

$$S = -k \sum_i n_i \ln \frac{e^{-\beta \epsilon_i}}{q}$$

$$S = -k \sum_i n_i \ln e^{-\beta \epsilon_i} - \ln q$$

$$= -k \sum_i n_i (-\beta \epsilon_i) + k \sum_i n_i \ln q$$

$$= k\beta \sum_i n_i \epsilon_i + k \sum_i n_i \ln q$$

$$= N\langle \epsilon \rangle \quad N$$

$$S = k\beta N\langle \epsilon \rangle + kN \ln q$$

Inserting the canonical partition func instead of / not part func.

$$S = \frac{U - U(0)}{T} + Nk \ln q$$

$$S = \frac{U - U(0)}{T} + Nk \ln q \quad S = \frac{U - U(0)}{T} + k \ln Q$$

For independent, indistinguishable molecules

→ W is reduced by $N!$

∴ $N!$ permutations among the energy states that would result in the same system

$$S = \frac{U - U(0)}{T} + Nk \ln q - k \ln N!$$

$$= \frac{U - U(0)}{T} + Nk \ln q - k[N \ln N - N]$$

$$= \frac{U - U(0)}{T} + Nk \ln q - Nk \ln N + Nk$$

$$= \frac{U - U(0)}{T} + Nk \ln \frac{q}{N} + Nk \ln \frac{e^1}{1}$$

$$= \frac{U - U(0)}{T} + Nk \ln \frac{q e^1}{N}$$

$$S = \frac{U - U(0)}{T} + Nk \ln \frac{q e^1}{N}$$

Residual entropy:

entropy @ $T = 0K$ is > 0

due to disorder present in the solid

Thermodynamics (mixing)

Mixtures: material system made up of 2 or more diff substances that are mixed, but not chemically combined

Solutions: 2 or more components mixed homogeneously to form a single phase

Gibbs energy:

$$dG = dH - TdS = Vdp - SdT$$

criterion of spontaneous change:

$$dG \leq 0 \quad (p, T = \text{constant})$$

eqⁿ of a system @ fixed p, T corresponds to the min Gibbs free energy

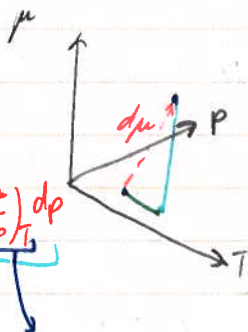
[pure substance]
for a one-component system:
molar Gibbs energy = chemical potential

(state function) $\mu = G_m = \frac{G}{n}$

See also phase diagrams in T1

$$\mu = G_m = \frac{G}{n}$$

$$d\mu = \left(\frac{\partial \mu}{\partial T} \right)_P dT + \left(\frac{\partial \mu}{\partial P} \right)_T dP$$

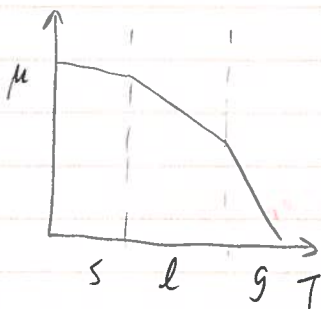


$$\left(\frac{\partial \mu}{\partial T} \right)_P = -S_m \quad (1)$$

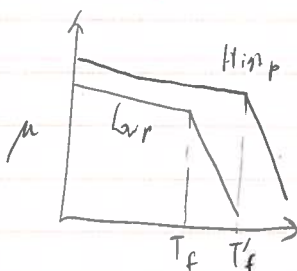
$$\left(\frac{\partial \mu}{\partial P} \right)_T = V_m \quad (2)$$

$$d\mu = -S_m dT + V_m dP$$

(1) $S_m = - \left(\frac{\partial \mu}{\partial T} \right)_P$ [Temperature dependence of a system]



(2) $V_m = \left(\frac{\partial \mu}{\partial P} \right)_T$ [Pressure dependence of a system]



Constituent: chemical species in the system

Component: chemically independent constituent of a system
[C = number of components in a system]

Gibb's Phase rule:

$$F = C - P + 2$$

Gibb's Criterion of phase eq^{ry}:

@ eq^{ry}: μ of a system is the same for all phases present in a sample

Mole fraction: x_j

how mol of a substance is present in the mixture

$$x_j = \frac{n_j}{n}$$

$$\sum_j x_j = 1$$

$$x_i = \frac{n_i}{\sum_j n_j}$$

for binary mixtures:

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

$$x_A + x_B = 1$$

Partial Molar Volume: V_j

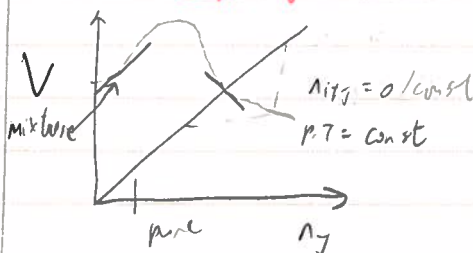
defining the contribution to the volume of each component in the mixture

=> change in V per mole of j added in the mixture

$$V_j = \frac{\partial V}{\partial n_j}$$

=> also the slope of V vs n_j @ const T, P

$n_i \neq 0$



In a binary mixture:

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

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

$$V = V_A n_A + V_B n_B$$

∴ volume is a state func
 ∴ does not depend on
 how the mixture is prepared

↳ we can calculate total V of mixture by
 knowing only the partial volume
 of the components at the desired
 final composition

Partial molar Gibbs energy: μ_j

$$\mu_j = \frac{\partial G}{\partial n_j}$$

$$G = \mu_A n_A + \mu_B n_B \quad (\text{derivation same as above})$$

⇒ Generalizing:

$$G = Vdp - SdT + \sum_j \mu_j dn_j$$

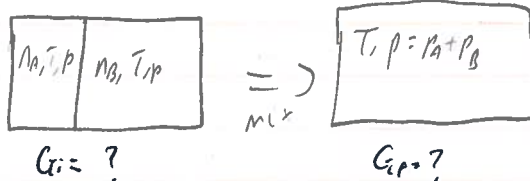
$$\text{@ const } p, dT: G = \sum_j \mu_j dn_j$$

⇒ accounting for any additional non-expansion
 work that can arise in a system
 due to changes of its composition (change moles)
 eg. consequences of phase changes / chemical Rx,
 (eg. redox rx or electrical work)

for binary systems:

$$dG = Vdp - SdT + \mu_A dn_A + \mu_B dn_B$$

Mixing of perfect gases:

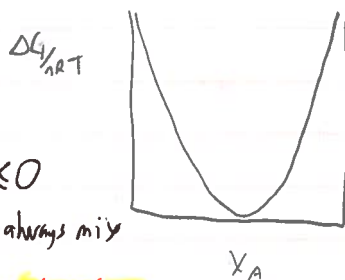


$dG = \mu_A dn_A + \mu_B dn_B$ - need to know
 $G_i = \mu_A n_A + \mu_B n_B$ the chemical potentials
 $\Delta_{\text{mix}} G = G_f - G_i$ of the gas before mixing

$$\mu(p) = \mu^0 + RT \ln \frac{p}{p^0}$$

(derivation in 1.2)

$$\Rightarrow \Delta_{\text{mix}} G = nRT (x_A \ln x_A + x_B \ln x_B)$$



$$\Delta_{\text{mix}} G \leq 0$$

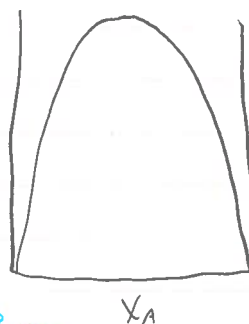
Ideal gases always mix

$$\Rightarrow \Delta_{\text{mix}} S = - \frac{\partial \Delta_{\text{mix}} G}{\partial T}$$

$$= -nR (x_A \ln x_A + x_B \ln x_B)$$

$$\Delta_{\text{mix}} S \geq 0$$

ΔS_{nr}



$$\Delta_{\text{mix}} H = 0$$

∴ no interaction
 between gas mol.

⇒ driving force
 entirely from ↑ entropy

Prob 6:

by mixing

$$G_i = \mu_A n_A + \mu_B n_B = n_A \left(\mu_A^0 + RT \ln \frac{P}{P^0} \right) + n_B \left(\mu_B^0 + RT \ln \frac{P}{P^0} \right)$$

after mixing:

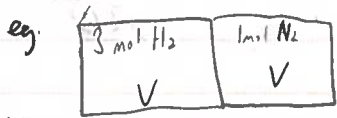
$$G_f = \mu_A n_A + \mu_B n_B = n_A \left(\mu_A^0 + RT \ln \frac{P_A}{P^0} \right) + n_B \left(\mu_B^0 + RT \ln \frac{P_B}{P^0} \right)$$

$$\Delta G = G_f - G_i$$

$$= n_A RT \ln \frac{P_A}{P} + n_B RT \ln \frac{P_B}{P}$$

for mole fractions: $x_A = \frac{n_A}{n}$; $x_B = \frac{n_B}{n}$

$$\Delta G = n x_A RT \ln \frac{P x_A}{P} + n x_B RT \ln \frac{P x_B}{P} = nRT (x_A \ln x_A + x_B \ln x_B)$$



by:

$$P_{H_2} = \frac{RT}{V} n_{H_2}; P_{N_2} = \frac{RT}{V} n_{N_2}$$

$$= \frac{3RT}{V} = 3P; \quad = \frac{RT}{V} = P$$

$$G_i = n_{H_2} (\mu_{H_2}^0 + RT \ln 3P) + n_{N_2} (\mu_{N_2}^0 + RT \ln P)$$

After:

$$P_{H_2} = n_{H_2} \frac{RT}{2V} = \frac{3}{2}P; \quad P_{N_2} = \frac{P}{2}$$

$$G_f = n_{H_2} (\mu_{H_2}^0 + RT \ln \frac{3}{2}P) + n_{N_2} (\mu_{N_2}^0 + RT \ln \frac{P}{2})$$

$$\Delta G = n_{H_2} RT \left(\ln \frac{3}{2} \times \frac{1}{3} \right) + n_{N_2} RT \ln \left(\frac{1}{2} \times \frac{1}{P} \right)$$

$$= n_{H_2} RT \ln \left(\frac{1}{2} \right) + n_{N_2} RT \ln \left(\frac{1}{2} \right)$$

$$= - \ln(2) RT(4)$$

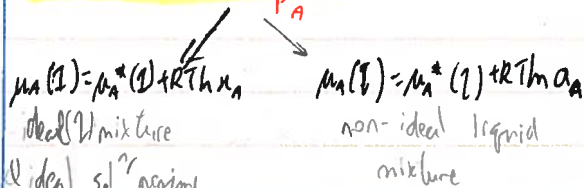
$$= -6.9 kJ$$

Chemical Potential of Ideal liquids

$$\mu(g) = \mu^*(g) + RT \ln \frac{P}{P^0} \quad [\text{chem pot. for I. gas}]$$

$$\mu_A(g) = \mu_A^*(g) + RT \ln \frac{P_A}{P^0} \quad \begin{matrix} \nearrow \text{partial pressure} \\ \text{[chem pot for ideal gas mixture]} \end{matrix}$$

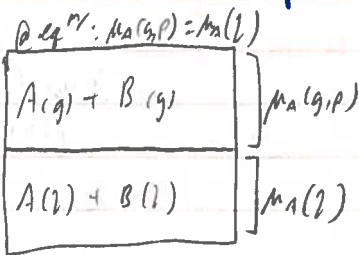
$$\mu_A(l) = \mu_A^*(l) + RT \ln \frac{P_A}{P_A^*}$$



do not have the chem pot of 1/2 mixtures
[no eqⁿ of state for an ideal liquid]

* criterion of phase eqⁿ:

@ eqⁿ, the chemical pot. of a substance is equal to its chemical pot in the liquid



In the absence of solute B:

$$\mu_A^* = \mu_A^*(l) = \mu_A^*(g) = \mu_A^0 + RT \ln \frac{P_A^0}{P^0}$$

*: pure substance

In the presence of solute B:

$$\mu_A = \mu_A^0 + RT \ln \frac{p_A}{p^0}$$

$\mu_A = \text{有 B} - \text{有 B}$

$$\mu_A = \mu_A^* - RT \ln \frac{p_A^*}{p^0} + RT \ln \frac{p_A}{p^0}$$

$$= \mu_A^* + RT \ln \frac{p_A}{p_A^*}$$

Simplifying using Raoult's Law:

\downarrow pure
 $p_A = x_A p_A^*$
 for closely related substances
 e.g. benzene / toluene in expt

rate of vaporization: $k x_A$

rate of condensation: $k' p_A$

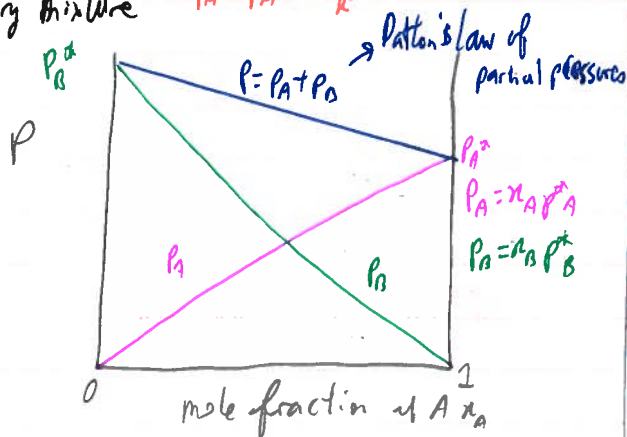
@ eqⁿ: $k x_A = k' p_A$

$$p_A = \frac{k}{k'} x_A$$

for a pure liquid $p_A = p_A^*$
 $\Rightarrow x_A = 1$

$$p_A = p_A^* = \frac{k}{k'}$$

for a binary mixture



Ideal solutions:

mixtures that follow Raoult's Law throughout the composition range
 all interactions of all molecules are same

$$\mu_A = \mu_A^* + RT \ln \frac{p_A}{p_A^*} \quad \text{using Raoult's Law:}$$

$$p_A = x_A p_A^*$$

$$\mu_A = \mu_A^* + RT \ln \frac{p_A}{p_A^*} = \mu_A^* + RT \ln x_A$$

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

A(g)	B(g)
A(l)	B(l)

A(g) + B(g)
A(l) + B(l)

$$\Delta_{mix} G = nRT (x_A \ln x_A + x_B \ln x_B) \leq 0$$

$$\Delta_{mix} S = -nR (x_A \ln x_A + x_B \ln x_B) \geq 0$$

$$\Delta_{mix} H = 0$$

W.P. entropy of mixing @ 25°C

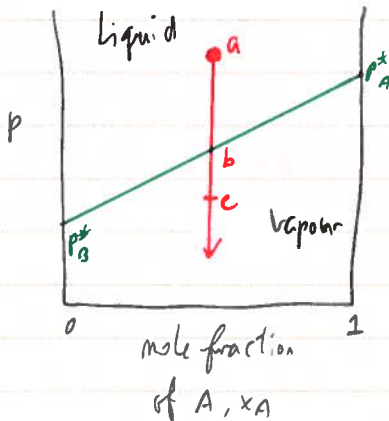
when 2 mole of C_6H_6 is mixed

w/ 2 mole of $C_6H_5CH_3(l)$

$$n_A = \frac{2}{3}, n_B = \frac{1}{3}$$

$$\Delta_{mix} S = -n (8.314) \left(\frac{2}{3} \ln \frac{2}{3} + \frac{1}{3} \ln \frac{1}{3} \right) = 5.3 \text{ J K}^{-1}$$

Vapour pressure diagram



$$p = p_A + p_B = p_B^* + (p_A^* - p_B^*)x_A$$

a: 1 phase present (liquid)

b: bubble-pt line

- evaporation starts

↳ more volatile component dominates in the vapour phase

c: dew-pt line

1 phase present (vapour)

↳ composition of the vapour phase is same as for the original liquid phase

Fractional distillation

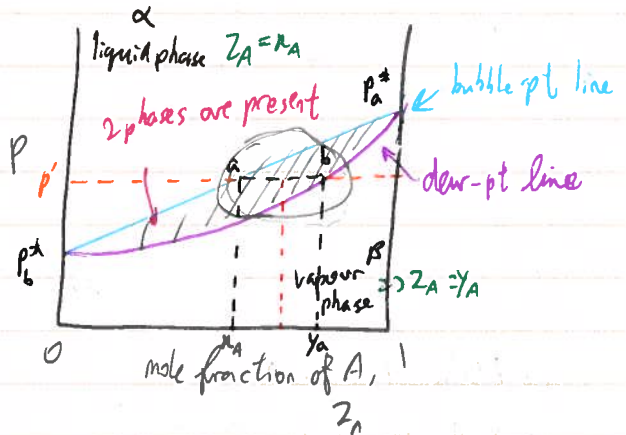
↳ several boiling pts & condensation cycles

efficiency: \propto no. of tie lines

[theoretical plates]



replotting:

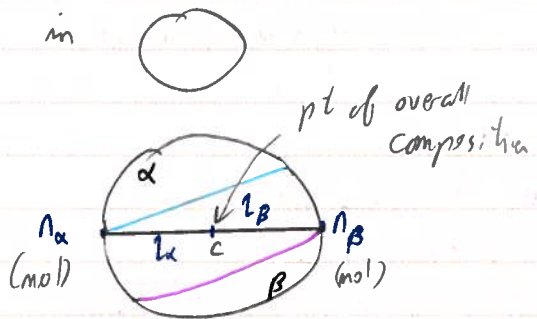


- vertical line: isopleth (const composition)

- Horizontal lines in two-phase region = tie lines

Lever rule:

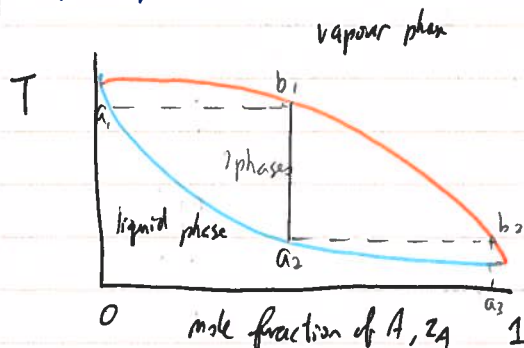
in



$$n_\alpha x_A = n_\beta y_A$$

lengths of the segments along the tie line along x_A , c , & y_A

Temp-composition diagrams:



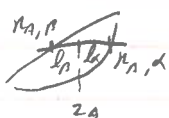
W.P. 3

$$\frac{n_A}{n_B}$$

$$z_A = 0.4, x_{A,A} = 0.6$$

$$x_{A,B} = 0.2$$

$$n_A z_A = n_B z_B$$



$$\frac{n}{n} = \frac{z_B}{z_A}$$

$$= \frac{z_A - x_{A,B}}{z_A - x_{A,A}} = \frac{0.4 - 0.2}{0.4 - 0.61} = \frac{0.2}{0.2} = 1$$

Colligative Properties

Solute (B) is dissolved in solvent (A)

Assuming solute B is:

- non-volatile

↳ not present in the vapour phase

- non-soluble in the solid solvent

↳ Solute fully separates from the solvent upon freezing

Only the chemical potential of the liquid phase is affected by the presence of the solute

Colligative properties

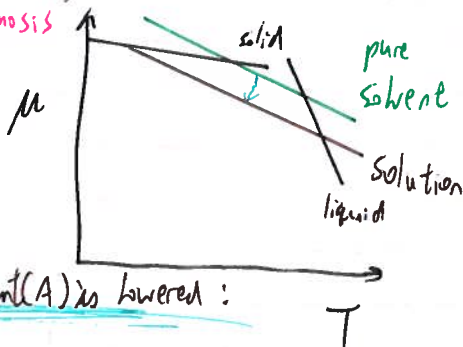
(depend on number, not on identity)

a. → elevation of B.P.

b. → depression of freezing point (F.P.)

→ (solubility)

c. → osmosis

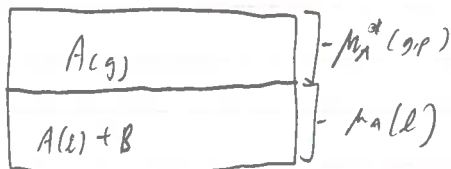


μ of solvent (A) is lowered:

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

This lowering justifies the emergence of colligative properties

a. Elevation of B.P.



$$@ eq^m: \mu_A^*(g.p) = \mu_A(l)$$

eq^m condition:

$$\mu_A(g) = \mu_A(l)$$

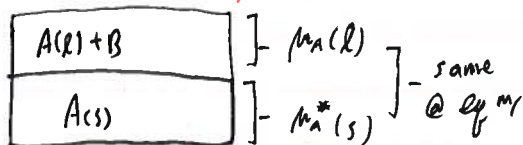
$$\Rightarrow \mu_A^*(g) = \mu_A^*(l) + RT \ln x_A$$

$$\Rightarrow \Delta T = \frac{RT_b^2}{\Delta_{vap}H} x_B$$

wt %?

Colligative property: only depends on x_B , number of solute quantity, not type/identity

b. Freezing Point depression



eq^m condition

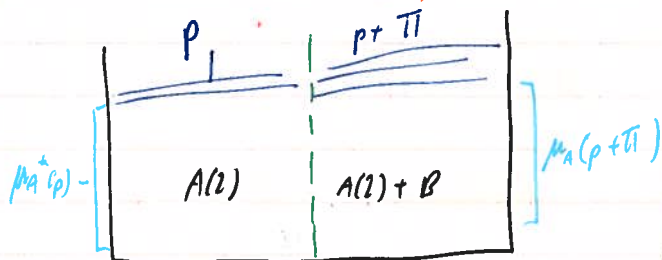
$$\mu_A(s) = \mu_A(l)$$

$$\Rightarrow \mu_A^*(s) = \mu_A^*(l) + RT \ln x_A$$

$$\Delta T = \frac{RT_f}{\Delta_{fus}H} x_B$$

C. Osmosis

osmotic pressure arises when
 $x_A(l) \neq x_A(g)$



@ eq^m $\Rightarrow \mu_A^*(p) = \mu_A(p + \pi)$

$\mu_A(x_A, p + \pi) = \mu_A^*(p + \pi) + RT \ln x_A$

$$\frac{d\mu}{dp} = V_m \Rightarrow d\mu = V_m dp$$

$$\int_{\mu_A^*(p)}^{\mu_A^*(p+\pi)} d\mu = \int_p^{p+\pi} V_m dp$$

$\Rightarrow \mu_A^*(p + \pi) = \mu_A^*(p) + \int_p^{p+\pi} V_m dp$

$\Rightarrow \mu_A(x_A, p + \pi) = \mu_A^*(p) + \int_p^{p+\pi} V_m dp + RT \ln x_A$

@ eq^m

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

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

↑
Taylor expansion

$$RT x_B = V_m \pi \quad \left| \begin{array}{l} x_B \approx \frac{n_B}{n_A} \\ V = n_A V_m \end{array} \right.$$

$$\pi = \frac{RT n_B}{n_A V_m} \approx \frac{RT n_B}{V} = RT [B]$$

$\pi = [B] RT$

\rightarrow Van't Hoff eq^m

Chemical Equilibrium

$dG = V dp - S dT + \sum_j \mu_j dn_j$

extend of $R_x: \xi$

\Rightarrow any change by $d\xi$ changes the amount of any species j by:

$d\xi = \frac{1}{\nu_j} dn_j$

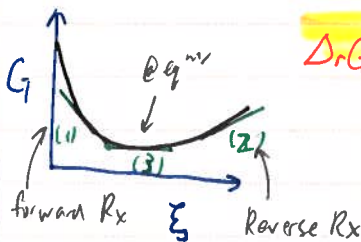
eg.



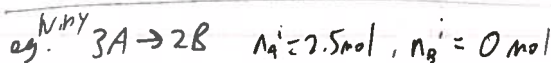
$\Rightarrow 3C + D - 2A - B = 0$

$d\xi = \frac{1}{3} dn_C = dn_D = -\frac{1}{2} dn_A = -dn_B$

R_x Gibbs Energy:



$\Delta_r G = \frac{\partial G}{\partial \xi}$



$\Delta \xi = 0.5 \text{ mol}$

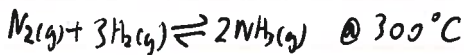
$\Delta \xi = -\frac{1}{3} \Delta n_A = \frac{1}{2} \Delta n_B$

$\Delta n = -3 \Delta \xi = -1.5 \text{ mol}, \Delta n_B = 2 \Delta \xi = 1 \text{ mol}$

$n_A^f = n_A^i - 1.5 \text{ mol} = 1 \text{ mol A}$

$n_B^f = 0 + 1 \text{ mol} = 1 \text{ mol B}$

eg. WP5



$$K = 4.34 \times 10^{-3} \quad p = 5 \text{ bar}$$

$$n_{\text{N}_2} = n_{\text{H}_2} = n_{\text{NH}_3}$$

$$\Delta_R G = \frac{\partial G}{\partial \xi}$$

$$G = \mu_{\text{N}_2} n_{\text{N}_2} + \mu_{\text{H}_2} n_{\text{H}_2} + \mu_{\text{NH}_3} n_{\text{NH}_3}$$

$$dG = \mu_{\text{N}_2} dn_{\text{N}_2} + \mu_{\text{H}_2} dn_{\text{H}_2} + \mu_{\text{NH}_3} dn_{\text{NH}_3}$$

$$= -\mu_{\text{N}_2} d\xi - 3\mu_{\text{H}_2} d\xi + 2\mu_{\text{NH}_3} d\xi$$

$$\Delta_R G = -\mu_{\text{N}_2} - 3\mu_{\text{H}_2} + 2\mu_{\text{NH}_3}$$

$$= -(\mu_{\text{N}_2}^\circ + RT \ln \frac{p_{\text{N}_2}}{p^\circ}) - 3(\mu_{\text{H}_2}^\circ + RT \ln \frac{p_{\text{H}_2}}{p^\circ}) + 2(\mu_{\text{NH}_3}^\circ + RT \ln \frac{p_{\text{NH}_3}}{p^\circ})$$

$$= \underbrace{2\mu_{\text{NH}_3}^\circ - \mu_{\text{N}_2}^\circ - 3\mu_{\text{H}_2}^\circ}_{\Delta_R G^\circ} + RT \ln \left(\frac{p_{\text{NH}_3}^2 p^\circ}{p_{\text{N}_2} p_{\text{H}_2}^3} \right)$$

$$\Delta_R G = \Delta_R G^\circ + RT \ln \left(\frac{p_{\text{NH}_3}^2 p^\circ}{p_{\text{N}_2} p_{\text{H}_2}^3} \right)$$

$$p = 5 \text{ bar} = p_{\text{NH}_3} + p_{\text{H}_2} + p_{\text{N}_2} \quad \frac{p_j}{p} = \frac{1}{3} = \frac{1}{3}$$

$$p_j = \frac{1}{3} p = \frac{5}{3} \text{ bar} = 1.67$$

$$\Delta_R G = \Delta_R G^\circ + RT \ln \left(\frac{(1.67)^2 \cdot 1}{(1.67) \times (1.67)^3} \right)$$

$$= \Delta_R G^\circ + RT \ln \left(\frac{1}{1.67^2} \right)$$

$$K = \left(\frac{p_{\text{NH}_3}^2}{p_{\text{N}_2} p_{\text{H}_2}^3} \right)_{\text{eq}} = 4.34 \times 10^{-3}$$

$$@ 400^\circ\text{C}: \Delta_R G_{i=0} = \Delta_R G^\circ + RT \ln K$$

$$\Delta_R G^\circ = -RT \ln K = 25.92 \text{ kJ mol}^{-1}$$

$$\Rightarrow \Delta_R G = 25.92 + RT \ln \frac{1}{1.67^2}$$

$$= 21.04 \text{ kJ mol}^{-1}$$

Reverse rx will tel. plus, product go back to form reactants

Mixing of Non-ideal gases/liquids

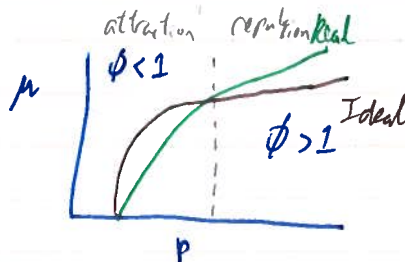
→ Fugacity

correction term

$$\mu = \mu^\circ + RT \ln \frac{p}{p^\circ} + RT \ln \phi \quad \phi: \text{fugacity coeff}$$

$$= \mu^\circ + RT \ln \left(\frac{p \phi}{p^\circ} \right) = \mu^\circ + RT \ln \left(\frac{f}{p^\circ} \right)$$

$f = p\phi$

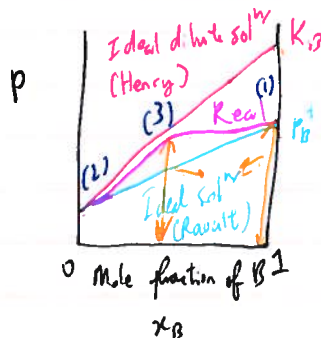


→ as $p \rightarrow 0$ $\mu_{\text{ideal}} = \mu_{\text{real}}$

✳ Ideal mixtures obey Raoult's law @ all compositions ($p_j = x_j p_j^*$)

Henry's law:

$$p_A = x_A K_B$$



$$p_A \approx x_A K_B$$

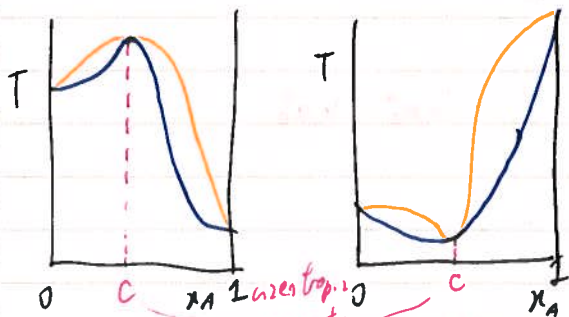
$$p_B \approx x_B p_B^*$$

- Raoult's Law still applicable for real mixture if mole fractions ≈ 1

✳ Mixtures for which the solute (B) obeys Henry's law & solute A obeys Raoult's laws are called Ideal-dilute Solution

Azeotropes

- mixtures where the vapour & the liquid have the exact same composition c
- @ the maximum/minimum of the phase diagram w/ important consequences for distillation



-ve azeotrope
eg. $\text{HCl} + \text{H}_2\text{O}$

+ve azeotrope
eg. ethanol & water

The Chemical Potential of Liquids

see graph

(1) Ideal solⁿ regime: use $p_A = x_A p_A^*$
 $\mu_A(l) = \mu_A^*(l) + RT \ln \frac{p_A}{p_A^*}$

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

(2) Ideal solⁿ regime use Henry's Law:
 $p_B = x_B K_B$

(3) general non-ideal liquid mixture
 \Rightarrow replacing x_A by a_A

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

a_A ... activity (effective mole fraction)

Activity: a_A
(determined experimentally)

$$a_A = \frac{p_A}{p_A^*}$$

$$a_A = \gamma_A x_A$$

γ_A activity coefficient
(indicates deviation from ideal behaviour)

Ideal mixtures: $\gamma_A = 1$

Real mixtures: $\gamma_A < 1$ or $\gamma_A > 1$

$$\mu_A = \mu_A^* + RT \ln a_A = \underbrace{\mu_A^* + RT \ln x_A}_{\text{ideal}} + \underbrace{RT \ln \gamma_A}_{\text{correction}}$$

W.P. 6

$$p = \left(1 + \frac{B}{V_m}\right) \frac{RT}{V_m}$$

$$V_m = \frac{V}{n_2} = \frac{0.775}{0.104} = 7.45 \text{ dm}^3 \text{ mol}^{-1}$$

$$p = \left(1 + \frac{(-1.475 \times 10^{-4})}{7.45 \times 10^{-3}}\right) \frac{R(100)}{2.16 \times 10^{-3}} = 350 \text{ kPa}$$

$$p_i = \frac{RT}{V_m} = 385 \text{ kPa} \text{ } 10\% \text{ higher for Ideal behaviour}$$

Attractive interactions

W.P. 7 $x_{\text{H}_2\text{O}} = 0.938$ $p = 2.638 \text{ kPa}$ @ 298 K

$$\gamma_{\text{H}_2\text{O}} = ?$$

$$\gamma_{\text{H}_2\text{O}} = \frac{p_{\text{H}_2\text{O}}}{x_{\text{H}_2\text{O}} p_{\text{H}_2\text{O}}^*} = \frac{0.872}{0.938} = 0.93 < 1$$

$$a_{\text{H}_2\text{O}} = \frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2\text{O}}^*} = \frac{0.872}{3.169} = 0.274$$

\Rightarrow favourable interaction of molecules in the solution

$$p_{\text{H}_2\text{O}}^* = 3.169 \text{ kPa}$$

-ve

$$p_{\text{NaCl}}^* = 0 \text{ @ } 25^\circ\text{C} \rightarrow \text{doesn't melt @ } 25^\circ\text{C}$$

$$\Rightarrow p_{\text{tot}} = p_{\text{H}_2\text{O}} = 2.638 \text{ kPa}$$

using Colligative Properties again

- osmosis in real solutions
 \Rightarrow van't Hoff eqⁿ

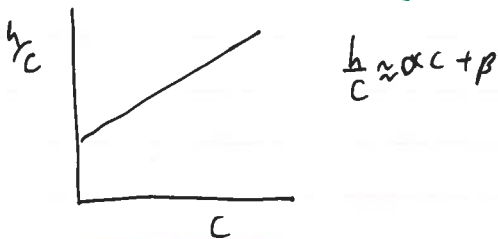
$$\Pi = [J]RT$$

- for real / non-ideal solⁿ
 \Rightarrow virial expansion

$$\Pi = [J]RT(1 + B[J] + \dots)$$

2nd + terms account for
 non-ideal behaviour

B : osmotic virial coefficient
 [accounting for non-ideal
 behaviour]



Excess functions: G^E

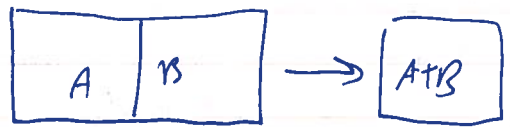
\rightarrow difference between an observed
 thermodynamic function of mixing
 & the function for an ideal mixture

$$G^E = \Delta_{mix} G^{real} - \Delta_{mix} G^{ideal}$$

$$= nRT(x_A \ln \gamma_A + x_B \ln \gamma_B)$$

(i.e. ideal: $\gamma_A = 1$; $\gamma_B = 1$; $G^E = 0$)
 definition: A-B more favourable than
 A-A or B-B

$G^E = ?$



$P, T = \text{const}$

BY mixing:

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

After mixing: [using activities instead
 of mole fractions]

$$G_f = n_A \mu_A + n_B \mu_B$$

$$= n_A(\mu_A^* + RT \ln a_A) + n_B(\mu_B^* + RT \ln a_B)$$

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

by

$$G = \Delta_{mix} G^{real} = G_f - G_i$$

$$= n_A \mu_A^* + n_A RT \ln x_A + n_A RT \ln \gamma_A + n_B \mu_B^* + n_B RT \ln x_B + n_B RT \ln \gamma_B - n_A \mu_A^* - n_B \mu_B^*$$

$n_A = n x_A$
 $n_B = n x_B$

$$= nRT(x_A \ln \gamma_A + x_B \ln \gamma_B)$$

$$\Delta_{mix} G^{ideal} = nRT(x_A \ln x_A + x_B \ln x_B)$$

[∵ ideal: $\gamma_i = 1$]

$$\Delta_{mix} G^E = \Delta_{mix} G^{real} - \Delta_{mix} G^{ideal} = nRT(x_A \ln \gamma_A + x_B \ln \gamma_B)$$

Other excess functions:

$$S^E = \Delta_{mix} S^{real} - \Delta_{mix} S^{ideal}$$

$$= -nR(x_A \ln x_A + x_B \ln x_B)$$

$$H^E = \Delta_{mix} H^{real}$$

$$V^E = \Delta_{mix} V^{real}$$

exactly equal to
measured value
ideal values of
these functions
are null

Determining G^E for Chloroform (A)

Acetone (B) @ $T = 35^\circ\text{C}$

1. Measure the vapour pressure of A/B mixtures

2. Calculate activities

$$a_A = \frac{P_A}{P_A^*}; a_B = \frac{P_B}{P_B^*}$$

3. Calculate activity coefficients

$$\gamma_A = \frac{a_A}{x_A}; \gamma_B = \frac{a_B}{x_B}$$

4. Calculate excess free Gibbs energy

$$G^E = nRT(x_A \ln \gamma_A + x_B \ln \gamma_B)$$

W.P. 8

$$\Pi = [J]RT(1 + B[J])$$

$$[B] = \frac{C}{M}$$

$$\Pi = \frac{CRT}{M} \left(1 + \frac{BC}{M}\right)$$

$$\frac{\Pi}{C} = \frac{RT}{M} + \frac{BRT}{M^2} C$$

$$y = \alpha + \beta x$$

$$\beta = \frac{\langle xy \rangle - \langle x \rangle \langle y \rangle}{\langle x^2 \rangle - \langle x \rangle^2} = \frac{\langle \Pi \rangle - \langle C \rangle \langle \frac{\Pi}{C} \rangle}{\langle C^2 \rangle - \langle C \rangle^2}$$

$$\alpha = \langle y \rangle - \beta \langle x \rangle$$

$$= \left\langle \frac{\Pi}{C} \right\rangle - \beta \langle C \rangle$$

$$\beta = 7.29 \text{ kg}^{-1} \text{ m}^3 \text{ s}^{-2}, \alpha = 19.44 \text{ m}^2 \text{ s}^{-2}$$

$$M = \frac{RT}{\alpha} = 127 \text{ kg mol}^{-1}, B = \frac{\beta M^2}{RT} = -47.62 \text{ m}^3 \text{ mol}^{-1}$$

W.P. 9

$$H^E = nRT \ln a_A a_B \beta \quad x_A = x_B = \frac{1}{2}$$

$$\beta = \frac{H^E}{nRT \ln a_A a_B} = \frac{4(710)}{(8.314)(298)} = 1.14$$

$$\Delta_{mix} G^{real} = \Delta_{mix} H^{real} - T \Delta_{mix} S^{real}$$

$$= (H^E + \Delta_{mix} H^{ideal}) - T(\Delta_{mix} S^{ideal} + \Delta_{mix} S^{real})$$

$$= H^E - T \Delta_{mix} S^{real}$$

$$= nRT \ln a_A a_B + nRT(x_A \ln x_A + x_B \ln x_B)$$

$$\Rightarrow \frac{\Delta_{mix} G^{real}}{n} = RT(\ln a_A a_B + x_A \ln x_A + x_B \ln x_B)$$

$$= (8.314)(298) \left(1.14 \frac{1}{4} + \frac{1}{2} \ln \frac{1}{2}\right)$$

$$= -1.02 \text{ kJ mol}^{-1}$$

more favourable \rightarrow -ve