Ideal Gases cont'd :

Reversible, adiabatic : $d\varphi = 0$

$dU = dW = -PdV$ $C_v dT = -PdV$

$$\frac{dT}{T} = -\frac{R}{C_v}\frac{dV}{V}$$ let $\gamma = \frac{C_p}{C_v} = $ const. (approx.)

$$\ln \frac{T_2}{T_1} = -(\gamma-1)\ln\frac{V_2}{V_1}$$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$$ $$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{(\gamma-1)/\gamma}$$

$$\boxed{P_1 V_1^{\gamma} = P_2 V_2^{\gamma} = PV^{\gamma} = \text{constant}}$$

Poly tropic : $PV^{\delta} = K = \text{constant}$

Van der Waals Eqn : $$P = \frac{RT}{V-b} - \frac{a}{V^2}$$ eqn. of state

See Figure 3.12   plot of eqn

dln accurately predict region in liquid-vapor transition - non analytic

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

Generalized : $$Z = \frac{1}{1-h} - \frac{4.9340}{T_r^{1.5}}\left(\frac{h}{1+h}\right)$$ $$h = \frac{0.08664\, P_r}{Z\, T_r}$$

$P_r = P/P_c$, $T_r = T/T_c$

Use with any gas, only need P_c + T_c
all fluids deviate from ideal gas similarly

Liquids : Rackett : $V^{sat} = V_c Z_c^{(1-T_r)^{0.2857}}$

$e_r = e/e_c = V_c/V$

Lennard- Jones Potentials

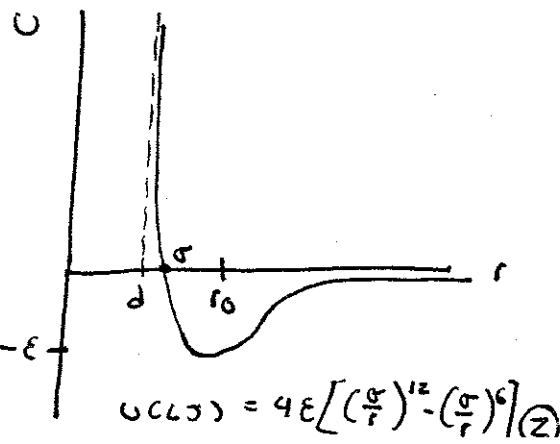U = intermolecular potential energy
F = intermolecular force

$$F(r) = -\frac{dU(r)}{dr}$$

d = hard-core diameter $(U + F \to \infty)$
σ = collision diameter $(U = 0)$
r_0 = equil. sep $(U_{min}$ at $-\varepsilon)$ $(F=0)$
ε = well depth

$$U(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{2}$$

Scond Virial Coefficient (B)

$$B = \frac{2}{3}\pi N_A d^3 \left[1 - (\ell^3 - 1)(e^{\mathcal{E}/kT} - 1) \right]$$

relative contributions of attraction and repulsion

$B = -$ attractions dominate (low T)

$B = +$ repulsions dominate (high T)

$B = 0$ Boyle temp T_B balanced

$$T_B = \frac{\mathcal{E}/k}{\ln\left(\frac{\ell^3}{\ell^3 - 1}\right)}$$

Ch. 4   Heat Effects

Sensible Heat   (T changes)

   homogeneous soln of const comp , $F = 2$

let $U = U(T, V)$

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

$$= C_V dT + \underbrace{\left(\frac{\partial U}{\partial V}\right)_T dV}_{=0 \text{ if } \text{const V process} \quad \text{or} \quad \text{if } U \neq U(V)}$$

$$dU = C_V dT$$
$$\Delta U = \int C_V dT$$

mech reversible, const V : $Q = \Delta U$

$$Q = \int_{T_1}^{T_2} C_V dT$$

$$\underbrace{\quad\quad\quad\quad}_{=0 \text{ if const P or}}$$
$$H \neq H(P)$$

let $H = H(T, P)$

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

$$dH = C_P dT$$
$$\Delta H = \int C_P dT$$

mech reversible const. P : $Q = \Delta H$ (or $\Delta E_P = 0, \Delta E_k = 0, W_S = 0$)

$$Q = \int_{T_1}^{T_2} C_P dT$$

To prove $C_p = \frac{3}{2}R$ ideal gas:

use canonical ensemble

$$A = -kT \ln Q$$

$$\left(\frac{\partial A}{\partial T}\right)_V = -k T_n Q - kT \frac{\partial \ln Q}{\partial T}$$

$$A = U - TS$$

$$dA = dU - TdS - SdT$$

$$\left(\frac{\partial^2 A}{\partial T^2}\right)_V = -k \frac{\partial \ln Q}{\partial T} - \frac{k \partial \ln Q}{\partial T}$$

$$= TdS - PdV - TdS - SdT$$

$$- kT \frac{\partial^2 \ln Q}{\partial T^2}$$

$$dA = -PdV - SdT$$

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

$$dU = TdS - PdV$$

$$dS = \frac{1}{T}dU + \frac{P}{T}dV$$

$$\left(\frac{\partial^2 A}{\partial T^2}\right)_V = -\left(\frac{\partial S}{\partial T}\right)_V$$

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V$$

$$= -\frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V$$

$$-2k\frac{\partial \ln Q}{\partial T} \quad -kT\frac{\partial^2 \ln Q}{\partial T^2} = -\frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V$$

$$-\frac{k}{T}\frac{\partial}{\partial T}\left[T^2\frac{\partial \ln Q}{\partial T}\right] = -\frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V$$

$$\left(\frac{\partial U}{\partial T}\right)_V = +k\frac{\partial}{\partial T}\left[T^2\frac{\partial \ln Q}{\partial T}\right]$$

$$U = +kT^2\left(\frac{\partial \ln Q}{\partial T}\right)_V$$

Now look at page 3.

2.5

empirical equation for C_p:

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

$$C_{p\ mix}^{is} = Y_A\, C_{p_A}^{is} + Y_B\, C_{p_B}^{is} + Y_C\, C_{p_C}^{is}$$

Internal Energy of Ideal Gases - Stat Mech

partition function Z

$$U = kT^2 \left(\frac{\partial \ln Z}{\partial T}\right)_V \qquad \text{total energy of a macroscopic system}$$

$$Z = \frac{Z_{translation}\ Z_{intramolecular}}{N!} \rightarrow \text{distinguishable}$$

$$\ln Z = \ln Z_{trans} + \ln Z_{intra} - \ln N!$$

$$Z_{trans} = V^{N_A}\left(\frac{2\pi m kT}{h^2}\right)^{(3/2)N_A}$$

$$\ln Z_{trans} = N_A \ln V + \frac{3}{2} N_A \ln \frac{2\pi m kT}{h^2}$$

sub into $\ln Z$ formula, take $\left(\frac{\partial}{\partial T}\right)_V$

$$U^{is} = \frac{3}{2} N_A kT + kT^2 \underbrace{\left(\frac{\partial \ln Z_{intra}}{\partial T}\right)_V}_{F(T)}$$

$$U^{is} = \frac{3}{2} RT + F(T)$$

$$H^{is} = U^{is} + RT$$

$$H^{is} = \frac{3}{2} RT + F(T)$$

$$C_p = \frac{5}{2} R, \qquad C_V = \frac{3}{2} R$$

monatomic and low T:
$$F(T) = 0$$

Latent Heat of Pure Substances

$$\boxed{\Delta H = T \Delta V \frac{d p^{sat}}{dT}}$$

Clapeyron Equations

Heat of Vap. at normal T_b: Riedel

$$\frac{\Delta H_n / T_n}{R} = \frac{1.092 (\ln P_c - 1.013)}{0.930 - T_{r_n}}$$

Watson:

Vaporization $\frac{\Delta H_2}{\Delta H_1} = \left(\frac{1 - T_{r_2}}{\cdots}\right)^{0.38}$

Standard heat of rxn : $\varphi = \Delta H$

Standard heat of formation

- rxn which forms a single compound from its constituent element
- ΔH_f°'s are additive, use to get ΔH rxn of a different rxn that isn't a formation rxn
- ΔH_f° of an element is 0
- ΔH° = products − reactants

Temp Dependence of ΔH° :

$$\Delta H^\circ = \Delta H_0^\circ + R \int_{T_0}^{T} \frac{C_p^\circ}{R} \, dT$$

$$\Delta H^\circ = \Delta H_0^\circ + \langle C_p^\circ \rangle_H \, (T - T_0)$$

Theoretical Flame Temp = Max attainable temp in a rxn
let $\varphi = 0$

Since $\Delta P_E = 0, \Delta K_E = 0, W_s = 0,$
$\Delta H = 0$

To solve for T in a given rxn: $\Delta H = \Delta H_{298}^\circ + \Delta H_p^\circ = 0$ ← heat products

$$\Delta H_p^\circ = \langle C_p^\circ \rangle_H \, (T - 298.15) \longrightarrow \text{solve for } T$$

if reactants not at 298k: $\Delta H = \Delta H_R^\circ + \Delta H_{298}^\circ + \Delta H_p^\circ$

heat or cool   rxn   heat
to 298   products to T_{max}

Ch 5   The Second Law

1. no apparatus can operate in such a way that its only effect is to convert heat absorbed by a system completely into work done by a system

2. no process is possible which consists solely of the transfer of heat from one temp level to a higher one

Heat Engines

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

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

Carnot engine : completely reversible, $m = 1$ (ideal)

Carnot's theorem : no engine can have a higher m than a Carnot engine

proof : assume engine with mth $|Q_H'|$ and $|W|$ greater m

$$\frac{|W|}{|Q_H'|} > \frac{|W|}{|Q_H|} \quad , \quad |Q_H| > |Q_H'|$$
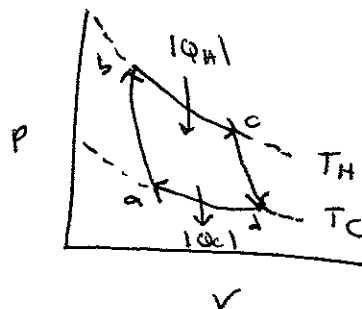
let this engine drive the Carnot engine backward as a refrigerator, net heat extracted from the cold reservoir is :

$$|Q_H| - |W| - (|Q_H'| - |W|) = |Q_H| - |Q_H'|$$

heat delivered to hot reservoir is also $|Q_H| - |Q_H'|$

$\longrightarrow$ violates 2nd law

Carnot cycle :

$a \to b$ adiabatic compression
$b \to c$ isothermal expansion
$c \to d$ adiabatic expansion
$d \to a$ isothermal compression

Prove Carnot's eqns

Isothermal : $dU = 0$, $Q = RT \ln \frac{V_1}{V_2}$

$$\frac{|Q_H|}{|Q_C|} = \frac{T_H \ln(V_c/V_b)}{T_C \ln(V_d/V_a)}$$

$Q = -W = P\,dV$
$= \frac{RT}{V} dV$

adiabatic : $dQ = 0$

$$C_V\, dT = dU = dW = -P\,dV$$

(4)

$$C_V dT = -p\,dV = -\frac{RT}{V}\,dV$$

$$\int_{T_c}^{T_H} \frac{C_V}{R}\frac{dT}{T} = \ln\frac{V_a}{V_b}$$

$$\int_{T_c}^{T_H} \frac{C_V}{R}\frac{dT}{T} = \ln\frac{V_d}{V_c}$$

$$\Rightarrow \ln\frac{V_a}{V_b} = \ln\frac{V_d}{V_c}$$

thus,

$$\frac{|Q_H|}{|Q_c|} = \frac{T_H}{T_c}\frac{\ln(V_c/V_b)}{\ln(V_d/V_a)} \qquad \text{Carnot's Eqns}$$

$$\eta = 1 - T_c/T_H$$

Entropy

$$\oint \frac{d\varphi_{rev}}{T} = 0$$

for total S, reversible

$$ds^+ = \frac{d\varphi_{rev}}{T} \qquad\qquad d\varphi_{rev} = T\,ds^+$$

<u>Entropy change of heat reservoir is always ϕ/T</u>
(effect is the same regardless of temperature)
 – irreversible or reversible

Isentropic : reversible and adiabatic $d\varphi_{rev} = 0$, $ds^+ = 0$

ideal gas :
$$\frac{\Delta S}{R} = \int_{T_0}^{T} \frac{C_p^{is}}{R}\frac{dT}{T} - \ln\frac{r}{r_0}$$

Second law : $\Delta S_{total} \geq 0$

$(= \text{is reversible adiabatic process})$

<u>Any engine</u> :
$$|W| = -T_c\,\Delta S_{total} \; (\text{lost work}) + |Q_H|\,(1 - T_c/T_H)$$

max work : $\Delta S_{total} = 0$, Carnot engine

Third Law of Thermo

Absolute entropy of all perfect crystalline substances at absolute temperature is 0.

$$du = Tds - pdV$$

$$H = U + pV$$

$$A = U - TS$$

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

(const. composition)

$$du = Tds - pdV$$

$$dH = Tds + Vdp$$

$$dA = -pdV - SdT$$

$$dG = Vdp - SdT$$

Maxwell's Equations

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

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

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

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

Canonical:

$$S = k \ln z + \frac{U}{T}$$

$$A = -kT \ln z$$

Residual properties:

$$G^R = G - G^{is}, \quad V^R = V - V^{is} = V - \frac{RT}{P} = \frac{RT}{P}(z-1)$$

we to solve for $H = H^{is} + H^R$ and $S = S^{is} + S^R$

Two-Phase Systems

$$G^\alpha = G^\beta \text{ at equilibrium}$$

derive the Clapeyron eqn

To derive Clausius-Clapeyron:
vapor-ideal gas
V^ℓ negligible

$$\Delta V = V^V = RT/p^{sat}$$

$$dG^\alpha = dG^\beta$$

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

$$\frac{dp^{sat}}{dT} = \frac{S^\beta - S^\alpha}{V^\beta - V^\alpha} = \frac{\Delta S^{\alpha\beta}}{\Delta V^{\alpha\beta}}$$

$$\frac{d\ell^{sat}}{p^{sat}} = \frac{\Delta H^{ev}}{R}\frac{dT}{T^2}$$

$$\Delta H^{ev} = \frac{-R d \ln p^{sat}}{d(1/T)}$$

at constant $P + T$: $\quad dH = Tds + V dp^{\nearrow 0}$

$$\frac{dp^{sat}}{dT} = \frac{\Delta H^{\alpha\beta}}{T\Delta V^{\alpha\beta}}$$

Antoine Eqn : $\ln P^{sat} = A - \dfrac{B}{T+C}$

Wagner Eqn : $\ln P_r^{sat} = \dfrac{A\tau + B\tau^{1.5} + C\tau^3 + D\tau^6}{1-\tau}$

$$\tau = 1 - T_r$$

$$P_r = P/P_c, \quad T_r = T/T_c$$

— valid over a wide temp range

Thermo diagrams :

T vs. S, $\ln P$ vs. H, H vs. S (Mollier diagram)

Ch. 7   Thermo of Flow Processes

Mass balance : $\dfrac{dm_{cv}}{dt} + \Delta(\dot{m})_{fs} = 0$ $\dfrac{dm_{cv}}{dt} = \Delta(\rho u A)_{fs} = 0$

steady state : $\rho_2 u_2 A_2 - \rho_1 u_1 A_1 = 0$

$\dot{m} = $ constant $= \rho_2 u_2 A_2 = \rho_1 u_1 A_1 = \dfrac{u_1 A_1}{V_1}$

Energy Balance :

$$\dfrac{d(mU)_{cv}}{dt} + \Delta\left[\left(H + \tfrac{1}{2}u^2 + zg\right)\dot{m}\right]_{fs} = \dot{Q} + \dot{W}$$

if KE & PE change negligable :

$$\dfrac{d(mU)_{cv}}{dt} + \Delta(H\dot{m})_{fs} = \dot{Q} + \dot{W}$$

Steady State Processes

→ implies no expansion of the control volume   (no PV work)

$$\Delta\left[\left(H + \tfrac{1}{2}u^2 + zg\right)\dot{m}\right]_{fs} = \dot{Q} + \dot{W}_s$$

↳ indicates applies to all flowing streams

if only 1 stream :

$$\Delta H + \dfrac{\Delta u^2}{2} + g\Delta z = Q + W_s$$

Entropy Balance

$$\sum_j \dfrac{\dot{Q}_j}{T_{\sigma,j}} - \Delta(S\dot{m})_{fs} + \dot{S}_G = \dfrac{d(mS)_{cv}}{dt}$$

Duct Flow of Compressible Fluids

adiabatic, steady state, 1-D, compressible, $W_s = 0$, $\Delta P_E = 0$

$$\Delta H + \frac{\Delta u^2}{2} = 0 \longrightarrow dH = -u\,du = T\,dS + V\,dP$$

$$d\left(\frac{uA}{V}\right) = 0 \quad \text{mass balance}$$

$$\boxed{\frac{dV}{V} - \frac{du}{u} - \frac{dA}{A} = 0}$$

$$-\frac{du}{u} = \frac{T\,dS + V\,dP}{u^2} \quad \text{sub into boxed eqn}$$

$$dH = T\,dS + V\,dP$$

$$dV = \left(\frac{\partial V}{\partial S}\right)_P dS + \left(\frac{\partial V}{\partial P}\right)_S dP$$

$$\left(\frac{\partial V}{\partial S}\right)_P = \underbrace{\left(\frac{\partial V}{\partial T}\right)_P}_{V\beta} \underbrace{\left(\frac{\partial T}{\partial S}\right)_P}_{(C_P/T)^{-1}} = \frac{V\beta T}{C_P}$$

$$c^2 = -V^2 \left(\frac{\partial P}{\partial V}\right)_S$$

$$\frac{dV}{V} = \frac{\beta T}{C_P} dS - \frac{V}{c^2} dP \longrightarrow \text{sub into boxed eqn}$$

eliminate $V\,dP$ with $dH = T\,dS + V\,dP$
divide by dx

Pipe Flow : $dA/dx = 0$

Nozzles : changing cross sectional area
  designed to be nearly frictionless
  in limit of reversible flow : $dS/dx = 0$
  ideal gas, constant heat capacities, isentropic expansion :
  $$PV^\gamma = \text{constant}$$

$$\frac{P_2}{P_1} = \left(\frac{2}{\gamma+1}\right)^{\gamma/(\gamma-1)}$$

Throttling : flow through a restriction with no ΔKE.
  $\longrightarrow$ pressure drop in the fluid
  if $Q = 0$, $\Delta H = 0 \longrightarrow H_1 = H_2$

Turbines (Expanders)
  expansion of a gas in a nozzle to produce high-velocity steam
  converts internal energy into KE, KE is converted
  to W_s when steam impinges on blades attached to a rotating shaft
  steam-turbines, high-P gas - expander

(6)

$\Delta PE = 0$, Q is negligible , $V_1 = V_2$ (usually)

$\dot{W}_s = \dot{m}\,\Delta H$

Isentropic $(Q=0,$ reversible$)$: $W_s = (\Delta H)_s$

$$\eta = \frac{W_s}{W_s\,(isentropic)} = \frac{\Delta H}{(\Delta H)_s}$$

Compression Processes $(P\uparrow)$

Compressors : rotating blades or reciprocating pistons

Same design equations as expanders

Isentropic work = min. shaft work required

$$\eta = \frac{W_s\,(isentropic)}{W_s} = \frac{(\Delta H)_s}{\Delta H}$$

Pumps : Some eqns as above

Isentropic : $dH = V\,dP$ $(S = const)$

$W_s\,(isentropic) = (\Delta H)_s = \int_{P_1}^{P_2} V\,dP = V(P_2 - P_1)$

(enthalpies of compressed liquids seldom available)

Ejectors : remove gases or vapors from an evacuated space
and compress them or discharge at a higher pressure
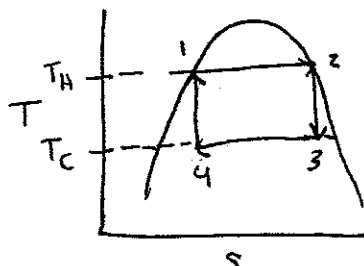
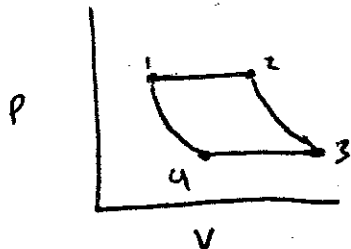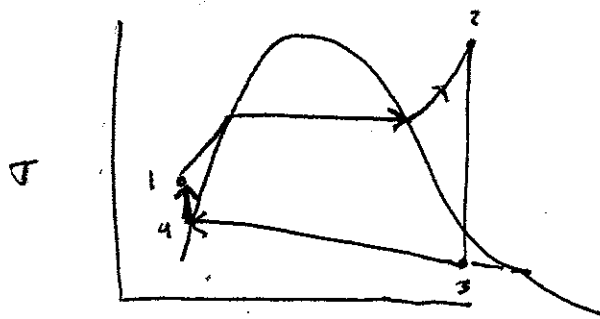## Ch. 8 Production of Power from Heat

Steam Power Plant
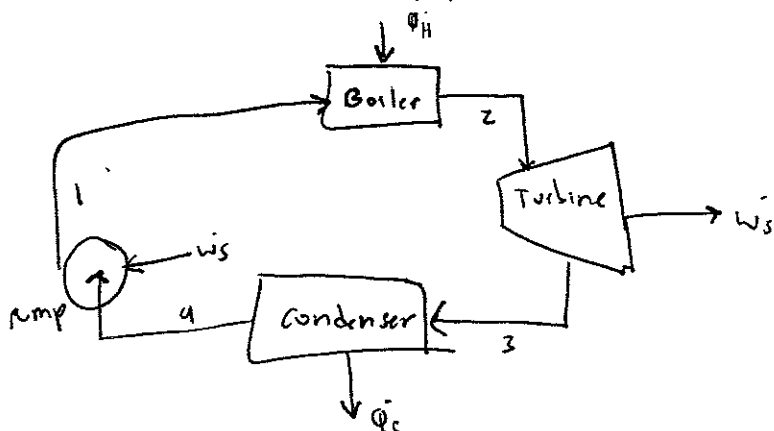
Problems with Carnot cycle
- turbines that take in sat. steam produce an exhaust w/ high liquid content - erosion
- difficult to design a pump that takes in a vapor-liq mixture and discharges a sat liquid

Carnot :

Rankine Cycle:

1-2   P is constant

A) heating subcooled liquid water to saturation temp

B) vaporization at const $T + P$

C) superheating vapor to $T > T_{sat}$

2-3   reversible, adiabatic expansion of vapor in a turbine

3-4   const $p + T$ in condenser to produce sat liquid

4-1   reversible, adiabatic pumping of sat liquid to the pressure of the boiler, producing a subcooled liquid

Internal Combustion engine — fuel is burned within engine products from combustion serve as working medium

Otto Engine (Internal combustion) — Cars
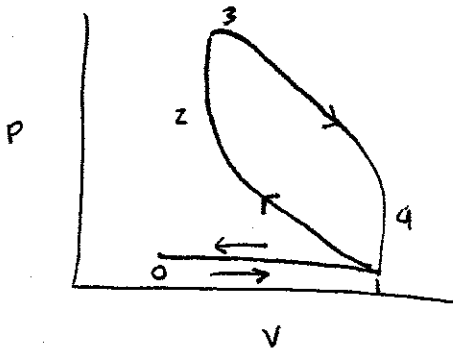
$0 \rightarrow 1$ const P, piston moving outward draws a fuel/air mix into cylinder

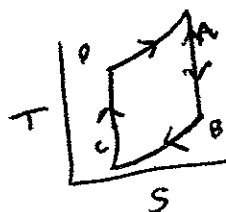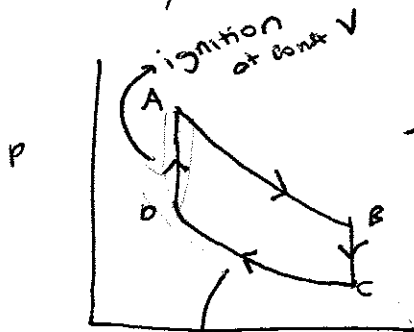$1 \rightarrow 2 \rightarrow 3$ all valves closed

fuel/air mix is compressed, adiabatically $1 \rightarrow 2$, mixture is ignited and combustion occurs rapidly (V const) $2 \rightarrow 3$

$3 \rightarrow 4$ expansion

$4 \rightarrow 1$ exhaust valve opens and $p \downarrow$ at const V

$1 \rightarrow 0$ piston pushes gases from cylinder

idealized cycle: air standard

happens fast in a real engine — model as adiabatic also reversible

$$PV^\gamma = const.$$

for ad, rev steps : $PV^\gamma = const$

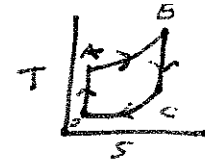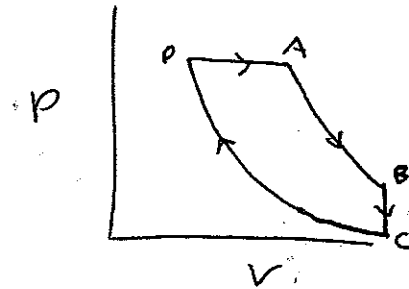$$\eta = \frac{-W_s (net)}{Q_{0A}} = \frac{Q_{0A} + Q_{BC}}{Q_{0A}}$$

$$\eta = 1 - \left(\frac{1}{r}\right)^{\gamma-1}$$

$r = V_C / ...$ compress. (7)

Diesel Engine

- combustion occurs spontaneously
- higher r and m than Otto
- now heat absorption at const. P (combustion process)
- fuel not injected until end of compression, added slowly so r is constant

Jet Engine — compression, combustion and a nozzle

Rocket — engine contains oxidizing agent (don't need air)

Ch. 9   Refrigeration and Liquefaction

Carnot Refrigerator

$$|W| = |\phi_H| - |\phi_C|$$

$\omega = $ coefficient of performance $= \dfrac{|\phi_C|}{W}$

$$\dfrac{W}{|\phi_C|} = \dfrac{|\phi_H|}{|\phi_C|} - 1 \qquad \omega = \dfrac{T_C}{T_H - T_C} \qquad \max \omega = \text{Carnot}$$
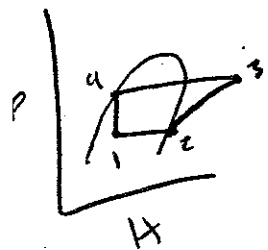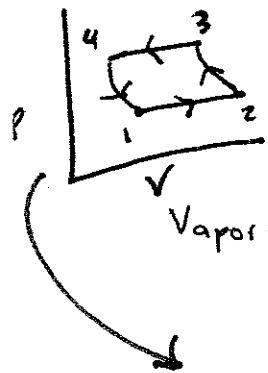
Vapor - Compression Cycle

liquid evaporating at const P provides means for heat absorption at const T
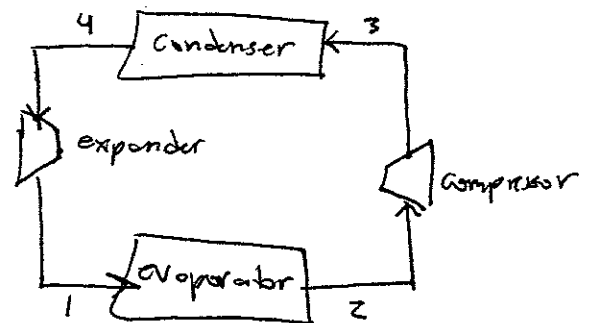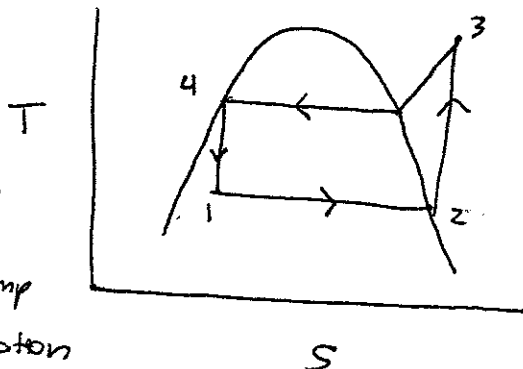
condensation of vapor, after compression to higher P, provides for rejection of heat at const T

liquid from condenser returned to normal state by expansion in a turbine where work is obtained

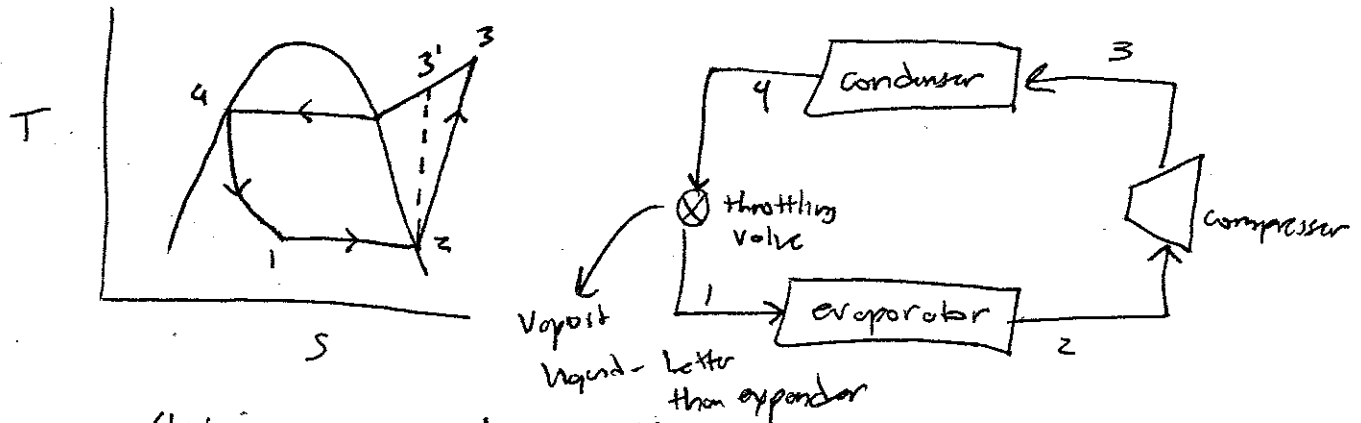if compression and expansion isentropic :

equivalent
= Carnot
except superheated
vapor (3) is
cooled to sat temp
before condensation

$$w = \frac{H_2 - H_1}{(H_3 - H_4) - (H_2 - H_1)}$$

if expansion is accomplished thrugh throttling:

$4 \to 1$ constant enthalpy throttling

$2 \to 3$ slopes in direction of $\uparrow S$ (irreversible)

$2 \to 3'$ if isentropic

Gas-Turbine (Brayton)

$$w = \frac{H_2 - H_1}{H_3 - H_2} \; ?? \qquad (H_4 = H_1)$$
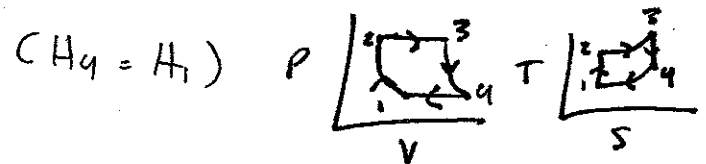
Absorption Refrigeration — compression supplied by an electric motor is vapor-compression refrig.

now use direct use of heat as energy source

$T_S = $ surroundings

$$\frac{W}{|Q_c|} = \frac{T_S - T_C}{T_C}$$

$$\eta = 1 - \frac{T_S}{T_H}$$

refrigerant —
$p^{vap} >$ atmospheric
so air not inside
p^{vap} not to high,
high cost

Heat pump — in winter, absorbs heat from surroundings and rejects heat into building

in summer — flow of refrigerant is reversed
heat absorbed from building and rejected to outside air

Liquefaction — gas cooled to the 2-phase region
— heat exchange at const P — throttling
— expansion in turbine

Ch. 10 Solution Thermo

At equilibrium : $\mu_i{}^\alpha = \mu_i{}^\beta$

partial molar property : $\overline{M}_i = \left[\dfrac{\partial (nM)}{\partial n_i}\right]_{P,T,n_j}$

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

$$nM = \sum_i n_i \overline{M}_i \quad , \quad M = \sum_i x_i \overline{M}_i$$

Ideal gas :

$$\boxed{\overline{M}_i{}^{is}(T,P) = M_i{}^{is}(T, P_i) \xrightarrow{P=P_i}}$$

↗ Gibbs mixing rule

$H \neq H(P)$ for ideal gas

$$\overline{H}_i{}^{is} = H_i{}^{is} = \sum_i x_i H_i{}^{is}$$

$$S^{is} = \sum_i x_i S_i{}^{is} - R \sum_i x_i \ln x_i$$

$$\mu_i{}^{is} = \overline{G}_i{}^{is} = G_i{}^{is} + RT \ln x_i$$

Fugacity of pure species i :

$$dG_i{}^{is} = V_i{}^{is} dP \quad (\text{const } T)$$

$$= \frac{RT}{P} dP = RT \, d\ln P$$

$$\boxed{G_i{}^{is} = \underbrace{\Gamma_i(T)}_{\text{integration constant}} + RT \ln P}$$

$G = E + PV - TS + PV$

$dG = dE - T dS - S dT + P dV + V dP$

$dG = T dS - P dV - T dS - S dT + P dV + V dP$

$dG = -S dT + V dP$

now, for a real fluid :

$$\boxed{G_i = \Gamma_i(T) + RT \ln f_i}$$

$f_i = $ fugacity of i (units of pressure)

$$G_i - G_i{}^{is} = RT \ln \frac{f_i}{P} = G_i{}^R$$

$$\boxed{\phi_i = \frac{f_i}{P} = \text{fugacity coefficient}}$$

$$f_i{}^{is} = P$$

ideal gas : $G_i{}^R = 0$, $\phi_i = 1$ → second virial coefficient

$$\ln \phi_i = \int_0^P (Z_i - 1) \frac{dP}{P} = \frac{B_{ii} P}{RT}$$

Criterion for equilibrium: $\quad f_i^V = f_i^\ell = f_i^{sat}$

$$\phi_i^V = \phi_i^\ell = \phi_i^{sat}$$

this is because

$$G_i^V = \Gamma_i(T) + RT \ln f_i^V$$

$$G_i^\ell = \Gamma_i(T) + RT \ln f_i^\ell$$

$$G_i^V - G_i^\ell = RT \ln f_i^V / f_i^\ell$$

At equil., $G_i^V = G_i^\ell$, thus $f_i^V = f_i^\ell$

$$\underline{G_i - G_i^{sat} = RT \ln f_i / f_i^{sat}}$$

$$dG = Vd\Gamma - Sd\Gamma$$

$$G_i - G_i^{sat} = \int_{f_i^{sat}}^{P} V_i \, dP \qquad \text{constant } T$$

$$\ln \frac{f_i}{f_i^{sat}} = \frac{1}{RT} \int_{f_i^{sat}}^{P} V_i \, dP$$

$$\longrightarrow f_i = \phi_i^{sat} \, P_i^{sat} \, \exp \underbrace{\frac{V_i^\ell (P - P_i^{sat})}{RT}}_{\text{Poynting factor}}$$

use when not at saturation

In Solution

$$\boxed{\mu_i = \Gamma_i(T) + RT \ln \hat{f}_i}$$

↳ fugacity of i in solution

in equil.: $\mu_i^\alpha = \mu_i^\beta$

$$\hat{f}_i^\alpha = \hat{f}_i^\beta \qquad \text{since all at same temp}$$

$$nG^R = nG - nG^{is}$$

$$\bar{G}_i^R = \bar{G}_i - \bar{G}_i^{is}$$

$$\mu_i - \mu_i^{is} = RT \ln \frac{\hat{f}_i}{x_i P} \qquad\qquad \mu_i = \bar{G}_i$$

$$\bar{G}_i^R = RT \ln \hat{\phi}_i$$

$$\boxed{\hat{\phi}_i = \hat{f}_i / x_i P}$$

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ideal gas : $\overline{G_i}^R = 0$ and $\hat{\phi}_i^{is} = 1$ $\longrightarrow$ $\hat{f}_i^{is} = x_i P$

$$d\left(\frac{nG}{RT}\right) = \frac{1}{RT} d(nG) - \frac{nG}{RT^2} dT \qquad (math)$$

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

$$dG = dU + PdV + VdP - TdS - SdT$$

$$= TdS - PdV + PdV + VdP - TdS - SdT + u_i dn_i$$

$$dG = VdP - SdT + u_i dn_i$$

$$d\left(\frac{nG}{RT}\right) = \frac{1}{RT}\left[nV dP - nS dT + u_i dn_i \right] - \frac{nH - nTS}{RT^2} dT$$

$$= \frac{nVdP}{RT} + \sum_i \frac{\overline{G_i} dn_i}{RT} - \frac{nH}{RT^2} dT$$

$$d\left(\frac{nG^R}{RT}\right) = \frac{nV^R}{RT} dP - \frac{nH^R}{RT^2} dT + \sum_i \ln \hat{\phi}_i dn_i$$

$$\frac{G^R}{RT} = \sum_i x_i \ln \hat{\phi}_i \qquad\qquad \sum_i x_i d\ln \hat{\phi}_i = 0$$

$$(const\ T, P)$$

from Gibbs - Duhem

Ideal Solutions

$$\boxed{\overline{G_i}^{id} = G_i + RT \ln x_i}$$

definition of on ideal solution
derive all other eqns from this

$$G = U + PV - TS$$

$$dG = VdP - SdT + u_i dn_i$$

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

$$\overline{S_i}^{id} = S_i - R \ln x_i$$

$$\overline{V_i}^{id} = V_i$$

$$\overline{H_i}^{id} = H_i$$

$$H = U + VP = G + TS$$

$$\cancel{dH =}$$

$$\overline{H_i}^{id} = G_i + RT\ln x_i + T\overline{S_i}^{id}$$

$$= G_i + RT \ln x_i + T S_i - RT \ln x_i$$

$$= G_i + TS_i = H_i$$

$$\bar{G}_i^{\,id} = G_i + RT \ln x_i$$

$$\mu_i^{\,id} = \bar{G}_i^{\,id} = \Gamma_i(T) + RT \ln \hat{f}_i^{\,id}$$

<u>Lewis / Randall Rule</u> : $\hat{f}_i^{\,id} = x_i f_i$

fugacity of i mole   fugacity of
in ideal   fraction   pure species i
solution

$$\rightarrow \quad \hat{\phi}_i^{\,id} = \phi_i$$

Excess properties : $M^E = M - M^{id}$

(analogous to M^R) $\bar{M}_i^{\,E} = \bar{M}_i - \bar{M}_i^{\,id}$

$$\bar{G}_i = \Gamma_i(T) + RT \ln \hat{f}_i$$

$$\bar{G}_i^{\,id} = \Gamma_i(T) + RT \ln x_i f_i$$

$$\bar{G}_i - \bar{G}_i^{\,id} = RT \ln \frac{\hat{f}_i}{x_i f_i}$$

Activity coefficient : $\boxed{\gamma_i = \dfrac{\hat{f}_i}{x_i f_i}}$

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

$$\frac{G^E}{RT} = \sum_i x_i \ln \gamma_i$$

$$\sum_i x_i \, d \ln \gamma_i = 0 \qquad (\text{Gibbs-Duhem})$$

$$\rightarrow \quad M = \text{~~~~~~} \sum_i x_i \bar{M}_i$$

$$dM = \sum_i x_i \, d\bar{M}_i + \sum_i \bar{M}_i \, dx_i$$

$$dM = \left(\frac{\partial M}{\partial P}\right)_{T,N} dP + \left(\frac{\partial M}{\partial T}\right)_{P,N} dT + \left(\frac{\partial M}{\partial n_i}\right)_{P,T} dn_i$$

$$0 = \sum \bar{M}_i \, dx_i \quad \text{at const } T, P$$

$$\bar{M}_i \, dx_i$$
$$\sum_i \text{~~~~~~}$$

(10)

Ch 11

Applications of Solution Thermodynamics

Liquid Phase Properties from VLE Data

$$f_i^v = y_i \hat{\phi}_i P = f_i^\ell \quad (\text{equil})$$

if assume ideal gas : $\hat{\phi}_i = 1$

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

Lewis-Randall : $\hat{f}_i^{id} = x_i f_i$

Actinty coefficient : $\gamma_i = \dfrac{\hat{f}_i}{x_i f_i} = \dfrac{\hat{f}_i}{\hat{f}_i^{id}} = \dfrac{y_i P}{x_i P_i^{sat}}$

Henry's Constant $K_i = \lim\limits_{x_i \to 0} \dfrac{\hat{f}_i}{x_i} = \left(\dfrac{d\hat{f}_i}{dx_i}\right)_{x_i = 0}$

$$\hat{f}_i = x_i K_i \quad \underline{\text{Henry's Low}} \quad -\text{applies when } x_i \to 0$$

other limit, as $x_i \to 1$:

$$\left(\dfrac{d\hat{f}_i}{dx_i}\right)_{x_i = 1} = f_i \qquad \underline{\text{Lewis-Randall}}$$

Excess Gibbs Energy

$$\dfrac{G^E}{RT} = x_1 \ln \gamma_1 + x_2 \ln \gamma_2$$

Gibbs-Duhem : $x_1 \dfrac{d \ln \gamma_1}{dx_1} + x_2 \dfrac{d \ln \gamma_2}{dx_1} = 0$

$$\boxed{\ln \gamma_1 = \left[\dfrac{\partial (nG^E/RT)}{\partial n_1}\right]_{P, T, n_2}}$$

$$\dfrac{G^E}{RT} = (A_{21} x_1 + A_{12} x_2) x_1 x_2$$

$$\ln \gamma_1 = x_2^2 \left[A_{12} + 2(A_{21} - A_{12}) x_1\right]$$

$$\ln \gamma_2 = x_1^2 \left[A_{21} + 2(A_{12} - A_{21}) x_2\right]$$

$\left.\begin{array}{c}\\ \\ \end{array}\right\}$ Margules Equations

$$y_1 P = x_1 \gamma_1 P_1^{sat}, \quad x_2 \gamma_2 P_2^{sat} = y_2 P$$

$$P = x_1 \gamma_1 P_1^{sat} + x_2 \gamma_2 P_2^{sat} \longrightarrow \text{plug into and solve for } y_1$$

$$Y_1 = \dfrac{x_1 \gamma_1 P_1^{sat}}{x_1 \gamma_1 P_1^{sot} + x_2 \gamma_2 P_2^{sot}}$$

Models for G^E

$$\frac{G^E}{RT} = g(x_1, x_2 \ldots x_N) \quad (\text{const } T)$$

$\longrightarrow$ Margules equations

$$\frac{G^E}{x_1 x_2 RT} = a + b x_1 + c x_1^2 + \ldots \quad (\text{const } T)$$

$$\frac{G^E}{x_1 x_2 RT} = B + C(x_1 - x_2) + D(x_1 - x_2)^2 + \ldots$$

$\longrightarrow$ Redlich / Kister Equations

$$\ln \gamma_1 = B x_2^2$$

$$\ln \gamma_2 = B x_1^2$$

$$\frac{x_1 x_2}{G^E/RT} = B'(x_1 + x_2) + C'(x_1 - x_2)$$

$\longrightarrow$ von Laar equations

$$\ln \gamma_1 = A'_{12} \left(1 + \frac{A'_{12} x_1}{A'_{21} x_2}\right)^{-2}$$

$$\ln \gamma_2 = A'_{21} \left(1 + \frac{A'_{21} x_2}{A'_{12} x_1}\right)^{-2}$$

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

$\longrightarrow$ Wilson

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

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

Also, NRTL (3 parameters), UNIQUAC, UNIFAC

Property Change of Mixing : $\Delta M = M - \sum_i x_i M_i$

$$G^E = \Delta G - RT \sum_i x_i \ln x_i$$

$$S^E = \Delta S + R \sum_i x_i \ln x_i$$

$$V^E = \Delta V$$

$$H^E = \Delta H$$

Heat of solution $\Delta \widetilde{H} = \dfrac{\Delta H}{x_1}$

basis 1 mol solute
solids or gases dissolved in liquids

Ch. 12   VLE at Low To Moderate Pressures

intensive state of PVT system containing N chemical species
and π phases in equilibrium is characterized by T, P and
$N-1$ mole fractions for each phase ($\sum_i x_i = 1$)

F = (# phase rule variables) - (# of equations connecting them)

$\downarrow$

$2 + (N-1)\pi$

$x_1 + x_2 \ldots x_n = 1$

$\downarrow$

$\mu_i^\alpha = \mu_i^\beta = \ldots = \mu_i^\pi$

$\hat{f}_i^\alpha = \hat{f}_i^\beta = \ldots = \hat{f}_i^\pi$

$i = 1, 2 \ldots N$

$(\pi-1)N$ ind equations

$$F = 2 + (N-1)\pi - (\pi-1)N = 2 - \pi + N$$

Proof of Gibbs phase rule

Duremi's theorem - for closed systems in which the intensive
and extensive states are fixed

variables = $2 + (N-1)\pi + \pi$

equations = $(\pi-1)N + N$

$\hookrightarrow$ extensive variable (mass or mol)

$\hookrightarrow$ material balances
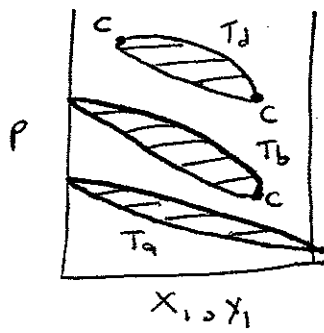
~~Reo~~

For any closed system, equilibrium state is
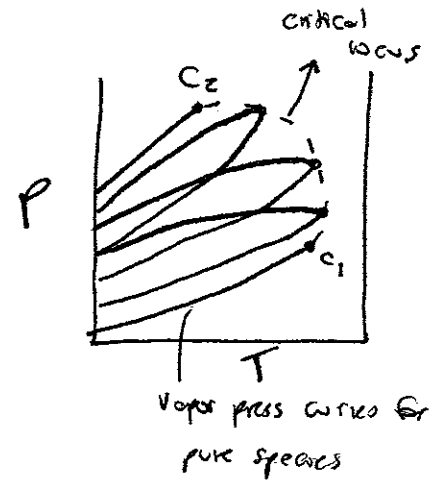determined completely by 2 variables.
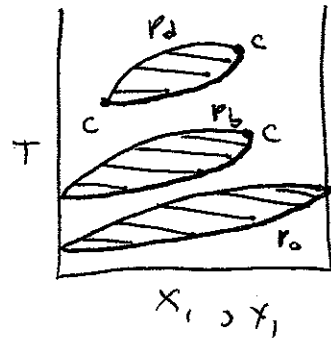
(F = # intensive variables) $F = 1$, 1 variable is extensive, $F = 0$ both extensive

T_d above 2 c's
T_b above 1 c
T_a below c's

$$y_i \, \underline{\Phi}_i \, P = x_i \, \gamma_i \, P_i^{sat} \quad , \quad \ln P_i^{sat} = A_i - \frac{B_i}{T + C_i}$$

$$\underline{\Phi}_i = \frac{\hat{\phi}_i}{\phi_i^{sat}} \exp\left[- \frac{V_i^{\ell}(P - P_i^{sat})}{RT} \right] \cong \frac{\hat{\phi}_i}{\phi_i^{sat}}$$

Dew point and Bubble point Calculations

		calculate	and	given	and
Bubl P :		$\{y_i\}$ and P,		$\{x_i\}$ and T	
Dew P :		$\{x_i\}$	P	$\{y_i\}$	T
Bubl T :		$\{y_i\}$	T	$\{x_i\}$	P
Dew T :		$\{x_i\}$	T	$\{y_i\}$	P

To calculate :

$$y_i = \frac{x_i \, \gamma_i \, P_i^{sat}}{\underline{\Phi}_i \, P} \quad , \quad x_i = \frac{y_i \, \underline{\Phi}_i \, P}{\gamma_i \, P_i^{sat}}$$

$$\sum_i y_i = 1 \quad , \quad \sum_i x_i = 1$$

$$P = \sum_i \frac{x_i \, \gamma_i \, P_i^{sat}}{\underline{\Phi}_i} \qquad P = \frac{1}{\sum_i y_i \underline{\Phi}_i / \gamma_i P_i^{sat}}$$

Bubl P :

1. T, x_i given. Set $\underline{\Phi}_i = 1.0$. Evaluate P_i^{sat} and γ_i.
   calc. P

2. calc y_i, evaluate $\underline{\Phi}_i$ ⟵

3. calc P again

4. if $P_{new} - P_{old} < \epsilon$, print P   if no ⟶

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Dew P:

- 1. T, y_i given. set $\Phi_i = 1.0$, $\gamma_i = 1.0$

  evaluate P_i^{sat}.

  calculate P and x_i

  evaluate γ_i

  calculate P again

2. evaluate Φ_i

3. calculate x_i, evaluate γ_i

4. is $\gamma_{i\,new} - \gamma_{i\,old} < \xi$? if no

5. calc. P

6. is $P_{new} - P_{old} < \xi$? if no

   if yes, print P

for bubble and dew T,

$$T_i^{sat} = \frac{B_i}{A_i - \ln P} - C_i \quad , \quad T = \frac{B_6}{A_j - \ln P_j^{sat}} - C_j$$

$$P_j^{sat} = \frac{P}{\sum_i (x_i \gamma_i / \Phi_i)(P_i^{sat}/P_j^{sat})} \quad , \quad P_j^{sat} = P \sum_i \frac{y_i \Phi_i}{\gamma_i}\left(\frac{P_j^{sat}}{P_i^{sat}}\right)$$

Roolt's Law — ideal gas in vapor, ideal solution in liquid

$$\Phi_i = 1 \quad , \quad \gamma_i = 1$$

$$\boxed{y_i P = x_i P_i^{sat}}$$

Modified Roolt's Law — ideal gas in vapor only

$$\boxed{y_i P = x_i \gamma_i P_i^{sat}}$$

Flash — liquid at $p \geq$ bubblepoint p flashes (partially evaporates)
  when p is ↓ below bubblepoint p → produces a
  2 - phase system in equilibrium

to describe fluid mixtures, use same eqns of state to describe PVT behavior

- parameters are now dependent on composition

2nd virial coefficient: $Z = 1 + \dfrac{BP}{RT}$

$B = \sum_i \sum_j y_j y_i B_{ij}$ binary mix: $B = y_1^2 B_{11} + 2 y_1 y_2 B_{12} + y_2^2 B_{2_1}$

3rd virial coefficient:

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

binary: $C = y_1^3 C_{111} + 3 y_1^2 y_2 C_{112} + 3 y_1 y_2^2 C_{122} + y_2^3 C_{222}$

Residual Properties easily calculated:

$$\dfrac{G^R}{RT} = \int_0^P (Z-1)\dfrac{dP}{P}$$

Cubic eqns of state — cubic in V can describe liquid + vapor phases
 — use mixing rules to describe parameters

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

$a = \sum_i \sum_j y_i y_j a_{ij}$, $b = \sum_i y_i b_i$

Pitzer correlations ~ $Z = Z^0 + \omega Z^1$

$T_{pc} = \sum_i y_i T_{ci}$, $P_{pc} = \sum_i y_i P_{ci}$, $\omega = \sum_i y_i \omega_i$

$T_{pr} = T/T_{pc}$, $P_{pr} = P/P_{pc}$

approximately use this correlation for mixtures

VLE from Cubic Equation of state
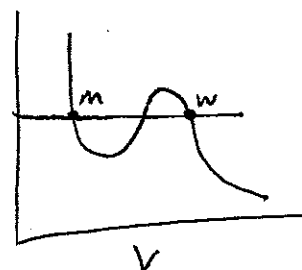   pure i : $\phi_i^v = \phi_i^\ell$
   On isotherm this must be true: P
      then $P = P^{sat}$ and M + W
      are saturated liquid and
      saturated vapor states at T

$$dS^+ + dS_{surr} \geqslant 0 \qquad (2^{nd} \text{ law})$$

↓ total S of system

$$dS_{surr} = \frac{dQ_{surr}}{T_{surr}} = \frac{-dQ}{T} \quad \rightarrow \text{system}$$

$$dS^+ T \geqslant dQ$$

$$dU^+ = dQ + dw = dQ - PdV^+$$

$$dU^+ + PdV^+ \leq TdS^+$$

$$dU^+ + PdV^+ - TdS^+ \leq 0$$

$$\boxed{\begin{array}{l} (dU^+)_{S^+, V^+} \leq 0 \\[2mm] (dS^+)_{U^+, V^+} \geqslant 0 \end{array}}$$

At const $T + P$:

$$\boxed{(dG^+)_{T,P} \leq 0}$$

At equilibrium G is minimum with respect to changes in $T + P$.

$$(dG^+)_{T,P} = 0 \qquad \text{at equilibrium}$$

$$\frac{d^2 \Delta G}{dx_1^2} \geqslant 0 \qquad (\text{const } T, P)$$

$$\frac{d\hat{f}_1}{dx_1} \geqslant 0 \qquad \text{"} \qquad \text{"}$$

$$\frac{d\mu_1}{dx_1} \geqslant 0 \qquad \text{"} \qquad \text{"}$$

$$\frac{d \ln \gamma_1}{dx_1} > -\frac{1}{x_1} \qquad \text{"} \qquad \text{"}$$

Liquid-Liquid Equilibrium — mix species 1 & 2 α-phase-rich in species 1

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

$$x_i^{\alpha} \gamma_i^{\alpha} f_i^{\alpha} = x_i^{\beta} \gamma_i^{\beta} f_i^{\beta}$$

β-phase-rich in Species 2
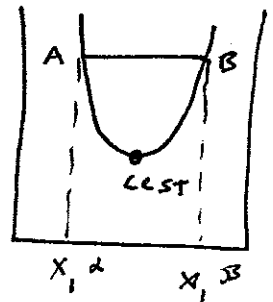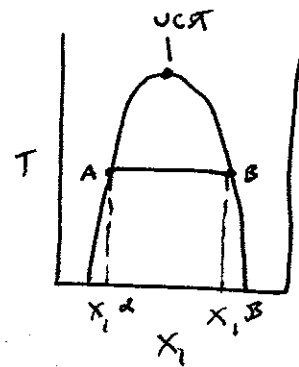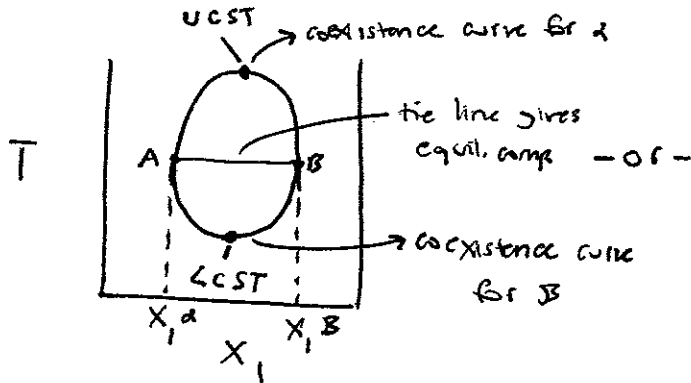
pure species liquid at T: $f_i^{\alpha} = f_i^{\beta}$

$$x_i^{\alpha} \gamma_i^{\alpha} = x_i^{\beta} \gamma_i^{\beta}$$

derive γ_i^{α} and γ_i^{β} from some function $\dfrac{G^E}{RT}$

UCST → coexistence curve for α

tie line gives equil. comp — or —

→ coexistence curve for β

LCST

X_1^{α} X_1^{β}

X_1

UCST

X_1^{α} X_1^{β} X_1

LCST

X_1^{α} X_1^{β}

Vapor-Liquid-Liquid Equilibrium

binodal curves representing LLE intersect VLE curve

V

$\alpha - V$ $\beta - V$

α β

$\alpha - \beta$

X_1, Y_1

locus of azeotropes

P_2

P_1

α, β binodal curve

X_1, Y_1

(14)
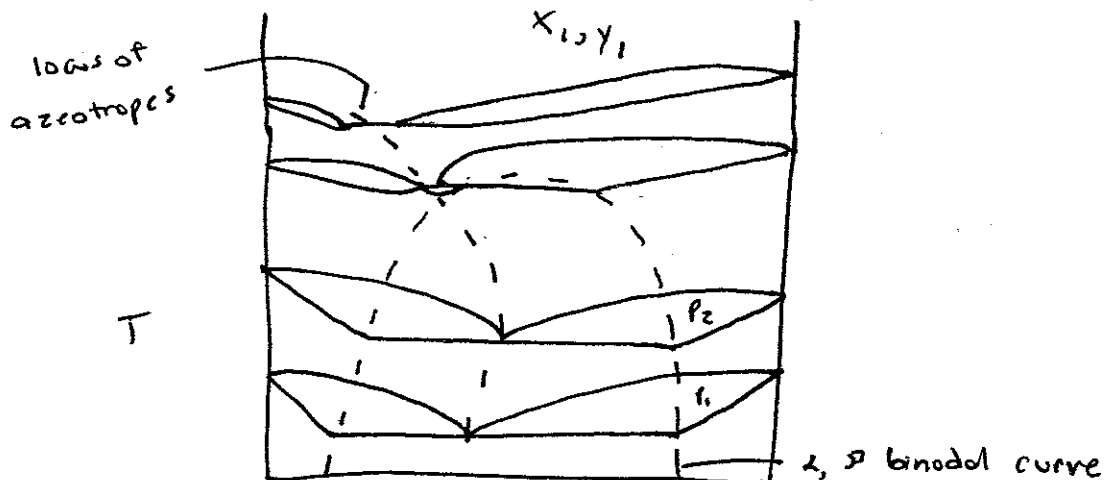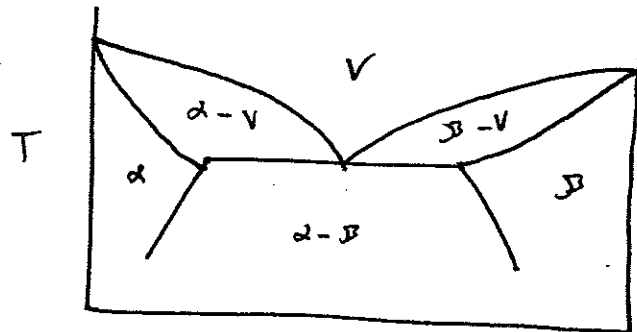
Solid-Liquid Equilibrium

$$\hat{f}_i^{\,\ell} = \hat{f}_i^{\,s}$$

$$x_i \, \sigma_i^{\,\ell} \, f_i^{\,\ell} = z_i \, \gamma_i^{\,s} f_i^{\,s}$$

$$\psi_i = f_i^{\,s} / f_i^{\,\ell} = \exp \frac{\Delta H_i^{\,s\ell}}{RT_{mi}} \left(\frac{T - T_{mi}}{T} \right)$$ ← assumed

$$x_i \, \sigma_i^{\,\ell} = z_i \, \sigma_i^{\,s} \, \psi_i$$

Solid - Vapor Equilibrium

Species 1 and 2

binary vapor mix in equil with pure solid (only species 1)

$$f_i^{\,s} = \hat{f}_i^{\,v}$$

$$f_1^{\,s} = \phi_1^{\,sat} P_1^{\,sat} \exp \frac{V_i^{\,s}(P - P_i^{\,sat})}{RT}$$

$$\hat{f}_i^{\,v} = y_1 \hat{\phi}_1 P$$

Equilibrium Adsorption of Gases on Solids

$$dG = VdP - SdT + \Sigma \mu_i dn_i$$

2-D phase :

$$dG = a \, d\pi - SdT + \Sigma \mu_i dn_i$$

$$nM = \sum_i n_i \, \overline{M}_i$$

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

$$dG = \sum_i n_i \, \overline{G}_i = \sum_i n_i \, \mu_i$$

$$d(nG) = \Sigma n_i d\mu_i + \Sigma \mu_i dn_i$$

$$0 = (na) \, d\pi - (ns) \, dT - \Sigma n_i d\mu_i$$

0 at const T

$$\boxed{S\cancel{dT} - a \, d\pi + \sum_i x_i d\mu_i = 0}$$

Gibbs adsorption isotherm

a = molar area

π = spreading pressure

$$E = PV - TS + \Sigma \mu_i n_i$$

$$dE = PdV + VdP - TdS - SdT$$
$$\quad + \Sigma \mu_i dn_i + \Sigma n_i d\mu_i$$

~~dE~~

$$G = E + PV - TS$$

$$dG = dE + PdV + VdP$$
$$\quad - TdS - SdT$$

$$dE = -PdV + TdS + \Sigma \mu_i dn_i$$

$$dG = VdP - SdT + \Sigma \mu_i dn_i$$

Pure Gas Adsorption

$$d\mu_i = d\mu_i^{g}$$

$$d\mu_i = d\mu_i^{g} = RT \, d\ln(y_i P) \quad \text{ideal gas assumed}$$

$$-\frac{a \, d\pi}{RT} + \cancel{\rule{2cm}{0.6cm}}_{d\ln P} + \sum_i x_i \, d\ln y_i = 0$$

pure species:

$$\frac{a}{RT} \, d\pi = d\ln P \quad, \quad z = \frac{\pi a}{RT}$$

$$dz = \frac{\pi}{RT} \, da + \frac{a}{RT} \, d\pi$$

$$-\frac{a}{RT} \, d\pi = -d\ln P = \frac{z}{a} \, da - dz$$

$$a = A/n \qquad da = -A \, dn/n^2$$

$$-d\ln P = -z \, \frac{dn}{n} - dz$$

Add dn/n to both sides

$$d\ln \frac{n}{P} = (1-z) \frac{dn}{n} - dz$$

$n = 0, \; P = 0$

$n = n, \; P = P$

$$\ln \frac{n}{P} - \ln \lim_{P \to 0} \frac{n}{P} = \int_0^n (1-z) \frac{dn}{n} + 1 - z$$

$$\lim_{P \to 0} \frac{n}{P} = \lim_{P \to 0} \frac{dn}{dP} = K \longrightarrow \text{Henry's constant adsorption}$$

$$\boxed{n = KP \exp \left[\int_0^n (1-z) \frac{dn}{n} + 1 - z \right]}$$

ideal gas analog: $z = 1$, $\boxed{n = KP}$

Langmuir: $\quad z = -\frac{m}{n} \ln\left(1 - \frac{n}{m}\right)$

plug into above eqn

$$n = \frac{(m-n)}{m} KP$$

full monolayer coverage:

$P \to \infty, \; n \to m$ saturation

$$\boxed{n = \frac{KbP}{1+b}} \qquad b = m/K$$

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Another way to derive Longmuir isotherm:

$$\text{rate adsorption} = \text{rate desorption}$$

$$\theta = \text{occupied sites}, \quad 1-\theta = \text{Vacant}$$

$$\theta = n/m \qquad 1-\theta = \frac{m-n}{m}$$

rate of adsorption $\propto$ rate strike surface $\propto$ pressure $\propto (1-\theta)$

rate of desorption $\propto \theta$

$$kP(1-\theta) = k'\theta$$

$$\boxed{n = \frac{mP}{\frac{1}{K}+P}}$$

$$K = k/k' = k/m$$

Valid as $\theta \to 0$ and $n \to 0$

Ch. 15 Chemical Reaction Equilibria

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

$\hat{a}_i = \dfrac{\hat{f}_i}{f_i^\circ}$ activity

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

$$\frac{d\ln K}{dT} = \frac{\Delta H^\circ}{RT^2}$$

$dG = VdP - SdT$
$G = G(P, T)$

$$\left(\frac{d(\Delta G^\circ/RT)}{dT} = -\frac{\Delta H^\circ}{RT^2}\right)$$

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

Gas phase: $\quad K = \prod_i \left(\frac{\hat{f}_i}{P^\circ}\right)^{v_i} \qquad \hat{a}_i = \frac{\hat{f}_i}{f_i^\circ} = \frac{\hat{f}_i}{P^\circ}$

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

$$\prod_i (y_i \hat{\phi}_i)^{v_i} = \left(\frac{P}{P_0}\right)^{-V} K \qquad \underbrace{}_{\text{usually 1}}$$

Liquid phase: $\quad \hat{a}_i = \frac{\gamma_i x_i f_i}{f_i^\circ} = \gamma_i x_i \left(\frac{f_i}{f_i^\circ}\right)$

Ch. 16   Thermo Analysis of Processes

Ideal Work

    reversible : $\dot{Q} = T \Delta (S\dot{m})_{fs}$

$$\Delta \left[(H + \tfrac{1}{2} u^2 + zg) \dot{m} \right]_{fs} = T \Delta (S\dot{m})_{fs} + \dot{W}_s (rev)$$

shaft work for a reversible process = ideal work

$$\dot{W}_{ideal} = \Delta \left[(H + \tfrac{1}{2} u^2 + zg) \dot{m} \right]_{fs} - T \Delta (S\dot{m})_{fs}$$

$$\eta = \frac{\dot{W}_{ideal}}{\dot{W}_s} \qquad \text{if } \dot{W}_{ideal} \text{ is } +$$

$$\eta = \frac{\dot{W}_s}{\dot{W}_{ideal}} \qquad \text{if } \dot{W}_{ideal} \text{ is } -$$

Lost work — wasted as a result of irreversibilities

$$\dot{W}_{lost} = \dot{W}_s - \dot{W}_{ideal}$$

$$\dot{W}_s = \Delta \left[(H + \tfrac{1}{2} u^2 + zg) \dot{m} \right]_{fs} - \dot{Q}$$

$$\dot{W}_{lost} = T \Delta (S\dot{m})_{fs} - \dot{Q}$$

$$\dot{W}_{lost} = T \underbrace{\dot{S}_{G, total}}_{\geqslant 0}$$