Elementary Principles of Chemical Processes

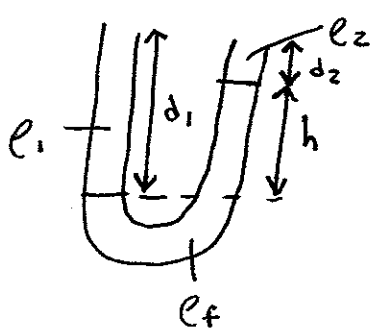
head = the height of a theoretical fluid that would exert the pressure at the base if the pressure at the top was zero.

Measuring pressure

- Bourdon gauge – hollow tube closed at one end and bent into a C configuration. Open end exposed to fluid. As $P \uparrow$, ~~fluid~~ tube straightens, rotating a pointer.

Bordon tube

- Manometers
  - open-open : one end exposed to fluid to be measured, other end exposed to atmosphere
  - ~~open~~ sealed-end : vacuum at one end
    - barometer – if other end open to atmosphere
  - differential : both ends exposed to fluid measured



$$P_1 + \rho_1 \frac{g}{g_c} d_1 = P_2 + \rho_2 \frac{g}{g_c} d_2 + \rho_f \frac{g}{g_c} h$$

$$\text{fractional conversion} = \frac{\text{moles reacted}}{\text{moles fed}}$$

$$\text{Selectivity} = \frac{\text{moles desired product formed}}{\text{moles undesired product formed}}$$

$$\text{Yield} = \frac{\text{moles desired product formed}}{\text{moles that would have been formed if no side rxns and limiting reactant was used up}}$$

$$\text{Overall conversion} = \frac{\text{reactant input to process} - \text{reactant output to process}}{\text{reactant input to process}}$$

$$\text{Single-pass conversion} = \frac{\text{reactant input to reactor} - \text{reactant output from reactor}}{\text{reactant input to reactor}}$$

Combustion

theoretical oxygen - oxygen needed for complete combustion of all fuel fed to reactor

theoretical air - quantity of air that contains theoretical oxygen

excess air - amount of air fed ~~to~~ reactor that exceeds theoretical air

$$\%\text{ excess air} = \frac{(\text{moles air})_{fed} - (\text{moles air})_{theor.}}{(\text{moles air})_{theor}} \times 100\%$$

Virial equation

$$\frac{P\hat{V}}{RT} = 1 + \frac{B(T)}{\hat{V}} + \frac{C(T)}{\hat{V}^2} + \dots$$

$\hat{V} \longrightarrow \infty$, ideal gas behavior

Redlich - Kwong

$$P = \frac{RT}{\hat{V}-b} - \frac{\alpha a}{\hat{V}(\hat{V}+b)}$$

$$a = 0.42747 R^2 T_c^2/P_c$$

$$b = 0.08664 T_c/P_c$$

$$Z = \frac{P\hat{V}}{RT}$$ compressibility factor

$$T_r = T/T_c$$

$$P_r = P/P_c$$

$$V_r = \frac{\hat{V}}{RT_c/P_c} = \frac{\hat{V}P_c}{RT_c}$$

Mixing of Real Gases : Kay's Rule

$$T_c' = y_a T_{ca} + y_b T_{cb} + y_c T_{cc} + \dots$$

$$P_c' = y_a P_{ca} + y_b P_{cb} + y_c P_{cc} + \dots$$

$$P_r' = P/P_c' , \quad T_r' = T/T_c'$$

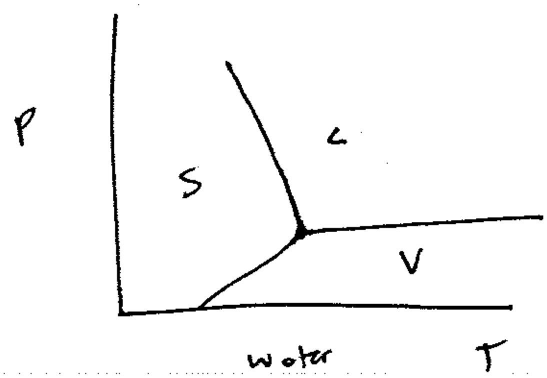
use compressibility chart to find z for mixture

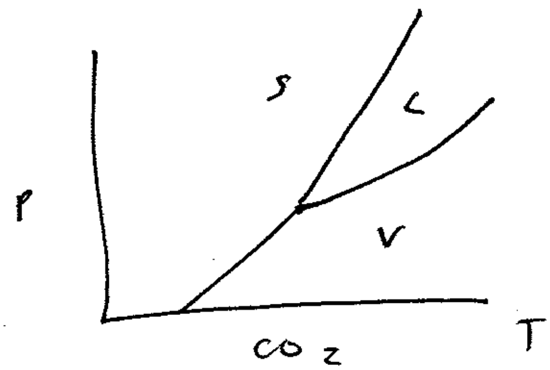
solve for $\hat{V}$ for mixture

Separations (if two things in same phase)

- distillation – 1 substance has a higher volatility
- crystallization – 1 substance has a lower melting pt
- liquid extraction – use a liquid that 1 substance is miscible in and 1 is immiscible in

Phase diagrams





normal boiling pt – at $P = 1$ atm

Clapeyron eqn

$$\frac{dp^*}{dT} = \frac{\Delta \hat{H}_v}{T(\hat{V}_g - \hat{V}_\ell)}$$

p^* = vapor pressure of a pure substance

Clausius – Clapeyron : $\hat{V}_g - \hat{V}_\ell \approx \hat{V}_g = RT/p^*$

$$\ln p^* = -\frac{\Delta \hat{H}_v}{RT} + B$$

Cox chart – plot $\log p^*$ vs $\log T$

Antoine eqn :

$$\log_{10} p^* = A - \frac{B}{T + C}$$

Gibbs phase rule : $F = 2 + N - \Pi$

F = # of intensive variables that can be specified

single condensable species

Saturation - rate of evaporation = rate of condensation

gas phase is saturated with liquid, can hold more

$$p_v = y_v P = p_v^*(T)$$

Superheated vapor - vapor present in gas less than its saturation amount

$$p_v = y_v P < p_v^*(T)$$

only a saturated vapor can condense

dew pt - gas containing single superheated vapor is cooled at constant P until saturation = dew pt

$$p_v = y_v P = p_v^*(T_{dp})$$

Relative humidity $= \dfrac{p_v}{p_v^*(T)} \times 100\%$

molal humidity $= \dfrac{p_v}{P - p_v}$

Absolute humidity $= \dfrac{p_v M_v}{(P - p_v) M_{dry}}$

percentage humidity $= \dfrac{100\ p_v/(P-p_v)}{p_v^*/(P-p_v^*)}$

$$\boxed{\begin{array}{lll} \text{Raoult's Law:} & y_A P = x_A p_A^*(T) & x_A \to 1 \\ \text{Henry's Law:} & y_A P = x_A H_A(T) & x_A \to 0 \end{array}}$$

Ideal solutions

bubble pt – first bubble forms

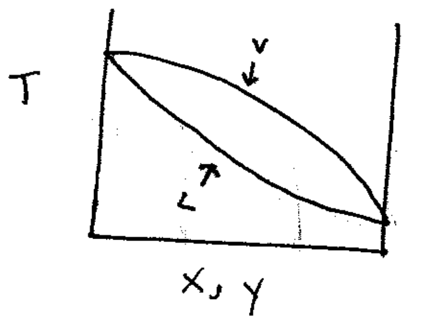
dew pt – first droplet of liquid forms

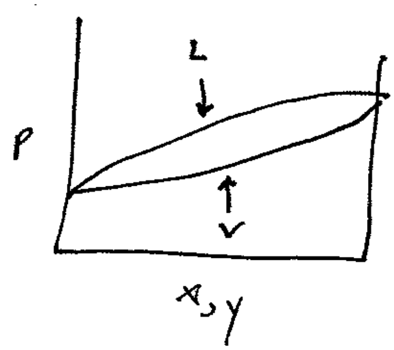
} use Raoult's Law

$$P = x_A p_A^*(T_{bp}) + x_B p_B^*(T_{Bp}) + \dots$$

$$\frac{y_A P}{p_A^*(T_{dp})} + \frac{y_B P}{p_B^*(T_{dp})} + \dots = 1$$

VLE for binary systems:





→ solution that contains as much of a dissolved species as it can hold is saturated with that species

if decrease T, solubility ↓ as some solute will precipitate out as crystals

Collisgative Properties: changes depend only on the conc. of a solute in solution, not on what the solute and solvent are

vapor pres lowering

$\Delta p_s^* = x p_s^*$

– Vapor pressure, boiling pt, freezing pt

Energy Balances

Closed systems:

$$\Delta U + \Delta E_K + \Delta E_P = Q + W$$

$$\Delta E_K \rightarrow \frac{mv^2}{2g_c} \qquad \Delta E_P \rightarrow \frac{mgz}{g_c} \qquad W \rightarrow W_s + W_f$$

$$W_f \rightarrow P_{in}V_{in} - P_{out}V_{out} \rightarrow \text{only in open systems}$$

$$\hat{H} = \hat{U} + P\hat{V}$$

Open systems:

$$\sum_{output} m_j \left(\hat{U}_j + (P_j \hat{V}_j) + \frac{V_j^2}{2g_c} + \frac{g}{g_c} z_j \right)$$

$$- \sum_{input} m_j \left(\hat{U}_j + (P_j \hat{V}_j) + \frac{V_j^2}{2g_c} + \frac{g}{g_c} z_j \right) = Q + W_s$$

$$\Delta H + \Delta E_K + \Delta E_P = Q + W_s$$

$$\Delta H = n(\hat{H}_{out} - \hat{H}_{in})$$

Mechanical Energy Balances

- when W_s, $\Delta E_K + \Delta E_P = 0$

$$\Delta U = Q \quad \text{(closed)}$$

$$\Delta H = Q \quad \text{(open)}$$

- Q and U are less important than W_s, $\Delta E_K + \Delta E_P$

Single incompressible fluid:

$$\frac{\Delta P}{\rho} + \frac{\Delta v^2}{2g_c} + \frac{g}{g_c}\Delta z + \underbrace{(\Delta \hat{U} - Q/m)}_{F \,=\, \text{friction loss}} = W_s/m$$

$$\frac{\Delta P}{\rho} + \frac{\Delta v^2}{2 g_c} + \frac{g}{g_c}\Delta z + F = W_s/m$$

- neglect Φ + $\hat{U}$ except in friction losses
- open system
- single incompressible fluid

If $F = 0$ and $W_s = 0$: Bernoulli Equation

$$\frac{\Delta P}{\rho} + \frac{\Delta v^2}{2 g_c} + \frac{g}{g_c}\Delta z = 0$$

Hypothetical process path:

If you want $\Delta \hat{H}$ for ice at $-5°C$, 1 atm $\rightarrow$ steam at 300°C, 5 atm

ice $-5°C$ 1 atm — — true path → vapor 300°C 5 atm

ice $-5°C$ 1 atm $\xrightarrow{\Delta \hat{H}_1}$ ice 0°C 1 atm $\xrightarrow{\Delta \hat{H}_2}$ liquid 0°C 1 atm $\xrightarrow{\Delta \hat{H}_3}$ liquid 100°C 1 atm $\xrightarrow{\Delta \hat{H}_4}$ Vapor 100°C 1 atm $\xrightarrow{\Delta \hat{H}_5}$ Vapor 300°C 1 atm $\xrightarrow{\Delta \hat{H}_6}$ vapor 300°C 5 atm

Changes in P at constant T:

Solids and liquids : U is ind of P

$$\Delta \hat{U} \approx 0 \quad \text{and} \quad \Delta \hat{H} \approx \hat{V}\Delta P$$

gases : U and H are ind of P

$$\Delta \hat{U} = 0, \quad \Delta \hat{H} = 0$$

Sensible heat : heat that must be transferred to raise or lower the temperature of a substance

$$Q = \Delta U \quad \text{(closed)}$$
$$Q = \Delta H \quad \text{(open)}$$

$\hat{U}$ is a strong function of T

$$C_v(T) = \left(\frac{d\hat{U}}{dT}\right)_V$$

$$d\hat{U} = C_v(T)\, dT$$
$$\Delta\hat{U} = \int_{T_1}^{T_2} C_v(T)\, dT \longrightarrow$$

Valid for
- ideal gases
- real gases, $\hat{V}$ const.
- solids + liquids (approx.)

if temp and volume change :

$$A(T_1, \hat{V}_1) \xrightarrow{\Delta\hat{U}_1} A(T_1, \hat{V}_2) \xrightarrow{\Delta\hat{U}_2} A(T_2, \hat{V}_2)$$

$$\Delta\hat{U} = \Delta\hat{U}_1 + \Delta\hat{U}_2$$

1st step : for ideal gases, and approximately solids and liquids this $= 0$ ($\hat{U}$ doesn't depend on $\hat{V}$, only T)

$$C_p(T) = \left(\frac{d\hat{H}}{dT}\right)_P$$

$$d\hat{H} = C_p\, dT$$

$$\Delta\hat{H} = \int_{T_1}^{T_2} C_p\, dT$$

$$A(T_1, P_1) \xrightarrow{\Delta\hat{H}_1} A(T_1, P_2) \xrightarrow{\Delta\hat{H}_2} A(T_2, P_2)$$

$$\Delta\hat{H} = \Delta\hat{H}_1 + \Delta\hat{H}_2$$

$$\Delta\hat{H}_1 = 0 \quad \text{(ideal gas)}$$
$$= \hat{V}\Delta P \quad \text{(solid or liquid)}$$

so use:

$$\Delta \hat{H} = \int_{T_1}^{T_2} C_p \, dT$$ ideal gases
real gases, $\hat{V}$ const.

$$\Delta \hat{H} = \hat{V} \Delta P + \int_{T_1}^{T_2} C_p \, dT$$ solid or liquid

liquids and solids : $C_p \approx C_v$
ideal gases : $C_p = C_v + R$

mean heat capacity : $\Delta \hat{H} = \overline{C_p} \Delta T$

$$\Delta \hat{H} = \hat{H}(T_2) - \hat{H}(T_1) = \overline{C_p}_{T_2} (T_2 - T_{ref}) - C_{p\,T_1} (T_1 - T_{ref})$$

Kopp's rule : $(C_p)_{Ca(OH)_2} = (C_{pa})_{Ca} + 2(C_{pa})_O + 2(C_{pa})_H$

Mixtures : $C_{pm}(T) = \sum_{\text{all comp}} y_i C_{pi}(T)$

$$\Delta \hat{H} = \int_{T_1}^{T_2} C_{pm}(T) \, dT$$

Latent heats :

Vaporization $\Delta \hat{H}_v$
fusion $\Delta \hat{H}_m$
Sublimation $\Delta \hat{H}_s$

In closed system : to sub into energy balance

$$\Delta \hat{U} = \Delta \hat{H} - \Delta P \hat{V}$$

liquids and solids $\Delta \hat{U}_m \approx \Delta \hat{H}_m$
ideal gas : $\Delta \hat{U}_v \approx \Delta \hat{H}_v - RT$

use if $\Delta\hat{H}_v$ dln vary with T

Clausius - Clapeyron : $\ln p^* = \dfrac{-\Delta\hat{H}_v}{RT} + B$

Clapeyron : $\dfrac{d(\ln p^*)}{d(1/T)} = \dfrac{\Delta\hat{H}_v}{R}$

if $\Delta\hat{H}_v$ varies w/ T

~~plot d(ln p*)~~

plot $\ln p^*$ vs. $1/T$

Slope $= \Delta\hat{H}_v / R$

Psychrometric charts :

Absolute humidity vs. dry bulb temp

↓

mass ratio of water vapor to dry air

saturation curve - 100% relative humidity $\left(\dfrac{p_{H_2O}}{p^*_{H_2O}}\right)$

wet - bulb temp - water evaporates from the wick,

↓ the temp

saturated gas around wick : $T_{db} = T_{wb}$

humid air : 1 phase, 2 components

$F = 2 + 2 - 1 = 3$

adiabatic saturation curve : specify T_1 and abs humidity

outlet T and humidity on this curve

- humidifying a gas

adiabatic sat temp - outlet air is saturated with water

intersection of adiabatic sat curve and 100% RH curve heat of solution $-\Delta\hat{H}_s$ - 1 mol of solute dissolved in n mols solvent

n is large $\rightarrow \Delta\hat{H}_s \rightarrow$ heat of soln at infinite dilution

heat of mixing $-\Delta\hat{H}_m$

- can ignore for gas ($\hat{H}$ mix = $\hat{H}$ pure substance) and liquid mix of similar components

- enthalpy per mol solute (not solution)

ex - Mix HCl + water $\longrightarrow$ HCl (aq)

$$\underset{100°C}{HCl} + \underset{25°C}{\text{water}} \longrightarrow \underset{40°C}{HCl\,(aq)}$$

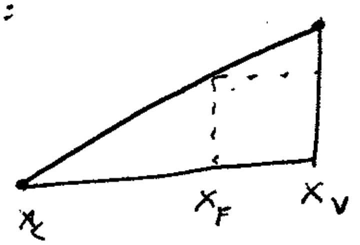
$$Q = \Delta H = \Sigma n_{out}\hat{H}_{out} - \Sigma n_{in}\hat{H}_{in}$$

$$= n_{out}\left(\Delta\hat{H}_s(25°C, n) + \int_{25}^{40} C_p\,dT\right)$$

$$- \underset{HCl}{n_{in}}\left(\int_{25}^{100} C_p\,dT\right) - \underset{H_2O \text{ at } T_{ref}}{0}$$

tie line :

enthalpy conc. chart



$$\frac{L}{V} = \frac{x_V - x_F}{x_F - x_L}$$

From : $F = L + V$

$$x_F F = x_L L + x_V V$$

$$\frac{L}{F} = \frac{x_V - x_F}{x_V - x_L} \qquad \frac{L}{F} = \frac{x_F - x_L}{x_V - x_L}$$

Heat of rxn

$\Delta\hat{H}_r\ (T, P) = \text{prod} - \text{reac.}$

$$\Delta H = \frac{\Delta\hat{H}_r(T_0)}{\nu_A} n_A$$ (n_A moles of A are consumed or producted at T_0)

$\Delta\hat{H}_r(T) < 0$ exo.

$\Delta\hat{H}_r(T) > 0$ endo.

if constant volume:

$$\Delta\hat{U}_r = U_{prod} - U_{reac} = \Delta\hat{H}_r(T) - RT\left(\sum_{prod} \nu_i - \sum_{reac} \nu_i\right)$$

if not gases: $\Delta\hat{U}_r = \Delta\hat{H}_r$

Hess' law: add heats of rxn together to get overall rxn

Heat of formation - formed from its atomic constituents as they occur in nature

$\Delta\hat{H}_f^\circ = 0$ for an element

$$\Delta\hat{H}_r^\circ = \sum_{prod} \nu_i \Delta\hat{H}_{f,i}^\circ - \sum_{reac} \nu_i \Delta\hat{H}_{f,i}^\circ$$

Heat of combustion $\Delta\hat{H}_c^\circ$

Solutions $(\Delta\hat{H}_f^\circ)_{solution} = (\Delta\hat{H}_f^\circ)_{solute} + \Delta\hat{H}_s^\circ(n)$

Fuels

- solid : coal (carbon, H_2O, ash, hydrocarbons, sulfur)
  coke (carbon mostly - solid after coal or petroleum is heated)
- liquid : hydrocarbons from distilling crude oil (petroleum)
- gas : natural gas (80-95% CH_4, ethane, other)

higher heating value : $-\Delta \hat{H}_c^\circ$ w/ $H_2O(l)$ as a product
lower heating value : $-\Delta \hat{H}_c^\circ$ w/ $H_2O(v)$ as a product

$$HHV = LHV + n \Delta \hat{H}_v (H_2O, 25°C)$$

Adiabatic flame temp : highest achievable temp if $Q = 0$

$$\Delta H = n_f \Delta \hat{H}_c^\circ + \sum_{out} n_i \hat{H}_i (T_{ad}) - \sum_{in} n_i \hat{H}_i (T_{feed}) = 0$$

ignition - rate of an oxidation rxn increases abruptly when the reaction mix exceeds a certain temp

lower flammability limit - just enough fuel
upper flammability limit - just enough O_2
in between those two : ignition can occur
At these limits, T_{ad} = ignition temp

flash pt - temp when liquid gives off enough vapor to form an ignitable mix with the air above the liquid surface

Transient Processes

$$\frac{dm}{dt} = q_{in} - r_{gen} - q_{out} + r_{cons}$$

$$\frac{d(VC_A)}{dt} = Q C_{A0} - Q_A C_A - k C_A V$$

open system :

$$MC_v \frac{dT_{sys}}{dt} = mC_p (T_{in} - T_{sys}) + Q + W_s$$

closed system :

$$MC_v \frac{dT_{sys}}{dt} = Q + W$$

Soda Ash

Production of sodium carbonate Na_2CO_3

Naturally occurring brines and ores

Separation from brine :

$$Na_2CO_3\,(aq) + CO_2\,(g) + H_2O\,(l) \rightarrow \underset{\text{sodium}}{2\,NaHCO_3}\,(aq)$$

sodium bicarbonate is crystallized and filtered bicarbonate from the liquor.

The crystals are heated (calcination), driving off CO_2 and H_2O.

$$2\,NaHCO_3\,(s) \rightarrow \underset{\text{light ash}}{\underset{\downarrow}{Na_2CO_3}}\,(s) + H_2O\,(g) + CO_2\,(g)$$

Bleach and feed to a crystallizer where $Na_2CO_3 \cdot H_2O$ crystallizes.

Separate crystals from solution (mother liquor) in a centrifuge and dry in a steam drier to form dense ash.

$$Na_2CO_3 \cdot H_2O\,(s) \rightarrow \underset{\downarrow}{Na_2CO_3}\,(s) + H_2O\,(g)$$

Production of Chemicals from Coal

- liquefaction
- gasification

$$C + H_2O\,(v) \longrightarrow CO + H_2$$

$CO + H_2$ then separated and used as fuel

$$C + O_2 \longrightarrow CO_2$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \quad \text{water-gas shift}$$

other rxn s

$$S + H_2 \longrightarrow H_2S$$

$$C + 2H_2 \rightarrow CH_4$$

synthesis gas - contains $CO + H_2$ + other gases
- when Hydrocarbon feed stocks are used in the production of chemicals

Convert coal to acetic anhydride:
- add water and grind coal
- send to gassification reactor -
  entrained flow gassifier, send in water - coal mixture and O_2

Claus process

$$H_2S + 1.5\,O_2 \longrightarrow SO_2 + H_2O$$

$$2H_2S + SO_2 \longrightarrow 2H_2O + 3S$$