 + RT \ln \left(f / P_0 \right) \quad \textbf{f: fugacity}$ $f = \phi \times P \quad f \rightarrow P \text{ or } \phi \rightarrow 1 \text{ when } P \rightarrow 0$ $\ln \phi = \int_0^P \frac{Z - 1}{P} dP$
Liquid (solution): Solvent	$P_A \approx x_A \times P_A^*$ $\mu_A \approx \mu_A^* + RT \ln x_A$ <p>when $x_A \rightarrow 1$</p>	$\mu_A = \mu_A^* + RT \ln \left(P_A / P_A^* \right)$ <div> $\mu_A = \mu_A^* + RT \ln a_A$ </div> <p>a: activity</p> $a_A = \gamma_A \times x_A \quad a_A \rightarrow x_A \text{ or } \gamma_A \rightarrow 1 \text{ when } x_A \rightarrow 1$ <div> $a_A = P_A / P_A^*$ </div>

Phase

Approximation

Exact equation

Liquid (solution):
Solute

$$P_B \approx x_B \times K_B$$

$$\mu_B \approx \mu_B^* + RT \ln \left(K_B / P_B^* \right) + RT \ln x_B$$

when $x_B \rightarrow 0$

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

$$\mu_B = \mu_B^* + RT \ln \left(K_B / P_B^* \right) + RT \ln a_B$$

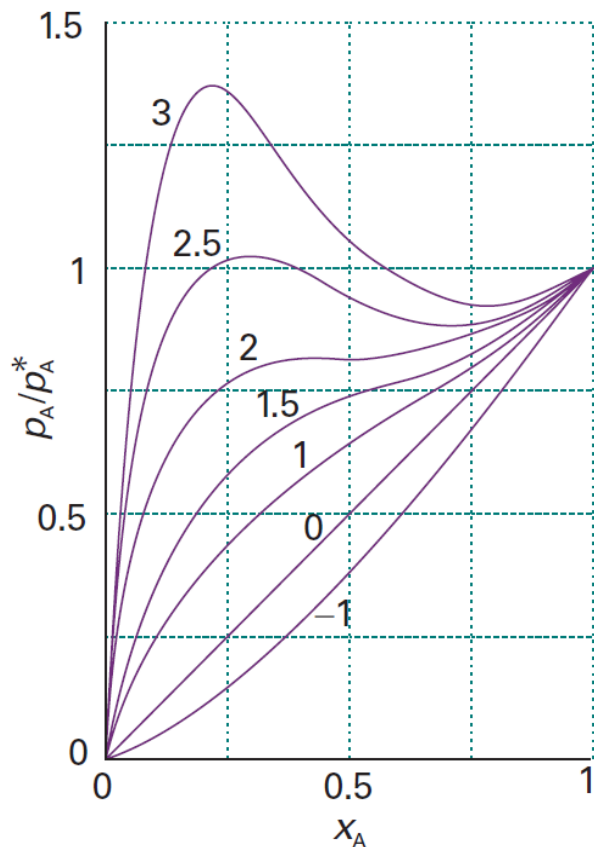
a: activity

$$a_B = \gamma_B \times x_B \quad a_B \rightarrow x_B \text{ or } \gamma_B \rightarrow 1 \text{ when } x_B \rightarrow 0$$

$$a_B = P_B / K_B$$

Activity of regular solution: Margules equation

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



Justification 5.4 *The Margules equations*

The Gibbs energy of mixing to form a nonideal solution is

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

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

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

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

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

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

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

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