fundamental relations

pure components

$$dU = TdS - PdV + \underline{G}dN$$

$$dH = TdS + VdP + \underline{G}dN$$

$$dA = -PdV - SdT + \underline{G}dN$$

$$dG = VdP - SdT + \underline{G}dN$$

mixtures

$$dU = TdS - PdV + \sum_{i=1}^{C} \mu_i dN_i$$

partial def of variables

$$\underline{G} = \left(\frac{\partial U}{\partial N}\right)_{S,V} = \left(\frac{\partial H}{\partial N}\right)_{P,S} = \left(\frac{\partial A}{\partial N}\right)_{T,V}$$

$$= \left(\frac{\partial G}{\partial N}\right)_{T,P} = -T\left(\frac{\partial S}{\partial N}\right)_{U,V}$$

$$\bar{G}_i = \left(\frac{\partial U}{\partial N_i}\right)_{S,V,N_{j\neq i}} = \left(\frac{\partial A}{\partial N_i}\right)_{T,V,N_{j\neq i}}$$

$$= \left(\frac{\partial H}{\partial N_i}\right)_{S,P} = \left(\frac{\partial G}{\partial N_i}\right)_{T,P,N_{j\neq i}}$$

$$S = -\left(\frac{\partial G}{\partial T}\right)_P = -\left(\frac{\partial A}{\partial T}\right)_V$$

ideal gas things

$$\underline{U}^{\mathrm{IG}} = C_v^* T$$

$$\underline{H}^{\mathrm{IG}} = C_p^* T$$

$$\Delta S^{\mathrm{IG}} = C_p \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}$$

$$\Delta G^{\mathrm{IG}}\bigg|_T = RT \ln \frac{P_2}{P_1}$$

legendre (wrt ξ_1)

$$\tilde{\theta} \equiv \theta - \left(\frac{\partial \theta}{\partial \xi_1}\right)_{\xi_{j\neq 1}} \xi_1 = \theta - \tilde{\xi}_1 \xi_1$$

$$\left(\frac{\partial \tilde{\theta}}{\partial \tilde{\xi}_1}\right)_{\xi_2,\xi_3\dots} = -\xi_1$$

volterra

$$\left(\frac{\delta g}{\delta x_i}\right) = \left(\frac{\partial g}{\partial x_i}\right) - \frac{1}{C}\sum_{j=1}^{C}\left(\frac{\partial g}{\partial x_j}\right)$$

$$\bar{g}_i = g + \left(\frac{\partial g}{\partial x_i}\right) - \sum_{j=1}^{C}\left(\frac{\partial g}{\partial x_j}\right)x_j$$

partial molar property

$$\bar{\theta}_i(T,P,\underline{x}) = \left(\frac{\partial(N\underline{\theta})}{\partial N_i}\right)_{T,P,}$$

$$\Delta_{\mathrm{mix}}\theta = \sum_{i=1}^{c} N_i\left[\bar{V}_i - \underline{V}_i\right] = \theta - \sum_{i=1}^{c} N_i\underline{\theta}_i$$
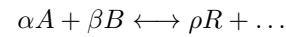
gibbs-duhem

$$\sum N_i d\bar{\theta}\big|_{T,P} = 0$$

$$\sum x_i d\bar{\theta}\big|_{T,P} = 0$$

$$x_1\left(\frac{\partial\bar{\theta}_1}{\partial x_1}\right)_{T,P} + x_2\left(\frac{\partial\bar{\theta}_2}{\partial x_1}\right)_{T,P} = 0$$

reactions

$$\alpha A + \beta B \longleftrightarrow \rho R + \dots$$

- products positive, reactants negative, inerts 0

$$X \equiv \frac{N_i - N_{i,0}}{\nu_i}$$

$$N_i = N_{i,0} + \nu_i X$$

independent reactions

given reactions, use $\underline{\underline{k}}$

- column for each component, row for each reaction

$$\mathrm{rank}(\mathbf{k}) = \text{number of independent reactions}$$

given components, use $\underline{\underline{a}}$

- column for each component, row for elements

$$S = \mathrm{rank}(\mathbf{a})$$

$$I = C - S$$

reacting systems

mass balance for reacting system

$$\frac{dN}{dt} = \sum_k^K \dot{N}_k + \sum_i\sum_j \nu_{ij}\dot{X}_j$$

energy balance for reacting system

$$\frac{dU}{dt} = \sum_k^K (\dot{N}\underline{H})_k + \dot{Q} + W_s - P\frac{dV}{dt}$$

for CSTR

$$\frac{dU}{dt} = \sum^C (\dot{N}\underline{H})_{in} + \sum^C (\dot{N}\underline{H})_{out} + \dot{Q}$$

standard state heats of reactions

$$\Delta_{\mathrm{rxn}}H^\circ = \sum_i \nu_i \Delta_{\mathrm{form}}\underline{H}_i^\circ$$

pmp from experiment

$$\Delta_{\mathrm{mix}}\underline{V} - x_1\left(\frac{\partial \Delta\underline{V}}{\partial x_1}\right)_{T,P} = (\bar{V}_2 - \underline{V}_2)$$

gibbs phase rule

$$\mathcal{F} = C - M - P + 2$$

partial pressure; fugacity

$$P_i = x_i P_{\mathrm{total}}$$

fugacity using ideal gas mixture as reference

$$\bar{f}(T,P,\underline{x}) = P_i \exp\left(\frac{\bar{G}_i(T,P,\underline{x}) - \bar{G}_i^{\mathrm{IGM}}(T,P,\underline{x})}{RT}\right)$$

$$= P_i \exp\left(\frac{1}{RT}\int_0^P (\bar{V}_i - \bar{V}_i^{\mathrm{IG}})\,dP\right)$$

ideal mixture

$$\bar{f}_i^{\mathrm{IM}} = x_i f_i(T,P)$$

ideal gas mixture

$$\bar{f}_i^{\mathrm{IGM}} = x_i P_{\mathrm{total}}$$

from eos

$$\ln\bar{\phi} = \frac{1}{RT}\int_\infty^{ZRT/P}\left[\frac{RT}{V} - N\left(\frac{\partial P}{\partial N_i}\right)_{T,V,N_{j\neq i}}\right]d\underline{V} - \ln Z$$

$$= \ln\frac{\bar{f}_i}{x_i P}$$

fugacity coefficient

$$\bar{\phi}_i = \frac{\bar{f}_i}{x_i P}$$

property	ideal gas mixture	$\Delta_{\mathrm{mix}}\theta$
$\bar{U}^{\mathrm{IGM}}$	$\underline{U}^{\mathrm{IG}}$	0
$\bar{H}^{\mathrm{IGM}}$	$\underline{H}^{\mathrm{IG}}$	0
$\bar{V}^{\mathrm{IGM}}$	$\underline{V}^{\mathrm{IG}}(T,P)$	0
$\bar{S}^{\mathrm{IGM}}$	$\underline{S}^{\mathrm{IG}}(T,P) - R\ln x_i$	$-R\sum x_i \ln x_i$
$\bar{G}^{\mathrm{IGM}}$	$\underline{G}^{\mathrm{IG}}(T,P) + RT\ln x_i$	$RT\sum x_i \ln x_i$
$\bar{A}^{\mathrm{IGM}}$	$\underline{A}^{\mathrm{IG}}(T,P) + RT\ln x_i$	$RT\sum x_i \ln x_i$

property	ideal mixture	$\Delta_{\mathrm{mix}}\theta$
$\underline{U}^{\mathrm{IM}}$	$\sum x_i \underline{U}_i$	0
$\underline{H}^{\mathrm{IM}}$	$\sum x_i \underline{H}_i$	0
$\underline{V}^{\mathrm{IM}}$	$\sum x_i \underline{V}$	0
$\underline{S}^{\mathrm{IM}}$	$\sum x_i \underline{S}_i - R\sum x_i \ln x_i$	$-R\sum x_i \ln x_i$
$\underline{A}^{\mathrm{IM}}$	$\sum x_i \underline{A}_i + RT\sum x_i \ln x_i$	$RT\sum x_i \ln x_i$
$\underline{G}^{\mathrm{IM}}$	$\sum x_i \underline{G}_i + RT\sum x_i \ln x_i$	$RT\sum x_i \ln x_i$
$\bar{S}_i^{\mathrm{IM}}$	$\underline{S}_i(T,P) - R\ln x_i$	$-R\sum x_i \ln x_i$
$\bar{A}_i^{\mathrm{IM}}$	$\underline{A}_i(T,P) + RT\ln x_i$	$RT\sum x_i \ln x_i$
$\bar{G}_i^{\mathrm{IM}}$	$\underline{G}_i(T,P) + RT\ln x_i$	$RT\sum x_i \ln x_i$

excess properties

$$\bar{\theta}_i^{\mathrm{ex}} = \bar{\theta}_i - \bar{\theta}_i^{\mathrm{IM}}$$

$$\Delta_{\mathrm{mix}}\underline{\theta}(T,P,\underline{x}) = \Delta_{\mathrm{mix}}\underline{\theta}^{\mathrm{IM}}(T,P,\underline{x}) + \underline{\theta}^{\mathrm{ex}}$$

excess gibbs

$$\bar{G}_i^{\mathrm{ex}} = \left(\frac{\partial N\underline{G}^{\mathrm{ex}}}{\partial N_i}\right)_{T,P,N_{j\neq i}} = RT\ln\left(\frac{\bar{f}_i}{x_i f_i}\right)$$

$$= RT\ln\left(\frac{\bar{\phi}_i}{\phi_i}\right) = \int_0^P \bar{V}_i - \underline{V}_i\,dP$$

activity coefficient

$$\gamma_i = \frac{\bar{f}_i}{x_i f_i} = \frac{\bar{\phi}_i}{\phi_i}$$

$$RT\ln(\gamma_i) = \bar{G}_i^{ex}$$

g-d for activity coefficients

$$\sum x_i d\ln\gamma_i = 0$$

lewis randall rule (low or high pressure)

$$\bar{f}_i^V = y_i f_i^V$$

VLE

low pressure vle

$$x_i \gamma_i P_i^{\mathrm{vap}} = y_i P_{\mathrm{total}}$$

low pressure; ideal liquid; raoults

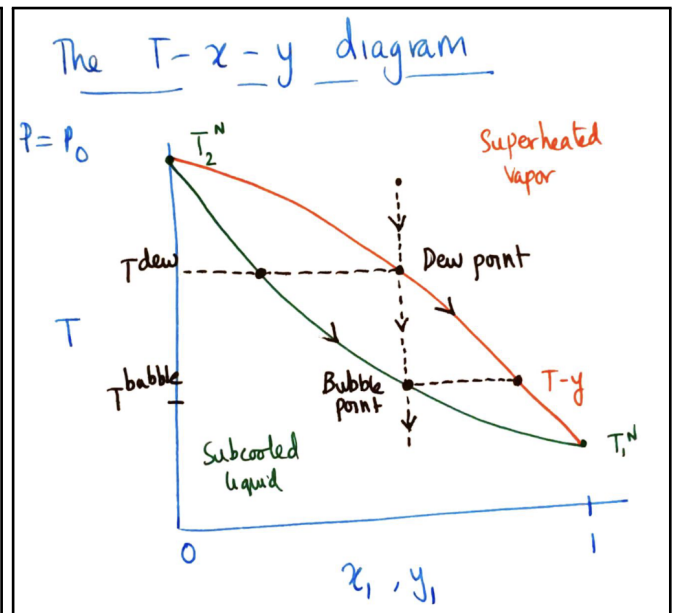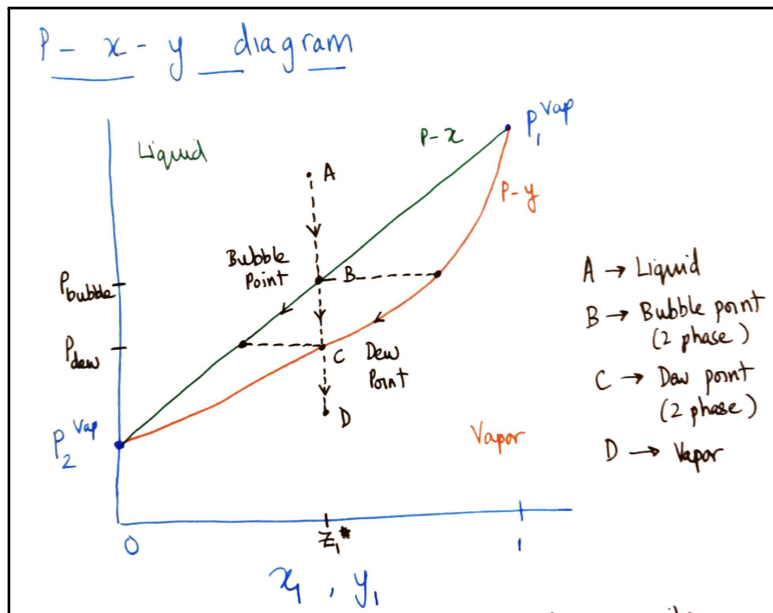$$x_i P_i^{\mathrm{vap}} = y_i P_{\mathrm{total}}$$

useful vle problem solutions

bubble pressure

$$\sum x_i \gamma_i P_i^{\mathrm{vap}}(T) = P_{\mathrm{total}}$$

dew pressure

$$P_{\mathrm{total}} = \frac{1}{\sum \dfrac{y_i}{P_i^{\mathrm{vap}}}} = \frac{1}{\sum \dfrac{y_i}{\gamma_i P_i^{\mathrm{vap}}}}$$

2

P-x-y diagram

The T-x-y diagram

$$k_i \equiv \frac{y_i}{x_i} = \frac{\gamma_i P_i^{\text{vap}}}{P_{\text{total}}}$$

$$y_i = \frac{z_i k_i}{1 + V(k_i - 1)} \qquad x_i = \frac{z_i}{1 + V(k_i - 1)}$$

positive azeotrope

- minimum boiling T; maximum pressure
- $k_i > 1$ before x_{az} (for more volatile)
- positive deviation from raoults

negative azeotrope

- maximum boiling T minimum pressure
- $k_i < 1$ before x_{az} (for more volatile)
- negative deviation from raoults

relative volatility

$$\alpha_{12} = \frac{K_1}{K_2} = \frac{\gamma_1 P_1^{\text{vap}}}{\gamma_2 P_2^{\text{vap}}}$$

- relative volatility $= 1$ at azeotrope
- if pure component limits are on opposite sides of 1, an azeotrope likely exists

reflux ratio, q

$$q = \frac{L}{D}$$

upper operating line

$$y = \frac{x_D}{1 + q} + \frac{x_i q}{1 + q}$$

slope less than 1 lower operating line

$$y = x\left(\frac{q + \frac{F}{D}}{q + 1}\right) - x_b\left(\frac{\frac{F}{D} - 1}{q + 1}\right)$$

slope greater than 1

fugacity of species in mixture

vapor

$$\bar{f}_i = y_i P\left(\frac{\bar{f}_i}{y_i P}\right) = y_i P\left(\frac{f}{P}\right)$$

liquid

$$\bar{f}_i = x_i \gamma_i f_i$$

poynting correction

$$f^{\text{L}}(T, P) = P^{\text{vap}}(T)\left(\frac{f}{P}\right)_{\text{sat}, T} \exp\left[\frac{1}{RT} \int_{P^{\text{vap}}(T)}^{P} \underline{V} \, dP\right]$$

$$= f_{\text{sat}}(T) \exp\left[\frac{1}{RT} \int_{P^{\text{vap}}(T)}^{P} \underline{V} \, dP\right]$$

henry law forms

$$\bar{f}_i^L(T, P, \underline{x}) = x_i \gamma_i^*(T, P, \underline{x}) H_i(T, P) \qquad \text{(molarity)}$$

$$\bar{f}_i^L(T, P, M_i) = M_i \gamma_i^{\square}(T, P, M_i) \mathcal{H}(T, P) \qquad \text{(molality)}$$
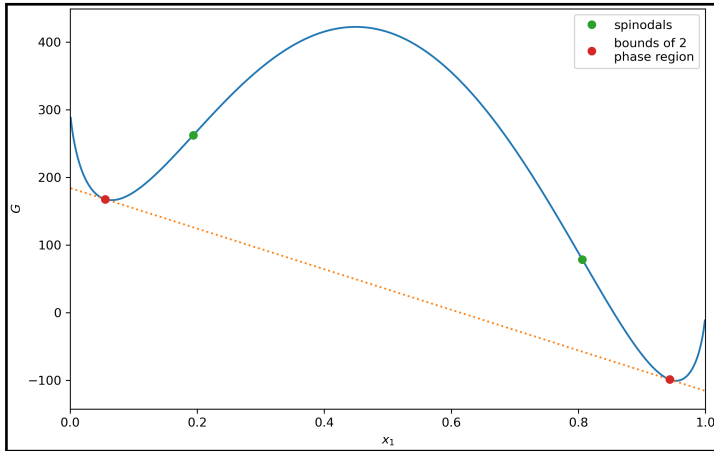
molality henry law

molality eqn

$$M_{\text{i}} = \frac{n_{\text{i}} \, 1000}{m_{\text{s}} n_{\text{s}}}$$

relating henry coeffs

$$\mathcal{H}_i = \frac{x_{\text{i}} \, 1000}{m_{\text{s}} M_{\text{i}}} H_i$$

3

LLE

$$x_i^I \gamma_i^I = x_i^{II} \gamma_i^{II} \qquad \text{(important LLE eqn)}$$

- spinodal points are inflection points

- binodals share common tangent line

- composition of liquid phases given by binodals

- between the bounds and the spinodals is the 'metastable region'

- between spinodal points is the region of absolute instability

stability criteria

$$\left(\frac{\partial^2 G}{\partial x^2} \right) > 0$$

various activity coefficient models

one constant margules

$$\underline{G}^{ex} = A x_1 x_2 \qquad \ln \gamma_1 = \frac{A}{RT} x_2^2$$

upper consulate temperature

$$T_{uc} = \frac{A}{2R}$$

redlich-kister

$$\underline{G}^{ex} = x_1 x_2 (A + B(x_1 - x_2) + C(x_1 - x_2)^2 + \dots)$$

two constant margules

$$RT \ln \gamma_1 = \alpha_1 x_2^2 + \beta_1 x_2^3$$

- α, β are related to A, B in redlich-kister expansion

regular solution

- a regular solution has $\underline{V}^{ex} = \underline{S}^{ex} = 0$

$$\Phi_i \equiv \frac{x_i \underline{V}_i}{x_1 \underline{V}_1 + x_2 \underline{V}_2} \qquad \delta_i \equiv \left(\frac{\Delta_{vap} \underline{U}_i}{V_i} \right)^{1/2}$$

activity coeff

$$RT \ \ln \gamma_1 = \underline{V}_1 \Phi_2^2 [\delta_1 - \delta_2]^2$$
$$RT \ \ln \gamma_2 = \underline{V}_2 \Phi_1^2 [\delta_1 - \delta_2]^2$$

van laar model

$$\ln \gamma_1 = \frac{\alpha}{\left[1 + \frac{\alpha x_1}{\beta x_2} \right]^2} \qquad \ln \gamma_2 = \frac{\beta}{\left[1 + \frac{\beta x_2}{\alpha x_1} \right]^2}$$

from infinite dilution

$$\alpha = \ln \gamma_1^\infty \qquad \beta = \ln \gamma_2^\infty$$

from one point

$$\alpha = \left(1 + \frac{x_2 \ln \gamma_2}{x_1 \ln \gamma_1} \right)^2 \ln \gamma_1$$

$$\beta = \left(1 + \frac{x_1 \ln \gamma_1}{x_2 \ln \gamma_2} \right)^2 \ln \gamma_2$$

from regular solution

$$\alpha = \frac{V_1}{RT} (\delta_1 - \delta_2)^2 \quad \beta = \frac{V_2}{RT} (\delta_1 - \delta_2)^2$$

- the δ are solubility parameters

from critical properties

$$\alpha = \frac{b_1}{RT} \left[\frac{\sqrt{a_1}}{b_1} - \frac{\sqrt{a_2}}{b_2} \right]^2 \quad \beta = \frac{b_2}{RT} \left[\frac{\sqrt{a_1}}{b_1} - \frac{\sqrt{a_2}}{b_2} \right]^2$$

three diff methods for a and b

$$a = \frac{27 R^2 T_C^2}{64 P_C} \text{ and } b = \frac{RT_C}{8 P_C}$$

$$a = 3 P_C \underline{V}_C^2 \text{ and } b = \frac{V_C}{3}$$

$$a = \frac{9 \underline{V}_C RT_C}{8} \text{ and } b = \frac{V_C}{3}$$

two-parameter wilson model

$$\frac{G^{ex}}{RT} = -x_1 \ln(x_1 + x_2 \Lambda_{12}) - x_2 \ln(x_2 + x_1 \Lambda_{21})$$

and activity coeffient equations

$$\ln \gamma_1 = -\ln(x_1 + x_2 \Lambda_{12}) + x_2 \left[\frac{\Lambda_{12}}{x_1 + x_2 \Lambda_{12}} - \frac{\Lambda_{21}}{x_1 \Lambda_{21} + x_2} \right]$$

$$\ln \gamma_2 = -\ln(x_2 + x_1 \Lambda_{21}) - x_1 \left[\frac{\Lambda_{12}}{x_1 + x_2 \Lambda_{12}} - \frac{\Lambda_{21}}{x_1 \Lambda_{21} + x_2} \right]$$

infinite dilution

$$\ln \gamma_1^\infty = -\ln \Lambda_{12} + 1 - \Lambda_{12}$$

$$\ln \gamma_2^\infty = -\ln \Lambda_{21} + 1 - \Lambda_{21}$$

4

- interestingly the wilson model cannot predict two liquid phases (no solutions to $x_1^I \gamma_1^I = x_1^{II} \gamma_1^{II}$ where $x^I \neq x^{II}$)

VLLE

$$\mathcal{F} = \mathcal{C} - \mathcal{M} - \mathcal{P} + 2 = 2 - 0 - 3 + 2 = 1$$

- at a given temperature there is only one pressure with VLLE !

- higher pressure $\longrightarrow$ two liquids

- lower pressure $\longrightarrow$ single liquid and vapor

- may be broken into LLE problem for liquid phases for simplicity

usually the liquid phases will be nearly pure components so the calculations would be greatly simplified

$$P_{\text{total}} = P_1^{\text{vap}} + P_2^{\text{vap}}$$

solubility of gas in liquid mixtures

(letting component 1 be the solute)

$$x_1 \gamma_1 f_1^L = y_1 P_{\text{total}}$$

but this kinda creates an issue since usually the temperature will be above the critical temperature of the solute (think CO_2 in water). may use corresponding states to get $\frac{f^L}{P_c}$ at $P = 1.013\,\text{bar}$ and then the following correction

$$f_1^L(T, P_{\text{total}}) = f_1^L(T, P = 1.013\,\text{bar})$$
$$\times \exp\left(\frac{V_1^L(P_{\text{total}} - 1.013\,\text{bar})}{RT}\right)$$

this is like super gay and annoying, so thankfully there's a simpler way with henry's law coefficients

$$H_1(T, P) = \lim_{x_1 \to 0} \frac{\bar{f}_1^L}{x_1} = \gamma_1^\infty f_1^L$$

which for an ideal application gives this relationship

$$x_1 H_1 = y_1 P_{\text{total}}$$

temperature dependence

$$\left(\frac{\partial \ln x}{\partial T}\right)_P \approx -\frac{\Delta_{\text{vap}} H}{RT^2}$$

- when $T < T_c$ the enthalpy of vaporization will always be positive

- for $T > T_c$ it could be negative, and solubility could increase with temperature

solubility of a gas in a salt solution

we have an empirical relationship for this equilibria

$$\log\left(\frac{S(M)}{S_0}\right) = -k_s M$$

- k_s "Satchenow coeff" is specific to every salt and gas pair

- M is the molality of the salt

meaning of k_s

- positive means gas solubility decreases with salt molality "salting out"

- negative k means solubility increases with salt molality "salting in"

  - you could add a fuck ton of salt and get the gas "out"

solute partitioning

$$K_{x,i}^{I/II} = \frac{x_i^I}{x_i^{II}}$$

- typically subscript gives information about what ratio it relates to (mole fractions or mass fractions or molarities or molalities)

- superscript tells you which phase is numerator and which is denominator

n-octanol and water

- "amphiphatic" molecule w/ hydrophilic and hydrophobic parts

- fairly good model for fatty tissue in animals

$$K_{OW,i} = \frac{C_i^O}{C_i^W} = 0.114 \frac{x_i^O}{x_i^W}$$

- convention to put organic phase in numerator!

- usually very high, so tabulated data is in $\log K_{OW}$

solute extraction

- separating based on solubility differences

- rinsing toluene with water

q is the proportion of solute left after each rinse, V^{II} is the volume of the phase being rinsed, V^I is the volume of solvent being used to rinse

$$q = \frac{V^{II}}{V^{II} + K_i V^I}$$

- independent of system size

if you do n solvent extractions the q at the end is

$$q_n = q^n$$

- conclude that more steps = more efficient mixing (on a solvent use basis of what you consider efficiency)

osmotic equilibrium

two phases separated by a semi-permeable membrane.

- since not all components may go through membrane, the $P^I = P^{II}$ equilibrium condition no longer applies
- by same reasoning $\bar{f}_i^I = \bar{f}_i^{II}$ only holds for the components which may move, too

$$\pi = P^{II} - P^I = \frac{RT}{\underline{V}_{\text{solvent}}} x_{\text{solute}} = \frac{RT}{M_{\text{solute}}} C_{\text{solute}}$$

- only a function of x_{solute} not of chemistry (colligative properties)
- may be used to measure molecular masses for polymers or biomolecules
- looks a lot like ideal gas law - only valid for tiny concentrations

viral expansion

$$\frac{\pi}{RT} = \frac{C_{\text{solute}}}{M_{\text{solute}}} \left[1 + B_2 \left(\frac{C_{\text{solute}}}{M_{\text{solute}}} \right) \dots \right]$$

- a few ways of fitting data to find parameters B_2, M
  - literally no way this shows up on the exam... but could directly curve fit $\frac{\pi}{RT}$ vs. C_{solute} for params

2nd order polynomial fit version

$$\frac{\pi}{RT} = \left(\frac{1}{M} \right) C_s + \left(\frac{B_2}{M^2} \right) C_s^2$$

linear fit version

$$\frac{\pi}{RTC_s} = \left(\frac{1}{M} \right) + \left(\frac{B_2}{M^2} \right) C_s$$

what about the units of B_2 and M (for R and T in SI units).

$$B_2 \ [=] \ \frac{\text{m}^3}{\text{mol}} \qquad M \ [=] \ \frac{\text{kg}}{\text{mol}}$$

physical meaning of B_2?

- think about pressure deviating from ideal and what that means for interactions
- negative B_2 indicates favorable interactions by that logic

van't hoff factor

to correct our π expression we need to account for different molecules dissolving/dissociating different

$$i = \frac{\text{apparent \# molecules in solution}}{\text{moles of solute dissolved}}$$

now using this to correct our π

$$\pi = i \frac{RTC_s}{M_s}$$

- now our π accounts for salts dissociating while sugars, proteins, polymers don't

Solid Liquid Equilibrium

of course this starts the same place every equilibrium starts. also daddy sandy treats solids as pure components

$$f_i^S = \bar{f}_i^L = x_i \gamma_i f_i^L$$

at the melting point

$$f_i^S = f_i^L \longrightarrow 1 = x_i^L \gamma_i^L$$

- when not at the melting point it gets a bit harder

$$f_1^L(T, P) = f_1^S(T, P) \times \exp\left[\frac{1}{RT} \left(\Delta_{\text{fus}} H(T) \left(1 - \frac{T}{T_m} \right) \right. \right.$$
$$\left. \left. + \int_{T_m}^T \Delta C_P \, dT - T \int_{T_m}^T \frac{\Delta C_P}{T} \, dT \right) \right]$$

if we apply this to 1 we get

$$\ln x_1 \gamma_1 = -\frac{\Delta_{\text{fus}} H(T_m)}{RT} \left[1 - \frac{T}{T_m} \right]$$
$$- \frac{1}{RT} \int_{T_m}^T \Delta C_P \, dT$$
$$+ \frac{1}{R} \int_{T_m}^T \frac{\Delta C_P}{T} \, dT$$

if ΔC_p constant

$$\ln x_1 \gamma_1 = -\frac{\Delta_{\text{fus}} H(T_m)}{RT} \left[1 - \frac{T}{T_m} \right]$$
$$- \frac{\Delta C_P}{R} \left[1 - \frac{T_m}{T} + \ln \left(\frac{T_m}{T} \right) \right]$$
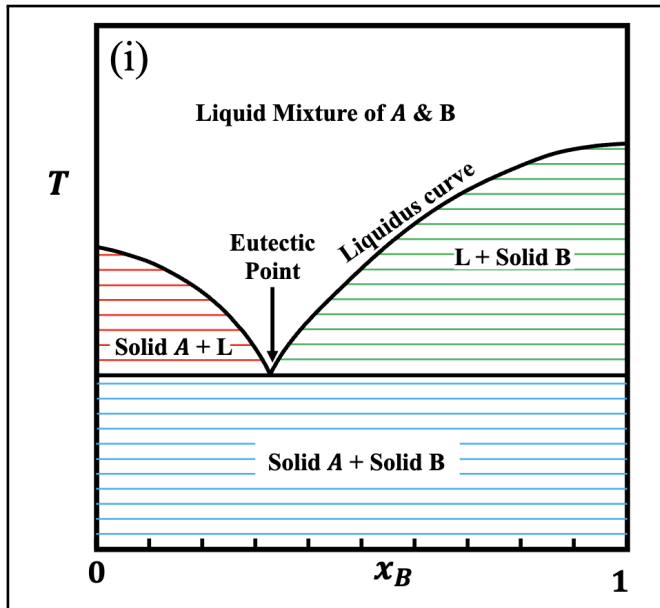
if $\Delta C_p = 0$

$$\ln x_1 \gamma_1 = -\frac{\Delta_{\text{fus}} H(T_m)}{RT} \left[1 - \frac{T}{T_m} \right]$$

clausius claperyon equation could be useful

$$\frac{\Delta_{\text{sub}} H}{RT^2} = \frac{d \ln P^{\text{sub}}}{dT} = \ln(10) \frac{d \log_{10} P^{\text{sub}}}{dT}$$

different types of points on phase diagram

- eutectic: 3 phases present, minimum melting temperature
- peritectic: liquid and solid cool and then eventually form a different solid phase
- horizontal tie lines
- line names (liquidus, solidus)
- 2 dof in liquid mixture; 1 dof in any region with tie lines; 0 dof at eutectic

(i)

Liquid Mixture of *A* & *B*

T

Liquidus curve

Eutectic Point

L + Solid B

Solid *A* + L

Solid *A* + Solid B

0 x_B 1

reactions

stoich coefficients (ν) convention

- positive for products
- negative for reactants
- 0 for bystanders

stoich constraint (A_i are components)

$$\sum \nu_i A_i = 0$$

equilibrium condition

$$\sum \nu_i \bar{G}_i = 0$$

activity

$$a = \frac{\bar{f}_i}{\bar{f}_i^{\,\circ}}$$

gibbs compared to standard state

$$\bar{G}_i = \bar{G}_i^{\circ} + RT \ln a_i$$

equlibrium constant

$$K_a(T) = \prod a_i^{\nu_i} = \exp\left(-\frac{\Delta_{\mathrm{rxn}} G^{\circ}}{RT}\right)$$

relating $\Delta_{\mathrm{rxn}} G$ to formation energies

$$\Delta_{\mathrm{rxn}} G^{\circ}(T = 25^{\circ}\mathrm{C}) = \sum \nu_i \Delta_{\mathrm{f}} G_i$$

adjusting K_a for different temperatures

$$\ln \frac{K_a(T_2)}{K_a(T_1)} = \int_{T_1}^{T_2} \frac{\Delta H_{\mathrm{rxn}}^{\circ}(T)}{RT^2}\, dT = -\frac{\Delta_{\mathrm{rxn}} H^{\circ}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

different types of systems

gas phase

$$\frac{-\sum \nu_i \underline{G}_i}{RT} = \ln\left[\prod_i \left(\frac{y_i(\bar{f}_i/y_i P)}{(f/P)_i}\right)^{\nu_i}\right]$$

ideal gas phase

$$\frac{-\sum \nu_i \underline{G}_i}{RT} = \ln\left[\prod_i y_i^{\nu_i}\right]$$

liquid mixture

$$K_a = \prod_i a_i^{\nu_i} = \prod_i (x_i \gamma_i)^{\nu_i} = K_x K_\gamma$$

ideal liquid mixture

$$\frac{-\sum \nu_i \underline{G}_i}{RT} = \ln\left(\prod_i x_i^{\nu_i}\right)$$

activities for certain reference states

species in gaseous mixture

$$a_i = \frac{y_i P}{1\ \mathrm{bar}} = \frac{P_i}{1\ \mathrm{bar}}$$

liquid mixture; reference of pure liquid

$$a_i = x_i \gamma_i$$
$$(\gamma_i \to 1 \text{ as } x_i \to 1)$$

liquid mixture; reference 1 molal soln

$$a_i = M_i \gamma_i^{\square}/(M_i = 1)$$
$$(\gamma_i^{\square} \to 1 \text{ as } M_i \to 0)$$

liquid mixture; reference is infinite dilution

$$a_i = x_i \gamma_i^{*}$$
$$(\gamma_i^{*} \longrightarrow 1 \text{ as } x_i \to 0)$$

K based on concentrations

$$K_c = \prod_i C_i^{\nu_i} = C^{\sum \nu_i} K_a/K_\gamma$$

what reference state to use

- Gas phase
  - Pure component as an ideal gas at reference pressure
- Liquid; exists at conditions of mixture
  - Pure liquid component at reference pressure
  - "Liquids that may act as a solvent"
- Liquid; does not exist at conditions
  - Use Henry law stuffs

ternary systems

7

Ternary diagram with Nitrobenzene (top), Methanol (bottom left), and Isooctane (bottom right) vertices. Point P is marked.

Ternary diagram with Wt. fraction of water (left axis), Wt. fraction of HMF (right axis), and Wt. fraction of n-butanol (bottom axis). Values shown: 0.417, 0.167, 0.417.

Ternary diagram with vertices P, Q, R and point M marked.