

1st Law of Thermodynamics

← you can't get something for nothing!

Although energy assumes many forms, the total quantity of energy is constant, and when energy disappears in one form it appears simultaneously in other forms. - Law of Conservation of energy

Most basic form:

$$\Delta(\text{Energy of the system}) + \Delta(\text{Energy of surroundings}) = 0$$

General form:

$$\sum_i (H_{in} + E_k + E_p) - \sum_o (H_{out} + E_k + E_p) + \dot{Q} + \dot{W} = \frac{dU}{dt}$$

~ includes k_e, p_e , and any other changes in the system

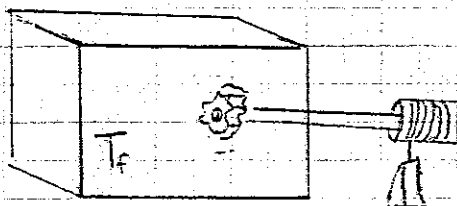
$$\sum_i [\Delta H + \Delta E_k + \Delta E_p] + \dot{Q} + \dot{W} = \frac{dU}{dt}$$

$$\Delta E_k = \frac{1}{2} \Delta U^2 \sim ?$$

{ negligible for most processes

$$\Delta E_p = g \Delta z \sim ?$$

~ How would you describe conversion of energy?



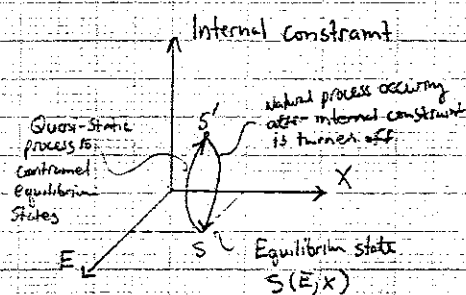
Closed insulated box, (adiabatic)

at $t=0$ $T_o = T_f$

by doing work on the system

The temperature of the fluid rises, and hence, a relationship between work and heat exists, therefore, heat is a form

Variational Statement of the Second Law of Thermodynamics



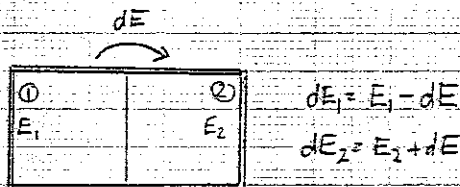
to lift the system off the manifold of equilibrium states (E, X plane) from S to S' requires work & since there is no change in E there must be heat flow.

2nd law states that $S - S' > 0$

$$S(E, \vec{X}) > S(E, \vec{X}, \text{internal constraint}) \quad \leftarrow \text{entropy maximum principle}$$

$$\text{also } E(S, \vec{X}) < E(S, \vec{X}, \text{internal constraint}) \quad \leftarrow \text{energy minimum principle}$$

Application:



$$dS = \frac{1}{T} dE + \frac{P}{T} dV - \frac{\mu}{T} dN$$

$$\text{for composite system } dS = \frac{1}{T_1} dE_1 + \frac{1}{T_2} dE_2 + \frac{P_1}{T_1} dV_1 + \frac{P_2}{T_2} dV_2 + \frac{\mu_1}{T_1} dN_1 + \frac{\mu_2}{T_2} dN_2$$

① Adiabatic wall \rightarrow diathermal

$$dE_1 = -dE_2 \quad \text{at equilibrium } T_1 = T_2 \quad \text{a } dS = 0$$

for a spontaneous process

$$dS = \left(\frac{1}{T_1} - \frac{1}{T_2} \right) dE_1 > 0$$

if dE_1 is negative then $T_1 > T_2$, so energy must transfer from hot to cold.

3rd Law of Thermodynamics

Nernst postulate:

The entropy of any system vanishes in the state for which

$$\left(\frac{\partial U}{\partial S}\right)_{V,N} = 0$$

The absolute entropy is zero for substances at an absolute temperature of zero.

$$S = 0 \text{ at } T = 0 \text{ K}$$

Significance of this postulate is that it allows calc. of absolute entropies (assuming no solid structural transitions)

$$S = \int_0^{T_f} \frac{(C_p)_s}{T} dT + \frac{\Delta H_f}{T_f} + \int_{T_f}^{T_l} \frac{(C_p)_l}{T} dT + \frac{\Delta H_l}{T_l} + \int_{T_l}^T \frac{(C_p)_g}{T} dT$$

Heat

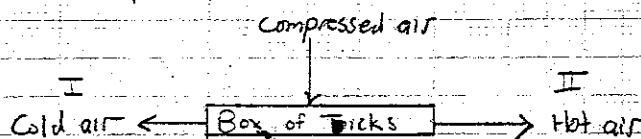
Quantitative definition of heat;

The heat flux to a system in any process (at constant mole numbers) is simply the difference in internal energy between the final and initial states, diminished by the work done in that process.

$$dQ = dU - dW \text{ at const. mole numbers}$$

Application of 1st and 2nd Laws

- 1) Apply 1st and 2nd laws together to determine if a process is feasible.



Consider an ideal gas and determine if this process is possible.

$$dU = dQ - dW \quad dQ = TdS \quad dW = PdV$$

$$EoS: PV = nRT \quad \text{let } n = 1 \text{ mol}$$

$$PV = RT$$

$$dU = TdS - PdV$$

$$d(PV) = d(RT) \quad PdV + VdP = RdT \quad PdV = RdT - \overset{\frac{RT}{P}}{VdP}$$

$$dU = TdS + RdT - \frac{RT}{P} dP$$

$$\text{for an ideal gas } dU = C_v dT$$

$$C_v dT = TdS - RdT + \frac{RT}{P} dP$$

$$TdS = \underset{C_p}{(C_v + R)} dT - \frac{RT}{P} dP$$

$$dS = C_p \frac{dT}{T} - \frac{R}{P} dP$$

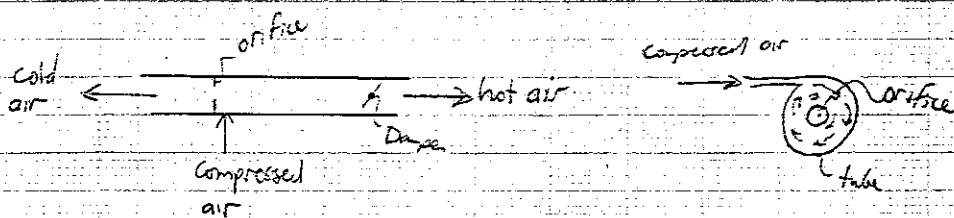
Integrating:

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

Determine $\Delta S_I + \Delta S_{II} \geq 0$ \leftarrow if this is true
(cold-compressed air) (hot-compressed air) then the process
is possible

Strategy: 1) Check for first law violation
2) Check for second law violation

Hilsch-Ranque vortex tube



gas in the middle of the tube (lowest KE) flows through the orifice, while the faster moving air eventually gives up its KE as it moves down the tube due to turbulence and friction, which causes it to heat up.

Classical Thermodynamics

Postulate 1 There exists states (equilibrium states) of simple systems that, macroscopically, are characterized completely by the internal energy U , the volume V , and the mole numbers of the chemical components.

Postulate 2 There exists a function (called the entropy S) of the extensive parameters of any composite system, defined for all equilibrium states and having the following property: The values assumed by the extensive parameters in the absence of an internal constraint are those that maximize the entropy over the manifold of constrained equilibrium states.

Postulate 3 The entropy of a composite system is additive over the constituent subsystems. The entropy is continuous and differentiable and is a monotonically increasing function of the energy.

Any system is completely defined by

1. fundamental eqn. U, S, H, A, G

2. knowledge of all eqns. of state of a system

$$\left. \begin{aligned} T &= T(S, V, N) \\ P &= P(S, V, N) \\ \mu &= \mu(S, V, N) \end{aligned} \right\} \text{intensive parameters in terms of} \\ \text{the independent extensive} \\ \text{parameters.}$$

Fundamental Relations: (State functions)

$$U = TS - PV + \sum_k \mu_k N_k$$

$$F = U - TS$$

$$G = U - TS + PV = H - TS$$

$$H = U + PV$$

$$\left. \begin{aligned} dU &= TdS - PdV \\ dA &= -SdT - PdV \\ dH &= TdS + VdP \\ dG &= -SdT + VdP \end{aligned} \right\} \text{Exact differentials}$$

$\frac{\partial^2 U}{\partial S \partial V} = \frac{\partial^2 U}{\partial V \partial S} \Leftarrow$ having this property from which maxwell's relations are derived

Thermodynamic Temperature scale:

~ if using EoS with classical thermo both temp scales must be consistent

Throttling (Joule-Thompson Expansion)



Ideal Gas

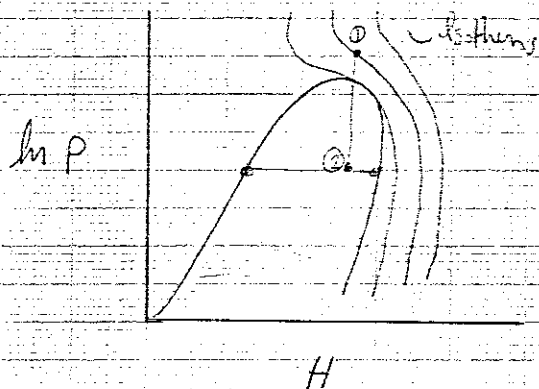
$$T_1 = T_2$$

typically for a real gas $T_2 < T_1$, but

it is possible to have $T_2 > T_1$ (hydrogen, helium)

In the absence of heat transfer $\Delta H = 0$

To find T_2 :



determine using a P-H diagram, where $\Delta H = 0$

$$H_{in} = \alpha H_{vap} + \beta H_{liq}$$

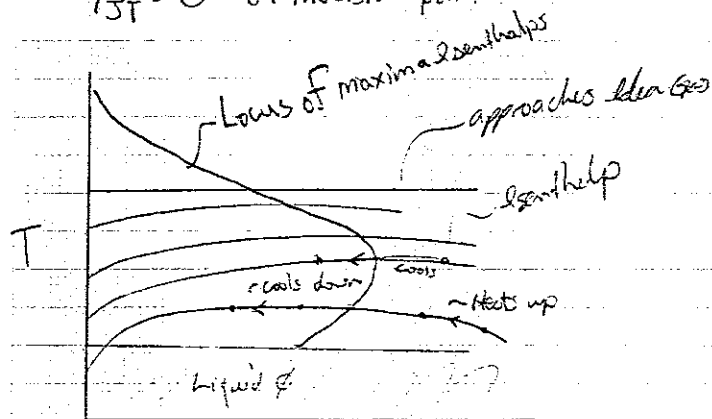
Joule-Thompson coefficient:

$$\eta_{JT} = \left(\frac{\partial T}{\partial P} \right)_H = \frac{T \left(\frac{\partial V}{\partial T} \right)_P - V}{C_p}$$

$$\left(\frac{\partial T}{\partial P} \right)_H \left(\frac{\partial H}{\partial T} \right)_P \left(\frac{\partial P}{\partial H} \right)_T = -1$$

$$\left(\frac{\partial T}{\partial P} \right)_H = - \frac{\left(\frac{\partial H}{\partial P} \right)_T}{C_p} = - \frac{V - T \left(\frac{\partial V}{\partial T} \right)_P}{C_p}$$

$\eta_{JT} = 0$ at inversion point



$$dH = TdS + VdP$$

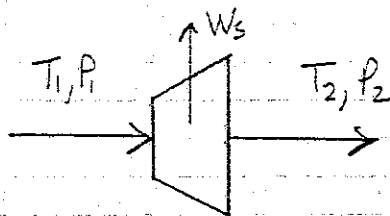
$$\left(\frac{\partial H}{\partial P} \right)_T = T \left(\frac{\partial S}{\partial P} \right)_T + V$$

$$\left(\frac{\partial S}{\partial P} \right)_T = - \left(\frac{\partial T}{\partial V} \right)_P$$

$$\left(\frac{\partial H}{\partial P} \right)_T = V - T \left(\frac{\partial T}{\partial V} \right)_P$$

If initial T & P lie to the left of the maxima then the process necessarily cools the gas
If initial T & P lie to the right of the maxima then the process can heat or cool depending on the final pressure

Turbo-Expander



In the absence of heat transfer

$$\Delta S = 0$$

from first Law:

$$\Delta H = W_s$$

Expander efficiency:

$$\eta = \frac{W_s}{W_s(\text{isentropic})} \leftarrow \text{ideal (max. work)}$$

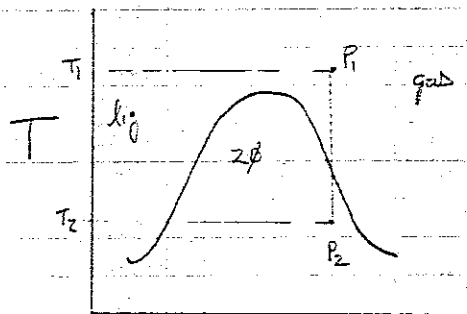
Algorithm to determine T_2

given T_1, P_1, P_2

use $\Delta S = 0$
to find T_2 using
EoS or Residuals

Calc. $W_s = \Delta H$ once
 T_2 is known

from efficiency $\approx 75\%$
calc $W_s(\text{actual})$ at then
calc $T_2(\text{actual})$ from
 $W_s(\text{actual}) = \Delta H$



T_2 can also be determined using
a T-S diagram and W_s can
be determined using a P-H diagram

Production of Power from Heat

Heat Engines :

Essential to all heat-engine cycles are the absorption of heat at high temperature, the rejection of heat at a lower temperature, and the production of work.

The first law $\Delta U_{\text{total}} = 0$:

$$|W| = |Q_H| - |Q_C|$$

The thermal efficiency is defined as

$$\eta = \frac{\text{net work output}}{\text{heat input}} = \frac{|W|}{|Q_H|} = 1 - \frac{|Q_C|}{|Q_H|}$$

for $\eta = 100\%$ $|Q_C|$ must equal zero \leftarrow some heat must always be rejected to the cold reservoir, so this will not happen

Completely reversible heat engine is called a Carnot engine

Four steps of a Carnot cycle :

- 1) A system initially in thermal equilibrium with a cold reservoir at temp. T_C undergoes a reversible adiabatic process that causes its temp. to rise to that of a hot reservoir at T_H .
- 2) System maintains contact with the hot reservoir at T_H , and undergoes a reversible isothermal process during which heat $|Q_H|$ is absorbed from the hot reservoir.
- 3) The system undergoes a reversible adiabatic process in the opposite direction of step 1 that brings the temperature back to that of the cold reservoir at T_C .
- 4) The system maintains contact with the reservoir at T_C , and undergoes a reversible isothermal process in the opposite direction of step 2 that returns it to its initial state with rejection of heat $|Q_C|$ to the cold reservoir.

Carnot's equations follow:

$$\frac{|Q_H|}{|Q_C|} = \frac{T_H}{T_C} \quad (1)$$

Temperature is the absolute temp. on the Kelvin scale

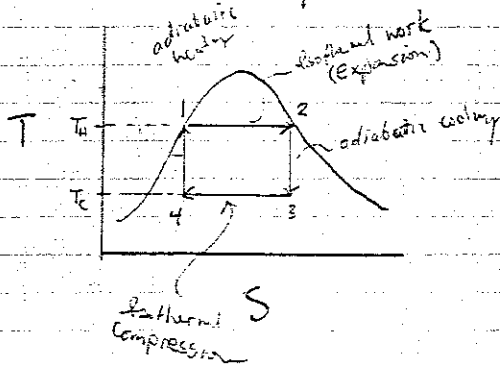
$$\eta = 1 - \frac{T_C}{T_H} \quad (2)$$

Tough practical limit for a Carnot engine is

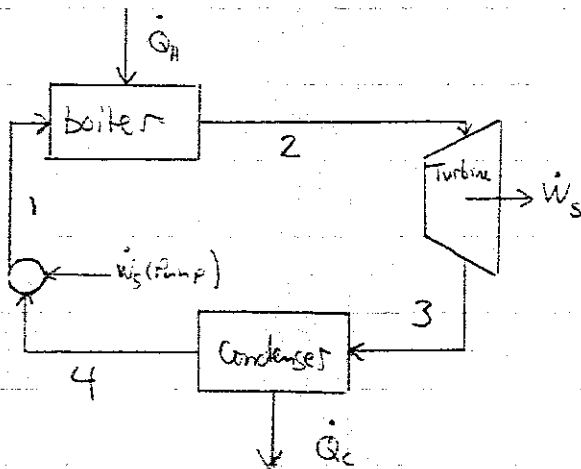
$$\eta = 50\%$$

however, actual heat engines are irreversible, and their thermal efficiencies rarely exceed 35%

Carnot Cycle on a T-S diagram



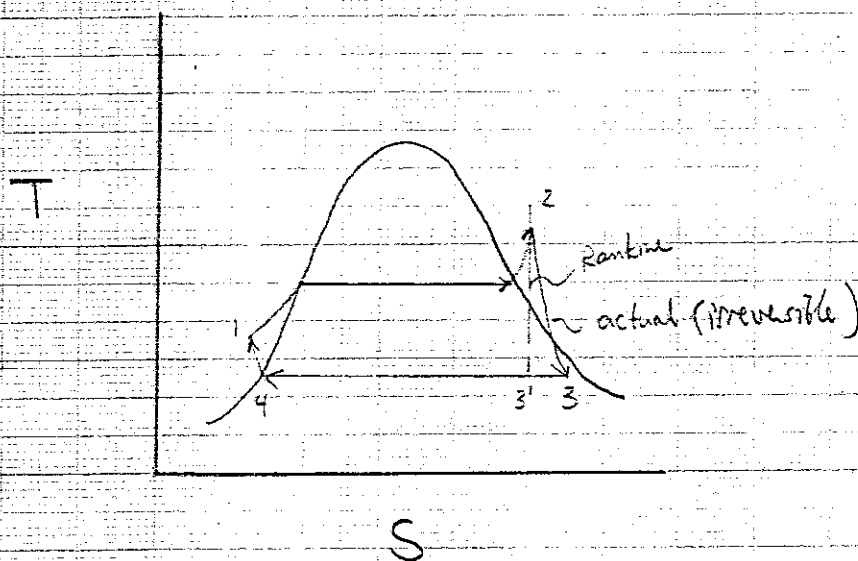
Simple Steam power plant:



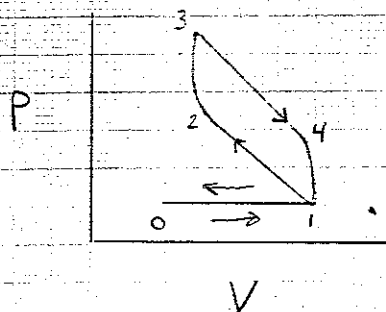
Although this process can be described by the Carnot cycle, severe practical limits exist, which makes this cycle unfeasible.

- expansion through the turbine produces a liquid that causes severe erosion problems
- design of a pump that takes in gas + liq. and discharges only a liq.

Because actual power plants have irreversibilities a more realistic T-S diagram is as follows:



Internal Combustion Engine: Otto Cycle



0 \rightarrow 1 cylinder draws in fuel/air mixture at essentially const. P

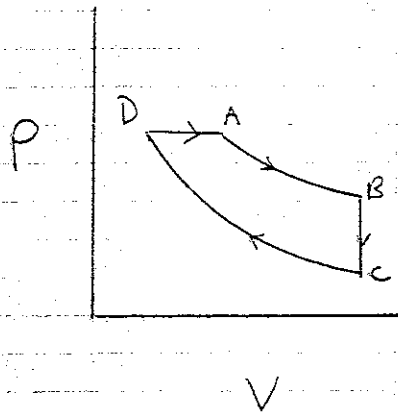
1 \rightarrow 2 \rightarrow 3 (second stroke) all valves are closed and the mixture is compressed approximately adiabatically along line 1 \rightarrow 2; the mixture is then ignited, and combustion occurs so rapidly that the volume remains nearly const. while the pressure rises along line 2 \rightarrow 3.

3 \rightarrow 4 \rightarrow 1 (third stroke) ~ production of work: The high T & P products expand, approx.

adiabatically, along line 3 \rightarrow 4; the exhaust valve opens & the pressure falls rapidly at nearly const. V along lines 4 \rightarrow 1.

1 \rightarrow 0 (fourth stroke) Exhaust stroke - the piston pushes the remaining gases out.

Diesel Engine



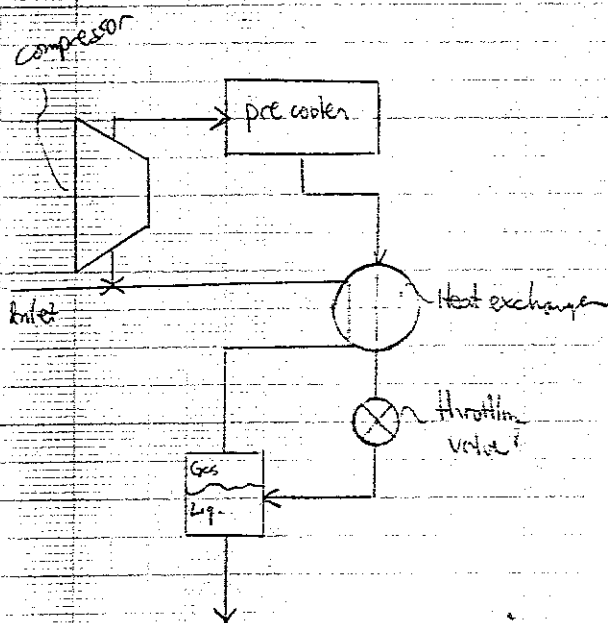
The primary difference between the Otto & Diesel engine is that for the Diesel engine the temperature at the end of the compression is sufficiently high that combustion initiates spontaneously. The higher temp. results because of a higher compression ratio that carries the compression step to a higher pressure. The fuel is not injected until the end of the compression step, and then is added slowly enough that the combustion occurs at approximately const. pressure.

η is higher for the Otto engine at the same compression ratio as the Diesel engine, however, preignition limits the compression ratio in an Otto engine. The Diesel engine operates at higher compression ratios and therefore higher efficiencies.

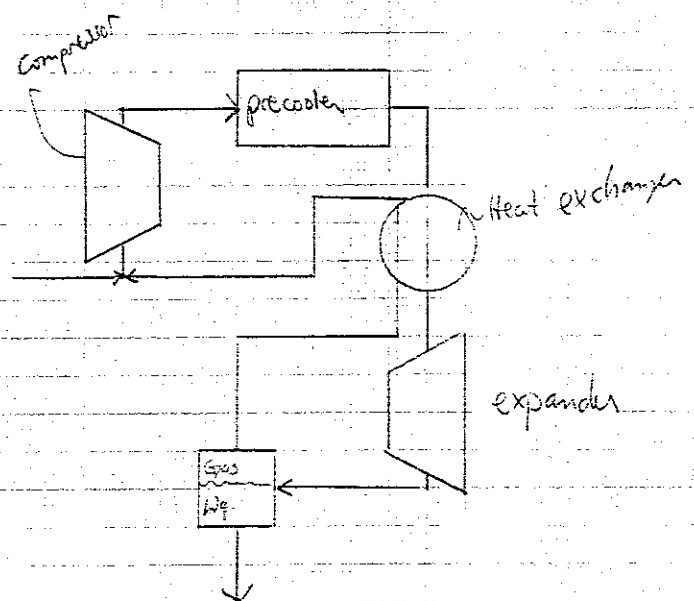
Liquefaction Processes

Several methods to liquify gases include

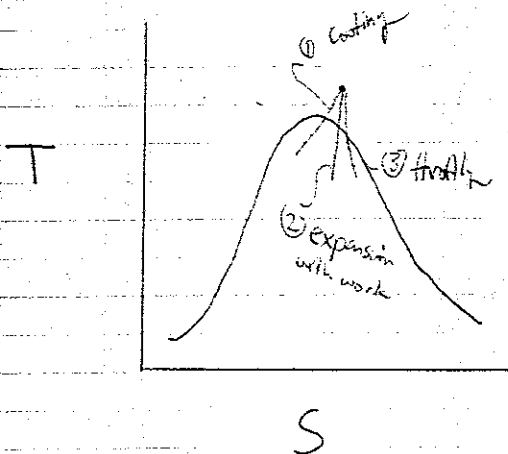
1. heat exchange at constant pressure
2. expansion in a turbine from which work is obtained
3. throttling process



Linde liquefaction process



Claude liquefaction process



From the T-S diagram it is evident that the Feasibility of the process depends on the initial state as well as the properties of the gas.

Thermodynamic Properties of Fluids

Often properties of fluids are needed at temperatures and pressures different from a standard state, and more importantly the difference between the states is needed.

— Thermodynamic properties can be found using

1) Classical Thermodynamic and an egn. of state

2) Residual Functions

Amagat's Law

Amagat's law states that at fixed temperature and pressure, the volume of a mixture is a linear function of mole numbers

$$V = \sum_i n_i v_i$$

where v_i is the molar volume of pure i .

In other words at constant P and T the components mix isometrically.

$$\bar{v}_i = \left(\frac{\partial V}{\partial n_i} \right)_{T, P, n_j} \approx v_i \quad \leftarrow \text{almost never true}$$

Mixing and Partial Molar Quantities

a partial molar property is defined as

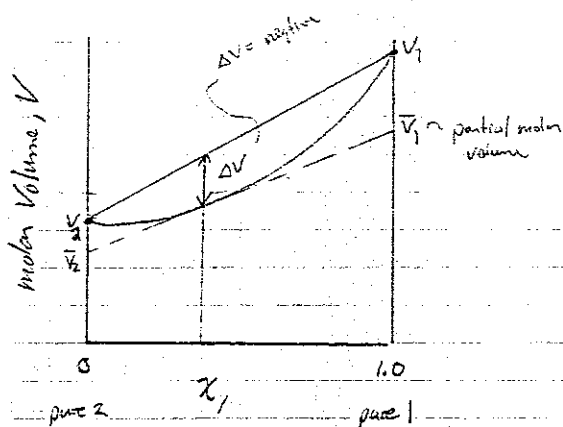
$$\bar{M}_i \equiv \left[\frac{\partial(nM)}{\partial n_i} \right]_{P, T, n_j}$$

or

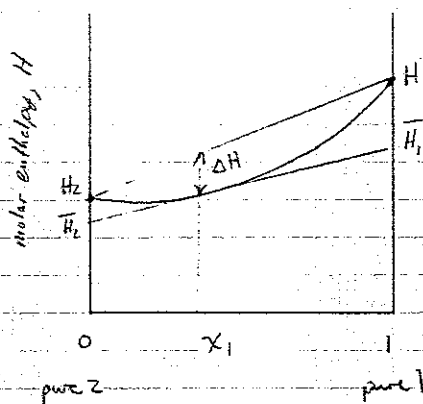
$$M = \sum_i x_i \bar{M}_i$$

$$nM = \sum_i n_i \bar{M}_i$$

Partial Molar Volume :



Partial Molar heat capacity :



The heat of mixing

$$\Delta H = H - \sum_i x_i \bar{H}_i$$

$$H = \sum_i x_i \bar{H}_i$$

if a negative deviation then $\Delta H < 0$ gives off heat

If a positive deviation then $\Delta H > 0$ takes in heat

VLE Properties from an EoS

From Classical Thermodynamics

$$dH = \underbrace{\left(\frac{\partial H}{\partial T}\right)_P}_{C_p} dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P$$

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

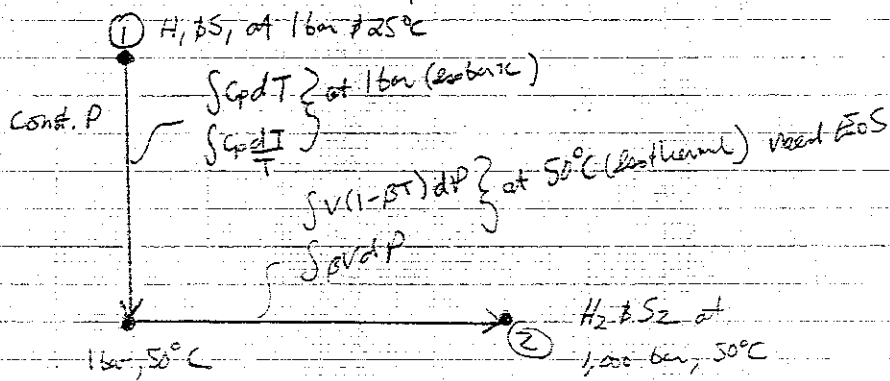
Similarly

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

for an Ideal Gas

$$dH^{ig} = C_p^{ig} dT \quad dS^{ig} = C_p^{ig} \frac{dT}{T} - R \frac{dP}{P}$$

Use Path Integration to determine ΔH and ΔS



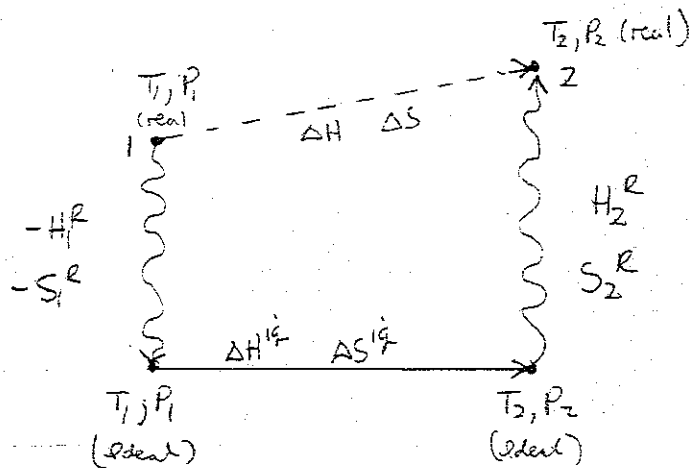
General Considerations:

for incompressible fluids —

$$\left. \begin{aligned} dH &= C_p dT + V dP \\ dS &= C_p \frac{dT}{T} \\ dU &= C_v dT \end{aligned} \right\} \begin{array}{l} \text{volume changes little with} \\ P \text{ \& } T \end{array}$$

Generalized Property Correlations For Gases: Residuals

Path for Property Changes:



$$\Delta H = \Delta H^{ig} + H_2^R - H_1^R$$

$$\Delta S = \Delta S^{ig} + S_2^R - S_1^R$$

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

$$\Delta S^{ig} = \int_{T_1}^{T_2} \frac{C_p^{ig}}{T} dT - R \ln \frac{P_2}{P_1}$$

Lee-Kessler Correlations

$$\frac{H^R}{RT_c} = \frac{(H^R)^0}{RT_c} + \omega \frac{(H^R)^1}{RT_c}$$

where $(H^R)^0$, $(H^R)^1$, $(S^R)^0$, and $(S^R)^1$

are tabulated as functions of T_r and P_r

$$\frac{S^R}{R} = \frac{(S^R)^0}{R} + \omega \frac{(S^R)^1}{R}$$

where

$$T_r \equiv T/T_c$$

$$P_r \equiv P/P_c$$

Pitzer type mixing rules:

$$T_{pc} = \sum y_i T_{c,i}$$

$$P_{pc} = \sum y_i P_{c,i}$$

$$\omega = \sum y_i \omega_i$$

$$T_{pc} = \frac{\sum y_i T_{c,i}}{\sum y_i} \quad P_{pc} = \frac{\sum y_i P_{c,i}}{\sum y_i}$$

Residuals

In general, the definition of a residual property is

$$M^R \equiv M - M^ig$$

where M is the molar value of any extensive variable

$$G^R = G - G^ig$$

$$d\left(\frac{G^R}{RT}\right) = \frac{V^R}{RT} dP$$

$$V^R = V - V^ig$$

$$PV = ZRT$$

$$V = \frac{ZRT}{P}$$

$$Z=1 \text{ (Ideal Gas)}$$

$$V^R = \frac{ZRT}{P} - \frac{RT}{P}$$

$$d\left(\frac{G^R}{RT}\right) = (Z-1) \frac{dP}{P}$$

$$\frac{G^R}{RT} = \int_0^P (Z-1) \frac{dP}{P} \quad (\text{const } T)$$

$$\frac{H^R}{RT} = -T \int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} \quad (\text{const } T)$$

$$\frac{S^R}{R} = -T \int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} - \int_0^P (Z-1) \frac{dP}{P} \quad (\text{const } T)$$

$$G^R = H^R - TS^R$$

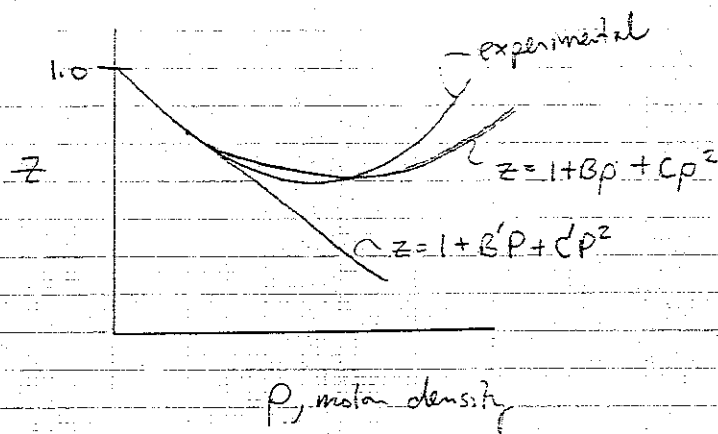
Virial Equation

The virial equation is an expansion of the compressibility factor where the parameters have physical significance (i.e. can be directly related to intermolecular potential)

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

$$B = \lim_{\rho \rightarrow 0} \left(\frac{\partial Z}{\partial \rho} \right)_T \quad C = \lim_{\rho \rightarrow 0} \frac{1}{2!} \left(\frac{\partial^2 Z}{\partial \rho^2} \right)_T$$

For pure components the virial coefficients are independent of pressure or density, they are functions of temperature only.



For many gases the virial EoS give good representation of the compressibility factor up to about one half of the critical density and fair representation up to nearly the critical density.

The significance of the virial coefficients is that they can be directly related to intermolecular forces.

The Second virial coefficient, B

- Takes into account deviations from ideal behavior that result from interactions between two molecules.

$$B = \lim_{p \rightarrow 0} \left(\frac{\partial Z}{\partial p} \right)_T = 2\pi N_A \int_0^{\infty} \left[1 - e^{\Gamma(r)/kT} \right] r^2 dr$$

The Third virial coefficient, C

- Takes into account deviations from ideal behavior that result from the interaction of three molecules.

$$C = \lim_{p \rightarrow 0} \frac{1}{2!} \left(\frac{\partial^2 Z}{\partial p^2} \right)_T = -\frac{8\pi^2 N_A^2}{3} \int_0^{\infty} \int_0^{\infty} \int_{|r_{12}-r_{13}|}^{r_{12}+r_{13}} f_{12} f_{13} f_{23} r_{12} r_{13} r_{23} dr_{12} dr_{13} dr_{23}$$

$$\text{where } f_{ij} = \exp(-\Gamma_{ij}/kT) - 1$$

These eqns. apply for spherically symmetric molecules, however, a more detailed analysis could give the potential for more complicated molecules.

The virial eqn. can easily be applied to mixtures using the following mixing rules:

$$B_{mix} = \sum_{i=1}^m \sum_{j=1}^m y_i y_j B_{ij}$$

$$C_{mix} = \sum_{i=1}^m \sum_{j=1}^m \sum_{k=1}^m y_i y_j y_k C_{ijk}$$

The major use of the virial equation is for the calculation of gas ϕ fugacities using a truncated form (i.e. omitting quadratic and higher density terms)

$$\ln \phi_i = \frac{2}{v} \sum_{j=1}^m y_j B_{ij} - \ln Z_{mix}$$

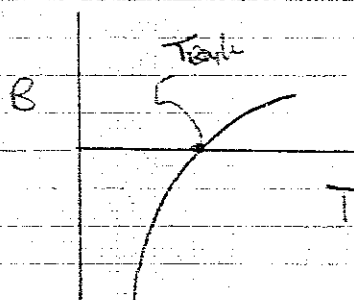
where $Z_{mix} = 1 + \frac{B_{mix}}{v}$

Boyle Temperature:

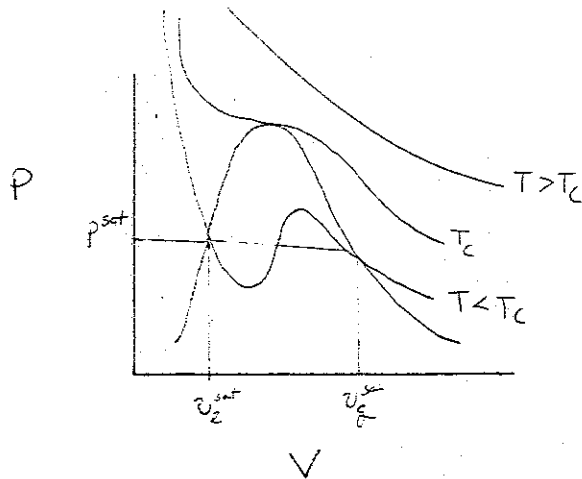
where the second virial coefficient equals zero

$$T_{Boyle} \Rightarrow B(T) = 0$$

at $B(T) = 0$ the attractions are exactly balanced by repulsive interactions



Cubic Equations of State



Isotherms given by an Equation of State

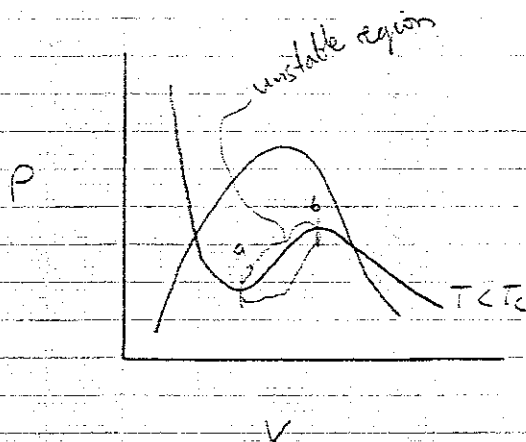
Van der Waals Equation of State

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

$b \sim$ corrects volume to account for volume occupied by the molecules

$a \sim$ accounts for molecular interactions

consider an isotherm in the 2 ϕ region

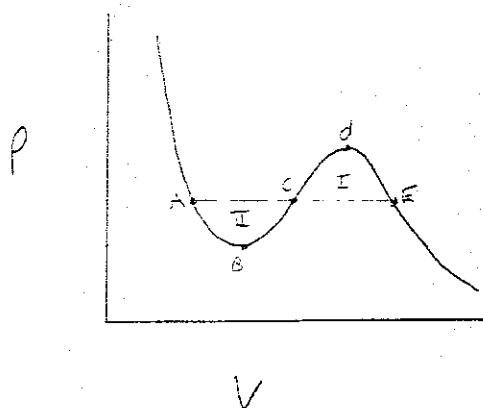


between points A and B

$\left(\frac{\partial P}{\partial V}\right)_T > 0$ this violates the stability criterion

Stability

$$K_T > 0 \text{ or } \left(\frac{\partial P}{\partial V}\right)_T < 0$$



Equal Area Construction (Maxwell Construction)

$$\mu_A = \mu_E \quad \mu_A - \mu_E = \int_A^E v dp = 0$$

$$\underbrace{\int_E^d v dp + \int_d^C v dp}_{\text{Area I}} = \underbrace{\int_C^E v dp + \int_E^A v dp}_{\text{Area II}}$$

This is how points A and E are determined.

The fraction of the system that exists in each of the two phases is governed by the lever rule.

$$V = N\bar{v} = N x_L \bar{v}_L + N x_G \bar{v}_G$$

x_L & x_G are the mole fractions of each β , $x_L + x_G = 1$

then

$$x_L = \frac{\bar{v}_G - \bar{v}}{\bar{v}_G - \bar{v}_L} \quad \text{and} \quad x_G = \frac{\bar{v} - \bar{v}_L}{\bar{v}_G - \bar{v}_L} \quad \leftarrow \text{quality}$$

Evaluation of constants a and b in the VDW EOS

1. fit to PVT data

2. Estimates from critical constants, T_c, P_c

at the critical point the isotherm inflects, so

$$\left(\frac{\partial P}{\partial V}\right)_{T_c} = \left(\frac{\partial^2 P}{\partial V^2}\right)_{T_c} = 0$$

$$a = \frac{27 R^2 T_c^2}{64 P_c}$$

$$b = \frac{R T_c}{8 P_c}$$

The EOS can be written in terms of the critical constants providing 3 equations and 5 unknowns, P_c, V_c, T_c, a , and b

Other Equations of State:

Redlich-Kwong:
$$P = \frac{RT}{v-b} - \frac{a}{T^{1/2} v(v+b)}$$

Peng-Robinson:
$$P = \frac{RT}{v-b} - \frac{a}{v(v+b) + b(v-b)}$$

Generic Equation of State:

$$P = \frac{RT}{v-b} - \frac{\Theta(v-\eta)}{(v-b)(v^2 + \delta v + \epsilon)}$$

the parameters $b, \Theta, \delta, \epsilon$, and η in general depend on Temperature and composition.

Mixing Rules:

R-K
$$a_m = \left(\sum_{i=1}^n y_i a_i^{1/2} \right)^2 \quad b_m = \sum_{i=1}^n y_i b_i$$

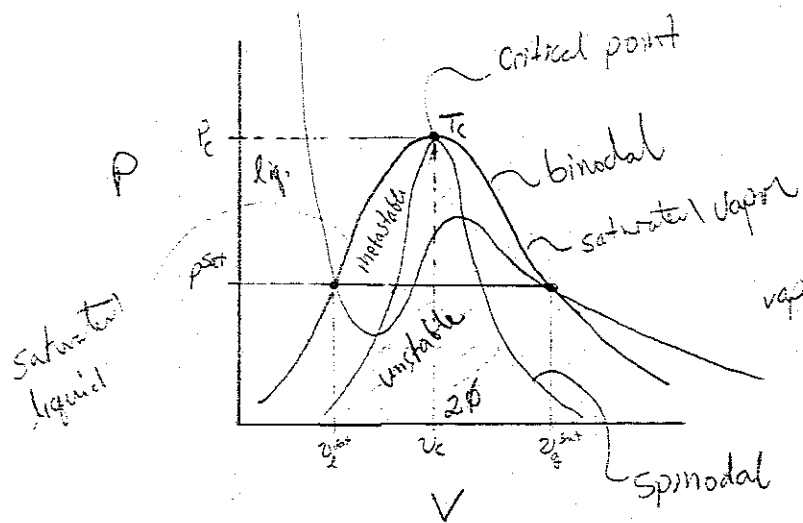
P-R
$$a_m = \sum_i \sum_j y_i y_j a_{ij} \quad b_m = \sum_i y_i b_i$$

$$a_{ij} = (1 - \delta_{ij}) (a_i a_j)^{1/2} \quad \delta_{ij} = \text{binary interaction parameter}$$

In General: arithmetic average is often used for size parameters

geometric mean is used for energy parameters

The P-V Diagram



The binodal marks the transition between the pure phases and the 2ϕ region. Between the spinodal and binodal is a metastable region (This is why fluids can be supercooled and superheated). The spinodal marks the point where a phase transition must occur.

Corresponding States

Classical or macroscopic theory of corresponding states

Van der Waals showed from the principle of continuity of gaseous & liquid phases that at the critical point

$$\left(\frac{\partial P}{\partial V}\right)_T = \left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0$$

These relations led van der Waals to the general result that for variables V , T , and P there exists a universal function such that

$$F\left(\frac{V}{V_c}, \frac{T}{T_c}, \frac{P}{P_c}\right) = 0$$

is valid for all substances. Stated another way, if an equation of state for any one fluid is written in reduced coordinates (i.e. V/V_c , T/T_c , P/P_c), that equation is valid for any other fluid.

Two parameter corresponding states only adequately describes simple molecules (heavier noble gases; argon, krypton, xenon). A simple molecule is one whose force field has a high degree of symmetry (the potential is determined by the degree of separation and not the relative orientation between the molecules). Nearly simple molecules are: CH_4 , O_2 , N_2 , and CO .

Extension to Complicated Molecules

- for complex molecules it is necessary to introduce at least one additional parameter.

In the three parameter theory of corresponding states the function $F(\mathcal{V}_c, T_c, P_c)$ still applies, but now the generalized function is different for each class of molecules.

Pitzer's parameter is perhaps most useful and is defined as the acentric factor, ω , that is a measure of the acentricity, i.e., the non-central nature of intermolecular forces.

three-parameter corresponding states theory:

$$Z(P, T, \omega) = Z^{(0)}(P, T, \omega=0) + \omega Z^{(1)}(P, T)$$

$\omega \approx 0$ for simple fluids $\omega > 0$ for complicated molecules.

Heat Capacity of Gases & Liquids

Ideal Monatomic gas $C_V = \frac{3}{2} RT$

$$C_p = \frac{5}{2} RT$$

$$C_p = C_V + R$$

Ideal heat capacity is correct in general in the limit that $P \rightarrow 0$

The most common expression for $C_p(T)$ is

$$\frac{C_p}{R} = A + BT + CT^2 + DT^{-2}$$

Fugacity

Form of the fundamental eqn. for equilibria:

$$f^{\alpha} = f^{\beta}$$

fugacity was proposed by Lewis and is defined by

$$\mu_i - \mu_i^{\circ} = RT \ln \frac{f_i}{f_i^{\circ}}$$

f_i° & μ_i° are chosen arbitrarily for convenience, however, when one is chosen the other is fixed

Fugacity of a pure component:

for a Pure Gas at const. T

$$dG_i = -S_i dT + V_i dP$$

$$= V_i dP \text{ (at const. T)}$$

for an Ideal gas $V_i = \frac{RT}{P}$

$$dG_i = RT d \ln P \quad (1)$$

$$\mu_i = \bar{G}_i = \left(\frac{\partial G}{\partial n_i} \right)_{T, P, n_{j \neq i}}$$

for a Pure Non-ideal gas at constant T

$$dG_i = RT d \ln f_i \quad (2)$$

equate (1) & (2)

$$d \ln f_i = d \ln P$$

Integrate

$$\ln f_i = \ln P + \ln \phi$$

$$\text{or } f_i = \phi P$$

Fugacity in gas ϕ is the corrected pressure

$$\lim_{P \rightarrow 0} \frac{f_i}{P} = 1.0$$

$\phi = 1.0$ for an Ideal Gas

Fugacity for a mixture:

In this case:

$$d\bar{G}_i = RT d \ln \hat{f}_i^{\sim \text{mixture}} \quad (\text{const. } T)$$

similarly to the analysis for a pure component

$$\hat{f}_i = \hat{\phi}_i y_i P \Leftarrow \text{fugacity for a mixture is a corrected partial pressure}$$

$$\lim_{P \rightarrow 0} \frac{\hat{f}_i}{y_i P} = 1.0$$

Calculation of Fugacity Coefficients:

$$\ln \phi_i = \int_0^P (Z-1) \frac{dP}{P}$$

$$RT \ln \phi_i = RT \ln \frac{\hat{f}_i}{y_i P} = \int_V^\infty \left[\left(\frac{\partial P}{\partial n_i} \right)_{T, y_{j \neq i}} - \frac{RT}{V} \right] dV - RT \ln Z$$

∞ ideal gas limit

Considering the virial EoS

$$Z-1 = \frac{BP}{RT}$$

$$\ln \phi_i = \frac{B_i P}{RT} \Leftarrow \text{generally good to 10 atm}$$

for a pure fluid:

$$f_i = \phi_i^{\text{sat}} P_i^{\text{sat}} \exp \left[\frac{v_i^L (P - P^{\text{sat}})}{RT} \right]$$

Lewis fugacity Rule:

$$\hat{f}_i = y_i f_{i, \text{pure}} \quad \left. \begin{array}{l} \text{good approx. at low } P \\ \text{good when } y_i > 0.9 \end{array} \right\}$$

$$\hat{\phi}_i = \phi_{i, \text{pure}}$$

Derivation of Poynting correction factor:

$$G_i - G_i^{\text{sat}} = \int_{P_i^{\text{sat}}}^P v^l dP = RT \ln \frac{f_i}{f_i^{\text{sat}}}$$

$$\ln \frac{f_i}{f_i^{\text{sat}}} = \frac{1}{RT} \int_{P_i^{\text{sat}}}^P v^l dP$$

$$\frac{f_i}{f_i^{\text{sat}}} = \exp \left[\int_{P_i^{\text{sat}}}^P v^l dP \right]$$

$$f_i = f_i^{\text{sat}} \exp \left[\int_{P_i^{\text{sat}}}^P v^l dP \right]$$

$$f_i^{\text{sat}} = \phi_i^{\text{sat}} P_i^{\text{sat}}$$

derivation of fundamental Phase equilibrium relationship:

$$\mu_i^\alpha - \mu_i^{\circ\alpha} = RT \ln \frac{f_i^\alpha}{f_i^{\circ\alpha}} \quad (1)$$

$$\mu_i^\beta - \mu_i^{\circ\beta} = RT \ln \frac{f_i^\beta}{f_i^{\circ\beta}} \quad (2)$$

$$\mu_i^\alpha = \mu_i^\beta$$

$$\mu_i^{\circ\alpha} + RT \ln \frac{f_i^\alpha}{f_i^{\circ\alpha}} = \mu_i^{\circ\beta} + RT \ln \frac{f_i^\beta}{f_i^{\circ\beta}} \quad (3)$$

if $\mu_i^{\circ\alpha} = \mu_i^{\circ\beta}$ then $f_i^{\circ\alpha} = f_i^{\circ\beta}$ (same P & T)

and $f_i^\alpha = f_i^\beta$

suppose the standard states are at the same T but different P , then

$$\mu_i^{\circ\alpha} - \mu_i^{\circ\beta} = RT \ln \frac{f_i^{\circ\alpha}}{f_i^{\circ\beta}}$$

substitution into (3) yields

$$f_i^\alpha = f_i^\beta$$

Activity

$$a_i(T, P, x) \equiv \frac{f_i(T, P, x)}{f_i(T, P^0, x^0)}$$

The activity coefficient is defined as

$$\gamma_i \equiv \frac{a_i}{x_i}$$

$\gamma < 1$ for attractive molecules

$\gamma > 1$ for repulsive molecules

using excess functions:

$$\bar{g}_i^E = \bar{g}_{i(\text{real})} - \bar{g}_{i(\text{ideal})}$$

an ideal solution is one where the activity is equal to the mole fraction, $\gamma_i = 1$, or where $f_i^L = K_i x_i$ (fugacity is proportional to the mole fraction)

$$\bar{g}_i^E = \bar{g}_{i(\text{real})} - \bar{g}_{i(\text{ideal})} = RT [\ln f_{i(\text{real})} - \ln f_{i(\text{ideal})}]$$

$$\bar{g}_i = RT \ln \frac{f_{i(\text{real})}}{f_{i(\text{ideal})}} = RT \ln \frac{f_i}{K_i x_i}$$

$$a_i = \gamma_i x_i = \frac{f_i}{K_i}$$

$$\bar{g}^E = RT \ln \gamma_i \quad \text{or} \quad g^E = RT \sum_i x_i \ln \gamma_i$$

Limiting Cases of Liquid ϕ fugacities

$$\lim_{x_2 \rightarrow 0} \frac{f_2}{x_2} = H_{2,1} \leftarrow \text{Henry's constant for solute 2 in solvent 1}$$

$$\lim_{x_2 \rightarrow 0} \frac{f_1}{x_1} = f_{1(\text{pure liquid})} = \phi_i^{\text{sat}} P_i^{\text{sat}} \exp\left[v_i^L \frac{(P - P^{\text{sat}})}{RT}\right]$$

Models for Activity Coefficients:

any expression for the molar excess Gibbs energy must obey the two boundary conditions:

$$g^E = 0 \quad \text{when } x_1 = 0$$

$$g^E = 0 \quad \text{when } x_2 = 0$$

the simplest expression is the Two-Suffix Margules Equation:

$$g^E = A x_1 x_2 \quad \text{or} \quad \ln \gamma_1 = \frac{A}{RT} x_2^2$$

$$\ln \gamma_2 = \frac{A}{RT} x_1^2$$

Margules } Parameters are Temp.
Van Laar } dependent

Other Models: (most sophisticated)

Wilson, NRTL, UNIQUAC, UNIFAC

universal quasi-chemical theory

combinatorial & residual parts

VLE

$$\mu_L = \mu_V$$

$$f_L = f_V \text{ or } \phi_L = \phi_V$$

Henry's Law:

$$\hat{f}_i^g = \hat{f}_i^L = x_i \gamma_i H_i \quad \lim_{x_i \rightarrow 1} \gamma_i = 1.0$$

$y_i P = x_i H_i \leftarrow$ only valid for dilute solution and H_i must be found Experimentally

Raoult's Law

$$y_i P = x_i p_i^{\text{sat}}$$

Techniques to determine Vapor-Liquid Equilibria in order of level of approximation

Level of approx.	Method	Advantages	Disadvantages
1	DePriester Charts	fast & easy ok for Paraffins	Limited components ideal solutions
1	Raoult's Law	Simple	Ideal gas & solution
3	Rigorous Raoult's Law	Hand Calc. (accurate)	Awkward for $T > T_c$
3	1 EoS for both phases	Accurate	Cannot deal with unusual fluids (polymers, highly polar, etc.)

Raoult's Law for Adults

$$\phi_i y_i P = x_i \gamma_i P_i^{\text{sat}} \phi_i^{\text{sat}} \exp\left[\frac{v_i^L (P - P_i^{\text{sat}})}{RT}\right]$$

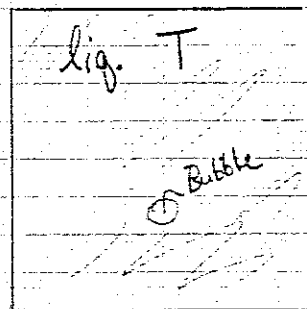
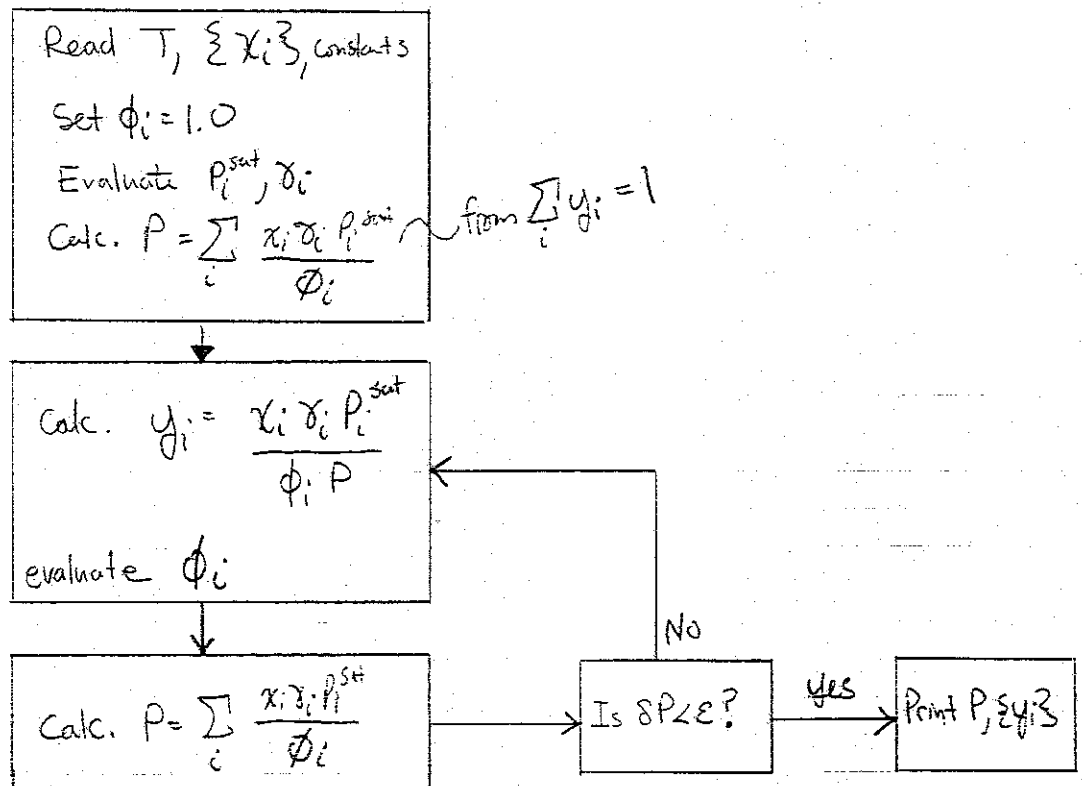
<u>Terms of the eqn.</u>	<u>details</u>	<u>contribution</u>
P y_i	total pressure gas ϕ mole fraction	major
ϕ_i	fugacity coefficient	≈ 1 for $P < 2 \text{ atm}$ for $2 < P < 10 \text{ atm}$ virial coefficient $P > 10 \text{ atm}$ major
P_i^{sat}	liq. ϕ vapor pressure	major
x_i	liq. ϕ mole fraction	
γ_i	activity coefficient	≈ 1 for dilute solutions $x_i \approx 0.9$
ϕ_i^{sat}	fugacity coefficient evaluate at P^{sat}	minor
$\exp\left[\frac{v_i^L (P - P_i^{\text{sat}})}{RT}\right]$	Poynting correction	Negligible for $P < 10 \text{ atm}$

$P_i^{\text{sat}} \rightarrow$ from Antoine eqn. $\ln P^{\text{sat}} = A - \frac{B}{T}$

$\alpha \text{ EoS } \phi_L = \phi_V$

Dew and Bubble Point Calculations

Bubble P (Given $T, \{x_i\}$) $\phi_i y_i P = x_i \gamma_i P_i^{sat}$

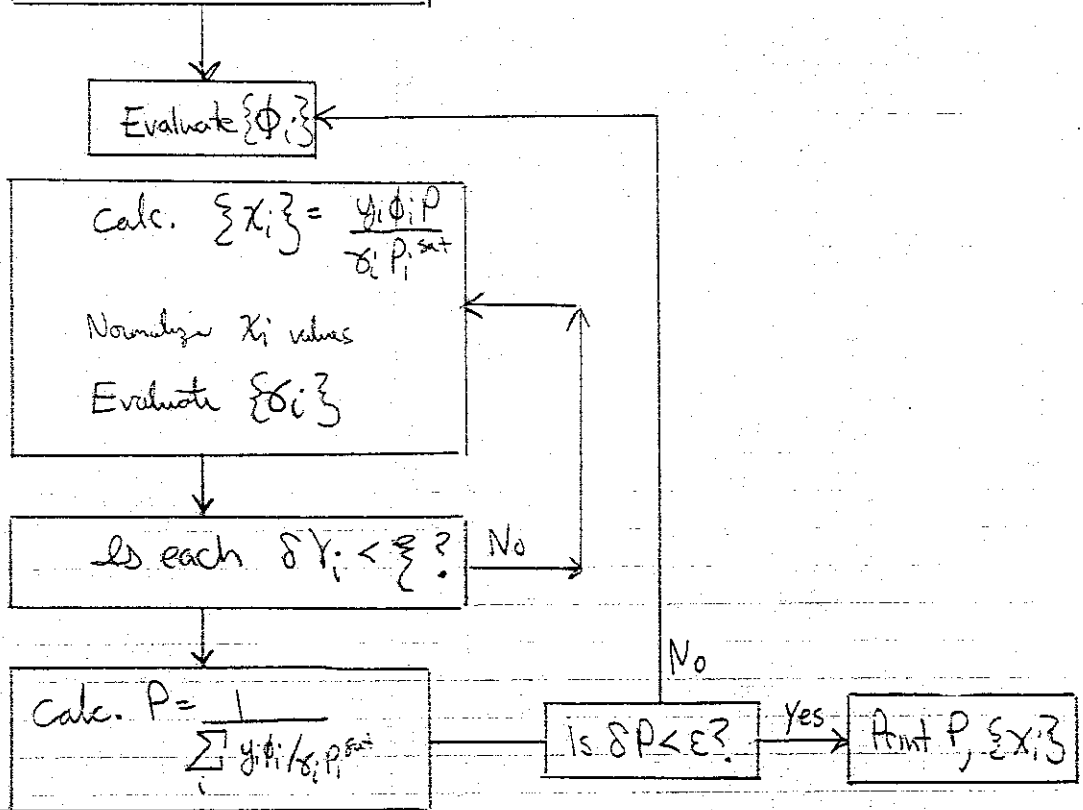


Decrease pressure to form bubble

Dew P (Given $T, \{y_i\}$)

Read $T, \{y_i\}, \text{constants}$
 Set all $\phi_i = 1.0$ & $\delta_i = 1.0$
 Evaluate $\{P_i^{\text{sat}}\}$
 Calc. $P = \frac{1}{\sum_i y_i \phi_i / \delta_i P_i^{\text{sat}}}$
 Calc. $\{x_i\} = \frac{y_i \phi_i P}{\delta_i P_i^{\text{sat}}}$
 evaluate γ_i

$$\sum_i x_i = 1$$



gas T
P_{drop}

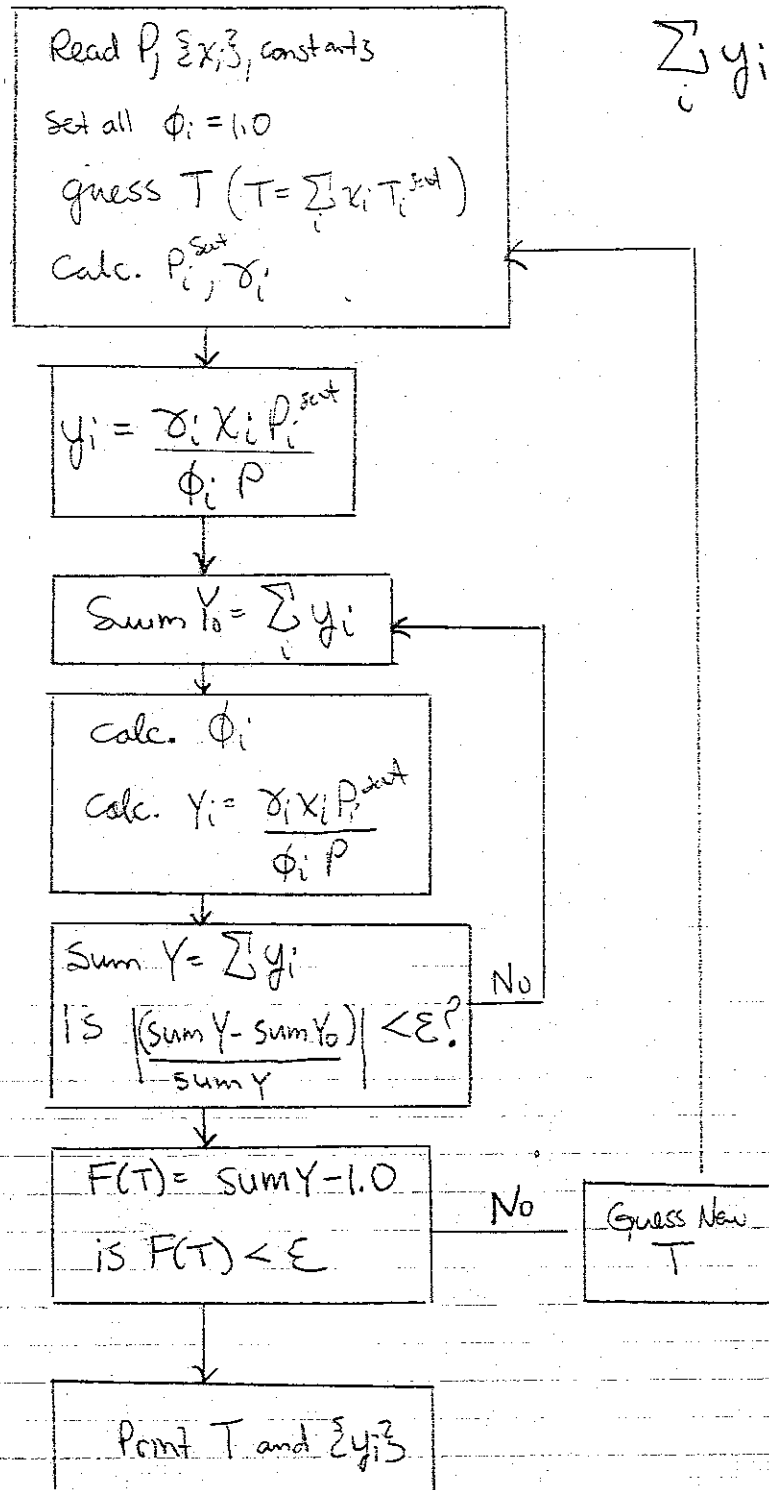
Pressure at which first drop
of liquid condenses

Bubble T (Given $P, \{x_i\}$)

$$\sum_i y_i = 1$$

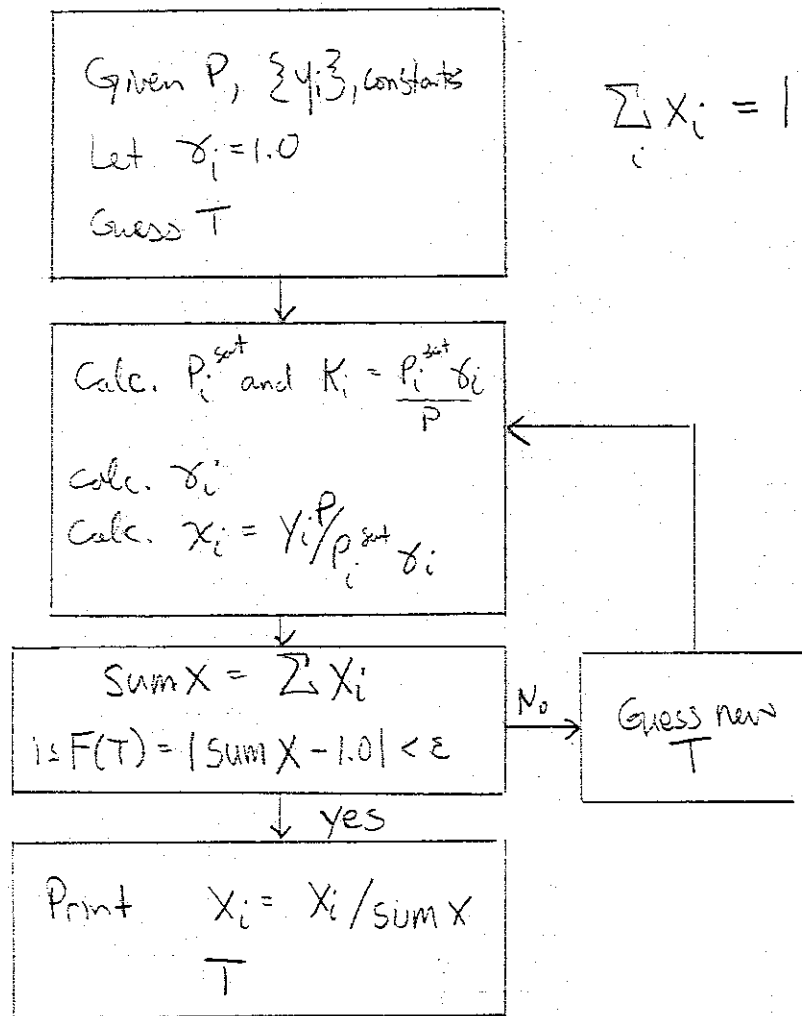
Successive
Substitution

Temperature at
which first bubble
of vapor forms



1/8. P
O-bubble

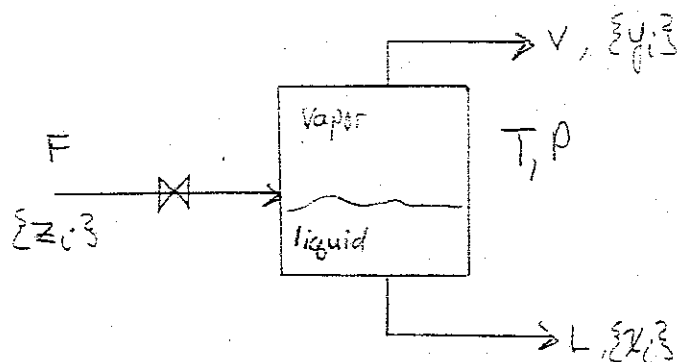
Dew T (Given P, $\{y_i\}$)



gas P
and drop

Temperature at which first
drop of liquid condenses

Flash Calculation



1) first do a dew or bubble calculation to determine if drum fluid is in the 2 ϕ region

Mass Balance:

$$L + V = 1$$

(if number is to 1 then L & V represent vapor & liquid ϕ fractions)
 $L \sim$ moles of liquid $V \sim$ moles of vapor

$$z_i = x_i L + y_i V$$

eliminate L

$$z_i = x_i (1 - V) + y_i V$$

for convenience define the partition coefficient

$$K_i \equiv \frac{y_i}{x_i}$$

then $y_i = \frac{z_i K_i}{1 + V(K_i - 1)}$ and $x_i = \frac{z_i}{1 + V(K_i - 1)}$

both $\sum_i y_i = 1$ and $\sum_i x_i = 1$

$$F_y = \sum_i y_i - 1 = \sum_i \frac{z_i K_i}{1 + V(K_i - 1)} - 1 = 0$$

$$F_x = \sum_i x_i - 1 = \sum_i \frac{z_i}{1 + V(K_i - 1)} - 1 = 0$$

a more convenient form

$$F = F_y - F_x$$

$$F = \sum_i \frac{z_i (K_i - 1)}{1 - V(K_i - 1)} = 0$$

$$\frac{dF}{dV} = - \sum_i \frac{z_i (K_i - 1)^2}{[1 - V(K_i - 1)]^2}$$

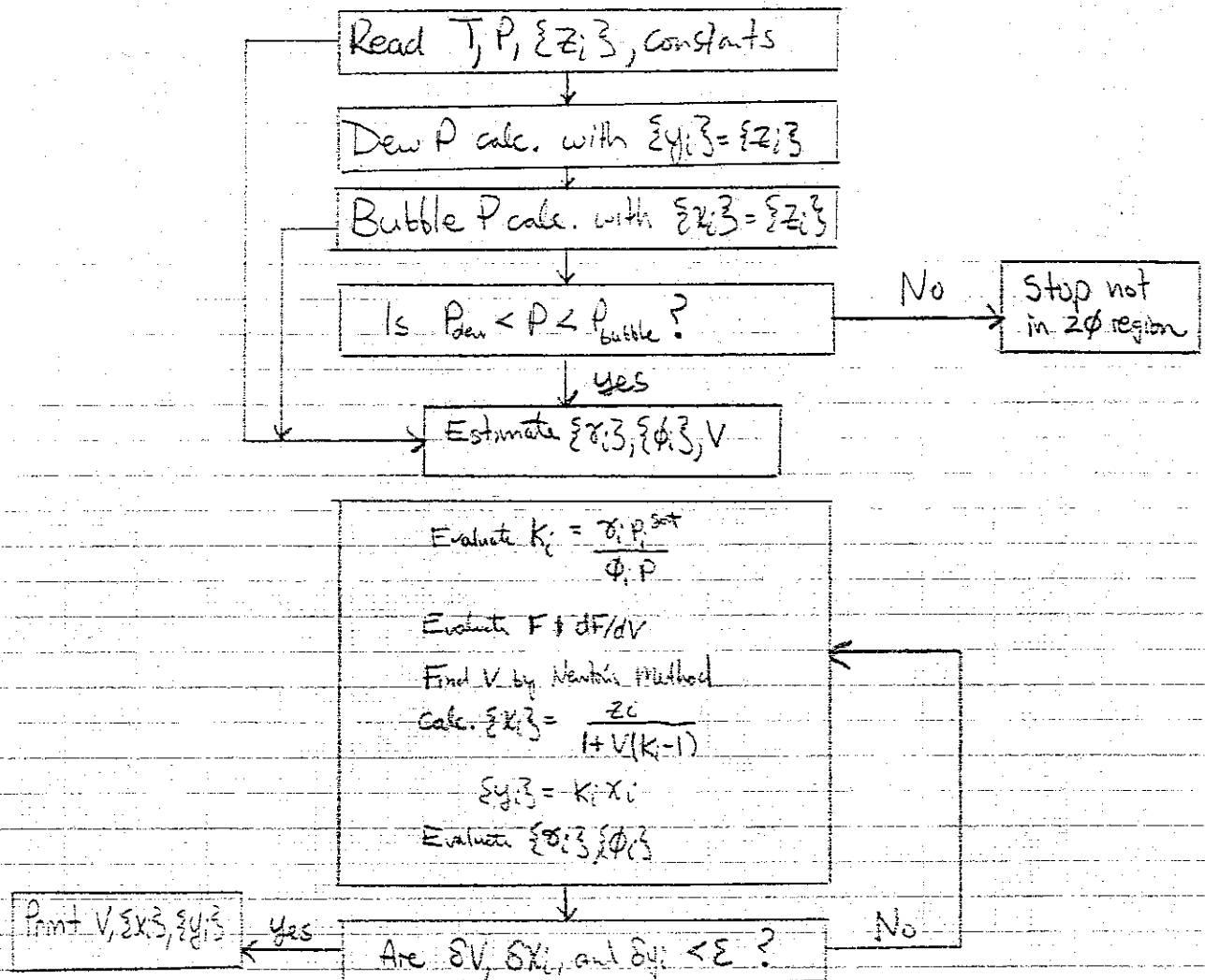
and Newton's method make iteration convergence rapid

$$F + \left(\frac{dF}{dV}\right) \Delta V = 0$$

then

$$K_i = \frac{y_i}{x_i} = \frac{\gamma_i P_i^{\text{sat}}}{\phi_i P}$$

Algorithm



Clapeyron & Clausius-Clapeyron

two phase systems

gas, β
Liq, α

P, T

$$\underbrace{P^{\text{sat}} = P^{\alpha} = P^{\beta} \quad T^{\alpha} = T^{\beta} = T}_{\text{true at equilibrium}}$$

for two phases of pure species coexisting in equilibrium

$$G^{\alpha} = G^{\beta}$$

then

$$dG^{\alpha} = dG^{\beta}$$

$$dG = -SdT + VdP$$

$$V^{\alpha}dP^{\text{sat}} - S^{\alpha}dT = V^{\beta}dP^{\text{sat}} - S^{\beta}dT$$

Rearrangement Gives

$$\frac{dP^{\text{sat}}}{dT} = \frac{S^{\beta} - S^{\alpha}}{V^{\beta} - V^{\alpha}} = \frac{\Delta S^{\alpha/\beta}}{\Delta V^{\alpha/\beta}}$$

for the entire system

$$G = H - TS$$

minimum at equilibrium

$$\Delta G = \Delta H - T\Delta S$$

at equilibrium

so it follows that

$$\Delta H^{\alpha/\beta} = T\Delta S^{\alpha/\beta}$$

$$\boxed{\frac{dP^{\text{sat}}}{dT} = \frac{\Delta H^{\alpha/\beta}}{T\Delta V^{\alpha/\beta}}}$$

← Clapeyron Equation

Clausius made a simple approximation of this equation using the following assumptions:

1. $V^{\beta} \gg V^{\alpha}$ ^{← gas & volume} which is true for gas-liquid systems

2. The gas & volume can be approximated using the ideal gas law (i.e. $PV = RT$)

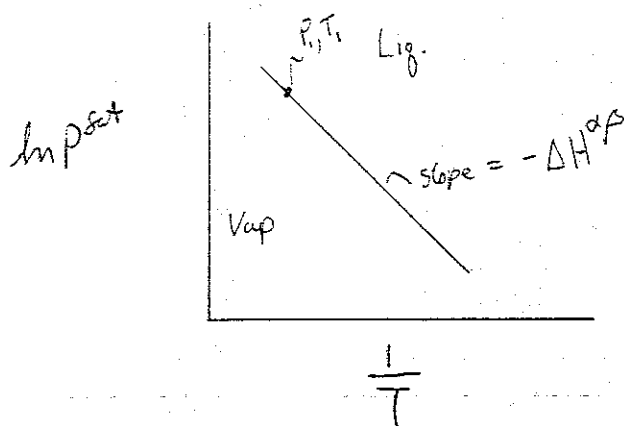
$$\frac{dp^{\text{sat}}}{dT} = \frac{\Delta H^{\alpha\beta}}{TV^{\beta}} = \frac{\Delta H^{\alpha\beta}}{T\left(\frac{RT}{p}\right)}$$

$$\frac{1}{p} \frac{dp^{\text{sat}}}{dT} = \frac{\Delta H^{\alpha\beta}}{RT^2}$$

or

$$\boxed{R \frac{d \ln p^{\text{sat}}}{d\left(\frac{1}{T}\right)} = -\Delta H^{\alpha\beta}} \Leftarrow \text{Clausius-Clapeyron Equation}$$

Applications



This equation suggests that by having one boundary condition (i.e. one phase equilibria point P_i, T_i) and knowledge of the enthalpy of vaporization $\Delta H^{\alpha\beta}$, then the incipient line can be extrapolated provided that $\Delta H^{\alpha\beta} = \text{const.}$, $V^{\beta} \gg V^{\alpha}$, and the gas ϕ behaves as an ideal gas.

Also, Antoine's Equation is derived from this relationship

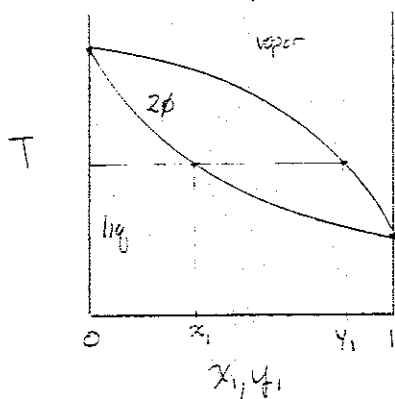
$$\ln p^{\text{sat}} = A - \frac{B}{T+C}$$

VLE - Phase Diagrams

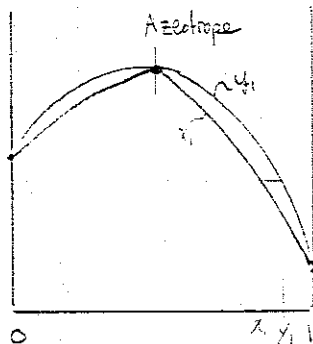
Binary Systems

$$F = C + 2 - P = 2$$

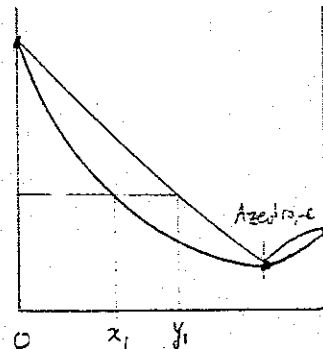
T-xy (Const. P)



Raoult's Law

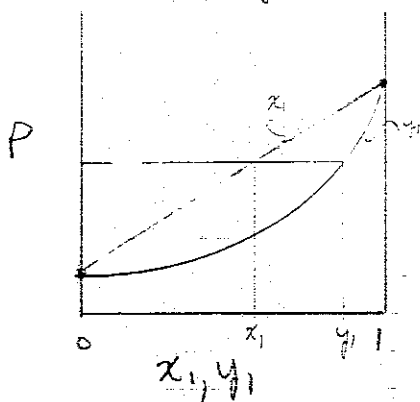


maximum boiling azeotrope

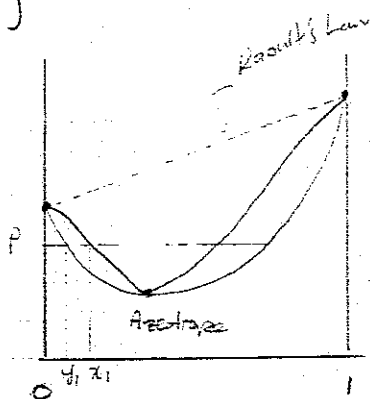


minimum boiling azeotrope

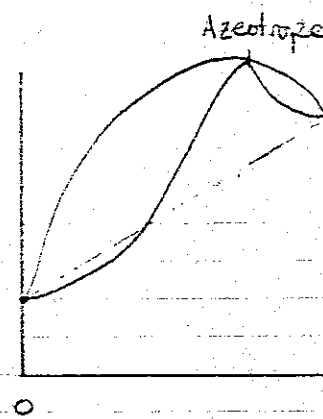
P-xy (Const. T)



Raoult's Law



Negative Deviation
minimum pressure azeotrope



maximum pressure azeotrope

for Raoult's Law: $y_A P = x_A P_A^{sat}$

$\sum y_i = 1$ (bubble P curve)

$$P = x_A P_A^{sat} + (1 - x_A) P_B^{sat}$$

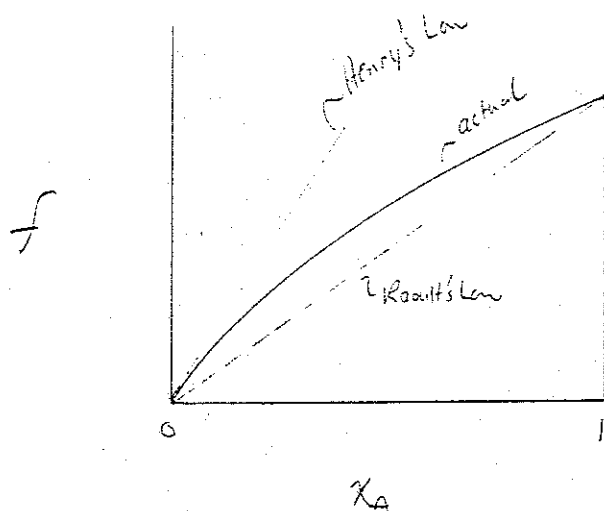
$$P = x_A (P_A^{sat} - P_B^{sat}) + P_B^{sat} \Leftarrow \text{straight line}$$

$\sum x_i = 1$ (dew P curve)

$$x_A + x_B = \left(\frac{y_A}{P_A^{sat}} + \frac{y_B}{P_B^{sat}} \right) P = \left[y_A \left(\frac{1}{P_A^{sat}} - \frac{1}{P_B^{sat}} \right) + \frac{1}{P_B^{sat}} \right] P$$

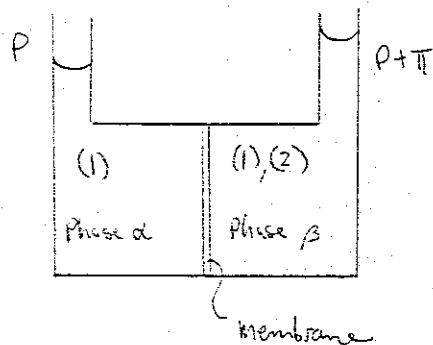
$$P = \left[\frac{1}{y_A} \left(\frac{1}{P_A^{sat}} - \frac{1}{P_B^{sat}} \right) + \frac{1}{P_B^{sat}} \right]^{-1}$$

P vs. y_A (non-linear)



if $\gamma < 1$ positive deviations from Raoult's Law (ideal solution)
 $\gamma > 1$ negative deviations " "

Osmotic Pressure



the membrane is permeable by component (1) only.

$$\mu_1^\alpha = \mu_1^\beta$$

$$\mu_1^\alpha = \mu_{1,\text{pure}}^\alpha(T, P) \quad \mu_1^\beta = \mu_{1,\text{pure}}^\beta(T, P+\pi) + RT \ln a_1$$

$$a_1 = \gamma_1 x_1$$

for a pure fluid $\left(\frac{\partial \mu}{\partial V}\right)_T = -P$

$$\mu_{\text{pure},1}(P+\pi) = \mu_{\text{pure},1}(P) + \pi V_{\text{pure},1}$$

for $\mu_1^\alpha = \mu_1^\beta$ $\mu_{1,\text{pure}}^\alpha = \mu_{1,\text{pure}}^\beta(P+\pi) + RT \ln a_1$

$$-\ln a_1 = \frac{\mu_{1,\text{pure}}^\beta(P+\pi) - \mu_{1,\text{pure}}^\alpha(P)}{RT} = \frac{\pi V_{\text{pure},1}}{RT}$$

assume: solution in phase β is dilute, x_1 is close to unity, so

$$\gamma_1 \approx 1$$

$$-\ln x_1 = \frac{\pi V_{\text{pure},1}}{RT}$$

Then $x_2 \ll 1$, $\ln x_1 = \ln(1-x_2) \approx -x_2$

$$\pi V_{\text{pure},1} = x_2 RT$$

Because $x_2 \ll 1$, $n_2 \ll n_1$ and $x_2 \approx \frac{n_2}{n_1}$

$$\pi v_{\text{pure},1} = \frac{n_2}{n_1} RT$$

$$\boxed{\pi V = n_2 RT} \Leftarrow \text{Van't Hoff equation}$$

Important assumptions:

- Solution is very dilute
- Solution is incompressible

Another way

$$f_{\text{soln}}^{\text{I}} = f_{\text{soln}}^{\text{II}}$$

I
Solvent

II

solvent + impurity

$$f_{\text{soln}}^{\text{I}} = x_i^{\text{II}} \gamma_i^{\text{II}} f_s^{\text{II}}(T, p^{\text{II}})$$

$$f_s^{\text{I}}(T, p^{\text{II}}) = f_s^{\text{I}}(T, p^{\text{I}}) \exp\left(\frac{v(p^{\text{II}} - p^{\text{I}})}{RT}\right)$$

$$f_{\text{soln}}^{\text{I}} = f_s^{\text{I}}(T, p^{\text{II}}) = x_i^{\text{II}} \gamma_i^{\text{II}} f_s^{\text{I}}(T, p^{\text{I}}) \exp\left(\frac{v(p^{\text{II}} - p^{\text{I}})}{RT}\right)$$

$$1 = x_i^{\text{II}} \gamma_i^{\text{II}} \exp\left(\frac{v(p^{\text{II}} - p^{\text{I}})}{RT}\right)$$

$$p^{\text{II}} - p^{\text{I}} = \pi = -\ln(x_i^{\text{II}} \gamma_i^{\text{II}}) \frac{RT}{v}$$

Phase Transitions

why does a fluid condense:

$$A = E - TS \leftarrow \begin{array}{l} \text{investigate the energy/entropy} \\ \text{competition} \end{array}$$

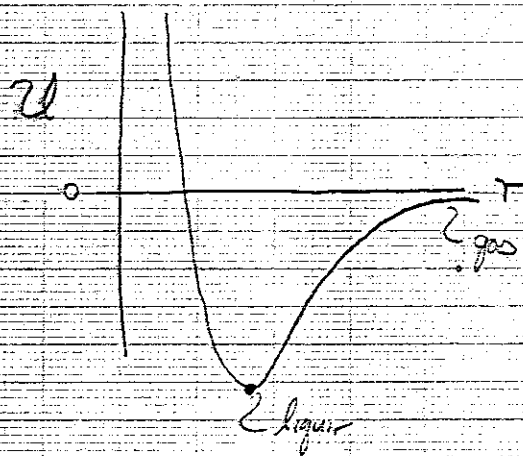
$A(T, V, N)$ at equilibrium: A is minimized

E is minimized

S is maximized

as the temperature, T , decreases the weight of the entropy decreases and the energetic effects become increasingly dominant until a phase transition occurs

for the energy of the fluid

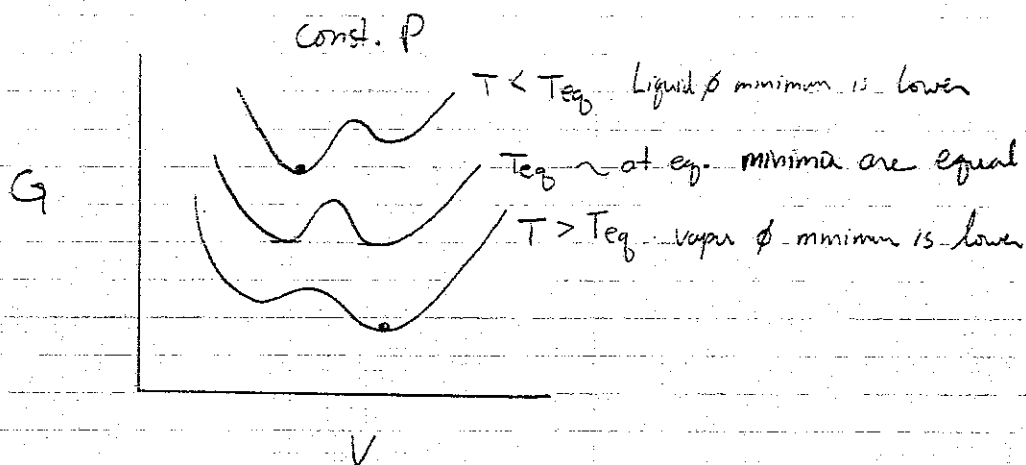


The energy of a liquid is less, hence, as T decreases the phase with minimum energy is the liquid phase

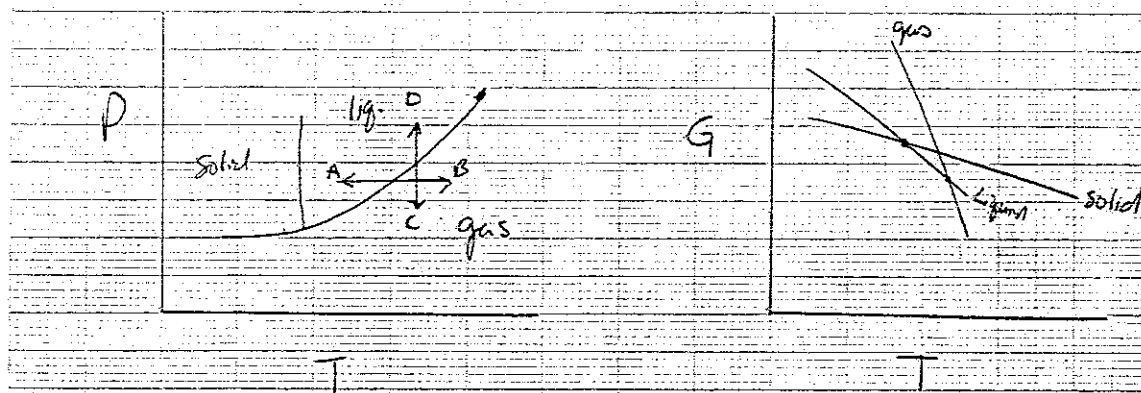
E = interaction between molecules

Phase Transitions

First order phase transition: G is the same, but U, A, H, S , and V are discontinuous across the transition



- latent heat is the stabilizing mechanism for density fluctuations
- C_v and K_T ~ diverge



Paths A-B and C-D
represent 1st order

Phase transitions

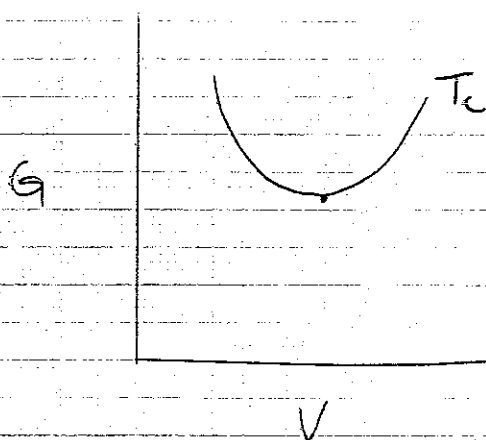
the stable ϕ is the one with
the lowest Gibbs free energy

Second order phase transition:

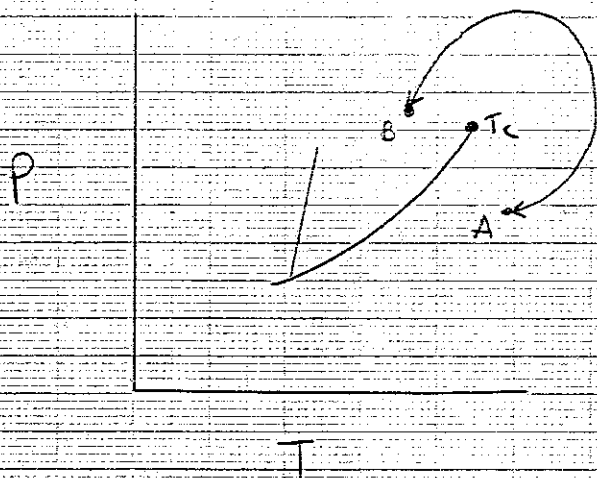
Continuous phase transition ~

large scale density fluctuations, critical opalescence
(no stabilizing mechanism)

- K_T & C_V diverge $\sim \Delta S = \frac{Q}{T}$ if Q is added some liquid
will vaporize, however, T
remains const. so
 $\frac{1}{T} \left(\frac{\partial S}{\partial T} \right) = \text{diverges}$



only one minimum at T_c and above



path A-B represents a
critical ϕ transition

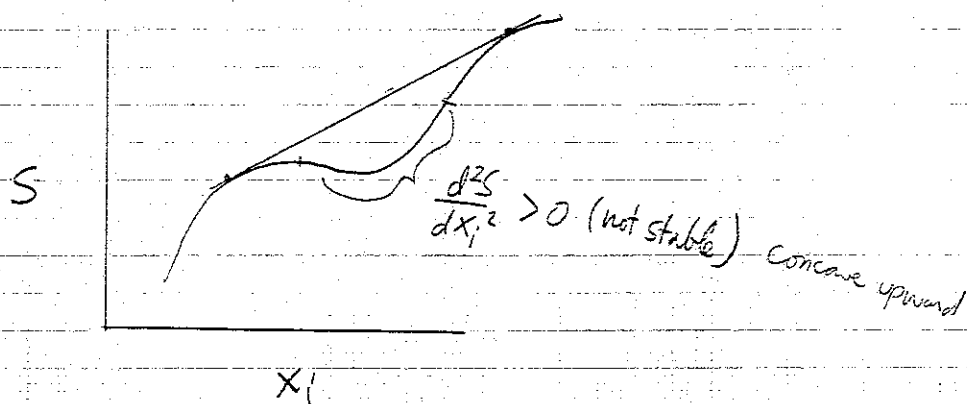
Stability

In General:

$$C_p > C_v > 0$$

$$K_T > K_S > 0$$

$$\left(\frac{\partial^2 S}{\partial U^2}\right)_{V,N} \leq 0 \quad \left(\frac{\partial^2 S}{\partial V^2}\right)_{U,N} \leq 0$$



$$\frac{\partial^2 U}{\partial S^2} = \frac{\partial T}{\partial S} \geq 0$$

$$\frac{\partial^2 U}{\partial V^2} = -\frac{\partial P}{\partial V} \geq 0$$

$$\left(\frac{\partial^2 F}{\partial T^2}\right)_{V,N} \leq 0$$

$$\left(\frac{\partial^2 F}{\partial V^2}\right)_{T,N} \geq 0$$

In General:

$$\frac{\partial^2 (\text{Free Energy})}{\partial (\text{Intensive Variable})^2} \leq 0$$

$$\left(\frac{\partial^2 H}{\partial P^2}\right)_{S,N} \leq 0$$

$$\left(\frac{\partial^2 H}{\partial S^2}\right)_{P,N} \geq 0$$

$$\frac{\partial^2 (\text{Free Energy})}{\partial (\text{Extensive Variable})^2} \geq 0$$

$$\left(\frac{\partial^2 G}{\partial T^2}\right)_{P,N} \leq 0$$

$$\left(\frac{\partial^2 G}{\partial P^2}\right)_{T,N} \geq 0$$

determination of ΔG°

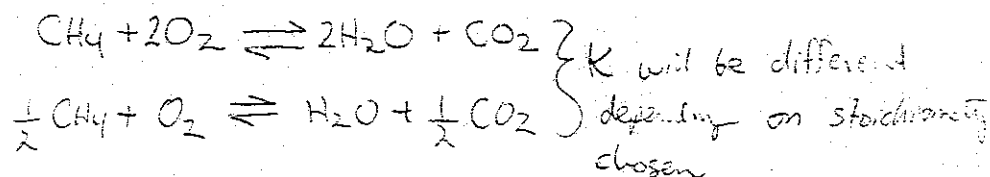
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\sum_i \nu_i G_i^\circ = \sum_i \nu_i H_i^\circ - T \sum_i \nu_i S_i^\circ$$

- reactants
+ products

$\Delta =$ products - reactants

Considering this \sim K is based upon the way the reaction is written



Gas ϕ Reactions

$$K = \prod_i \left(\frac{\hat{f}_i}{P^\circ} \right)^{\nu_i}$$

$$\hat{f}_i = \hat{\phi}_i \cdot y_i \cdot P$$

P° is standard state (i.e. 1 bar)

General Conclusions:

1) Effect of Temperature on K is determined by the sign of ΔH°

- Endothermic $\uparrow T \uparrow K$ (reaction shifts to the right at const. P)
- Exothermic $\uparrow T \downarrow K$ (reaction shifts to the left at const. P)

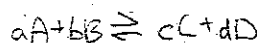
2) If the total stoichiometric $\# \nu = \sum \nu_i$

- $\nu =$ negative (moles of reactants > moles of products)

at const $T \quad \uparrow P \quad \uparrow K$ (shifts reaction to the right)

Liquid ϕ Reactions

$$K = \prod_i (\hat{a}_i)^{\nu_i} \quad \hat{a}_i = \frac{\gamma_i x_i f_i^\circ}{f_i^\circ}$$



$$\sim K = \frac{\hat{a}_C^c \hat{a}_D^d}{\hat{a}_A^a \hat{a}_B^b} = \frac{\frac{P_C^c P_D^d}{P_A^a P_B^b} \cdot \frac{\phi_C^c \phi_D^d}{\phi_A^a \phi_B^b}}{K_P \quad K_\phi}$$

$$\frac{d \ln K_p}{d(1/T)} = -\frac{\Delta H_{rxn}}{R}$$

If $\nu =$ positive (moles of products > moles of reactants)

at const. $T \quad \uparrow P \quad \downarrow K$

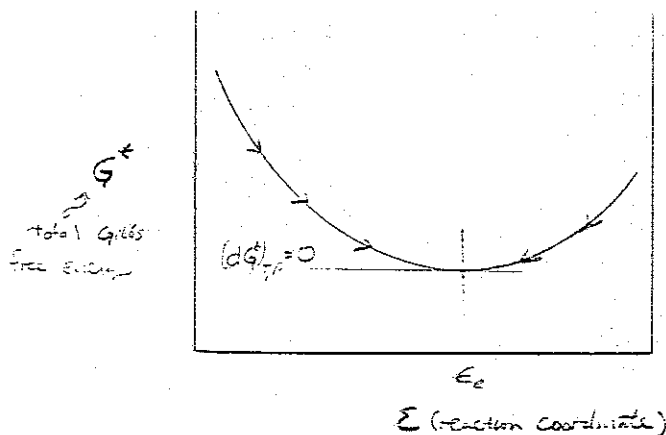
shifts reaction to the left

Reaction Equilibria

Rule of thumb : always consider rxn. equilibria first so that an evaluation as to whether the rxn. is economical can be made (best case scenario - rxn. goes to equilibrium)



For reaction equilibrium consider the Gibbs Free Energy



The condition for equilibrium is reached when G^* attains a minimum value

Two distinct features:

1) G^* is a minimum

2) $(dG^*)_{T,P} = 0$ its derivative is zero

Criterion of chemical reaction equilibrium

$$\sum_i \nu_i \mu_i = 0$$

↑ chemical potential

↑ stoichiometric coefficient

Definition of Equilibrium const.

$$K \equiv \prod_i (\hat{a}_i)^{\nu_i} = \exp \left[\frac{-\sum_i \nu_i G_i^\circ}{RT} \right]$$

$$-RT \ln K = \sum_i \nu_i G_i^\circ \equiv \Delta G^\circ$$

Equilibrium const. K is a function of Temperature only.