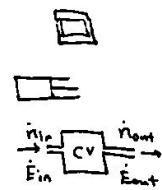


••• Thermodynamic Systems

- > isolated system - neither mass or energy can cross system boundary
- > closed system - only energy can cross system boundary
- > open system - both mass and energy can cross system boundary



••• Thermodynamic Properties

- > substance that is contained within the system is described by properties

[Ex1] gas in piston cylinder is described by P, V, T



- P - pressure
- T - temperature
- $V = \frac{V}{n}$ molar volume

[Ex2] Other properties

U, H, G, S, \dots

→ Distinction

> extensive - size dependent (e.g. V)

> intensive - size independent

$$\text{specific volume } \hat{v} = \frac{V}{m}$$

$$\text{molar volume } v = \frac{V}{n}$$

$$P, T$$

••• Thermodynamic State of System

> state condition at any given time

• the thermodynamic state of a system is defined by specifying values of a set of measurable properties sufficient to determine all other properties

••• Thermodynamic Process

> process - change of state

• When external conditions change, the state of system changes

> adiabatic - no heat transfer $q=0$

> isothermal - $\Delta T = 0$

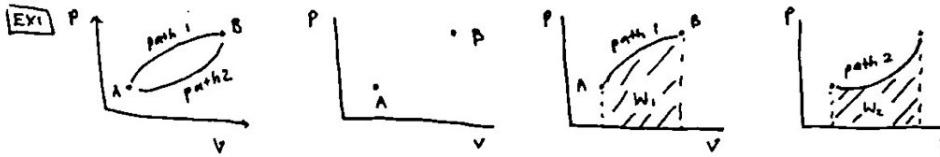
> isobaric - $\Delta P = 0$

> isochoric - $\Delta V = 0$

<< Path (In)dependence

> state function - process path independent properties
(point)

> path function - process path dependent properties



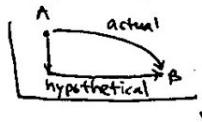
- thermo property define state function
 - regardless of path, $\Delta P = P_2 - P_1$
- heat and work are path functions
 - $W_1 \neq W_2$

> Internal energy is a state function, although heat and work are path functions

$$\Delta U = Q + W$$

→ Hypothetical Process path

- Because state functions are path independent, we can pick any path that helps us to determine the final state property
- Does not work for path functions



<< Phase of Matter

- > phase - has
- | | |
|---|---|
| { | uniform physical structure (e.g. solid, liq, gas) |
| | uniform chemical composition (e.g. brine, H ₂ O) |
- single phase (e.g. gas)
 - multiple phase (e.g. vapor-liquid eqm)
 - phases are separated by phase boundary

<< State Postulate

- If we have a system of a pure substance, the thermo state, and therefore its intensive thermo properties can be determined from 2 independent intensive properties.
- independent variable - the two intensive properties defining the system
- dependent variable - other intensive properties (constrained)
 - e.g. $v = f(T, P)$

<< Equation of States (EOS)

- Based on state postulate, thermo properties are related
- The relationships are called equation of states

[Ex2] Ideal gas EOS

$$Pv = RT$$

 $R = 8.314 \text{ J mol}^{-1}\text{K}^{-1}$ ideal gas constant

<< Equilibrium

> equilibrium - a state of balanced forces

- orig. system is never in eqm because driving force needed to move mass

> steady state - open system for which state does not change

→ Types of Eqm

> mechanical eqm: $P_{sys} = P_{sur}$ > thermal eqm: $T_{sys} = T_{sur}$ > chemical eqm: $\mu(t_1) = \mu(t_2)$

} thermodynamic equilibrium
requires all three

<< Gibbs Phase Rule

- Gibbs phase rule identifies degree of freedom of a multiphase system in eqm

$$F = 2 + m - \pi$$

$$F = 2 + c - p - r$$

- F - degree of freedom (# intensive property to fix state)
- m - (c) # species/component
- π - (p) # phase
- r - # fns

[Ex3] State Postulate

- single phase, pure substance $\Rightarrow m=1, \pi=1$

$$F = 2 + 1 - 1 = 2$$

[Ex4] Water VLE

$$m = 1, \pi = 2$$

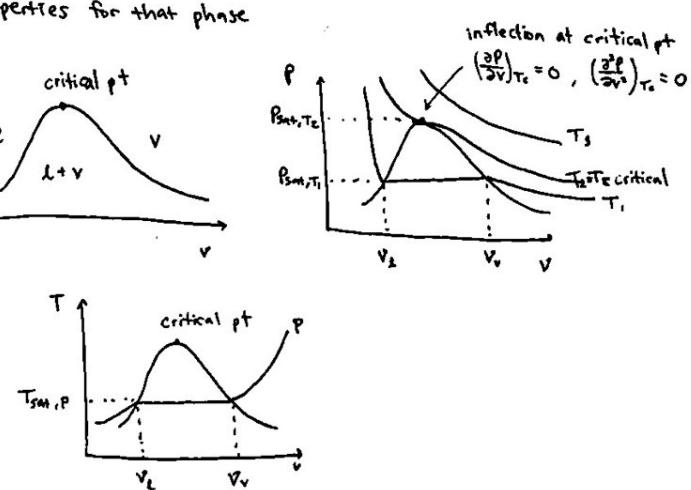
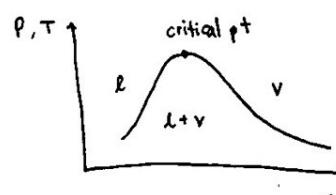
$$F = 2 + 1 - 2 = 1 \Rightarrow \text{need one property in each phase to constrain all other properties for that phase}$$

<< PVT phase Diagram

- pure substance
- ignore solid phase
- Liquid-vapor (saturation) dome
- At critical pt, L and V are no longer distinguishable.

> vapor quality

$$q = \frac{n_v}{n_v + n_L} = \frac{V - V_L}{V_v - V_L}$$



<< Heat and Work

→ Heat

- > heat - transfer of energy by temperature gradient
- > sensible heat - involve change in temperature & internal energy
- > latent heat - involve phase change ($\Delta T = 0$)
 - modes of heat transfer { conduction
 - path function { convection
 - radiation

→ Work

- > work - transfer of "useful" energy
- path function
- $W = P\Delta V$ if $\Delta P = 0$

<< Internal Energy

- > internal energy - associated with motion, position, and chemical-bonding configuration of molecules
 - molecular kinetic energy
 - molecular potential energy (interaction)
- ideal gas only has molecular KE.
- molecular PE_{ideal} = 0
- $U_{ideal} = u(T \text{ only})$
- real gas has molecular KE and PE
- molecular PE depends on distance
- $u_{real} = u(T, v) = u(T, P)$

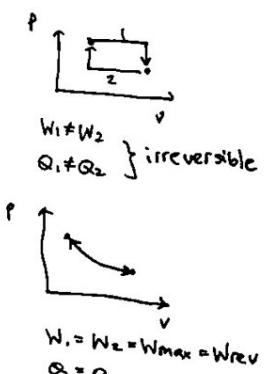
<< Reversible & Irreversible Process

- > irreversible process - not reversible, has friction and with finite driving force
- > reversible process - system can be returned to original state without any net (ideal) effect on surrounding. the driving force is infinitesimally small.
 - no heat to surrounding ($\alpha=0$, $W=W_{max} = W_{rev}$)
 - need ∞ time

> efficiency

$\eta_{expansion} = \frac{W_{irrev}}{W_{rev}}$	$\eta_{compression} = \frac{W_{rev}}{W_{irrev}}$
--	--

• reversible work of ideal gas - $W_{rev} = -P_1 V_1 \ln\left(\frac{V_2}{V_1}\right)$



••• 1st law for Closed System

$$\rightarrow \Delta U = Q + W \quad \cdot \text{neglect KE, PE}$$

$$\Delta u = q + w$$

$$du = dq + dw$$

••• 1st law for Open System

$$\rightarrow \frac{dU}{dt} = \sum_{in} \dot{m} \dot{h}_i - \sum_{out} \dot{m} \dot{h}_i + \dot{Q} + \dot{W}_s \quad \cdot \text{neglect KE, PE}$$

$$\cdot \text{Steady state} \quad 0 = \sum_{in} \dot{m} \dot{h}_i - \sum_{out} \dot{m} \dot{h}_i + \dot{Q} + \dot{W}_s$$

→ Enthalpy

→ enthalpy H - composition property associated with internal energy U and flow work PV

$$H = U + PV, \quad h = u + Pv$$

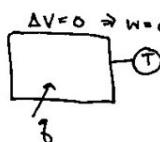
$$\cdot \text{for ideal gas, } h = u + Pv \\ = u(T) + RT \\ = h(T \text{ only})$$

••• Thermochemical Data

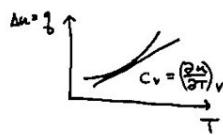
→ Heat capacity

· captures sensitivity to temperature of u at constant v and h at constant p .

· constant volume heat capacity



$$\Delta u = q + \cancel{\Delta PV} = q$$



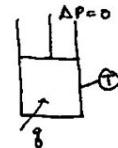
$$C_V = \left(\frac{\partial u}{\partial T} \right)_V$$

$$\cdot \text{ideal gas: } C_p = C_v + R$$

$$\cdot \text{liquid & solid: } C_p \approx C_v$$

$$\cdot \text{mean } C_p \text{ of gas: } \bar{C}_p = \frac{\int_{T_1}^{T_2} C_p(T) dT}{T_2 - T_1} \quad T_2 > T_1$$

· constant pressure heat capacity



$$\Delta u = q + w$$

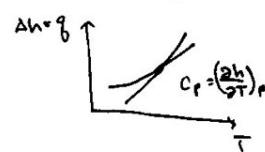
$$\Delta u = q - P \Delta V$$

$$\Delta u + P \Delta V = q$$

$$\Delta u + \Delta(PV) = q$$

($\Delta P = 0$)

$$\Delta h = q$$



$$C_p = \left(\frac{\partial h}{\partial T} \right)_p$$

<< Thermodynamic Data

→ Latent Heats

→ latent heat = change in h when changes phase

- $\Delta h_{\text{vap}} = h^v - h^l$

- $\Delta h_{\text{fus}} = h^f - h^s$

- $\Delta h_{\text{sub}} = h^v - h^s$

- At any temp T , $\Delta h_{\text{vap}}(T) = \int_T^{T_b} c_p^l dT + \Delta h_{\text{vap}}(T_b) + \int_{T_b}^T c_p^v dT$

→ Enthalpy of Reaction

formation method:

$$\Delta h_{\text{rxn}}^\circ = \sum_{\text{reactant}} \nu_i \Delta h_{f,i}^\circ + \sum_{\text{product}} \nu_i \Delta h_{f,i}^\circ$$

$$= \sum \nu_i \Delta h_{f,i}^\circ$$

ν - stoichiometric coeff

$\nu < 0$ reactant

$\nu > 0$ product

<< Reversible Process in Closed System

→ Isothermal

- ideal gas $W = nRT \ln\left(\frac{P_2}{P_1}\right)$

$$\Delta T = 0 \rightarrow \Delta U = 0$$

$$Q = -W = -nRT \ln\left(\frac{P_2}{P_1}\right)$$

- expansion, $P_2 < P_1$, $W < 0$, $Q > 0$

- compression, $P_2 > P_1$, $W > 0$, $Q < 0$

→ Adiabatic, constant C_p

- $Q = 0$

- $dU = \cancel{\delta Q} + \delta W = \delta W = -PdV \quad \} \quad nC_v dT = -PdV$

- $dU = nC_v dT$

$$nC_v d\left(\frac{PV}{nR}\right) = -PdV$$

$$C_v(PdV + VdP) = -RPdV$$

$$C_v V dP = -(R + C_v) PdV$$

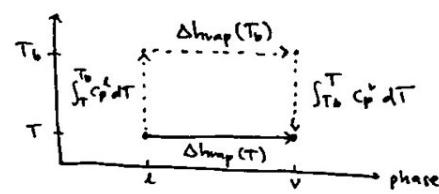
$$C_v V dP = -C_p PdV$$

$$\int -\frac{C_p}{C_v} \frac{dV}{V} = \int \frac{dP}{P}$$

$$-\ln\left(\frac{V_2}{V_1}\right) = \ln\left(\frac{P_2}{P_1}\right) \quad k = \frac{C_p}{C_v}$$

$$\ln(P_1 V_1^k) = \ln(P_2 V_2^k)$$

$$PV^k = \text{const.}$$



, T_b = normal boiling pt

*** Polytropic Process

> polytropic process - process that satisfies $PV^\gamma = \text{const}$

- $\gamma = 0$, $P = \text{const}$, isobaric
- $\gamma = 1$, $PV = \text{const}$, isothermal
- $\gamma = k = \frac{C_p}{C_v}$, $PV^k = \text{const}$, isentropic, adiabatic reversible
- $\gamma = \infty$, $V = \text{const}$, isochoric

*** Open System Balance on Process Equipment

→ Nozzle & Diffuser

- > nozzle - \downarrow cross section, $\uparrow v$, $\uparrow KE$
- > diffuser - \uparrow cross section, $\downarrow v$, $\downarrow KE$
- $\Delta PE = 0$
- $\dot{Q} = 0$
- $\dot{W}_s = 0$

$$\left. \begin{array}{l} \\ \end{array} \right\} U \leftrightarrow KE$$

→ Turbine, Pump, Compressor

- > turbine - generate power, \dot{W}_s
- > pump - raise pressure or PE of fluid, $\uparrow P$
- > compressor - raise pressure or PE of gas, $\uparrow P$
- $\Delta KE = 0$
- $\dot{Q} = 0$

$$\left. \begin{array}{l} \\ \end{array} \right\} \dot{W}_s$$

→ Heat Exchanger

- > heat exchanger - increase or decrease fluid temperature T
- $\Delta KE = 0$
- $\Delta PE = 0$
- $\dot{W}_s = 0$

$$\left. \begin{array}{l} \\ \end{array} \right\} \dot{Q}$$

→ Throttling Device

- > throttling device - reduce fluid pressure, $\downarrow P$

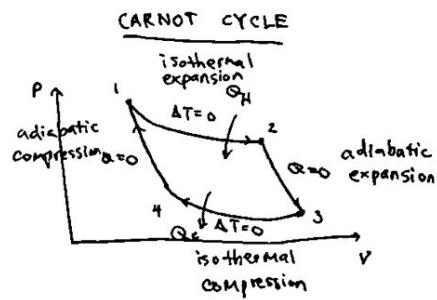
- $\dot{Q} = 0$
- $\dot{W}_s = 0$
- $\Delta KE = 0$
- $\Delta PE = 0$

$\left. \begin{array}{l} \\ \end{array} \right\}$ isentropic process

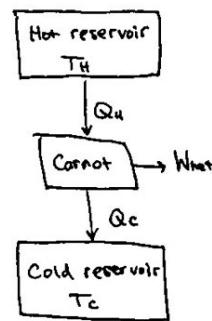
$$h_1 = h_2$$

Thermodynamic Cycle & Carnot Cycle

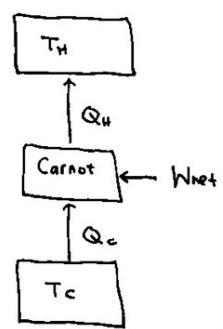
- thermo cycles produce power or refrigeration
- Carnot cycle - most efficient cycle
 - Net Work: $-W_{net} = |W_{12}| + |W_{23}| - |W_{34}| - |W_{41}|$
 - State property does not change after a cycle
 - $\Delta U_{cycle} = 0 = W_{net} + Q_{net}$
 - $-W_{net} = Q_{net}$
 - $-W_{net} = Q_{12} + \cancel{Q_{23}} + Q_{34} + \cancel{Q_{41}}$
 - $-W_{net} = |Q_H| - |Q_L|$



ENGINE
(power production)



REFRIGERATION
(cooling)



<< 2nd Law Statements & Directionality

- 2nd law impose constraint on the directionality of thermo process
 - state property entropy S
 - an isolated system tends towards the state of max entropy (multiplicity)
 - Clausius - heat cannot flow from cold to hot without external effect
 - Kelvin & Planck - impossible to build engine that operates in cycle that can convert all heat to work
 - no heat engine can have efficiency $\eta = 100\%$.
 - impossible for cyclic device to receive heat from a single reservoir and produce net work
 - For reversible process, $\Delta S_{\text{univ}} = 0$
 - For irreversible process, $\Delta S_{\text{univ}} > 0$
- $\left. \right\} \Delta S_{\text{univ}} \geq 0$

<< Entropy & 2nd Law Consequences

> entropy - incremental heat absorbed in reversible process divided by temperature

$$ds \equiv \frac{dq_{\text{rev}}}{T}$$

- s is a state function
 - path function q_{rev} is converted by $\frac{1}{T}$ into a state function s
 - $\frac{1}{T}$ is an integrating factor of q_{rev}
- For cyclic process, entropy does not change
 - $\Delta S_{\text{cyc}} = 0$
 - $\oint \frac{dq_{\text{rev}}}{T} = 0$
- $\Delta S = 0$ describes a reversible process
 - > reversible mechanical process - pressure change
 - infinitesimally slow, no direction
 - > reversible thermal process - temperature change
 - reversible heat exchange q_{rev}
 - Carnot Cycle

<< Carnot Cycle

- $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$
- $\Delta S_{\text{sys}} = \Delta S_{\text{cycle}} = 0$
- $\Delta S_{\text{surr}} = -\frac{q_H}{T_H} - \frac{q_C}{T_C} = 0$ for reversible process
- $\eta = 1 - \frac{T_C}{T_H}$

<< 2nd Law for Closed System

- $\Delta S_{\text{univ}} \geq 0$

$$\Delta S_{\text{sys}} + \Delta S_{\text{surr}} \geq 0$$

$$\Delta S_{\text{sys}} + \frac{Q_{\text{surr}}}{T_{\text{surr}}} \geq 0$$

$$\boxed{\Delta S_{\text{sys}} - \frac{Q_{\text{surr}}}{T_{\text{surr}}} \geq 0}$$

$$\Delta S_{\text{surr}} = \int_1^2 \frac{dQ_{\text{surr}}}{T_{\text{surr}}} = \frac{Q_{\text{surr}}}{T_{\text{surr}}}$$

$$Q_{\text{surr}} = -Q_{\text{sys}}$$



<< 2nd Law for Open System

$$\frac{dS_{\text{univ}}}{dt} \geq 0$$

$$\frac{dS_{\text{sys}}}{dt} + \frac{dS_{\text{surr}}}{dt} \geq 0$$

$$\frac{dS_{\text{surr}}}{dt} \geq 0$$

$$\frac{dS_{\text{surr}}}{dt} = 0 \quad \text{at steady-state}$$

$$\boxed{\sum_{\text{out}} n_i s_i - \sum_{\text{in}} n_i s_i - \frac{Q}{T_{\text{surr}}} \geq 0}$$

at steady state



<< Ideal Gas Processes

→ Reversible, Isothermal Process

- $\Delta T = 0 \rightarrow du = 0$

- $du = \delta q_{\text{rev}} + \delta w_{\text{rev}} = 0$

$$\delta q_{\text{rev}} = -\delta w_{\text{rev}} = P dv$$

- $\Delta S = \int \frac{\delta q_{\text{rev}}}{T} = \int \frac{P}{T} dV = \int \frac{RT}{V} dV = R \int \frac{dV}{V} = R \ln \left(\frac{V_f}{V_i} \right)$

$$\boxed{\Delta S = R \ln \left(\frac{V_f}{V_i} \right)}$$

$$\boxed{\Delta S = -R \ln \left(\frac{P_f}{P_i} \right)}$$

→ Reversible, Isobaric Process

- $du = \delta q_{\text{rev}} + \delta w_{\text{rev}}$

$$\delta q_{\text{rev}} = du - \delta w_{\text{rev}}$$

$$\delta q_{\text{rev}} = du - (-P dv)$$

$$\delta q_{\text{rev}} = dh$$

- $\Delta S = \int \frac{\delta q_{\text{rev}}}{T} = \int \frac{dh}{T} = \int \frac{C_p}{T} dT$

$$\boxed{\Delta S = \int \frac{C_p}{T} dT}$$

→ Reversible, Adiabatic Process (Isentropic)

- $\delta q_{\text{rev}} = 0$

> isentropic process - reversible adiabatic process

- $\Delta S = \int \frac{\delta q_{\text{rev}}}{T} = 0$

- $\Delta S = 0$

$$\boxed{\Delta S = 0}$$



<< Ideal Gas Processes

→ Reversible, Isochoric Process

- $dV = 0 \Rightarrow dW_{rev} = 0$

- $dU = \delta q_{rev} + dW_{rev} = 0$

- $\Delta S = \int \frac{\delta q_{rev}}{T} = \int \frac{dU}{T} = \int \frac{C_V}{T} dT$

$$\boxed{\Delta S = \int \frac{C_V}{T} dT}$$

→ Compound Process

- $(T_1, P_1) \rightarrow (T_2, P_2)$

- isothermal + isobaric hypothetical path

- $\Delta S = \int \frac{C_P}{T} dT - R \ln\left(\frac{P_2}{P_1}\right)$

- $(T_1, V_1) \rightarrow (T_2, V_2)$

- isothermal + isochoric hypothetical path

- $\Delta S = \int \frac{C_V}{T} dT + R \ln\left(\frac{V_2}{V_1}\right)$

<< Mechanical Energy Balance & Bernoulli Equation

- 1st law: $dH + d(K_e) + d(Pe) = dq + dw_{is}$

- 2nd law: $dS + \frac{\delta q_{rev}}{T} = 0$

$$\delta q_{rev} = T dS$$

- enthalpy: $dH = dH + d(Pv)$

$$= (dq + dw) + (Pdv + vdp)$$

1st law, chain rule

$$= TdS - PdV + PdV + vdp$$

$$= TdS + vdp$$

- substitute, rearrange

$$dw_{is} = dH + d(K_e) + d(Pe) - dq$$

$$= TdS + vdp + d(K_e) + d(Pe) - TdS$$

$$\boxed{dw_{is} = vdp + d(K_e) + d(Pe)}$$

- Integrate,

$$\boxed{w_{is} = \int vdp + \Delta K_e + \Delta Pe}$$

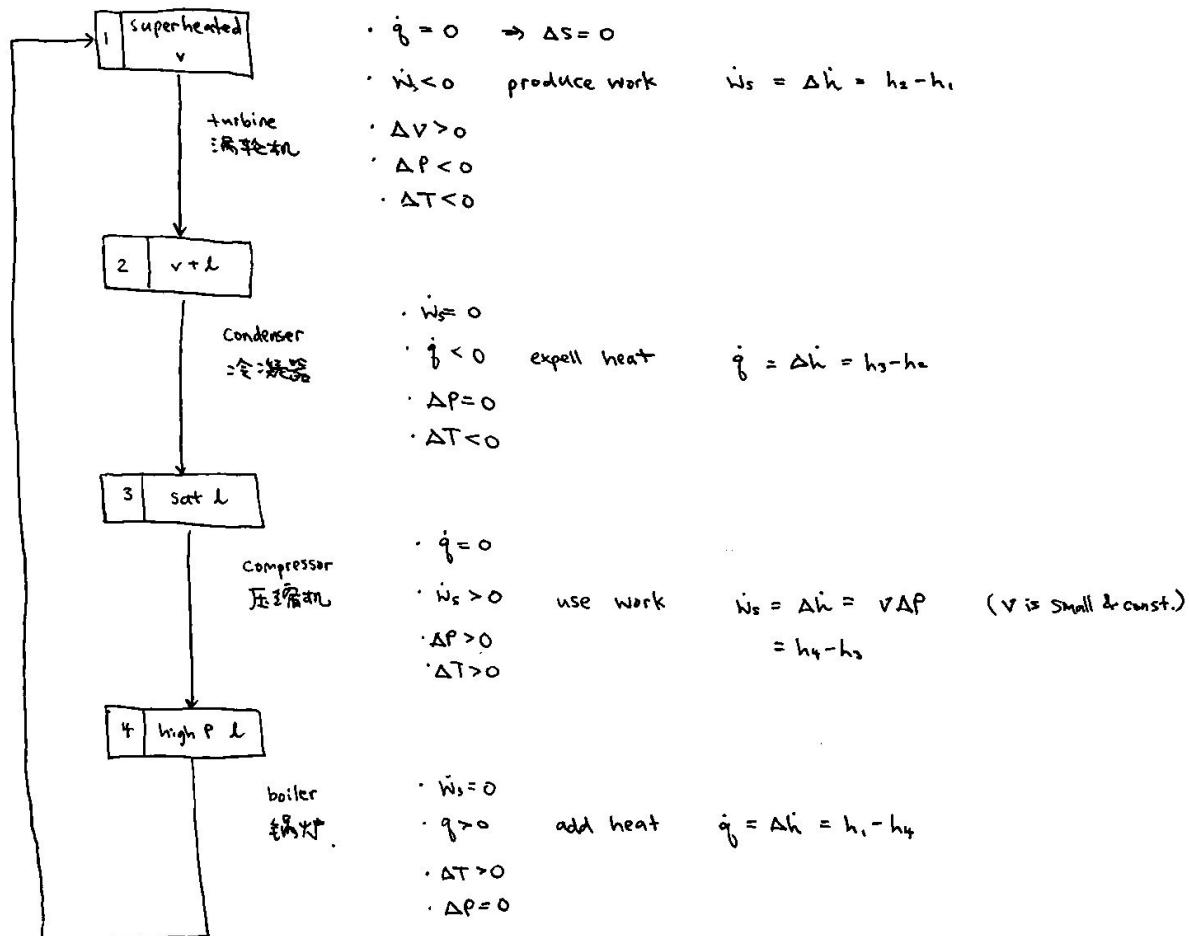
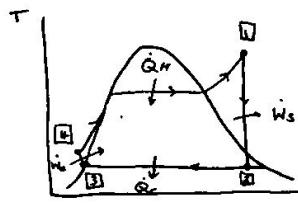
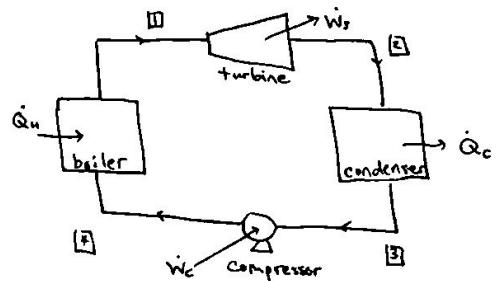
- nozzle, diffuser: $w_{is} = 0 \Rightarrow$ Bernoulli eqn

- turbine, pump: $\Delta K_e, \Delta Pe = 0$

<< Vapor - Compression Cycles

→ Power Cycle (Rankine Cycle)

Rankine cycle converts fuel into electric power.

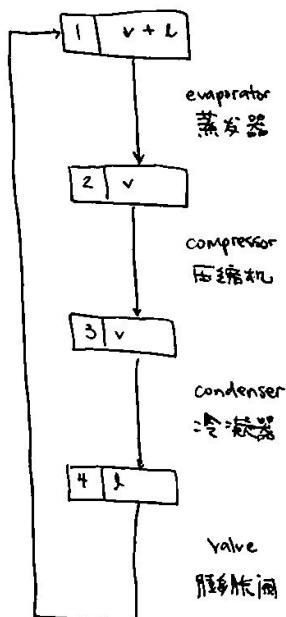
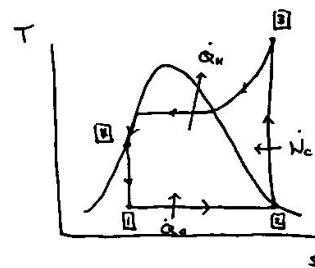
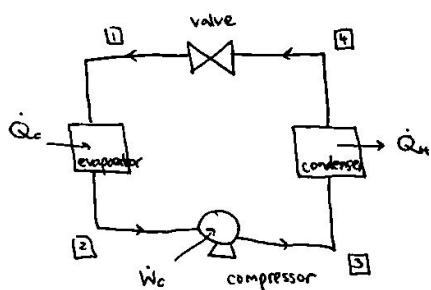


$$\eta = \frac{|\dot{w}_s| - \dot{w}_c}{\dot{q}_H} = \frac{|(h_2 - h_1)| - (h_4 - h_3)}{h_1 - h_4}$$

$$W_{net} = \dot{q}_H - |\dot{q}_C| = |\dot{w}_s| - \dot{w}_c$$

↔ Vapor - Compression Cycles

→ Refrigeration Cycle



- $\dot{W} = 0$
- $\dot{Q}_c = \dot{Q}_H = \Delta h = h_2 - h_1$
- $\Delta T = 0$

- $\dot{Q} = 0 \Rightarrow \Delta S = 0$
- $\dot{W} = \dot{W}_c = \Delta h = h_3 - h_2$
- $\Delta P > 0$

- $\dot{W} = 0$
- $\dot{Q} = \dot{Q}_H = \Delta h = h_4 - h_3$
- $\Delta T < 0$

- $\dot{Q} = 0$
- $\dot{W} = 0$
- $\Delta h = 0 \Rightarrow h_4 = h_1$
- $\Delta P < 0$

> Coefficient of performance

$$COP = \frac{\dot{Q}_c}{\dot{W}_c} = \frac{h_2 - h_1}{h_3 - h_2}$$

<< Motivation

- State postulate states that for pure species, only 2 intensive independent properties are needed to define all properties of a state.

- inconvenient to use graph & table for PVT calculation
- Equations for PVT relations needed

> Equation of state - equation use experimental data to fit PVT relation as $f(P, v, T) = 0$.

- constitutive eqn - constructed from measurable data, no physical basis
- not fundamental eqn

<< Ideal Gas Law & Compressibility factor

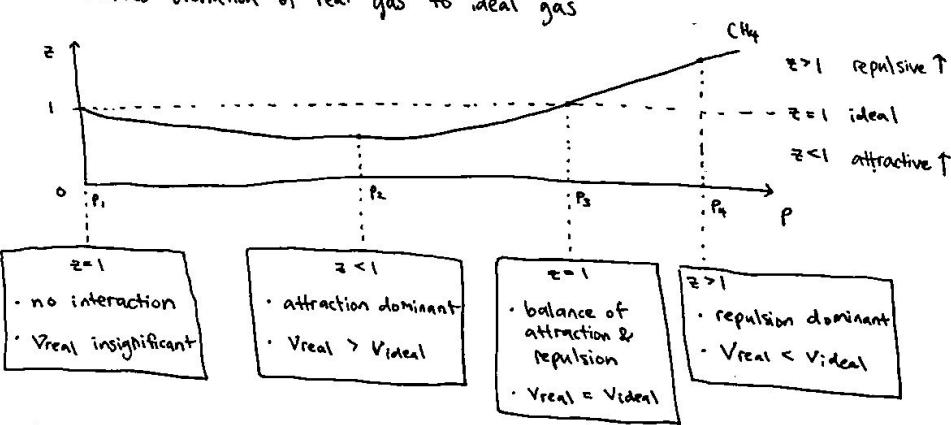
- Ideal gas law - assume molecules are infinitesimally small, hard round spheres that occupy negligible volume and exert force upon each other only through collisions

- no volume
 - no intermolecular forces between gas
- } high T, low P

$$P_v = RT$$

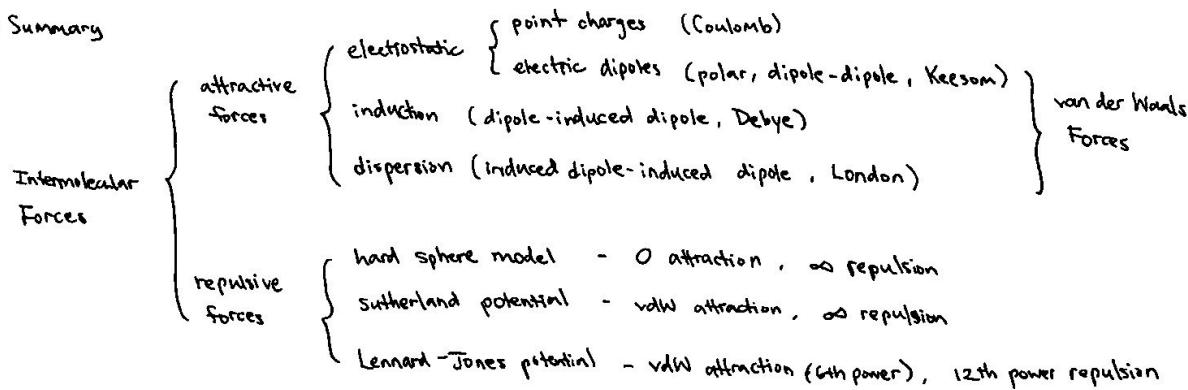
> Compressibility factor - measures deviation of real gas to ideal gas

$$\cdot z = \frac{P_v}{RT}$$



<< Intermolecular Forces & Potentials

→ Summary



» Intermolecular Potentials

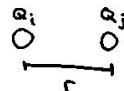
- For conservative forces, the potential is its negative integral

$$\Gamma_{ij}(\vec{r}) = - \int \mathbf{F}_{ij} d\vec{r} \quad \leftrightarrow \quad \mathbf{F}_{ij} = - \vec{\nabla} \Gamma_{ij}$$

→ Attractive Potentials

→ Coulomb Interaction (electrostatic, point charges)

$$\Gamma_{ij}(r) = \frac{Q_i Q_j}{4\pi\epsilon_0} \frac{1}{r} \quad (\text{SI})$$

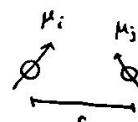


$$\Gamma_{ij}(r) = \frac{Q_i Q_j}{r} \quad (\text{CGS})$$

→ Dipole-Dipole Interaction (polar, electric dipole, Keesom)

- orientational

$$\Gamma_{ij}(r) = - \frac{(2)}{3} \frac{\mu_i^2 \mu_j^2}{(4\pi\epsilon_0)^2 kT} \frac{1}{r^6} \quad (\text{SI})$$

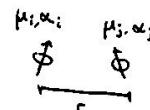


$$\phi = \oplus$$

$$\Gamma_{ij}(r) = - \frac{(2)}{3} \frac{\mu_i^2 \mu_j^2}{kT} \frac{1}{r^6} \quad (\text{CGS})$$

→ Dipole-Induced Dipole Interaction (induction, Debye)

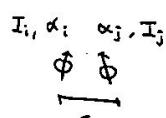
$$\Gamma_{ij}(r) = - \frac{(\alpha_i \mu_j^2 + \alpha_j \mu_i^2)}{(4\pi\epsilon_0)^2} \frac{1}{r^6} \quad (\text{SI})$$



$$\Gamma_{ij}(r) = - \frac{\alpha_i \mu_j^2 + \alpha_j \mu_i^2}{r^6} \quad (\text{CGS})$$

→ Induced-Dipole-Induced-Dipole Interaction (dispersion, London)

$$\Gamma_{ij}(r) \approx - \frac{3}{2} \frac{\alpha_i \alpha_j}{(4\pi\epsilon_0)^2} \frac{I_i I_j}{I_i + I_j} \frac{1}{r^6} \quad (\text{SI})$$



$$\Gamma_{ij}(r) \approx - \frac{3}{2} \frac{\alpha_i \alpha_j}{r^6} \frac{I_i I_j}{I_i + I_j} \quad (\text{CGS})$$

→ van der Waals Interaction

- Sum of Keesom, Debye, London interactions, all $1/r^6$ potentials

$$\Gamma_{ij}^{\text{vdW}} = \Gamma_{ij}^K + \Gamma_{ij}^D + \Gamma_{ij}^L = - \frac{C_{\text{vdW}}}{r^6}$$

$$C_{\text{vdW}} = C^K + C^D + C^L$$

→ Attractive Potentials (cont.)

→ Same Species Simplifications ($i=j$)

$$\left. \begin{aligned} C^F &= \frac{(z)}{3} \frac{\mu_i^4}{kT} \frac{1}{(4\pi\epsilon_0)^2} \\ C^D &= 2\alpha_i \mu_i^2 \frac{1}{(4\pi\epsilon_0)^2} \\ C^L &= \frac{3}{4} \alpha_i^2 I_i \frac{1}{(4\pi\epsilon_0)^2} \end{aligned} \right\} \text{(SI)}$$

→ Properties & Units

> vacuum permittivity $\epsilon_0 = 8.854 \times 10^{-12} \text{ C}^2/\text{N}\text{m}^2$

> Boltzmann constant $k_B = 1.38 \times 10^{-23} \text{ J/K}$

> Dipole moment μ

$$\cdot 1D = 3.336 \times 10^{-30} \text{ Cm} = 10^{-18} \sqrt{\text{Jerg cm}^3}$$

> Polarizability α

$$\cdot \text{SI: } \frac{\alpha_i}{4\pi\epsilon_0} \text{ fm}^3 \text{ Å} = 10^{-10} \text{ m}$$

$$\cdot \text{CGS: } \alpha_i \text{ fm}^3 10^{-25} \text{ cm}^3$$

> Ionization energy I

$$\cdot 1 \text{ eV} = 1.602 \times 10^{-19} \text{ J} = 1.602 \times 10^{-12} \text{ erg}$$

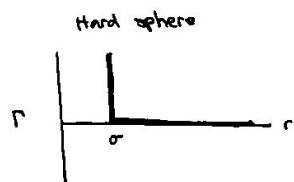
$$\cdot 1 \text{ J} = 10^7 \text{ erg}$$

→ Repulsive Potentials

→ Hard Sphere Model

• no attraction, ∞ repulsion

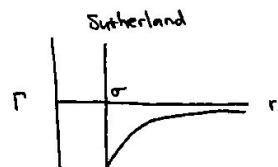
$$\boxed{\Gamma = \begin{cases} 0 & r > \sigma \\ \infty & r \leq \sigma \end{cases}} \quad (\text{Note, } \sigma = 0 \text{ for ideal gas})$$



→ Sutherland Model

• vdW attraction, ∞ repulsion

$$\boxed{\Gamma = \begin{cases} -\frac{C_{vdW}}{r^6} & r > \sigma \\ \infty & r \leq \sigma \end{cases}}$$



→ Lennard-Jones Potential

• vdW attraction, 12^{th} power empirical repulsion

$$\cdot \Gamma = \frac{C_{rep}}{r^{12}} - \frac{C_{vdW}}{r^6}$$

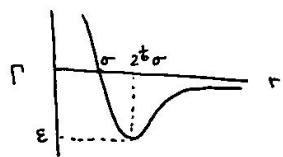
$$C_{rep} = 4\epsilon \sigma^{12}$$

$$C_{vdW} = 4\epsilon \sigma^6$$

$$\boxed{\Gamma = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right]}$$

• ϵ - energy of potential well

• σ - collision diameter



↔ Principle of Corresponding States

- Dimensionless potential energy is the same for all species
- Compressibility factor for diff. fluids exhibit similar behavior as function of reduced temp, pressure.
- > All fluids deviate from ideal gas behavior about the same (same compressibility factor) when compared at the same reduced temperature and pressure.

$$\cdot T_r = \frac{T}{T_c}$$

$$\cdot P_r = \frac{P}{P_c}$$

- Nonpolar molecules (esp. nonspherical ones) deviate from the principle.
• need correction factor
- > Pitzer acentric factor ω - accounts for nonsphericity of molecules
- $\omega = -1 - \log_{10} [P_r^{\text{sat}} (T_r = 0.7)]$
- $\omega \approx 0$ for simple molecules

↔ Equations of State

→ Cubic EOS

→ van der Waals EOS

- relax assumptions from ideal gas law

• account for molecule's volume with b : $P = \frac{RT}{V-b}$

• account for intermolecular force with a : $P = \frac{RT}{V-b} - \frac{a}{V^2}$
(a decrease in P with IMF)

$$> P = \frac{RT}{V-b} - \frac{a}{V^2}$$

$$PV^3 - (RT + Pb)V^2 + av - ab = 0$$

cubic form

• $T > T_c$, supercritical, one real root

• $T < T_c$, largest root as V_r , smallest root as V_e .

• By principle of corresponding states, vdW EOS at critical pt gives

$$a = \frac{27}{64} \frac{(RT_c)^2}{P_c}$$

$$b = \frac{RT_c}{8P_c}$$

, although experimental data is preferred

$$Z_c = \frac{P_c V_c}{R T_c} = \frac{3}{8}$$

$$\cdot P_r = \frac{8T_r}{3V_r - 1} - \frac{3}{V_r^2}$$

reduced form

<< Equations of State (cont.)

→ Cubic EOS (cont.)

→ Redlich - Kwong EOS

$$\rightarrow \boxed{P = \frac{RT}{v-b} - \frac{a}{\sqrt{v(v+b)}}}$$

$$a = \frac{0.42748 R^2 T_c^{2.5}}{P_c}, \quad b = \frac{0.08664 R T_c}{P_c}$$

$$\cdot z_c = \frac{1}{3}$$

→ Peng - Robinson EOS

$$\rightarrow \boxed{P = \frac{RT}{v-b} - \frac{a \alpha(T)}{v(v+b) + b(v-b)}}$$

$$a = 0.45724 \frac{R^2 T_c^2}{P_c}, \quad b = 0.07780 \frac{R T_c}{P_c}$$

$$\alpha(T) = [1 + K(1 - \sqrt{T_c})]^2$$

$$K = 0.37464 + 1.54226 \omega - 0.26992 \omega^2$$

→ Virial EOS

• With statistical mechanics, virial EOS assesses deviation from ideal behavior using power series expansion

$$\boxed{z = \frac{Pv}{RT} = 1 + \frac{B}{v} + \frac{C}{v^2} + \frac{D}{v^3} + \dots}$$

↓ ↓ ↑ ↓ ↓
 1-body 2-body 3-body interactions etc.
 no interaction ideal gas

• Second virial coefficient B

$$\cdot B = \frac{RT_c B_r}{P_c}$$

$$\cdot B_r = B^{(0)} + \omega B^{(1)}$$

$$\cdot B^{(0)} = 0.083 - \frac{0.422}{T_c^{1/6}}$$

$$\cdot B^{(1)} = 0.139 - \frac{0.172}{T_c^{1/2}}$$

* Benedict - Bridgeman EOS and
Benedict - Webb - Rubin EOS are
specific types of virial EOS

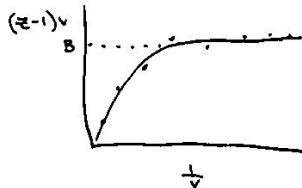
EX1 Determine B for water from steam table

$$z = \frac{Pv}{RT} = 1 + \frac{B}{v} + \frac{C}{v^2} + \dots$$

$$z - 1 = \frac{B}{v} + \frac{C}{v^2} + \dots$$

$$(z-1)v = B + \frac{C}{v} + \dots$$

Plot $(z-1)v$ vs $1/v$ using steam table values



<< Generalized Compressibility Charts

- Principle of corresponding states gives relation between \bar{z} and T_r, P_c .
- Account for diff. type of molecules,

$$\bar{z} = \bar{z}^{(0)} + \omega \bar{z}^{(1)}$$

Simple molecules Non-spherical correction

- Based on Lee-Kesler EOS, use Fig 4.13, 4.14, Appendix C.1, C.2

<< EOS Parameters for Mixtures

- Mixing rules - relate properties of mixtures to properties of pure substances
- Cubic EOS

- Weight attractive interactions with their relative proportions

$$a_{\text{mix}} = y_1^2 a_1 + 2y_1 y_2 a_{12} + y_2^2 a_2$$

binary mixture

$$a_{12} = \sqrt{a_1 a_2} (1 - k_{12})$$

k_{12} - binary interaction parameter

- Average excluded volume

$$b_{\text{mix}} = y_1 b_1 + y_2 b_2$$

binary mixture

$$b_{\text{mix}} = \sum_i y_i b_i$$

generally

→ Virial EOS

- Weight virial coeff (interactions)

$$B_{\text{mix}} = y_1^2 B_{11} + 2y_1 y_2 B_{12} + y_2^2 B_{22}$$

binary mixture

$$B_{\text{mix}} = \sum_i \sum_j y_i y_j B_{ij}$$

$$C_{\text{mix}} = \sum_i \sum_j \sum_k y_i y_j y_k C_{ijk}$$

→ Corresponding State

- Use pseudocritical properties

$$T_{pc} = \sum_i y_i T_{ci}$$

$$P_{pc} = \sum_i y_i T_{ci}$$

$$\omega_{pc} = \sum_i y_i \omega_{ci}$$

<< EOS for Liquids & Solids

- Volume of condensed phases has weak T dependence and P dependence

- use 1st term of Taylor expansion

> thermal expansion coefficient $\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$ [K⁻¹]

> isothermal compressibility $\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$ [Pa⁻¹]

- Benedict-Webb-Rubin EOS works for liquid

- Rackett equation

$$V^{L,\text{sat}} = \frac{RT_c}{P_c} (0.29056 - 0.08715 \omega)^{(1 + (1 - T_r)^{\frac{2}{3}})}$$

↔ Types of Thermo Properties

> measured properties - P, v, T, composition

> fundamental properties { u 1st law: conservation of energy
 s 2nd law: directionality of nature

> derived properties { $h = u + Pv$
 $a = u - Ts$
 $g = h - Ts$

↔ Thermo Relations

> total differential - by state postulate, intensive property can be written in terms of partial derivative of two independent intensive properties

- $z = z(x, y)$

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

- exact, path independent

→ Fundamental Property Relations

- assumed closed system with reversible Pv work

- $du = S_{rev} + S_{irrev} = Tds - Pdv$

- $dh = du + d(Pv) = Tds + v dP$

- $da = du - d(Ts) = -sdT - Pdv$

- $dg = dh - d(Ts) = -sdT + v dP$

- Assumptions relaxed because all state properties

- path independent (rev, irrev ok)

$$\begin{aligned} du &= Tds - Pdv \\ dh &= Tds + v dP \\ da &= -sdT - Pdv \\ dg &= -sdT + v dP \end{aligned}$$

→ Fundamental Grouping Relations

- Compare total differential with fundamental property relation

- $du(s, v) = \left(\frac{\partial u}{\partial s}\right)_v ds + \left(\frac{\partial u}{\partial v}\right)_s dv$

$$du = Tds - Pdv$$

- $dh(s, P) = \left(\frac{\partial h}{\partial s}\right)_P ds + \left(\frac{\partial h}{\partial P}\right)_s dP$

$$dh = Tds + v dP$$

- $da(T, v) = \left(\frac{\partial a}{\partial T}\right)_v dT + \left(\frac{\partial a}{\partial v}\right)_T dv$

$$da = -sdT - Pdv$$

- $dg(T, P) = \left(\frac{\partial g}{\partial T}\right)_P dT + \left(\frac{\partial g}{\partial P}\right)_T dP$

$$dg = -sdT + v dP$$

$$\left. \begin{aligned} T &= \left(\frac{\partial u}{\partial s}\right)_v, & -P &= \left(\frac{\partial u}{\partial v}\right)_s \\ T &= \left(\frac{\partial h}{\partial s}\right)_P, & V &= \left(\frac{\partial h}{\partial P}\right)_s \\ -S &= \left(\frac{\partial a}{\partial T}\right)_v, & -P &= \left(\frac{\partial a}{\partial v}\right)_T \\ -S &= \left(\frac{\partial g}{\partial T}\right)_P, & V &= \left(\frac{\partial g}{\partial P}\right)_T \end{aligned} \right\}$$

> fundamental grouping { $\{u, s, v\}$
 $\{h, s, P\}$
 $\{a, T, v\}$
 $\{g, T, P\}$

<< Thermo Relations

→ Maxwell's Relations

- Take second derivative of fundamental grouping relation
- Order of differentiation does not matter

$$\boxed{\begin{aligned} \left(\frac{\partial T}{\partial v}\right)_S &= - \left(\frac{\partial P}{\partial S}\right)_V, & \left(\frac{\partial S}{\partial V}\right)_T &= \left(\frac{\partial P}{\partial T}\right)_V \\ \left(\frac{\partial T}{\partial P}\right)_S &= \left(\frac{\partial v}{\partial S}\right)_P, & \left(\frac{\partial v}{\partial P}\right)_T &= - \left(\frac{\partial S}{\partial T}\right)_P \end{aligned}}$$

→ Useful Mathematical Relations

> chain rule $\boxed{\left(\frac{\partial z}{\partial x}\right)_a = \left(\frac{\partial z}{\partial y}\right)_a \left(\frac{\partial y}{\partial x}\right)_a}$

> inversion rule $\boxed{\left(\frac{\partial x}{\partial y}\right)_z = \left(\frac{\partial y}{\partial x}\right)_z^{-1}}$

> cyclic relation
(triple product rule) $\boxed{\left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z = -1}$

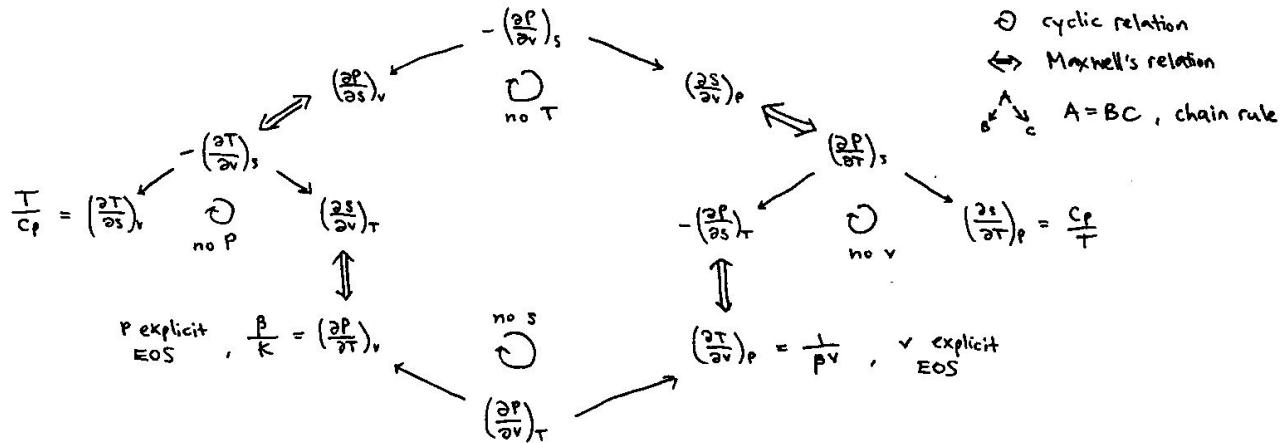
→ Thermodynamic Web

> thermal expansion coefficient $\boxed{\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P}$

> isothermal compressibility $\boxed{\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T}$

> constant volume heat capacity $\boxed{C_V = \left(\frac{\partial S}{\partial T}\right)_V T = \left(\frac{\partial U}{\partial T}\right)_V}$

> constant pressure heat capacity $\boxed{C_P = \left(\frac{\partial S}{\partial T}\right)_P T = \left(\frac{\partial H}{\partial T}\right)_P}$



<< Real Gas Heat Capacity

$$\cdot C_v = \left(\frac{\partial U}{\partial T}\right)_v = T \left(\frac{\partial S}{\partial T}\right)_v$$

$$\cdot C_p = \left(\frac{\partial H}{\partial T}\right)_p = T \left(\frac{\partial S}{\partial T}\right)_p$$

$$\cdot C_v^{\text{real}} = C_v^{\text{ideal}} + \int_{V_{\text{ideal}}}^{V_{\text{real}}} T \left(\frac{\partial P}{\partial T}\right)_v dV$$

$$\cdot C_p^{\text{real}} = C_p^{\text{ideal}} - \int_{P_{\text{ideal}}}^{P_{\text{real}}} T \left(\frac{\partial V}{\partial T}\right)_P dP$$

<< Entropy change

$$\cdot dS = \frac{C_v}{T} dT + \left(\frac{\partial P}{\partial T}\right)_v dV \quad (T, V)$$

$$\cdot dS = \frac{C_p}{T} dT - \left(\frac{\partial V}{\partial T}\right)_P dP \quad (T, P)$$

<< Internal Energy change

$$\cdot dU = C_v dT + [T \left(\frac{\partial P}{\partial T}\right)_V - P] dV \quad (T, V)$$

<< Enthalpy change

$$\cdot dH = C_p dT + [-T \left(\frac{\partial V}{\partial T}\right)_P + V] dP \quad (T, P)$$

<< Properties in terms of (T, P)

$$\cdot dS = \frac{C_p}{T} dT - \beta V dP$$

$$\cdot dV = \beta V dT - \kappa V dP$$

$$\cdot dU = (C_p - \beta P_V) dT + (\kappa P_V - \beta V T) dP$$

$$\cdot dH = (C_p - \beta P_V) dT + V dP$$

$$\cdot dA = -S dT + (\kappa P_V - \beta V T) dP$$

$$\cdot dG = -S dT + V dP$$

$$\Rightarrow \beta = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P \stackrel{\text{ideal gas}}{=} \frac{R}{P_V} = \frac{1}{T}$$

$$\Rightarrow \kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T \stackrel{\text{ideal}}{=} \frac{\kappa_T}{P^2 V} = \frac{1}{P}$$

⇒ Departure Function

> departure function - difference between real and ideal property

$$\cdot \Delta h_{\text{dep}} = h^{\text{real}} - h^{\text{ideal}}$$

→ Enthalpy Departure Function

$$> \boxed{\Delta h_{\text{dep}} = h^{\text{real}} - h^{\text{ideal}}}$$

$$> \boxed{\frac{\Delta h_{\text{dep}}}{RT_c} = \left[\frac{\Delta h_{\text{dep}}}{RT_c} \right]^{(0)} + w \left[\frac{\Delta h_{\text{dep}}}{RT_c} \right]^{(1)}}$$

General departure

Ex1 Derive an expression for enthalpy departure and total Δh

$$\cdot \Delta h_{T,P} = -\Delta h_{T,P_1}^{\text{dep}} + \Delta h_{T_1 \rightarrow T_2}^{\text{ideal}} + \Delta h_{P_1 \rightarrow P_2}^{\text{ideal}} + \Delta h_{T_1 \rightarrow T_2}^{\text{dep}}$$

$$\cdot \Delta h_{T_1 \rightarrow T_2}^{\text{ideal}} = \int_{T_1}^{T_2} c_p dT$$

$$\cdot \Delta h_{P_1 \rightarrow P_2}^{\text{ideal}} = 0 \quad (h = h(T))$$

$$\cdot \Delta h_{T,P}^{\text{dep}} = h_{T,P}^{\text{real}} - h_{T,P}^{\text{ideal}}$$

$$= (h_{T,P}^{\text{real}} - h_{T,P=0}^{\text{ideal}}) - (h_{T,P}^{\text{ideal}} - h_{T,P=0}^{\text{ideal}}) \quad (\text{constant } T)$$

$$= \int_{P_1}^P c_p dT + \int_{T_1}^T \left[-T \left(\frac{\partial v}{\partial T} \right)_P + v \right] dP \quad (\text{enthalpy change, constant } T)$$

$$= \int_{P_1}^P \left[-T \left(\frac{\partial z}{\partial T} \right)_P + \frac{zRT}{P} \right] dP \quad v = \frac{zRT}{P}$$

$$= \int_{P_1}^P \left[-T \left[\frac{\partial R}{P} + \frac{R}{P} \left(\frac{\partial z}{\partial T} \right)_P \right] + \frac{zRT}{P} \right] dP \quad \text{chain rule on } z, T$$

$$\boxed{\Delta h_{T,P}^{\text{dep}} = \int_{P_1}^P \left[-\frac{RT^2}{P} \left(\frac{\partial z}{\partial T} \right)_P \right] dP}$$

$$\frac{\Delta h_{\text{dep}}}{RT_c} = T_c^2 \int_{P_1}^P -\frac{1}{P} \left(\frac{\partial z}{\partial T} \right)_P dP$$

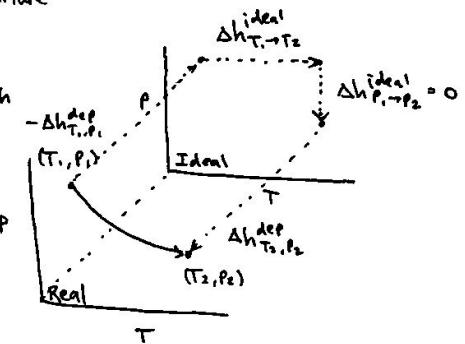
in reduced form

$$\cdot \Delta h_{T,P} = - \int_{P_1}^{P_2} -\frac{RT^2}{P} \left(\frac{\partial z}{\partial T} \right)_P dP + \int_{T_1}^{T_2} c_p dT + \int_{P_1}^{P_2} -\frac{RT^2}{P} \left(\frac{\partial z}{\partial T} \right)_P dP$$

→ Entropy Departure Function

$$> \boxed{\Delta s_{\text{dep}} = s^{\text{real}} - s^{\text{ideal}}}$$

$$> \boxed{\frac{\Delta s_{\text{dep}}}{R} = \left[\frac{\Delta s_{\text{dep}}}{R} \right]^{(0)} + w \left[\frac{\Delta s_{\text{dep}}}{R} \right]^{(1)}}$$



$$v = \frac{zRT}{P}$$

<< Joule-Thompson Expansion

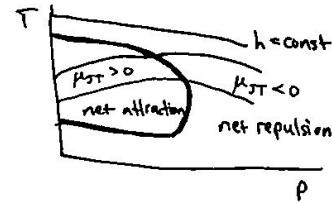
- > Joule-Thompson effect - a gas that suddenly expands without work or heat transfer cools
 - all real gases (except He, He) cools upon such expansion
 - throttling device, expansion valve

$$\left. \begin{array}{l} q = 0 \\ w_s = 0 \end{array} \right\} \boxed{\Delta h = 0} \text{ isenthalpic}$$

- > Joule-Thompson coefficient - measures change in T as P changes at constant h

$$\boxed{\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_h}$$

- > Boyle temperature - T at which $\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_h = 0$ at given pressure



Ex2 Derive an expression for μ_{JT} .

$$dh = c_p dT + [-T \left(\frac{\partial v}{\partial T}\right)_p + v] dP$$

$$0 = c_p dT + [-T \left(\frac{\partial v}{\partial T}\right)_p + v] dP \quad (\Delta h = 0)$$

$$\boxed{\left(\frac{\partial T}{\partial P}\right)_h = \frac{T \left(\frac{\partial v}{\partial T}\right)_p + v}{c_p} = \frac{T \left(\frac{\partial v}{\partial T}\right)_p + v}{c_p^{\text{ideal}} - \int_{P_{\text{ideal}}}^{P_{\text{real}}} T \left[\frac{\partial^2 v}{\partial T^2}\right]_p dP}} \quad (\text{real } c_p)$$

<< Gibbs Free Energy & 2nd Law

- describe system equilibrium using system properties
- consider closed system at mechanical & thermal eqm (constant T, P)

1st law : $dU = \delta Q + \delta W$

$$dU = \delta Q - PdV$$

$$\delta Q = dU + d(PV)$$

$$(dP=0 \rightarrow d(PV) = \cancel{\delta PV} + PdV = PdV)$$

$$\delta Q = dH$$

2nd law :

$$dS \geq \frac{\delta Q}{T}$$

$$0 \geq \delta Q - TdS$$

$$0 \geq dH - TdS$$

$$0 \geq dH - d(TS)$$

$$(dT=0 \rightarrow d(TS) = \cancel{\delta TS} + TdS = TdS)$$

$$0 \geq dg$$

> Gibbs free energy

$$g = h - TS$$

- For spontaneous process, Gibbs free energy decreases or stay constant at constant T, P

$$(dg)_{T,P} \leq 0$$

At equilibrium, $dg = 0$

<< Criteria of Chemical Equilibrium

$G = G^\alpha + G^\beta$

$$G = n^\alpha g^\alpha + n^\beta g^\beta$$

$$dG = \cancel{n^\alpha dg^\alpha} + g^\alpha dn^\alpha + \cancel{n^\beta dg^\beta} + g^\beta dn^\beta$$

$$0 \geq g^\alpha dn^\alpha + g^\beta dn^\beta$$

$$0 \geq (g^\alpha - g^\beta) dn^\alpha$$

$$dn^\alpha = -dn^\beta \text{ in closed sys}$$

- If $g^\alpha > g^\beta$, system evolves to pure β

- If $g^\alpha < g^\beta$, system evolves to pure α

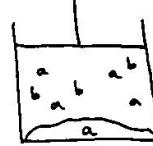
- If $g^\alpha = g^\beta$, system at chemical equilibrium

== Competition of Energy & Entropy in Phase Eqm

- $g = h - Ts$
- at diff T, g may have diff values
- at diff composition, g also have diff values of h and s

Ex1 Analyze g dependence on x_a

- Consider closed system with ideal gas a and b at constant T, P.
- Perfect crystal of a coexist, but b cannot condense



- Enthalpy
 - ideal gas $h = h(T)$ does not contribute
 - $s \rightarrow v$ process increase h by bond breaking, being proportional to x_a

- Entropy
 - at $x_a \rightarrow 0$, s increases linearly due to large increase in configurations
 - at $x_a \rightarrow 1$, s has less increase because substantial amount of a already exist in gas phase.

- System is at eqm when

$$g_a^v = g_a^s \rightarrow dg_a = 0$$

== Clapeyron Equation

- Construct relation between saturation T and P of two phases α, β

- At saturation (eqm),

$$g_i^\alpha = g_i^\beta$$

$$g_i^\alpha = g_i^\beta$$

$$g_i^\alpha + dg_i^\alpha = g_i^\beta + dg_i^\beta$$

$$h_i^\alpha - Ts_i^\alpha = h_i^\beta - Ts_i^\beta$$

$$dg_i^\alpha = dg_i^\beta$$

$$\Delta S = \frac{\Delta h}{T}$$

$$v_i^\alpha dP - s_i^\alpha dT = v_i^\beta dP - s_i^\beta dT$$

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V}$$



> Clapeyron eqn

$$\boxed{\frac{dP}{dT} = \frac{\Delta h}{T \Delta V}}$$

<< Clausius-Clapeyron Equation

- Vapor-liquid equilibrium case of Clapeyron eqn

- assume negligible liquid molar volume $v^l \rightarrow 0$

- assume ideal gas $v^v = \frac{RT}{P}$

- Substitute in Clapeyron eqn

$$\frac{dp}{dT} = \frac{\Delta h}{T\Delta v}$$

$$\frac{dp_{\text{sat}}}{dT} = \frac{\Delta h_{\text{vap}}}{T(T-0)} = \frac{P_{\text{sat}}^{\text{vap}} \Delta h_{\text{vap}}}{RT^2}$$

$$\frac{dp_{\text{sat}}}{P_{\text{sat}}} = \frac{\Delta h_{\text{vap}} \Delta T}{RT^2}$$

> Clausius-Clapeyron eqn

$$\ln\left(\frac{P_2^{\text{sat}}}{P_1^{\text{sat}}}\right) = -\frac{\Delta h_{\text{vap}}}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$$

assume Δh_{vap} indep. of T

> Antoine's eqn

$$\ln(P^{\text{sat}}) = A - \frac{B}{T+C}$$

<< Properties of Mixtures

→ Partial Molar Properties

- mixtures has multiple species interactions, having diff properties than pure species

> extensive property - $K = K(T, P, n_1, n_2, \dots, n_m)$

> intensive property - $k = \frac{K}{n} = k(T, P, n_1, n_2, \dots, n_m)$

> partial molar property - $\bar{k}_i = \left(\frac{\partial K}{\partial n_i}\right)_{T, P, n_j \neq i}$

- at constant T, P

- with respect to number of moles, not mole fraction

- $dK = \left(\frac{\partial K}{\partial T}\right)_{P, n_i} dT + \left(\frac{\partial K}{\partial P}\right)_{T, n_i} dP + \sum \left(\frac{\partial K}{\partial n_j}\right)_{T, P, n_j \neq i} dn_j$

$$dK = \left(\frac{\partial K}{\partial T}\right)_{P, n_i} dT + \left(\frac{\partial K}{\partial P}\right)_{T, n_i} dP + \sum \bar{k}_i dn_i \quad \text{partial molar property}$$

$$dK = \sum \bar{k}_i dn_i$$

assume constant T, P

$$K = \sum n_i \bar{k}_i$$

$$k = \sum x_i \bar{k}_i \quad \text{weighted avg}$$

→ Physical Interpretation of Partial Molar Properties \bar{k}_i

- \bar{k}_i represents species i 's contribution to total solution property K
- intensive property of individual species in mixture (with others)
- k_i represents intensive property of individual species in pure species (by itself)
- $\bar{k}_i - k_i$ compares species i 's behavior in mixture and pure species
 - $\bar{k}_i - k_i = 0$ for ideal behavior

<< Gibbs-Duhem Equation

- $K = \sum n_i \bar{k}_i$

$$dK = \sum [n_i d\bar{k}_i + \bar{k}_i dn_i]$$

- $dK = \sum \bar{k}_i dn_i$

$$\sum n_i d\bar{k}_i = 0$$

Gibbs-Duhem Eqn

[Ex1] Consider binary system a and b. Derive expression of \bar{V}_b in terms of x_a .

$$\sum n_i d\bar{V}_i = 0$$

$$n_a d\bar{V}_a + n_b d\bar{V}_b = 0$$

$$n_a \frac{d\bar{V}_a}{dx_a} + n_b \frac{d\bar{V}_b}{dx_b} = 0$$

$$\bar{V}_b = - \int \frac{x_a}{1-x_a} \left(\frac{d\bar{V}_a}{dx_a} \right) dx_a$$

<< Summary of Properties

→ Total solution properties

> properties of entire mixture

• extensive K • intensive k

→ Pure species properties

> property of species i as pure substance at T,P, phase of mixture• extensive K_i • intensive k_i

→ Partial Molar Properties

> contribution of species i to total mixture property• intensive \bar{K}_i • pure limit $\lim_{x_i \rightarrow 1} \bar{K}_i = k_i$ • infinite dilution $\lim_{x_i \rightarrow 0} \bar{K}_i = \bar{K}_i^\infty$

• interact only with unlike species

Property Changes of Mixing

- ΔK_{mix} - how much a property changes as result of mixing process

$$\Delta K_{\text{mix}} = K - \sum n_i k_i = \text{Mix} - \text{pure}$$

$$\Delta K_{\text{mix}} = \sum n_i (\bar{k}_i - k_i)$$

$$\Delta K_{\text{mix}} = k - \sum x_i k_i$$

$$\Delta K_{\text{mix}} = \sum x_i (\bar{k}_i - k_i)$$

- difference between partial molar property and pure species property
- how interaction between unlike species compare to like species

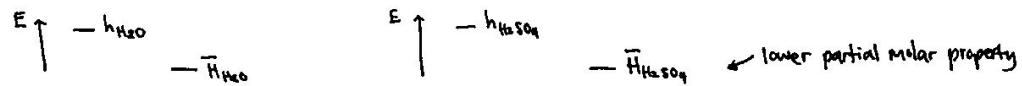
Enthalpy of Mixing Δh_{mix}

- Δh_{mix} - diff between energetic interactions of species in mixture and in pure species

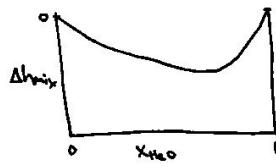
- $\Delta h_{\text{mix}} < 0$ mixture more stable, exothermic
- $\Delta h_{\text{mix}} > 0$ pure species more stable, endothermic
- $\Delta h_{\text{mix}} = 0$ identical interaction in mix & pure

Ex: Predict sign of Δh_{mix} of H_2O and H_2SO_4 mixing.

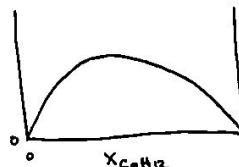
- After mixing, H_2SO_4 dissociates, allowing hydrogen bonding between H_2O and SO_4^{2-} , being energetically more favorable, so $\Delta h_{\text{mix}} < 0$, consistent with its exothermic nature.



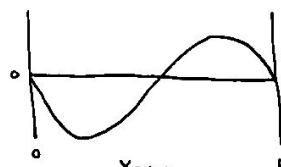
- Δh_{mix} depends on mixture composition and intermolecular interaction



$\text{H}_2\text{O} + \text{Methanol}$
- H-bonding and vdw attraction makes mixing favorable, so $\Delta h_{\text{mix}} < 0$



$\text{C}_6\text{H}_{12} + \text{toluene}$
- Dispersion interaction dominates, but strength of mixture is not as strong as in pure.
so $\Delta h_{\text{mix}} > 0$.



$\text{chloroform} + \text{methanol}$
- At low X_{CHCl} , H-bonding dominates, $\Delta h_{\text{mix}} < 0$
- At higher X_{CHCl} , dispersion effect dominates, where its mixture strength is less than in pure, so $\Delta h_{\text{mix}} > 0$

<< Property Changes of Mixing

→ Enthalpy of Solution $\tilde{\Delta h_s}$

> enthalpy of solution - enthalpy change when 1 mol pure solute is dissolved in n mol pure solvent

$$\cdot \tilde{\Delta h_s} = \frac{\Delta h_{mix}}{x_1} = \Delta h_{mix}(n+1)$$

$$\underbrace{\frac{J}{\text{mol solute}}}_{\tilde{\Delta h_s}} \times \underbrace{\frac{1 \text{ mol solute}}{(n+1) \text{ mol soln}}}_{x_1} = \underbrace{\frac{J}{\text{mol soln}}}_{\Delta h_{mix}}$$

$$\cdot \Delta h_{mix} = \frac{\tilde{\Delta h_s}}{1+n} = \tilde{\Delta h_s} x_1$$

→ Entropy of Mixing ΔS_{mix} > ΔS_{mix} - change in # of configurations caused by mixing process

- $\Delta S_{mix} > 0$ always true
- always more configuration in mixture than pure
- ideal gas at constant T, P

$$\cdot \Delta S_{mix} = -R \sum y_i \ln y_i$$

- $\Delta h_{mix} = 0$
 - $\Delta V_{mix} = 0$
- } no intermolecular interaction

> regular solution - liquid solution that mix completely randomly

- follow ideal gas $\Delta S_{mix} = -R \sum y_i \ln y_i$

- vdW liquids form regular soln

- deviation from regular soln
 - significant diff size of species
 - association & solvation occurs

→ Partial Molar Property change of Mixing

$$\begin{aligned} > \overline{\Delta K}_{mix,i} &= \left(\frac{\partial \Delta K_{mix,i}}{\partial n_i} \right)_{T,P,n_j \neq i} \\ &= \left(\frac{\partial K}{\partial n_i} \right)_{T,P,n_j \neq i} - \left(\frac{\partial \sum (m_k k_i)}{\partial n_i} \right)_{T,P,n_j \neq i} \end{aligned}$$

$$\cdot \overline{\Delta K}_{mix,i} = K_i - k_i$$

<< Determination of Partial Molar Properties

→ Analytical Method

> function of composition - analytical expression for total solution property K

• Use definition of partial molar property to differentiate function of composition

Ex1 Derive \bar{V}_i for binary mixture of 1 and 2 using virial EOS.

• Virial EOS

$$z = \frac{PV}{RT} = 1 + B'P \quad \text{truncated}$$

$$V = \frac{RT}{P} + B'RT$$

$$V = \frac{RT}{P} + B \quad B' = \frac{B}{RT}$$

$$V = \frac{RT}{P} + y_1^2 B_{11} + 2y_1 y_2 B_{12} + y_2^2 B_{22} \quad \text{mixing rule}$$

• Extensive property

$$V = (n_1 + n_2) \frac{RT}{P} + \frac{n_1^2 B_{11} + 2n_1 n_2 B_{12} + n_2^2 B_{22}}{n_1 + n_2}$$

• Partial molar property

$$\begin{aligned} \bar{V}_1 &= \left(\frac{\partial V}{\partial n_1} \right)_{T, P, n_2} \\ &= \frac{RT}{P} + \frac{2n_1 B_{11} + 2n_2 B_{12}}{n_1 + n_2} - \frac{n_1^2 B_{11} + 2n_1 n_2 B_{12} + n_2^2 B_{22}}{(n_1 + n_2)^2} \\ &= \frac{RT}{P} + (y_1^2 + 2y_1 y_2) B_{11} + 2y_1^2 B_{12} - y_2^2 B_{22} \end{aligned}$$

• Similarly,

$$\bar{V}_2 = \frac{RT}{P} - y_1^2 B_{11} + 2y_1^2 B_{12} + (y_2^2 + 2y_1 y_2) B_{22}$$

Ex2 Derive pure species molar volume V_i

$$\lim_{x_i \rightarrow 1} \bar{V}_i = \frac{RT}{P} + B_{ii}$$

$$\lim_{x_i \rightarrow 1} \bar{V}_i = \frac{RT}{P} + B_{ii}$$

Ex3 Derive volume change of mixing ΔV_{mix}

$$\Delta V_{\text{mix}} = V - (y_1 V_1 + y_2 V_2)$$

$$= \left(\frac{RT}{P} + y_1^2 B_{11} + 2y_1 y_2 B_{12} + y_2^2 B_{22} \right) - \left(y_1 \left(\frac{RT}{P} + B_{11} \right) + y_2 \left(\frac{RT}{P} + B_{22} \right) \right)$$

$$= 2y_1 y_2 \left(B_{12} - \frac{B_{11} + B_{22}}{2} \right)$$

• ΔV_{mix} determined by strength of unlike interaction B_{12} and avg of like interactions. $\underline{\underline{B_{11} + B_{22}}}$

c) Determination of Partial Molar Properties

→ Analytic Method (cont.)

Ex4 Derive general expression of \bar{K}_i with $\Delta K_{\text{mix},i}$ for binary mixture

$$k = x_1 k_1 + x_2 k_2 + \Delta K_{\text{mix}}$$

$$K = n_1 k_1 + n_2 k_2 + \Delta K_{\text{mix}}$$

$$\bar{K}_i = \left(\frac{\partial K}{\partial n_i} \right)_{T,P,n_{\text{tot}}} = k_i + \left(\frac{\partial \Delta K_{\text{mix}}}{\partial n_i} \right)_{T,P,n_{\text{tot}}}$$

$$\boxed{\bar{K}_i = k_i + \Delta K_{\text{mix},i}}$$

, which is consistent with $\Delta K_{\text{mix},i} = \bar{K}_i - k_i$

→ Graphical Method

$$k = \sum x_i \bar{K}_i$$

$$k = x_1 \bar{K}_1 + x_2 \bar{K}_2$$

$$dk = x_1 d\bar{K}_1 + \bar{K}_1 dx_1 + x_2 d\bar{K}_2 + \bar{K}_2 dx_2$$

$$dk = x_1 d\bar{K}_1 + \bar{K}_1 dx_1 + (1-x_1) d\bar{K}_2 - \bar{K}_2 dx_1$$

$$dk = \bar{K}_1 dx_1 - \bar{K}_2 dx_2$$

$$x_2 = 1-x_1$$

$$dx_2 = -dx_1$$

$$\text{Gibbs-Duhem eqn: } \sum x_i d\bar{K}_i = 0$$

$$\boxed{\frac{dk}{dx_1} = \bar{K}_1 - \bar{K}_2}$$

⇒ slope of $k(x_1)$ is difference of partial molar property

$$x_1 \frac{dk}{dx_1} = x_1 \bar{K}_1 - x_1 \bar{K}_2$$

$$x_1 \frac{dk}{dx_1} = x_1 \bar{K}_1 - (1-x_1) \bar{K}_2$$

$$x_1 \frac{dk}{dx_1} = x_1 \bar{K}_1 + x_2 \bar{K}_2 - \bar{K}_2$$

$$x_1 \frac{dk}{dx_1} = k - \bar{K}_2$$

$$k = \sum x_i \bar{K}_i$$

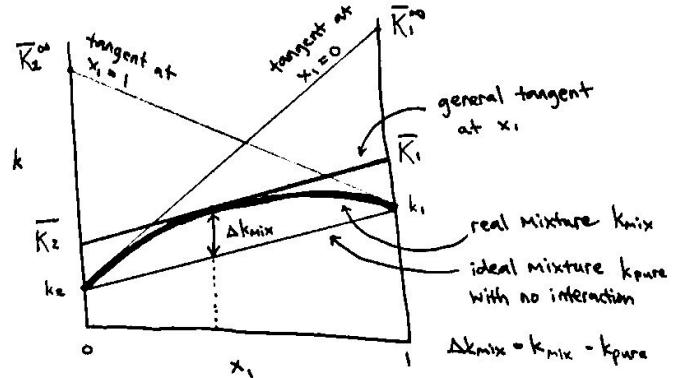
$$\boxed{k = x_1 \frac{dk}{dx_1} + \bar{K}_2}$$

⇒ \bar{K}_2 is intercept of tangent line of $k(x_1)$

$$\boxed{\bar{K}_2 = k - x_1 \frac{dk}{dx_1}}$$

• $\lim_{\substack{x_1 \rightarrow 0 \\ x_2 \rightarrow 1}} \bar{K}_2 = k$ (pure species)

• $\lim_{\substack{x_1 \rightarrow 1 \\ x_2 \rightarrow 0}} \bar{K}_2 = \bar{K}_2^{\infty}$ (infinite dilution)



$$\Delta K_{\text{mix}} = k_{\text{mix}} - k_{\text{pure}}$$

<< Relations among Partial Molar Properties

- Relations of regular properties apply to partial molar property.

[Ex5] Proof $\bar{H}_i = \bar{U}_i + PV_i$

$$H = U + PV$$

$$\left(\frac{\partial H}{\partial n_i}\right)_{T,P,n_j \neq i} = \left(\frac{\partial U}{\partial n_i}\right)_{T,P,n_j \neq i} + \left(\frac{\partial PV}{\partial n_i}\right)_{T,P,n_j \neq i}$$

$$\left(\frac{\partial H}{\partial n_i}\right)_{T,P,n_j \neq i} = \left(\frac{\partial U}{\partial n_i}\right)_{T,P,n_j \neq i} + P \left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_j \neq i}$$

$$\bar{H}_i = \bar{U}_i + P \bar{V}_i$$

Important partial molar gibbs free energy relations

$$\cdot \left(\frac{\partial \bar{G}_i}{\partial T}\right)_{P,n_i} = -\bar{S}_i$$

$$\cdot \left(\frac{\partial \bar{G}_i}{\partial P}\right)_{T,n_i} = \bar{V}_i$$

$$\cdot \left(\frac{\partial}{\partial T} \frac{\bar{G}_i}{T}\right)_{P,n_i} = -\frac{\bar{H}_i}{T^2}$$

<< Multicomponent Phase Equilibrium

→ Criteria of Chemical Equilibrium

$$\cdot dG = dG^\alpha + dG^\beta$$

$$0 = [-SdT + VdP + \sum \bar{G}_i dn_i]^\alpha + [-SdT + VdP + \sum \bar{G}_i dn_i]^\beta$$

$$0 = [\sum \bar{G}_i dn_i]^\alpha + [\sum \bar{G}_i dn_i]^\beta$$

$$0 = \sum (\bar{G}_i^\alpha - \bar{G}_i^\beta) dn_i$$

$$0 = \sum (\mu_i^\alpha - \mu_i^\beta) dn_i$$

$$\begin{aligned} dT^\alpha &= dT^\beta && \text{thermal eqn} \\ dP^\alpha &= dP^\beta && \text{mechanical eqn} \end{aligned}$$

$$dn_i^\alpha = -dn_i^\beta$$

$$\mu_i = \bar{G}_i$$

$$\boxed{\mu_i^\alpha = \mu_i^\beta} \quad \text{criteria of chem eqm}$$

→ chemical potential - $\boxed{\mu_i = \bar{G}_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j \neq i}}$

<< Multicomponent Equilibrium

→ T and P dependence of $\mu_i(T, P)$

• At eqm

$$\frac{\mu_i^x}{T} = \frac{\mu_i^p}{T}$$

$$\Delta \left[\left(\frac{\partial \frac{\mu_i}{T}}{\partial T} \right)_{P, x_i} dT + \left(\frac{\partial \frac{\mu_i}{T}}{\partial P} \right)_{T, x_i} dP + \left(\frac{\partial \frac{\mu_i}{T}}{\partial x_i} \right)_{T, P} dx_i \right] = 0$$

$$\Delta \left[\left(\frac{\partial \frac{\mu_i}{T}}{\partial T} \right)_{P, x_i} dT + \frac{1}{T} \left(\frac{\partial \mu_i}{\partial P} \right)_{T, x_i} dP + \frac{1}{T} \left(\frac{\partial \mu_i}{\partial x_i} \right)_{T, P} dx_i \right] = 0$$

$$\boxed{\Delta \left[-\frac{\bar{H}_i}{T^2} dT - \frac{\bar{V}_i}{T} dP + \frac{1}{T} \left[\frac{\partial \mu_i}{\partial x_i} \right]_{T, P} dx_i \right] = 0}$$

→ Ideal gas $\mu_i(T, P)$ with liquid

$$\cdot \bar{H}_i^v = h_i^v$$

$$\cdot \bar{V}_i^v = v_i^v = \frac{RT}{P}$$

$$\cdot \left(\frac{\partial \mu_i^v}{\partial x_i^v} \right)_{T, P} = \left(\frac{\partial g_i^v}{\partial x_i^v} \right)_{T, P} = \frac{RT}{y_i^v}$$

$$\frac{\mu_i^v}{T} = \frac{\mu_i^l}{T}$$

$$\frac{\mu_i^v}{T} = -\frac{h_i^v}{T^2} dT - R \frac{dP}{P} + R \frac{dx_i^v}{x_i^v}$$

$$-\frac{h_i^v}{T^2} dT - R \frac{dP}{P} + R \frac{dx_i^v}{x_i^v} = -\frac{\bar{H}_i^l}{T^2} dT + \frac{\bar{V}_i^l}{T} dP + \frac{1}{T} \left(\frac{\partial \mu_i^l}{\partial x_i^l} \right)_{T, P} dx_i^l$$

Defn of Fugacity

- chemical potential μ_i is hard to work with mathematically
- fugacity is developed inductively from specific to general case

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{T, n_i} = V_i$$

$$d\mu_i = V_i dP \quad * \text{Assume const. } T$$

$$\int_{\mu_i^0}^{\mu_i} d\mu_i = \int_{P^0}^P \left(\frac{\partial V}{\partial n_i}\right)_{T, P, n_j \neq i} dP \quad * \text{Ref state } T_{ref} = T^0 = T_{sys}$$

$$\mu_i - \mu_i^0 = \int_{P^0}^P \frac{RT}{P} dP \quad * \text{assume ideal gas } P_{ref} = P^0 = P_{low}$$

$$\mu_i - \mu_i^0 = RT \ln\left(\frac{P}{P^0}\right)$$

$$\mu_i - \mu_i^0 = RT \ln\left(\frac{P_i}{P_i^0}\right) \quad P_i = y_i P \quad \text{partial pressure}$$

problem with μ_i :

$$\lim_{x_i \rightarrow 0} \mu_i = -\infty \quad \text{infinite dilution}$$

$$\lim_{P_i \rightarrow 0} \mu_i = -\infty \quad \text{ideal gas}$$

> fugacity - tendency to escape, real gas analogous partial pressure at constant T

$$\boxed{\mu_i - \mu_i^0 = RT \left(\frac{f_i}{f_i^0}\right)}$$

$$\text{ref state } \hat{f}_i = 1$$

$$f_i^0 = y_i P^0 = y_i P_{low}$$

$$\boxed{\lim_{P \rightarrow 0} \left(\frac{f_i}{P_i}\right) = 1} \quad \text{ideal gas as ref state}$$

> fugacity coefficient - ratio of fugacity (real partial pressure) with ideal partial pressure

$$\boxed{\hat{f}_i = \frac{f_i}{P_i} = \frac{f_i}{y_i P}} = \frac{\text{real partial pressure}}{\text{ideal partial pressure}}$$

- $\hat{f}_i = 1$ for ideal gas or real gas with balanced attractive & repulsive force (as if ideal)
- $\hat{f}_i < 1$ dominant attractive force
- $\hat{f}_i > 1$ dominant repulsive force

> pure species fugacity

$$\boxed{\gamma_i - g_i^0 = RT \ln\left(\frac{f_i}{f_i^0}\right)}$$

$$\text{ref state } \gamma_i = 0$$

$$f_i^0 = P^0 = P_{low}$$

$$\boxed{\lim_{P \rightarrow 0} \left(\frac{f_i}{P}\right) = 1}$$

> pure species fugacity coefficient -

$$\boxed{\varphi_i = \frac{f_i}{P}}$$

↔ Criteria of Chemical Equilibrium (Fugacity version)

$$\mu_i^\alpha = \mu_i^P$$

$$\mu_i^{\alpha,0} + RT \ln\left(\frac{\hat{f}_i^\alpha}{\hat{f}_i^{\alpha,0}}\right) = \mu_i^{P,0} + RT \ln\left(\frac{\hat{f}_i^P}{\hat{f}_i^{P,0}}\right) \quad \text{def. of fugacity}$$

$$\mu_i^{\alpha,0} - \mu_i^{P,0} = RT \ln\left(\frac{\hat{f}_i^P}{\hat{f}_i^{P,0}}\right) - RT \ln\left(\frac{\hat{f}_i^\alpha}{\hat{f}_i^{\alpha,0}}\right)$$

$$\mu_i^{\alpha,0} - \mu_i^{P,0} = RT \ln\left(\frac{\hat{f}_i^P}{\hat{f}_i^{P,0}} \cdot \frac{\hat{f}_i^{\alpha,0}}{\hat{f}_i^\alpha}\right) \quad \text{log property}$$

$$\cancel{RT \ln\left(\frac{\hat{f}_i^{\alpha,0}}{\hat{f}_i^{P,0}}\right)} = \cancel{RT \ln\left(\frac{\hat{f}_i^{\alpha,0}}{\hat{f}_i^{P,0}}\right)} + RT \ln\left(\frac{\hat{f}_i^P}{\hat{f}_i^\alpha}\right) \quad \text{def. of fugacity}$$

$$\sigma = RT \ln\left(\frac{\hat{f}_i^P}{\hat{f}_i^\alpha}\right) \quad \text{log property}$$

$$\boxed{\hat{f}_i^\alpha = \hat{f}_i^P}$$

criterion of chemical eqm

↔ Fugacity in Vapor Phase

→ Single Component Pure Gas

• Reference State

$$\cdot T^0 = T_{sys}$$

$$\cdot P^0 = P_{low}$$

$$\cdot f^0 = r^0 = P_{low}$$

• Method of calculating fugacity

• Table of experimental data of h, s (steam table)

• Equation of state

• Generalized correlations

→ Fugacity from tables of h, s

Ex1 Find fugacity of saturated steam at 1 atm.

$$\begin{aligned} P &= 1 \text{ atm} & \hat{h} &= 26760 \text{ kJ/kg} & \hat{g} = \hat{h} - T\hat{s} &= -68.44 \text{ kJ/kg} \\ T &= 373.15 \text{ K} & \hat{s} &= 7.3548 \text{ kJ/kgK} \end{aligned}$$

$$\begin{aligned} P^0 &= 101.3 \text{ kPa} & \hat{h}^0 &= 2687.5 \text{ kJ/kg} & \hat{g}^0 = \hat{h}^0 - T\hat{s}^0 &= -464.83 \text{ kJ/kg} \\ T^0 &= 273.15 \text{ K} & \hat{s}^0 &= 8.4479 \text{ kJ/kgK} \end{aligned}$$

$$\hat{g}_i - \hat{g}_i^0 = RT \ln\left(\frac{\hat{f}_i}{\hat{f}_i^0}\right)$$

$$f_i = f_i^0 \exp\left(\frac{\hat{g} - \hat{g}^0}{RT}\right)$$

$$f_i = P^0 \exp\left(\frac{\hat{g} - \hat{g}^0}{RT}\right)$$

$$f_i = 99.73 \text{ kPa}$$

$$f_i^0 = P^0$$

$$\varphi_i = \frac{f_i}{P} = 0.984$$

<-- Fugacity in Vapor Phase

→ Single Component Pure Gas

→ Fugacity from EOS

- total differential

$$dg_i = v_i dP - s_i dT + \sum \bar{G}_i dn_i$$

$$dg_i = v_i dP$$

- def of fugacity

$$g_i - g_i^{\circ} = RT \ln \left(\frac{f_i}{f_i^{\circ}} \right)$$

equate

constant T
pure species, const. n_i

- fugacity from EOS

$$RT \ln \left(\frac{f_i}{f_i^{\circ}} \right) = \int_{P^{\circ}}^P v_i dP$$

$$f_i = P^{\circ} \exp \left[\frac{1}{RT} \int_{P^{\circ}}^P v_i dP \right]$$

with v-or-P-explicit EOS

→ Fugacity from generalized correlation

- fugacity from EOS

$$RT \ln \left(\frac{f_i}{f_i^{\circ}} \right) = \int_{P^{\circ}}^P v_i dP$$

$$\ln \left(\frac{f_i}{f_i^{\circ}} \right) = \int_{P^{\circ}}^P \frac{v_i}{RT} dP$$

$$\ln \left(\frac{f_i}{f_i^{\circ}} \right) - \int_{P^{\circ}}^P \frac{1}{P} dP = \int_{P^{\circ}}^P \frac{v_L}{RT} dP - \int_{P^{\circ}}^P \frac{1}{P} dP$$

$$\ln \left(\frac{f_i}{f_i^{\circ}} \cdot \frac{P^{\circ}}{P} \right) = \int_{P^{\circ}}^P \frac{v_L}{RT} - \frac{1}{P} dP$$

$$\ln \left(\frac{f_i}{P} \right) = \int_{P^{\circ}}^P \frac{z-1}{P} dP$$

$$f_i^{\circ} = P^{\circ}$$

$$\ln \varphi_i = \int_{P^{\circ}}^P (z-1) \frac{dP}{P}$$

$$\varphi_i = \frac{f_i}{P}$$

$$\ln \varphi_L = \int_{P_r^{\circ}}^{P_r} (z_i - 1) \frac{dP_r}{P_r}$$

reduced form

Lee-Kesler EOS chart

• Fig 7.1, 7.2, Appendix C.7, C.8

• $\log \varphi = \log \varphi^{(0)} + \omega \log \varphi^{(1)}$

• Fugacity in Vapor Phase

→ Multicomponent Mixture

• Reference State

$$\cdot T^{\circ} = T_{\text{sys}}$$

$$\cdot P^{\circ} = P_{\text{low}}$$

$$\cdot n_i^{\circ} = n_{i,\text{sys}}$$

$$\cdot f^{\circ} = P_i^{\circ} = y_i P^{\circ} = y_i P_{\text{low}}$$

- Method
 - EOS with mixing rules
 - Lewis fugacity rule (reduce to pure species)

→ Fugacity from EOS with mixing rules

$$\cdot \text{total differential } d\mu_i = d\bar{G}_i = \bar{V}_i dP - \bar{S}_i dT + \sum \bar{G}_j dn_j$$

$$d\mu_i = \bar{V}_i dP$$

$$\cdot \text{def of fugacity}$$

$$\mu_i - \mu_i^{\circ} = RT \ln \left(\frac{f_i}{f_i^{\circ}} \right) \quad \begin{cases} \text{const } T \\ \text{const } n_j \end{cases}$$

> fugacity from
v-explicit EOS

$$RT \ln \left(\frac{f_i}{f_i^{\circ}} \right) = \int_{P^{\circ}}^P \bar{V}_i dP$$

$$f_i = y_i P^{\circ} \exp \left[\frac{1}{RT} \int_{P^{\circ}}^P \bar{V}_i dP \right]$$

• rewrite expression for p-explicit EOS

• cyclic rule

$$\left(\frac{\partial V}{\partial n_i} \right)_{T,P} \left(\frac{\partial P}{\partial V} \right)_{T,n_i} \left(\frac{\partial n_i}{\partial T} \right)_{V,P} = -1$$

$$\left(\frac{\partial V}{\partial n_i} \right)_{T,P} \frac{dP}{dV} = - \left(\frac{\partial P}{\partial n_i} \right)_{T,V}$$

const T, n;
inverse rule

$$\left(\frac{\partial V}{\partial n_i} \right)_{T,P} dP = - \left(\frac{\partial P}{\partial n_i} \right)_{T,V} dV$$

> fugacity from
p-explicit EOS

$$RT \ln \left(\frac{f_i}{f_i^{\circ}} \right) = - \int_{V^{\circ}}^V \bar{P}_i dV$$

$$\hat{f}_i = y_i P^{\circ} \exp \left[\frac{1}{RT} \int_{V^{\circ}}^V \bar{P}_i dV \right]$$

$$V^{\circ} = \frac{nRT}{P^{\circ}}$$

→ Mixing rules (vdW)

$$\cdot a_{\text{mix}} = \sum y_i y_j a_{ij}$$

$$\cdot a_{ii} = a_i$$

$$\cdot a_{ij} = \sqrt{a_i a_j} (1 - k_{ij})$$

$$\cdot b_{\text{mix}} = \sum y_i b_i$$

• See pg 408 Table 7.1 for fugacity coeff from cubic EOS

<< Fugacity in Vapor Phase

→ Multicomponent Mixture (cont.)

→ Lewis Fugacity Rule

> Lewis fugacity rule - approximate fugacity coeff of species i in mixture by its pure species fugacity coeff.

$$\hat{\varphi}_i^v = \varphi_i^v$$

• approximates all interactions as i - i interactions (ideal mixture of real gas)

→ Level of Calculation Rigor

1. EOS with mixing rules

• i - j interactions

$$\hat{f}_i^v = y_i \hat{\varphi}_i^v P$$

2. Lewis fugacity rule

• i - i interactions

$$\hat{f}_i^v = y_i \varphi_i^v P = y_i f_i^v$$

assumptions
(valid regions)

- Ideal gas limit (low P , high T)
- Pure Species limit ($y_a \gg y_b$)
- Similar interactions ($a_{ab} \approx a_{bb}$)

3. Ideal gas

• no interactions

$$\hat{f}_i^v = y_i P$$

<< Property Changes of Mixing if Ideal Gas

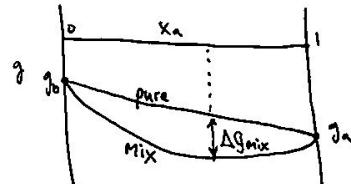
• $\Delta v_{mix} = 0$ (no interaction)

• $\Delta h_{mix} = 0$ (no interaction)

• $\Delta S_{mix} = -R \sum y_i \ln y_i$

• $\Delta g_{mix} = RT \sum y_i \ln y_i$

• mixing of ideal gas always decrease g ($\Delta g_{mix} < 0$), being spontaneous.



→ Alternative derivation

• $\Delta g_{mix} = g - \sum y_i g_i$

$= \sum y_i (\bar{G}_i - g_i)$

$= \sum y_i (\mu_i - g_i)$

$= \sum y_i RT \ln \left(\frac{f_i}{\bar{f}_i} \right)$

$= \sum y_i RT \ln \left(\frac{P}{P_i} \right)$

$= RT \sum y_i \ln y_i$

$\mu_i = \bar{G}_i$

def. of fugacity $\begin{cases} \mu_i \rightarrow \hat{f}_i & \text{mix} \\ g_i \rightarrow f_i & \text{pure} \end{cases}$

ideal gas

↔ Fugacity in Liquid Phase

→ Reference State

> ideal solution - solution whose mixing rules are the same as in ideal gas

- intermolecular interactions are same between all component of mixture.

- satisfies Lewis fugacity rule (all i - i interactions)

$$\hat{f}_i^{\text{ideal}} = x_i f_i^{\circ}$$

> Lewis/Randall rule - same species interactions dominate

- $\hat{f}_a^{\text{ideal}} = f_a^{\circ} = f_a$ (volatile)

- a - a interaction ($x_a \rightarrow 1$ for tangent line at $x_a \rightarrow 1$)

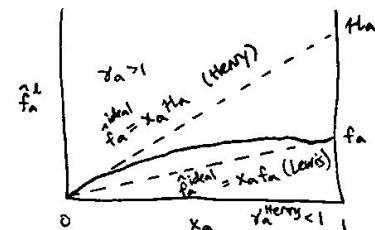
- > solvent - species defined by Lewis/Randall rule

> Henry's law - different species interactions dominate

- $\hat{f}_a^{\text{ideal}} = f_a^{\circ} = f_{\text{Henry}}$ (dilute)

- a - b interaction ($x_a \rightarrow 1$ for tangent line at $x_a \rightarrow 0$)

- > Solute - species defined by Henry's law



Curve and γ_a may change depending on species.

→ Activity Coefficient

> activity coefficient -

$$\gamma_i = \frac{\hat{f}_i}{\hat{f}_i^{\text{ideal}}} = \frac{\hat{f}_i^L}{x_i \hat{f}_i^{\text{ideal}}}$$

- $\lim_{x_a \rightarrow 1} \gamma_a^{\text{Henry}} = \gamma_a^{\text{Henry(pure a)}} = \frac{\hat{f}_a^L}{\hat{f}_a^{\text{ideal}}} = \frac{f_a}{f_a^{\circ}} = \frac{1}{\gamma_a^{\infty}}$

- $\lim_{x_a \rightarrow 0} \gamma_a = \gamma_a^{\infty} = \frac{f_a}{f_a^{\circ}}$

> activity -

$$a_i = x_i \gamma_i$$

- $a_i = x_i \gamma_i$

• compare

$$\left\{ \begin{array}{l} \text{fugacity coeff} = \frac{\text{fugacity in vapor}}{\text{fugacity in ideal gas}} \\ \text{activity coeff} = \frac{\text{fugacity in liquid}}{\text{fugacity in ideal soln}} \end{array} \right.$$

$$\hat{\phi}_i = \frac{\hat{f}_i^v}{y_i p^\circ}$$

$$\gamma_i = \frac{\hat{f}_i^L}{x_i \hat{f}_i^{\text{ideal}}} , \quad \hat{f}_i^{\text{ideal}} = \begin{cases} f_i & \text{Lewis/Randall} \\ f_{\text{Henry}} & \text{Henry} \end{cases}$$

<< Fugacity in Liquid Phase

→ Lewis/Randall Ref State: Calculating pure species fugacity f_i^* :

- $f_i^* = f_i$
- $f_i^* = x_i f_i$ } need to find pure species fugacity f_i

Ex] Derive fugacity dependence on P .

$$\cdot g_i - g_i^* = RT \ln\left(\frac{f_i}{P^*}\right)$$

$$g_i = g_i^* + RT \ln(f_i) - RT \ln(P^*)$$

$$\left(\frac{\partial g_i}{\partial P}\right)_T = RT \left[\frac{\partial}{\partial P}(\ln(f_i))\right]_T$$

$$\cdot \left(\frac{\partial g_i}{\partial P}\right)_T = \left(\frac{-S_i \partial T + V_i \partial P}{\partial P}\right)_T = V_i$$

Equate

$$\cdot V_i = RT \left[\frac{\partial}{\partial P}(\ln f_i)\right]_T$$

$$\int_{P_{\text{sat}}}^P \frac{V_i}{RT} dP = \int_{f_i(P_{\text{sat}})}^{f_i(P)} \frac{\partial \ln f_i}{\partial \ln f_i}$$

$$\int_{P_{\text{sat}}}^P \frac{V_i}{RT} dP = \ln\left(\frac{f_i(P)}{f_i(P_{\text{sat}})}\right)$$

$$f_i(P) = f_i(P_{\text{sat}}) \exp\left[\int_{P_{\text{sat}}}^P \frac{V_i}{RT} dP\right]$$

$$f_i^*(P_{\text{sat}}) = f_i^*(P_{\text{sat}}) = \varphi_i^{\text{sat}} P_i^{\text{sat}}$$

$$\boxed{f_i^L = \varphi_i^{\text{sat}} P_i^{\text{sat}} \exp\left[\int_{P_{\text{sat}}}^P \frac{V_i}{RT} dP\right]}$$

Poynting correction

decreasing accuracy

$$\cdot f_i^L = \varphi_i^{\text{sat}} P_i^{\text{sat}} \exp\left[\frac{V_i}{RT}(P - P_{\text{sat}})\right]$$

* Incompressible liquid ($V_i \text{ const}$)

$$\cdot f_i^L = \varphi_i^{\text{sat}} P_i^{\text{sat}}$$

* $P \approx P_{\text{sat}}$

$$\cdot f_i^L = P_i^{\text{sat}}$$

* Ideal gas $\varphi_i = 1$

→ Henry's law Ref State: Calculating Henry's constant H_i :

- $f_i^* = H_i$
- $f_i^* = x_i H_i$ } need to find Henry's constant H_i dependence on T, P

$$\cdot \left(\frac{\partial \ln H_i}{\partial P}\right)_T = \frac{V_i^{\infty}}{RT}$$

$$\Rightarrow H_i(P) = H_i(P_i) \exp\left[\int_{P_i}^P \frac{V_i^{\infty}}{RT} dP\right]$$

$$\cdot \left(\frac{\partial \ln H_i}{\partial T}\right)_P = \frac{h_i^* - \bar{H}_i^{\infty}}{RT^2}$$

$$\Rightarrow H_i(T) = H_i(T_i) \exp\left[\int_{T_i}^T \frac{h_i^* - \bar{H}_i^{\infty}}{RT^2} dT\right]$$

\leftrightarrow Thermodynamic Relations between γ_i :

→ Gibbs-Duhem Eqn

• applies to γ_i as well

$$\cdot 0 = \sum n_i d\bar{K}_i$$

$$0 = \sum n_i d\mu_i \quad \text{const } T, P$$

$$0 = RT \sum n_i d(\ln \hat{f}_i)$$

$$0 = - \sum n_i d(\ln(x_i f_i^\circ))$$

$$\left\{ \begin{array}{l} \mu_i = \mu_i^\circ + RT \ln \left(\frac{f_i}{f_i^\circ} \right) \\ d\mu_i = RT d \ln \hat{f}_i \end{array} \right.$$

$$0 = \sum n_i d(\ln \gamma_i) + \sum n_i d(\ln x_i) + \sum n_i d(\ln f_i^\circ) \quad \sum n_i d(\ln x_i) = \sum n_i (\ln x_i)$$

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

$$0 = x_a \left(\frac{\partial \ln \gamma_a}{\partial x_a} \right)_{T,P} + x_b \left(\frac{\partial \ln \gamma_b}{\partial x_b} \right)_{T,P}$$

$$= \sum n_i (\ln x_i)$$

$$= \sum n_i dx_i$$

$$= 0 \quad (\sum x_i = 1 \Rightarrow \sum dx_i = 0)$$

→ Excess Properties

$$\rightarrow \text{excess property} - \boxed{k^E = \bar{K}^{\text{real}} - \bar{K}^{\text{ideal}}}$$

at appropriate ref state

$$\boxed{k^E = \Delta k_{\text{mix}}^{\text{real}} - \Delta k_{\text{mix}}^{\text{ideal}}}$$

$$\rightarrow \text{partial molar excess property} - \boxed{\bar{K}_i^E = \bar{K}_i^{\text{real}} - \bar{K}_i^{\text{ideal}}}$$

• types of excess property

$$\left\{ \begin{array}{ll} \Delta k_{\text{mix}}^{\text{ideal}} = 0 & (u, h, v) \Rightarrow k^E = \Delta k_{\text{mix}}^{\text{real}} \\ \Delta k_{\text{mix}}^{\text{ideal}} \neq 0 & (g, s, a) \Rightarrow k^E = \Delta k_{\text{mix}}^{\text{real}} - \Delta k_{\text{mix}}^{\text{ideal}} \end{array} \right.$$

$$\boxed{g^E = \Delta g_{\text{mix}} - RT \sum x_i \ln \gamma_i}$$

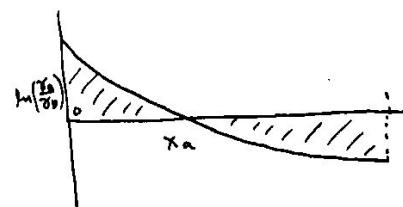
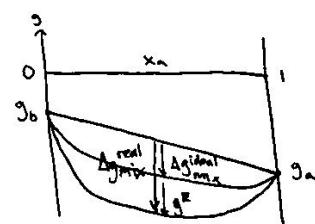
$$g^E = RT \sum x_i \ln \gamma_i$$

$$\boxed{\bar{G}_i^E = RT \ln \gamma_i}$$

• area test for thermodynamic consistency

$$\boxed{\int_0^1 \ln \left(\frac{x_a}{x_b} \right) dx_a = 0}$$

• Net area of $\ln \left(\frac{x_a}{x_b} \right)$ vs x_a from 0 to 1 is 0.



<< Activity Coefficient γ_i from Excess Gibbs Energy Model g^E

- We can relate γ_i with g^E with

$$\boxed{G_i^E = \left(\frac{\partial g^E}{\partial n_i}\right)_{T, P, n_{j \neq i}} = RT \ln \gamma_i}$$

- We need to develop models of g^E to solve for γ_i

→ Two-Suffix Margules Equation

- $g^E = Ax_a x_b$
- $\bar{G}_a^E = Ax_a^2$
- $\bar{G}_b^E = Ax_b^2$

γ_i can then be used to solve for f_i^L

$$\cdot f_i^L = x_i \gamma_i f_i^* \quad \begin{cases} x_i \gamma_i f_i^* & \text{Lewis ref} \\ x_i \gamma_i f_i^* & \text{Henry's ref} \end{cases}$$

- Parameter A is relative importance of unlike interaction and avg of like interactions

• $A < 0$ unlike interaction dominates, mixing favored

• $A > 0$ like interaction dominates, mixing entropically favored

vs.

- Symmetric model - same prediction for all species

- only London interaction

- same interaction strength

- same size

symmetric

asymmetric

- $A < 0, g^E < 0$

- unlike interaction dominates

- Mixing favored

- $A > 0, g^E > 0$

- small magnitude

- like interaction dominates

- mixing entropically favored

- $A > 0, g^E > 0$

- large magnitude

- like interaction dominates

- separation energetically favored

→ Asymmetric Models

- three-suffix Margules equation

- van Laar equation

- Wilson equation

- Nonrandom two-liquid model (NRTL)

- universal quasi-chemical theory (UNIQUAC) - pg 442

} pg 438

<< Excess Gibbs Energy g^E Models for Multicomponent Systems

- Two-Stage Margules equation for ternary system

$$\cdot g^E = A_{ab}x_a x_b + A_{ac}x_a x_c + A_{bc}x_b x_c$$

$$\cdot \bar{G}_a^E = A_{ab}x_b^2 + A_{ac}x_c^2 + (A_{ab} + A_{ac} - A_{bc})x_a x_c$$

$$\cdot \bar{G}_b^E = A_{ab}x_a^2 + A_{bc}x_c^2 + (A_{ab} + A_{bc} - A_{ac})x_a x_c$$

$$\cdot \bar{G}_c^E = A_{ac}x_a^2 + A_{bc}x_b^2 + (A_{ac} + A_{bc} - A_{ab})x_a x_b$$

- Wilson eqn
- NRTL
- UNIQUAC

} pg 446

<< T, P dependence of g^E

→ General

$$\cdot dG^E = V^E dP - S^E dT + \sum \bar{G}_i^E dn_i$$

$$\cdot \left(\frac{\partial g^E}{\partial P} \right)_{T, n_i} = V^E - \Delta v_{mix}$$

$$\cdot \left(\frac{\partial g^E}{\partial T} \right)_{P, n_i} = - \frac{h^E}{T^2} = - \frac{\Delta h_{mix}}{T^2}$$

→ Regular solution

- nonideality only from energetic effect
 - diff attraction forces
 - same size & shape

$$\cdot g^E = h^E - T s^E$$

$$g^E = h^E$$

$$s^E \approx 0$$

$$g^E = \Delta h_{mix}$$

$$\Delta h_{mix}^{\text{ideal}} = 0$$

$$\cdot \left(\frac{\partial g^E}{\partial T} \right)_{P, n_i} = - \frac{h^E}{T^2} + \frac{1}{T} \left(\frac{\partial g^E}{\partial P} \right)_{P, n_i}$$

$$\cdot \left(\frac{\partial g^E}{\partial P} \right)_{P, n_i} = - \frac{h^E}{T^2} = - \frac{g^E}{T^2}$$

$$\left[\rightarrow \left(\frac{\partial g^E}{\partial P} \right)_{P, n_i} = 0 \right]$$

$$g^E = RT \sum x_i \ln \gamma_i = \text{const}$$

→ Athermal solution

- nonideality only from entropic effect
 - same attraction forces
 - diff size & shape

$$\cdot g^E = h^E - T s^E \quad s^E \approx 0$$

$$\frac{h^E}{T} = - s^E$$

$$\left(\frac{\partial g^E}{\partial T} \right)_{P, n_i} = 0$$

$$\left[\frac{h^E}{T} = \text{const} = R \sum x_i \ln \gamma_i \right]$$

→ γ_i independent of T

$\propto T, P$ dependence of γ_i

$$\cdot \left(\frac{\partial \ln \gamma_i}{\partial P} \right)_{T, K} = \frac{V_i - v_i}{RT}$$

$$\cdot \left(\frac{\partial \ln \gamma_i}{\partial T} \right)_{P, K} = - \frac{\bar{H}_i - h_i}{RT^2}$$

\propto Fugacity in Solid Phase

→ Pure solid

- Activity coeff $\Gamma_i = 1$

- Fugacity $\hat{f}_i^s = f_i^s$

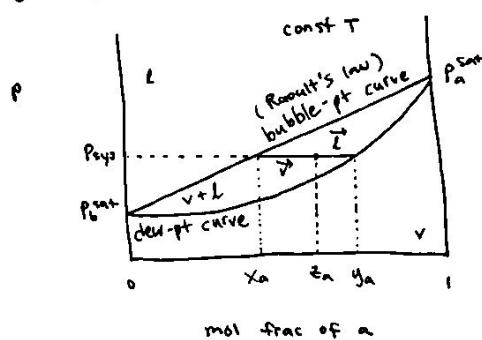
→ Solid solutions

- treat like liquid soln

- $\hat{f}_i^s = X_i \Gamma_i f_i^s$

↔ Phase Diagrams for VLE

→ Pxy diagram (Ideal)



- Lighter, more volatile component on x-axis

> tie line - connects composition in v and l at P_{sys} , z_a .

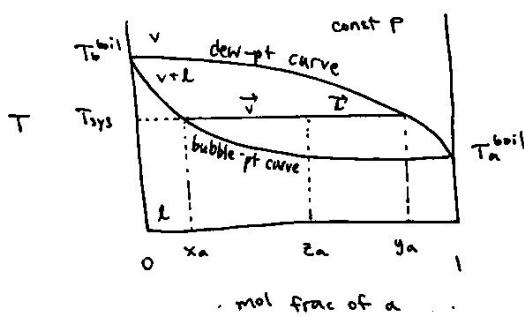
> horizontal $\therefore P_{sys} = P_v = P_L$

$$\text{lever rule} - \frac{n^v}{n^L} = \frac{z}{z_a}$$

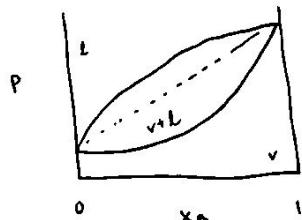
$$\cdot n^v = \frac{z}{z + z_a}$$

$$\cdot n^L = \frac{z_a}{z + z_a}$$

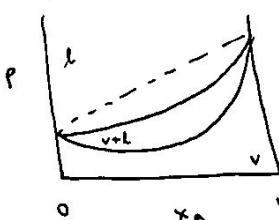
→ Txy diagram



→ Pxy diagram (Nonideal)

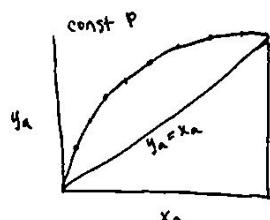


Positive deviation
 $\gamma_a > 1$



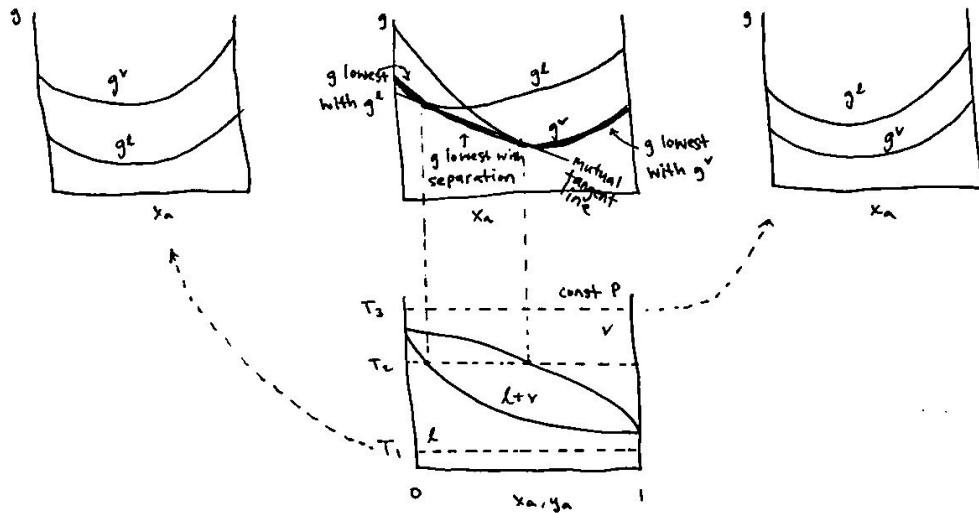
Negative deviation
 $\gamma_a < 1$

→ xy Diagram



→ Phase Diagrams for VLE (cont.)

→ Gibbs energy and Txy diagram



• system seeks to minimize g

- at T_1 , $g^L < g^V$, system entirely in l
 - at T_2 , $g^V < g^L$, system entirely in v
 - at T_2 , composition dependent
 - draw a mutual tangent line (not necessarily at minimum)
 - represents g if system separates into l and v
 - in between the intersection with g^L and g^V .
 - left to intersection at left, $g^L < g^V$, system entirely in l
 - right to intersection at right, $g^V < g^L$, system entirely in v
 - in between the intersections, the mutual tangent line (separation) gives lowest g , system separates to $v+l$.
- } common tangent construction

« Azeotrope 色沸點

> azeotrope - the point in phase diagram that P_x and P_y curve goes through max or min

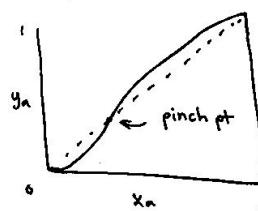
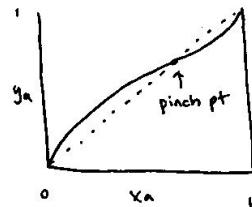
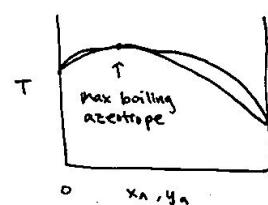
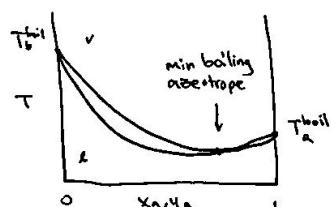
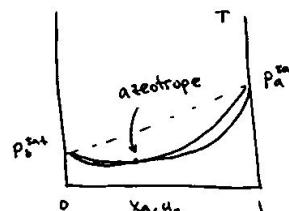
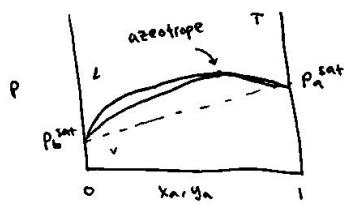
- P_x, P_y curves max or min at the same time at same composition

$$\boxed{x_i = y_i}$$

- Deviation from Raoult's law causes azeotrope

- unlike interaction very diff from like interactions

- P_i^{sat} of each species is close



- min boiling azeotrope

- positive deviation from Raoult's law

- unlike interaction < like interaction

→ Activity coefficient at azeotrope

$$\cdot y_i P = x_i \gamma_i P_i^{\text{sat}} \quad (x_i = y_i)$$

$$\cdot P = \gamma_i P_i^{\text{sat}}$$

$$\cdot P = \gamma_a P_a^{\text{sat}}$$

$$\cdot P = \gamma_b P_b^{\text{sat}}$$

- max boiling azeotrope

- negative deviation from Raoult's law

- like interaction < unlike interaction

$$\Rightarrow \boxed{\gamma_i = \frac{P}{P_i^{\text{sat}}}}$$

$$\Rightarrow \boxed{\frac{\gamma_a}{\gamma_b} = \frac{P_b^{\text{sat}}}{P_a^{\text{sat}}}}$$

<< Fitting > Model using VLE data

> objective function - measure of error written in terms of diff between calculated and experimental value

- minimize objective function to get optimal model parameter

$$\cdot f_p = \sum (P_{\text{exp}} - P_{\text{calc}})_i^2$$

$$\cdot f_g = \sum (g_i^{\text{exp}} - g_i^{\text{calc}})_i^2$$

$$\cdot f_x = \sum \left[\left(\frac{x_a - x_a^{\text{calc}}}{x_a} \right)^2 + \left(\frac{x_b - x_b^{\text{calc}}}{x_b} \right)^2 \right]_i$$

<< Solubility of Gases in Liquids

- Henry's ref state used for species that $T \gg T_c$

$$\cdot \left(\frac{\partial \ln H_i}{\partial P} \right)_T = \frac{V_i^{\infty}}{RT}$$

$$\cdot \left(\frac{\partial \ln H_i}{\partial T} \right)_P = \frac{h_i^{\circ} - \bar{H}_i^{\infty}}{RT^2} \Rightarrow \left(\frac{\partial \ln H_i}{\partial (1/T)} \right)_P = \frac{\bar{H}_i^{\infty} - h_i^{\circ}}{R}$$

- At eqm, $\hat{f}_i^v = f_i^l$

$$y_i \hat{\varphi}_i^v P = x_i \gamma_i^v H_i$$

- approximations:

		Ideal Gas ($\hat{\varphi}_i^v = 1$)	Nonideal Gas
Ideal liquid ($\gamma_i^v = 1$)	solute a	$y_a P = x_a H_a$	$y_a \varphi_a P = x_a H_a \exp \left[\int_{P_0}^P \frac{V_a^{\infty}}{RT} dP \right]$
	Solvent b	$y_b P = x_b P_b^{\text{sat}}$	$y_b \hat{\varphi}_b P = x_b \varphi_b^{\text{sat}} P_b^{\text{sat}} \exp \left[\int_{P_b^{\text{sat}}}^P \frac{V_b^{\infty}}{RT} dP \right]$
Nonideal liquid	solute a	$y_a P = x_a \gamma_a^v H_a$	$y_a \varphi_a P = x_a \gamma_a^v H_a \exp \left[\int_{P_0}^P \frac{V_a^{\infty}}{RT} dP \right]$
	Solvent b	$y_b P = x_b \gamma_b P_b^{\text{sat}}$	$y_b \hat{\varphi}_b P = x_b \gamma_b \varphi_b^{\text{sat}} P_b^{\text{sat}} \exp \left[\int_{P_b^{\text{sat}}}^P \frac{V_b^{\infty}}{RT} dP \right]$

- Mixing rule for Henry's const: $\ln H_a = \sum_i x_i \ln H_{ai}$

<< VLE Using EOS Method

- Use fugacity coefficient with EOS to describe both v and l phase.

$$\cdot \hat{f}_i^v = \hat{f}_i^l$$

$$\cdot y_i \hat{\varphi}_i^v P = x_i \hat{\varphi}_i^l P$$

$$\boxed{y_i \hat{\varphi}_i^v = x_i \hat{\varphi}_i^l}$$

- $\hat{\varphi}_i$ obtained from EOS that's valid over entire range

↳ Liquid-liquid Equilibrium (LLE)

→ Composition
at eqm

$$\hat{f}_i^x = \hat{f}_i^p$$

$$x_i^x \gamma_i^x f_i^x = x_i^p \gamma_i^p f_i^p$$

$$x_i^x \gamma_i^x = x_i^p \gamma_i^p \Rightarrow$$

$$\begin{cases} x_a^x \gamma_a^x = x_a^p \gamma_a^p \\ x_b^x \gamma_b^x = x_b^p \gamma_b^p \end{cases}$$

• If use two-suffix Margules eqn for γ_i ,

$$x_a^x \exp\left[\frac{\Delta}{RT}(x_b^x)^2\right] = x_a^p \exp\left[\frac{\Delta}{RT}(x_b^p)^2\right]$$

$$x_b^x \exp\left[\frac{\Delta}{RT}(x_a^x)^2\right] = x_b^p \exp\left[\frac{\Delta}{RT}(x_a^p)^2\right]$$

• Composition constraints

$$x_a^x + x_b^x = 1$$

$$x_a^p + x_b^p = 1$$

} solve for compositions

$$x_a^x, x_a^p, x_b^x, x_b^p$$

⇒ binodal curve

> binodal curve - compositions of coexisting liquid phases at any T

- T ↓, range of partial miscibility ↑.
- partial miscibility caused by energetic > entropic effect
- $\Delta > T_s$



> upper consolute temperature T_u - T above which liquid mixture no longer separates into two phases at any composition

> lower consolute temperature T_c - T below which liquid phase separation not possible

→ spontaneous separation

at any composition

- Gibbs energy concave down causes instability

$$\left(\frac{\partial^2 g}{\partial x_i^2}\right)_{T,p} < 0$$

For two-suffix Margules eqn,

$$g = g_{\text{pure}} + \Delta g_{\text{mix}}^{\text{ideal}} + g_E$$

$$= x_a g_a + x_b g_b + RT(x_a \ln x_a + x_b \ln x_b) + Ax_a x_b$$

$$\left(\frac{\partial^2 g}{\partial x_i^2}\right)_{T,p} = RT\left(\frac{1}{x_a} + \frac{1}{x_b}\right) - 2A < 0$$

$$\boxed{\frac{RT}{x_a x_b} < 2A}$$

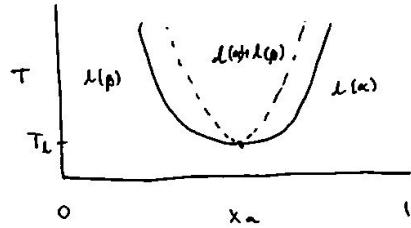
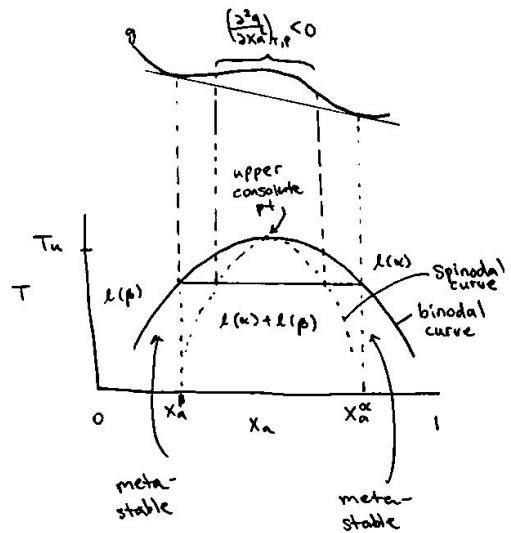
⇒ spinodal curve

> spinodal curve - not lowest g, but does not necessarily spontaneously separate

- with binodal curve, gives

$$\boxed{T_u = \frac{A}{2R}}$$

Liquid-Liquid Equilibrium (LLE)



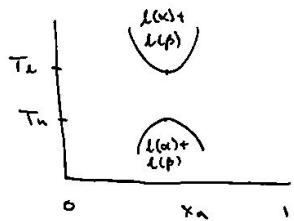
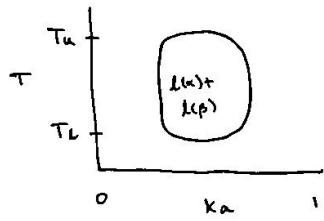
• $T \uparrow, A \downarrow$

- unlike interaction favored at high T
- mixing favored at high T
- upper consolute T

• $T \uparrow, A \uparrow$

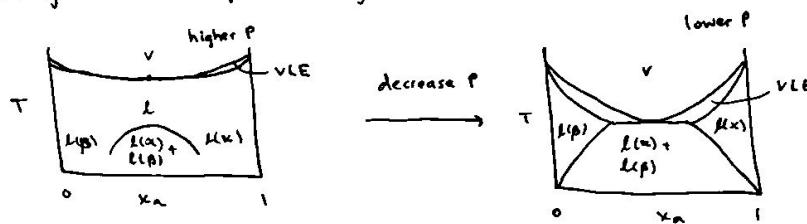
- unlike interaction favored at low T
- mixing favored at low T
- lower consolute T

→ other LLE phase diagrams

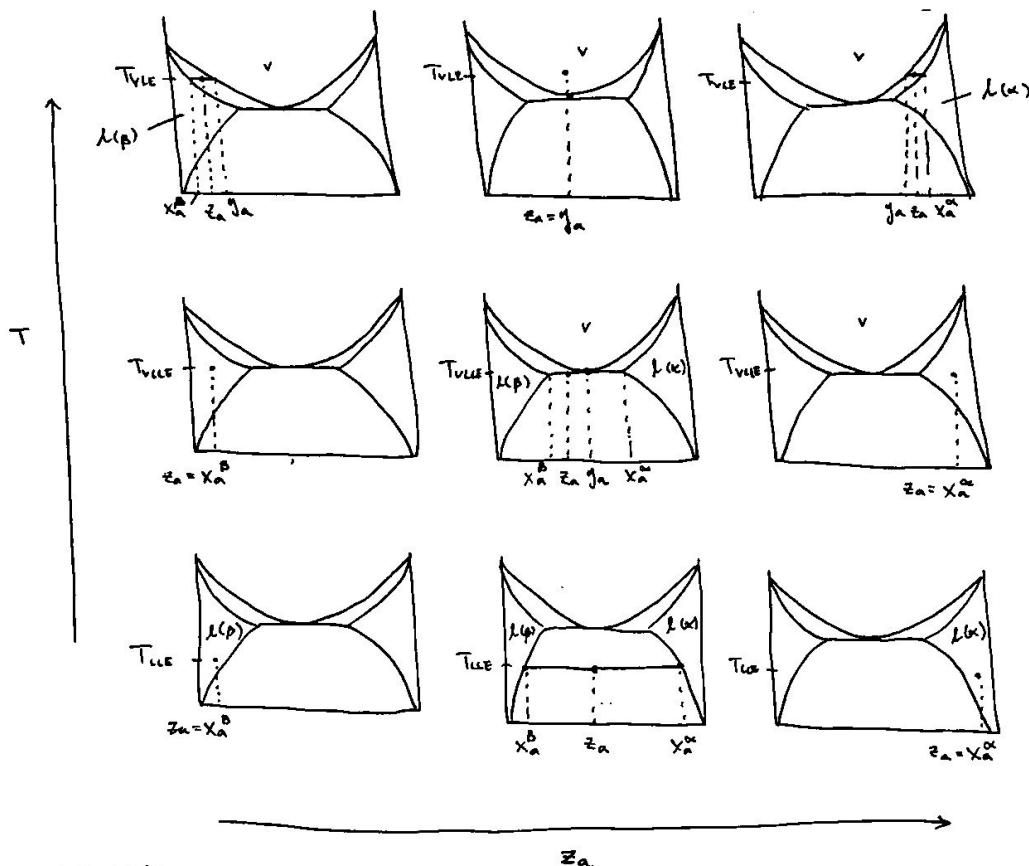


• VLLE

- lowering P causes phase diagram to fuse



- composition at diff T



→ Composition

$$\begin{cases} \cdot f_a^v = f_a^\alpha = f_a^p \\ \cdot f_b^v = f_b^\alpha = f_b^p \end{cases}$$

$$\begin{cases} \cdot y_{aP} = x_a^\alpha x_a^p P_a^{\text{sat}} = x_a^B x_a^p P_a^{\text{sat}} \\ \cdot y_{bP} = x_b^\alpha x_b^p P_b^{\text{sat}} = x_b^B x_b^p P_b^{\text{sat}} \end{cases}$$

$$\cdot y_a + y_b = 1$$

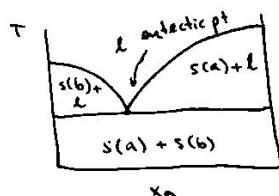
$$\cdot x_a^\alpha + x_b^\alpha = 1$$

$$\cdot x_a^B + x_b^B = 1$$

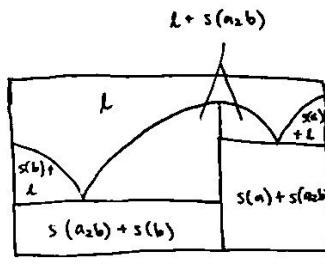
- } 7 eqns solve for 8 var
 $y_a, y_b, x_a^\alpha, x_b^\alpha, x_a^p, x_b^p, P, T$
- } specify one var to solve
- } γ_i use χ_i models
- } P_i use Antoine's eqn

\leftrightarrow Solid Equilibrium (SLE, SSE, SSLE)

→ Pure Solids



SLE in pure
immiscible solids



SLE in pure immiscible solids

• at eqm

$$\hat{f}_i^s = \hat{f}_i^l$$

$$f_i^s = x_i \gamma_i f_i^l$$

pure solid : Lewis(Randall) lig. ref.

$$\frac{f_i^s}{f_i^l} = x_i \gamma_i$$

$$\frac{\Delta g_{\text{fus}}}{RT} = \ln(x_i \gamma_i)$$

fugacity def. $\Delta g_{\text{fus}} = g_i^s - g_i^l = RT \ln\left(\frac{f_i^s}{f_i^l}\right)$

$$\ln(x_i \gamma_i) = \frac{\Delta h_{\text{fus}}}{RT} - \frac{\Delta s_{\text{fus}}}{R}$$

• use alternative path to get Δh_{fus} , Δs_{fus} at T

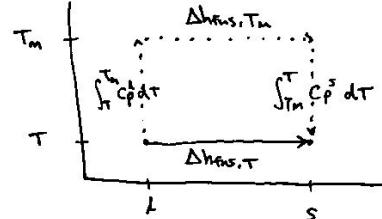
$$\Delta h_{\text{fus},T} = \int_{T_m}^T \Delta c_p^l dT + \Delta h_{\text{fus},T_m}$$

$$\Delta c_p^s = c_p^s - c_p^l$$

$$\Delta s_{\text{fus},T} = \int_{T_m}^T \frac{\Delta c_p^s}{T} dT + \Delta s_{\text{fus},T_m}$$

$$= \int_{T_m}^T \frac{\Delta c_p^{sl}}{T} dT + \frac{\Delta h_{\text{fus},T_m}}{T_m}$$

($\Delta g_{\text{fus}} = 0$ at T_m)



• substitute back, we have

$$\ln(x_i \gamma_i) = \frac{\Delta h_{\text{fus},T_m}}{R} \left[\frac{1}{T} - \frac{1}{T_m} \right] - \frac{1}{R} \int_{T_m}^T \frac{\Delta c_p^{sl}}{T} dT + \frac{1}{RT} \int_{T_m}^T \Delta c_p^l dT$$

$$\ln(x_i \gamma_i) = \frac{\Delta h_{\text{fus},T_m}}{R} \left[\frac{1}{T} - \frac{1}{T_m} \right] + \frac{\Delta c_p^{sl}}{R} \left[1 - \frac{T_m}{T} - \ln\left(\frac{T}{T_m}\right) \right]$$

const. Δc_p^{sl}

↔ Solid Equilibrium

→ Solid Solutions

• solid solutions form if crystal structure remains the same upon addition of other species

> substitutional solid soln - other species occupies lattice sites where original species once sat

> interstitial solid soln - other species sits in interstitial spaces between lattice sites of original species.

• at eqm,

$$f_i^s = f_i^l$$

$$\sum_i \Gamma_i f_i^s = \sum_i \Gamma_i f_i^l$$

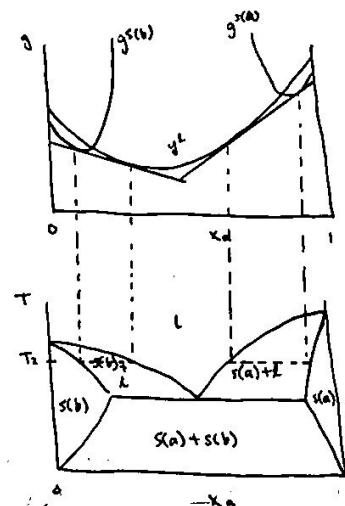
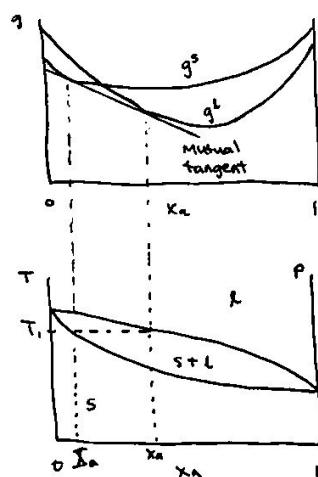
$$\frac{\sum_i \Gamma_i}{\sum_i \Gamma_i} = \frac{f_i^s}{f_i^l}$$

:

$$\ln \left(\frac{\sum_i \Gamma_i}{\sum_i \Gamma_i} \right) = \frac{\Delta h_{\text{vap}, T_m}}{R} \left[\frac{1}{T} - \frac{1}{T_m} \right] - \frac{1}{R} \int_{T_m}^T \frac{\Delta C_p^{\text{sl}}}{T} dT + \frac{1}{R T} \int_{T_m}^T \Delta C_p^{\text{sl}} dT$$

$$\boxed{\ln \left(\frac{\sum_i \Gamma_i}{\sum_i \Gamma_i} \right) = \frac{\Delta h_{\text{vap}, T_m}}{R} \left[\frac{1}{T} - \frac{1}{T_m} \right] + \frac{\Delta C_p^{\text{sl}}}{R} \left[1 - \frac{T_m}{T} - \ln \left(\frac{T}{T_m} \right) \right]}$$

const. ΔC_p^{sl}



<< Colligative Properties

> colligative properties - when mixture of pure liquid and small amount of solute form ideal soln, the change in properties depends only on amount of solute present, not the chemical nature of the solute.

→ Boiling point elevation vs Freezing point depression

> boiling point elevation - raise of boiling point when small amount of nonvolatile solute is added

> freezing point depression - decrease of freezing point when small amount of nonvolatile solute is added

- qualitative argument with Raoult's law

- pure liquid has sat pressure $P_a^{\text{sat},I} = P$

- mixture has sat pressure $y_a P = x_a P_a^{\text{sat},I}$, $y_a < 1$

$$P_a^{\text{sat},II} = \frac{P}{x_a}$$

$$P_a^{\text{sat},II} = \frac{P_a^{\text{sat},I}}{x_a} , x_a < 1$$

- compare sat pressure

$$P_a^{\text{sat},II} > P_a^{\text{sat},I}$$

- so boiling point

$$T_{\text{boil},II} > T_{\text{boil},I}$$

- qualitative argument with chemical potential

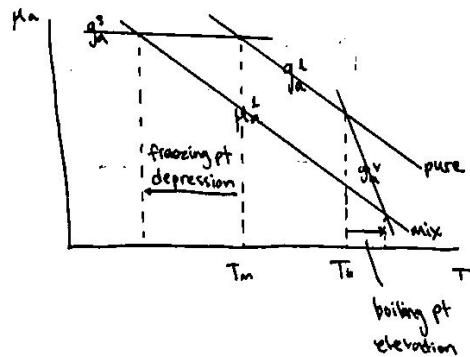
- pure liquid has chem potential μ_a

- mixture has chem potential μ_a

- by fugacity definition, $\mu_a - \mu_a = RT \ln \left(\frac{f_a^{\text{ideal}}}{f_a} \right) > RT \ln(x_a) < 0$

$$\mu_a < \mu_a$$

- lowered μ of mixture changes intersection of μ of solid and vapor phase



or Colligative Properties

→ Boiling point elevation (quantitative)

at eqm,

$$\hat{f}_i^v = \hat{f}_i^{\infty}$$

pure vapor
Lewis/Randall liq ref

$$f_i^v = x_i \gamma_i f_i^{\infty}$$

:

$$\ln(x_i \gamma_i) = \frac{\Delta h_{\text{vap},T_b}}{R} \left[\frac{1}{T} - \frac{1}{T_b} \right] + \frac{\Delta C_p^{\infty}}{R} \left[1 - \frac{T_b}{T} - \ln\left(\frac{T}{T_b}\right) \right]$$

$$\ln(x_a) = \frac{\Delta h_{\text{vap},T_b}}{R} \left[\frac{1}{T} - \frac{1}{T_b} \right]$$

ideal soln $\gamma_i = 1$
small boiling pt elevation

$$\ln(1-x_b) = \frac{\Delta h_{\text{vap},T_b}}{R} \left[\frac{1}{T} - \frac{1}{T_b} \right]$$

$$-x_b = \frac{\Delta h_{\text{vap},T_b}}{R} \left[\frac{1}{T} - \frac{1}{T_b} \right]$$

$$\ln(1-x_b) \approx x_b$$

$$T - T_b = \frac{RT_b x_b}{\Delta h_{\text{vap}}} \quad \begin{matrix} \text{depends on amount of } b \\ \text{depends on chem nature of } a \end{matrix}$$

• nonideal liquid

$$T - T_b = \frac{RT_b^2 x_b}{\Delta h_{\text{vap}}} \gamma_a x_b$$

$$T_b = T_{\text{boil of } a}$$

$$\text{experimentally determine } \gamma_a = \frac{(T - T_b) \Delta h_{\text{vap}}}{RT_b^2 x_b}$$

→ Freezing point depression (quantitative)

at eqm,

$$\ln(x_a) = \frac{\Delta h_{\text{fus},T_m}}{R} \left[\frac{1}{T} - \frac{1}{T_m} \right]$$

$$T - T_m = \frac{RT_m^2}{\Delta h_{\text{fus},T_m}} x_b$$

• nonideal liquid

$$T - T_m = \frac{RT_m^2}{\Delta h_{\text{fus},T_m}} \gamma_a x_b$$

$$\text{experimentally determine } \gamma_a = \frac{(T - T_m) \Delta h_{\text{fus}}}{RT_m^2 x_b}$$

<< Colligative Properties

→ Osmotic pressure

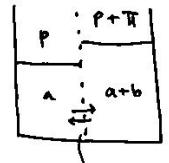
> osmosis - transport of pure solvent into solution through a semipermeable membrane

> osmotic pressure Π - diff of pressure between dilute liq solution and pure liq at eqm

- If $P_{\text{right}} < P + \Pi$, a flow from left to right \rightarrow
- If $P_{\text{right}} > P + \Pi$, a flow from right to left \leftarrow
- If $P_{\text{right}} = P + \Pi$, eqm \leftrightarrow

at eqm,

$$g_a(T, P) = \mu_a(T, P + \Pi)$$



fugacity def

$$g_a(T, P) = g_a(T, P + \Pi) + RT \ln \left(\frac{f_a}{f_a} \right)$$

$$g_a(T, P) = g_a(T, P + \Pi) + RT \ln(x_a y_a)$$

$$g_a(T, P + \Pi) - g_a(T, P) = -RT \ln(x_a y_a)$$

$$\int_{g_a(T, P)}^{g_a(T, P + \Pi)} dy = -RT \ln(x_a y_a)$$

rewrite with integral

$$\int_P^{P + \Pi} v_a dP = -RT \ln(x_a y_a)$$

thermodynamic web

$$\boxed{\nabla_a \Pi = -RT \ln(x_a y_a)}$$

incompressible

for dilute b, ideal soln,

$$x_a \approx 1, \ln(1-x_b) \approx x_b$$

$$\boxed{-\Pi = \frac{x_b R T}{v_a}}$$

Rewrite mol frac with mass concentration to calculate molar mass of macromolecules,

$$x_b = \frac{M_b}{M_a + M_b} = \frac{\frac{C_b}{M_b}}{\frac{C_a}{M_a} + \frac{C_b}{M_b}} \approx \frac{\frac{C_b}{M_b}}{\frac{C_a}{M_a}} \quad (C_a \gg C_b)$$

where $M_i = \frac{C}{M}$ (molar concentration = $\frac{\text{mass concentration}}{\text{molar mass}}$)

$$\frac{\text{mol}}{\text{m}^3} = \frac{\text{g}}{\text{m}^3} \cdot \frac{\text{mol}}{\text{g}}$$

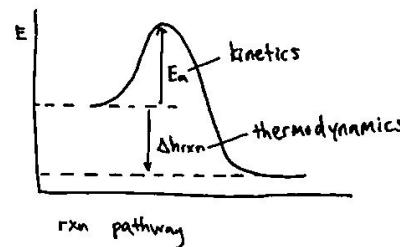
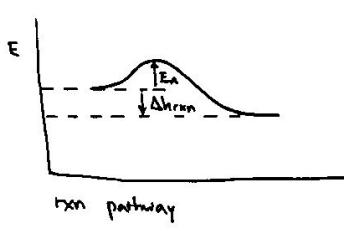
$$\Pi = \frac{C_b}{M_b} \frac{M_a}{C_a} \frac{R T}{v_a} \quad (v_a = \frac{M_a}{C_a})$$

$$\Pi = \frac{R T C_b}{M_b}$$

$$\boxed{M_b = \frac{R T C_b}{\Pi}}$$

<< Thermodynamics & Kinetics

- thermo - possibility of reaction (equilibrium conversion)
- kinetics - rate of reaction



- kinetically controlled at low T
- low Ea allows low energy molecules to react, even though the product is not the most stable
- thermodynamically controlled at high T
- high T allows molecules to sample all available bonding config., and overcome Ea
- more stable product is formed

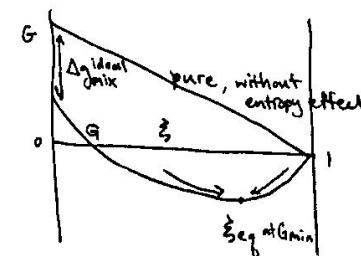
<< Chemical Reaction & Gibbs Energy

> extent of reaction ξ - moles of reaction proceeded

- Write Gibbs energy in terms of extent of reaction

reaction $1 + 2 \rightleftharpoons 3$

$$\begin{aligned}
 G &= \sum n_i \bar{G}_i^{\circ} + \Delta G_{\text{mix}} \\
 &= \sum n_i \mu_i + \Delta G_{\text{mix}} \\
 &= \sum n_i (g_i^{\circ} + RT \ln(\frac{P_i}{P_i^{\text{ref}}})) + \Delta G_{\text{mix}} \quad \text{ideal gas ref state at } T_{\text{ref}}, P_i^{\text{ref}} = 1 \text{ bar} \\
 &= n_1 g_1^{\circ} + n_2 g_2^{\circ} + n_3 g_3^{\circ} \\
 &\quad + RT(n_1 + n_2 + n_3) \ln P \\
 &\quad + RT[n_1 \ln y_1 + n_2 \ln y_2 + n_3 \ln y_3] \\
 &= (1-\xi)(g_1^{\circ} + g_2^{\circ}) + \xi g_3^{\circ} \\
 &\quad + 2RT \ln P \\
 &\quad + RT[(1-\xi)\ln y_1 + (1-\xi)\ln y_2 + \xi \ln y_3]
 \end{aligned}$$



Equilibrium for a single reaction

Stoichiometric coefficient - proportion a given species is reacted or produced given a reaction

- $\nu_{\text{reactant}} < 0$
- $\nu_{\text{product}} > 0$
- $\nu_{\text{nert}} = 0$
- Any reaction can be written as $\sum \nu_i A_i$
- change in moles proportion to ν_i :

$$\frac{dn_1}{dn_2} = \frac{\nu_1}{\nu_2} \Rightarrow \frac{dn_1}{\nu_1} = \frac{dn_2}{\nu_2}$$

$$d\xi \equiv \frac{dn_1}{\nu_1} = \frac{dn_2}{\nu_2} = \frac{dn_3}{\nu_3}$$

$$\xi^0 = 0 \quad \text{at start}$$

$$dn_i = \nu_i d\xi$$

$$n_i = n_i^0 + \nu_i \xi$$

eqm condition with G and ξ

$$\begin{aligned} dG &= \sum \mu_i dn_i \\ &= \sum \mu_i \nu_i d\xi \end{aligned}$$

$$\frac{dG}{d\xi} = 0 = \sum \mu_i \nu_i$$

$$0 = \sum \nu_i \left[g_i^0 + RT \ln \left(\frac{f_i}{f_i^0} \right) \right]$$

$$\ln \left[\prod \left(\frac{f_i}{f_i^0} \right)^{\nu_i} \right] = - \frac{\sum \nu_i g_i^0}{RT}$$

$$\rightarrow \text{Gibbs energy of rxn} - \Delta G_{\text{rxn}} = \sum \nu_i g_i^0$$

only function of T

$$\rightarrow \text{equilibrium constant} - K = \prod \left(\frac{f_i}{f_i^0} \right)^{\nu_i}$$

only function of T

$$\ln K = - \frac{\Delta G_{\text{rxn}}}{RT}$$

$\left. \begin{array}{l} \text{fugacity def} \\ \text{ref state: pure species, } T^0 = T_{\text{rxn}}, P^0 = 1 \text{ bar} \end{array} \right\}$

→ Calculation of K with Data

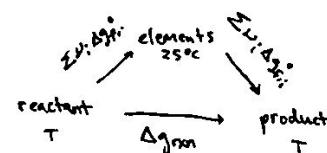
→ Δg_f° Method

> Gibbs energy of formation Δg_f° - energy diff between species and its natural elemental form

elements $\xrightleftharpoons{\Delta g_f^\circ}$ species i

$\Delta g_f^\circ = 0$ for pure elements in nature

$$\Delta g_{\text{rxn}}^\circ = \sum n_i \Delta g_{f,i}^\circ$$



→ T dependence of K

$$\ln K = \frac{\Delta g_{\text{rxn}}^\circ}{RT}$$

$$\frac{d}{dT} \ln K = \frac{d}{dT} \frac{\Delta g_{\text{rxn}}^\circ}{RT}$$

$$= \frac{\Delta h_{\text{rxn}}^\circ}{RT^2} - \frac{1}{R} \frac{d}{dT} \Delta g_{\text{rxn}}^\circ \quad \left(\frac{\partial g}{\partial T}\right)_P = -S$$

$$= \frac{\Delta h_{\text{rxn}}^\circ}{RT^2} + \frac{\Delta S_{\text{rxn}}^\circ}{RT}$$

$$\Delta g_{\text{rxn}}^\circ = \Delta h_{\text{rxn}}^\circ - T \Delta S_{\text{rxn}}^\circ$$

$$\frac{d}{dT} \ln K = \frac{\Delta h_{\text{rxn}}^\circ}{RT^2}$$

• $\Delta h_{\text{rxn}}^\circ < 0$, exothermic rxn, $T \uparrow, K \downarrow$

• $\Delta h_{\text{rxn}}^\circ > 0$, endothermic rxn, $T \uparrow, K \uparrow$

→ $\Delta h_{\text{rxn}}^\circ = \text{constant}$

$$\frac{d}{dT} \ln K = \frac{\Delta h_{\text{rxn}}^\circ}{RT^2}$$

$$d \ln K = \frac{\Delta h_{\text{rxn}}^\circ}{R} \frac{dT}{T^2}$$

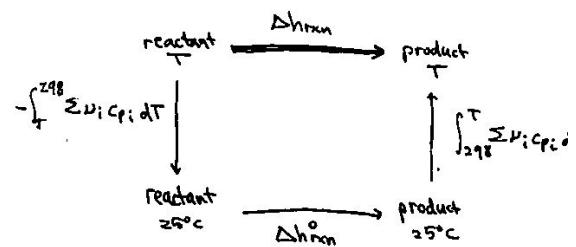
$$\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta h_{\text{rxn}}^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

→ $\Delta h_{\text{rxn}}^\circ = \Delta h_{\text{rxn}}(T)$

$$\Delta h_{\text{rxn}} = \Delta h_{\text{rxn}}^\circ + \int_{298}^T (\sum n_i c_{p,i}) dT$$

$$d \ln K = (\Delta h_{\text{rxn}}^\circ + \int_{298}^T \sum n_i c_{p,i} dT) \frac{dT}{RT^2}$$

$$\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta h_{\text{rxn}}^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right) + \int_{T_1}^{T_2} \frac{\int_{T_1}^T \sum n_i c_{p,i} dT}{RT^2} dT \quad \text{not number, still function of } T$$



<< K and concentration

→ Gas phase rxn

- $K = \prod \left(\frac{f_i}{f_i^0} \right)^{\nu_i}$

$$= \prod (y_i)^{\nu_i}$$

$f_i^0 = 1$ pressure unit (bar/atm)

$K = \prod (y_i; \varphi_i; P)^{\nu_i}$

- $K = \prod (y_i; \varphi_i; P)^{\nu_i}$

$K = P^\nu \prod (y_i; \varphi_i)^{\nu_i}$

Lewis fugacity rule $\varphi_i = \varphi_i$

$K = P^\nu \prod (y_i)^{\nu_i}$

Ideal gas $\varphi_i = 1$

→ Liquid, solid phase rxn

- $K = \prod \left(\frac{f_i}{f_i^0} \right)^{\nu_i}$

$K = \prod \left(\frac{x_i y_i f_i}{f_i^0} \right)^{\nu_i}$

$K = \prod (x_i; y_i)^{\nu_i}$

Low pressure - pressure dependence & negligible

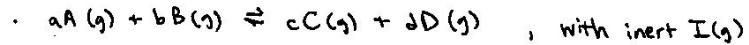
$K = \prod (x_i)^{\nu_i}$

Ideal soln $y_i = 1$

<< Understanding K and Le Chatelier's Principle

- $K = 1$ - equal fwd, backward rxn rate
- $K > 1$ - fwd rxn favored
- $K < 1$ - backward rxn favored

→ Le Chatelier's principle - eqm counteracts external perturbation



$$n^\nu = n_A + n_B + n_C + n_D + n_I$$

$$K = P^\nu \prod (y_i; \varphi_i)^{\nu_i} = \frac{\left(\frac{n_C}{n^\nu}\right)^c \left(\frac{n_D}{n^\nu}\right)^d}{\left(\frac{n_A}{n^\nu}\right)^a \left(\frac{n_B}{n^\nu}\right)^b} P^\nu \prod (\varphi_i)^{\nu_i}$$

$$\frac{K(n^\nu)^{\nu_i}}{P^\nu \prod (\varphi_i)^{\nu_i}} = \frac{(n_C)^c (n_D)^d}{(n_A)^a (n_B)^b}$$

↑ T, endothermic rxn, shift right
(↑T, K↑)

↑ T, exothermic rxn, shift left
(↑T, K↓)

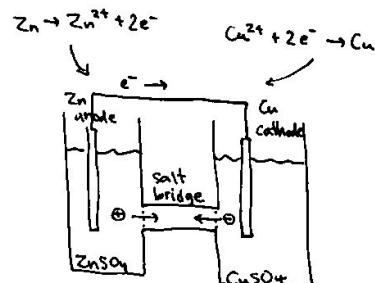
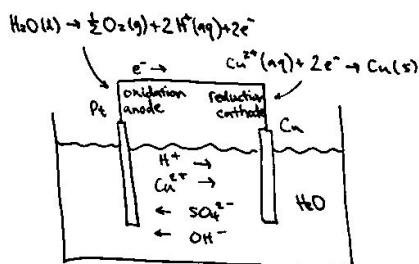
↑ P, shift to less gas moles (ν dependence of P)

↑ [I], shift to more gas moles (ν dependence of n^ν) - inhibit collision for more molecules

↑ [A], shift right

<< Electrochemical Cells

- > galvanic cell - use spontaneous reaction to do useful work ($\Delta G < 0, \Delta W^* < 0$)
- > electrolytic cell - use electrical work to induce reaction ($\Delta G > 0, \Delta W^* > 0$)
- > reduction - gain e^- , at cathode
- > oxidation - lose e^- , at anode
- > overall rxn obtained by adding oxidation & reduction half rxns.
 - no net charge
 - use H^+ , OH^- , H_2O to balance charge and species
- > electrolyte - medium with mobile charge carrier
 - could be solution or salt bridge



<< Electrochemical Equilibrium

- $\Delta W^* = (\delta E)_{T,P}$ non-PV work ΔW^*
- If $\Delta G > 0, \Delta W^* > 0$: If nonspontaneous rxn, work input needed: electrolytic cell
- If $\Delta G < 0, \Delta W^* < 0$: If work generated, rxn is spontaneous: galvanic cell
- $\Delta W^* = -E dQ$

$$\downarrow$$

$$\begin{aligned} \cdot dQ &= zFd\xi \\ \Delta W^* &= -zFE d\xi \end{aligned}$$

$\left\{ \begin{array}{l} z = \text{mol } e^- \text{ per mol rxn} \\ d\xi = \text{extent of rxn (mol rxn)} \end{array} \right\} n = z \xi \text{ total mol } e^-$

$F = 96485 C / \text{mol } e^-$

$$\cdot \Delta G = \sum \mu_i v_i d\xi$$

$$\cdot \text{for reversible, } \Delta W^* = \Delta G \Rightarrow \boxed{\Delta G = -z \xi FE}$$

$$-zFE d\xi = \sum \mu_i v_i d\xi$$

$$-zFE = \sum (g_i^\circ + RT \ln(\frac{f_i}{f_i^\circ})) v_i$$

$$-zFE = \sum g_i^\circ v_i + RT \sum \ln\left[\left(\frac{f_i}{f_i^\circ}\right)^{v_i}\right]$$

$$-zFE = \Delta g^\circ_{rxn} + RT \ln\left[\prod_{\text{vapor}} (y_i; \bar{q}; P)^{v_i} : \prod_{\text{liq}} (x_i; v_i)^{v_i}\right]$$

<< Electrochemical Equilibrium (cont.)

> molality = mol i per 1 kg of solvent

• Liq standard state = 1-m ideal soln, Henry's law ref state

$$-\nu F E = \Delta g_{rxn}^{\circ} + RT \ln \left[\prod_{\text{vap}} (y_i; \bar{a}; P)^{\nu_i} : \prod_{\text{liq}} (x_i; \gamma_i)^{\nu_i} \right]$$

ideal gas $\bar{a}_i = 1$
liq ref with molality b_i

$$-\nu F E = \Delta g_{rxn}^{\circ} + RT \ln \left[\prod_{\text{vap}} (P_i)^{\nu_i} : \prod_{\text{liq}} (b_i; \gamma_i)^{\nu_i} \right]$$

$$E = -\frac{\Delta g_{rxn}^{\circ}}{\nu F} - \frac{RT}{\nu F} \ln \left[\prod_{\text{vap}} (P_i)^{\nu_i} : \prod_{\text{liq}} (b_i; \gamma_i)^{\nu_i} \right]$$

$$E = E_{rxn}^{\circ} - \frac{RT}{\nu F} \ln \left[\prod_{\text{vap}} (P_i)^{\nu_i} : \prod_{\text{liq}} (b_i; \gamma_i)^{\nu_i} \right]$$

Nernst eqn

$$\rightarrow E_{rxn}^{\circ} = -\frac{\Delta g_{rxn}^{\circ}}{\nu F} \quad \rightarrow \quad \Delta g_{rxn}^{\circ} = -\nu F E_{rxn}^{\circ}$$

<< Half Cell Potential

> reference half cell rxn = $\text{H}_2(\text{g}) \rightleftharpoons 2\text{H}^+(\text{aq}) + 2\text{e}^- \quad E^{\circ} = 0\text{V}$

• standard potential of rxn E_{rxn}° obtained from data

• combine oxidation and reduction half cells

$$\cdot E_{rxn}^{\circ} = E_{\text{red}}^{\circ}(\text{cathode}) - E_{\text{red}}^{\circ}(\text{anode})$$

• $E_{rxn}^{\circ} > 0$, $\Delta g_{rxn}^{\circ} < 0$, spontaneous

• $E_{rxn}^{\circ} < 0$, $\Delta g_{rxn}^{\circ} > 0$, nonspontaneous

<< Activity Coefficient γ_i in Electrochemical Systems

• To solve $K = \prod (x_i; \gamma_i)^{\nu_i}$ for ideal soln, γ_i needed

• γ_+ and γ_- measured together in soln

$$\cdot \gamma_{\pm} = (\gamma_+^a \gamma_-^b)^{\frac{1}{a+b}} \quad \text{for} \quad X_a Y_b \rightleftharpoons aX^{(z+)^+} + bY^{(z-)^-}$$

$$\cdot \gamma_{\pm} = \sqrt{\gamma_+ \gamma_-} \quad \text{for} \quad XY \rightleftharpoons X^{z+} + Y^{z-}$$

$$\cdot \text{Debye-Hückel model} - \boxed{\ln \gamma_{\pm} = -A(z_+ z_-) \sqrt{I}}$$

$$\cdot \text{ionic strength} \quad I = \frac{1}{2} \sum z_i^2 b_i$$

$$\cdot \text{Correlation for real system} \quad \ln \gamma_{\pm} = \frac{A(z_+ z_-) \sqrt{I}}{I + B \sqrt{I}}$$

↔ ξ and K for R reactions

- independent reactions 1, 2, ..., k, ... R
 - in each rxn, species 1, 2, ..., i, ... m
 - multiple rxn in compact form
- $$\sum_{k=1}^R \sum_{i=1}^m \nu_{ki} A_i$$
- $$\cdot d n_i = \sum_{k=1}^R \nu_{ki} d \xi_k$$
- $$n_i = n_i^0 + \sum_{k=1}^R \nu_{ki} \xi_k \Rightarrow y_i \Rightarrow K$$

↔ Gibbs Phase Rule

$$R = m - F + 2 - \pi - S$$

- R = # independent rxn
- m = # species
- F = degree of freedom, # intensive var specified (e.g. T, P)
- π = # phase
- S = stoichiometric constraint (e.g. feed ratio)