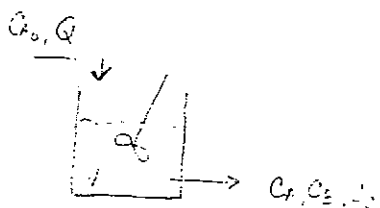
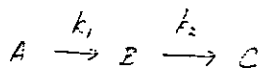


THERMODYNAMICS AND KINETICS PRELIMINARY QUESTIONS

- FOR A SERIES RXN, WHAT VARIABLES INFLUENCE THE AMT OF INTERMEDIATE FORMED? HOW WOULD YOU MAXIMIZE THE PRODUCTION OF INTERMEDIATE IN A CSTR? A PFR? OR IN A BATCH REACTOR?

CSTR



$$-r_A = k_1 C_A$$

kinetic expression:

$$A: C_{A0}Q - C_AQ - k_1 C_A V = V \frac{dC_A}{dt} = 0 \text{ at SS}$$

$$C_{A0}Q = C_A (Q + k_1 V)$$

$$C_A = C_A (1 + k_1 \tau)$$

$$\tau = \frac{V}{Q}$$

$$C_A = \frac{C_{A0}}{1 + k_1 \tau}$$

$$B: k_1 V C_A - k_2 V C_B - C_B Q = 0$$

no B in feed

$$k_1 \tau \left(\frac{C_{A0}}{1 + k_1 \tau} \right) = (k_2 \tau + 1) C_B$$

$$C_B = \frac{k_1 \tau \left(\frac{C_{A0}}{1 + k_1 \tau} \right)}{k_2 \tau + 1}$$

To maximize C_B , change τ : $\frac{dC_B}{d\tau} = 0 \rightarrow \tau = \left(\frac{1}{k_1 k_2} \right)^{1/2}$

BATCH

$$A: -k_1 C_A = \frac{dC_A}{dt} \rightarrow C_A = C_{A0} e^{-k_1 t}$$

$$B: k_1 C_A - k_2 C_B = \frac{dC_B}{dt}$$

$$k_1 C_{A0} e^{-k_1 t} - k_2 C_B = \frac{dC_B}{dt}$$

$$\frac{dC_B}{dt} + k_2 C_B = k_1 C_{A0} e^{-k_1 t}$$

$$\frac{d}{dt} [e^{k_2 t} C_B] = e^{k_2 t} \cdot k_1 C_{A0} e^{-k_1 t}$$

$$e^{k_2 t} C_B = \frac{k_1 C_{A0}}{k_2 - k_1} e^{(k_2 - k_1)t} + C_1 \quad t=0, C_B=0$$

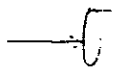
$$0 = \frac{k_1 C_{A0}}{k_2 - k_1} + C_1$$

$$e^{k_2 t} C_B = \frac{k_1 C_{A0}}{k_2 - k_1} [e^{(k_2 - k_1)t} - 1]$$

$$C_B(t) = \frac{k_1 C_{A0}}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t})$$

$$\text{To maximize } C_B, \frac{dC_B}{dt} = 0 \rightarrow \rightarrow \rightarrow t = \frac{\ln \frac{k_2}{k_1}}{k_2 - k_1}$$

PFR



$$A: \quad G C_{A0} - Q C_A - k_1 C_A \Delta x = 0 \quad \text{at S.S.}$$

$$-Q \frac{dC_A}{dx} = k_1 C_A$$

$$\frac{dC_A}{dV} + \frac{k_1 C_A}{Q} = 0 \rightarrow C_A = C_{A0} e^{-\frac{k_1 V}{Q}}$$

$$B: \quad Q C_B|_x - Q C_B|_{x+\Delta x} + k_1 C_A \Delta V - k_2 C_B \Delta V = 0$$

$$-Q \frac{dC_B}{dV} + k_1 C_A - k_2 C_B = 0$$

$$\frac{dC_B}{dV} + \frac{k_2}{Q} C_B = \frac{k_1}{Q} C_{A0} e^{-\frac{k_1 V}{Q}}$$

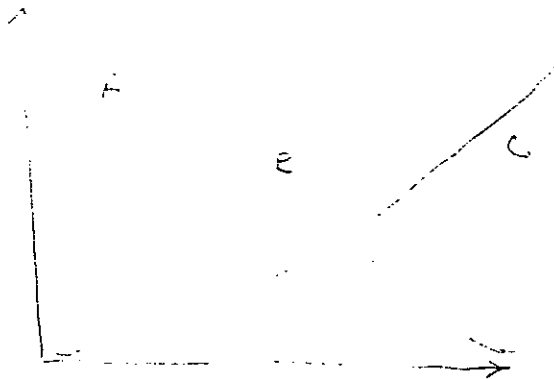
$$\frac{d}{dV} \left(C_B e^{\frac{k_2 V}{Q}} \right) = e^{\frac{k_2 V}{Q}} \cdot e^{-\frac{k_1 V}{Q}} \cdot \frac{k_1}{Q} C_{A0}$$

$$C_B e^{\frac{k_2 V}{Q}} = \frac{k_1 C_{A0}}{Q} \cdot \frac{Q}{k_2 - k_1} e^{(k_2 - k_1) \frac{V}{Q}} + C \quad \begin{matrix} V=0 \\ C_B=0 \end{matrix}$$

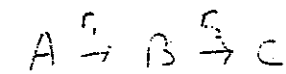
$$C_B = \frac{k_1 C_{A0}}{k_2 - k_1} \left[e^{-k_1 \tau} - e^{-k_2 \tau} \right]$$

To maximize C_B , $\frac{dC_B}{d\tau} = 0 \rightarrow \rightarrow \rightarrow \tau = \frac{\ln \frac{k_2}{k_1}}{k_2 - k_1}$

For series rxn. use PFR or Batch, not CSTR



1)



$$r_1 = k_1 A$$

$$r_2 = k_2 B$$

see Fogler p. 416
for PFR batch

Fogler's result shows that yield related to $\frac{k_1}{k_2} \tau = F(V, k)$

What influences k ?

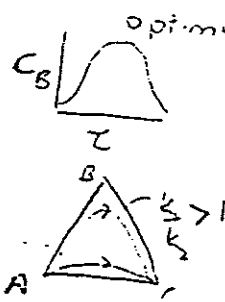
$$k = A \exp(-E_a/RT)$$

• E_a is fixed (unless consider catalysis)

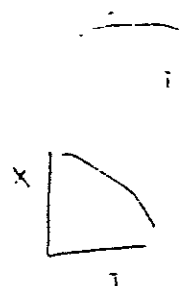
• τ can be varied (opt direction depends on E_a). This is most applicable in a CSTR which is at constant T within reactor.

his for maximum selectivity want low conversion of A; in this case a batch reactor or PFR would be best because of the delta function residence time distribution. You always get that optimum τ , unlike in a CSTR

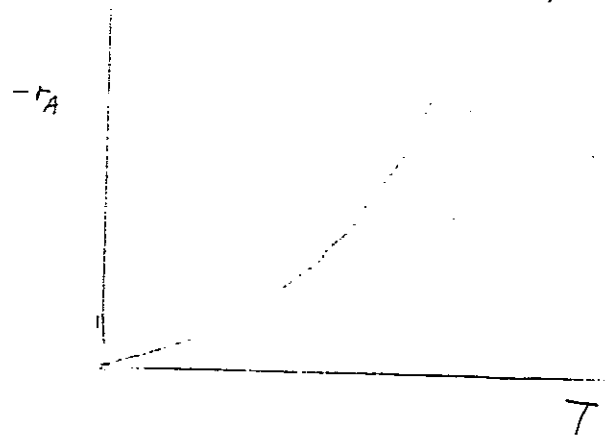
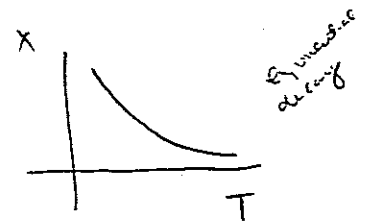
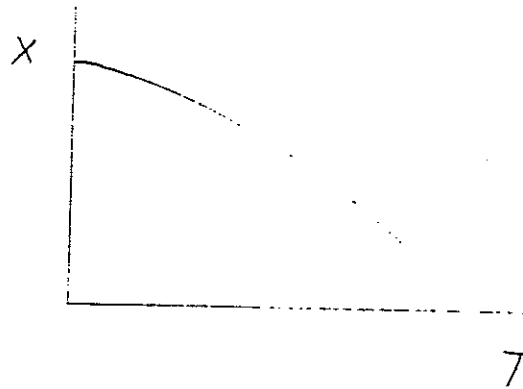
• also consider feed concentration which will influence conversion for a given reactor



2)



2. FOR AN EXOTHERMIC, 1ST ORDER RXN, PLOT EXTENT OF REACTION AND THE RXN RATE AS FUNCTIONS OF T .



$$-r_A = kC_A$$

3. WHEN CAN THE STEADY-STATE APPROXIMATION BE USED?

- The pseudo-steady-state hypothesis can be used when the forward rxn rate and the reverse rxn rates are large compared to the rds. In addition, the forward and reverse rates ought to be comparable in magnitude. We use PSSH when we deal with a reaction that has many steps and is usually applied to the reactive intermediates.

When conc. of intermediate is low

4. WHAT IS THE CHEMICAL POTENTIAL?

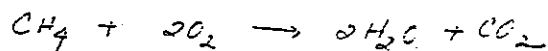
$$\mu \equiv \left. \frac{\partial G}{\partial n_i} \right|_{T, P, n_j} = \left. \frac{\partial U}{\partial n_i} \right|_{S, V, n_j} = \left. \frac{\partial H}{\partial n_i} \right|_{S, P, n_j} = \left. \frac{\partial A}{\partial n_i} \right|_{T, V, n_j}$$

- abstract concept introduced by Gibbs and used in phase-equilibrium.
- At equilibrium, chemical potential is the same in all phases
- Driving force for mass transfer.

5. EXPERIMENTALLY HOW WOULD YOU DETERMINE ΔH_f , ΔG_f , ΔS_f ?

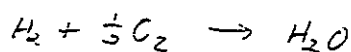
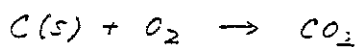
- ΔH_f calorimetry

eg



$$Q = \Delta H_{\text{rxn}} = 2H_f^{\text{H}_2\text{O}} + H_f^{\text{CO}_2} - H_f^{\text{CH}_4}$$

where $H_f^{\text{CO}_2}$, $H_f^{\text{H}_2\text{O}}$ can be gotten from



$$\Delta H_{\text{rxn}} = H_f^{\text{CO}_2}$$

$$\Delta H_{\text{rxn}} = H_f^{\text{H}_2\text{O}}$$

$$S_f^{CH_4} = S_{CH_4} - S_C - 2S_{H_2} \quad \text{from} \quad C(s) + 2H_2 \rightarrow CH_4$$

- S_i found by:

$$dS = \left. \frac{\partial S}{\partial T} \right|_P dT + \left. \frac{\partial S}{\partial P} \right|_T dP$$

$$= \frac{C_P}{T} dT + \text{pressure corrections}$$

$S=0$ for perfect crystalline solids at 0°K

$$S_i = \int_0^{T_m} \frac{C_P^S}{T} dT + \frac{\Delta H_m^S}{T_m} + \int_{T_m}^{T_b} \frac{C_P^L}{T} dT + \frac{\Delta H_b^L}{T_b} + \int_{T_b}^T \frac{C_P^V}{T} dT + \text{pressure correct.}$$

$$G^f = H^f - TS^f.$$

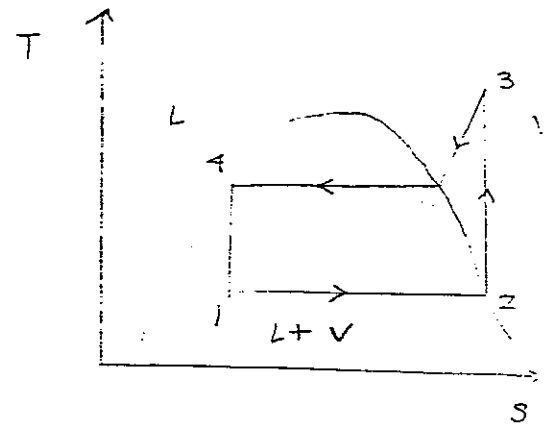
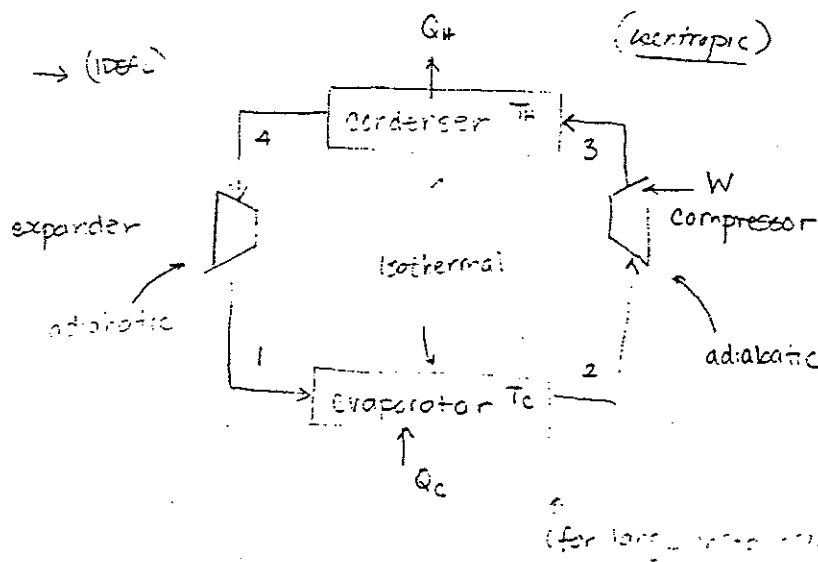
- need to measure C_P by flow calorimetry
- J-T expansion of gas to cool down to 0°K
- adiabatic demagnetization

④

chemical potential = driving force for mass transfer
= partial molar gibbs free energy
= criterion for eqbm $\mu^a = \mu^b$

$$\mu_i \equiv \left(\frac{\partial U}{\partial n_i} \right)_{S, V, n_j} = \left(\frac{\partial H}{\partial n_i} \right)_{S, P, n_j} = \left(\frac{\partial A}{\partial n_i} \right)_{T, V, n_j} = \left(\frac{\partial G}{\partial n_i} \right)_{T, P, n_j}$$

6 How DOES A REFRIGERATOR WORK? SKETCH T-S, P-V, and/or P-H DIAG.



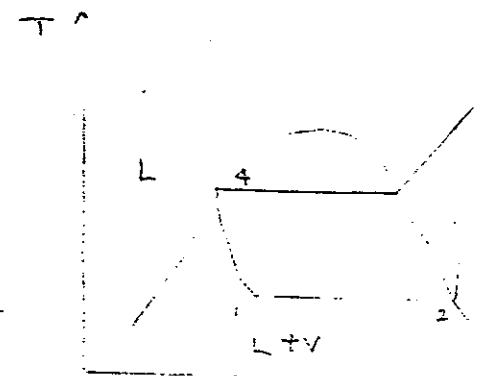
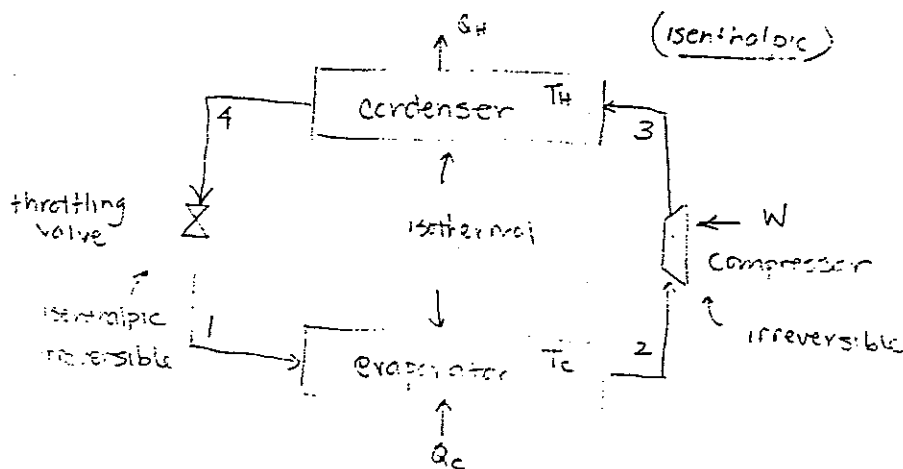
- ideal refrigerator operates on a Carnot cycle, consisting of two isothermal steps in which $|Q_c|$ is absorbed at the lower T_c and heat $|Q_h|$ is ejected at the higher T_h . Net work, W , is required for the system. ΔU of working fluid is zero →

$$|W| = |Q_h| - |Q_c|$$

usually performance of refrigerator is called coefficient of performance; ω .

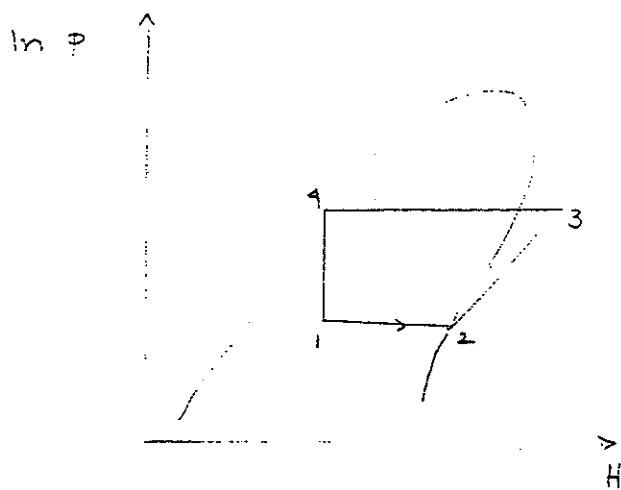
→ (NON-IDEAL)

$$\omega = \frac{|Q_c|}{|W|} = \frac{T_c}{T_h - T_c} \quad \frac{|Q_h|}{|Q_c|} = \frac{T_h}{T_c}$$

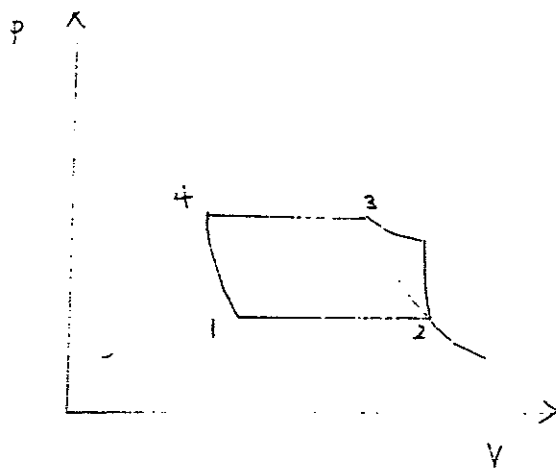


$$\omega = \frac{|Q_c|}{|W|} = \frac{H_2 - H_1}{(H_3 - H_4) - (H_2 - H_1)} = \frac{H_2 - H_1}{H_3 - H_2}$$

$$H_1 = H_4$$



for isenthalpic
refrigeration cycle



7. HOW DOES RATE CONSTANT VARY W/ T ?

$$k = A \exp\left(-\frac{E_a}{RT}\right)$$

↑
weak function of T

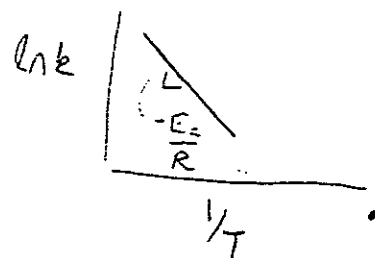
A = pre exponential factor
 E_a = activation energy

Arrhenius Law

$$\textcircled{7} \quad k = A \exp\left(-\frac{E_a}{RT}\right)$$

so

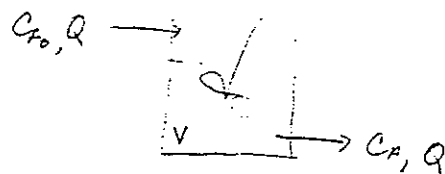
$$\ln k = \ln A - \frac{E_a}{R} \cdot \frac{1}{T}$$



$T \uparrow k \uparrow$

8 DERIVE DESIGN EQUATIONS FOR MASS AND ENERGY FOR CSTR, PFR, AND BATCH REACTORS.

• CSTR:



- mass balance:

$$QC_{A0} - QC_A + r_i V = \frac{dC_i}{dt} V = 0 \quad \text{at SS}$$

$$F_{i0} - F_i = -r_i V$$

$$V = \frac{F_{i0} - F_i}{-r_i}$$

- energy balance:

$E = \text{total energy}$

$$\rightarrow \frac{dE}{dt} = \dot{Q} - \dot{W} + \sum_i F_i e_{i, \text{in}} - \sum_i F_i e_{i, \text{out}}$$

$$\dot{W} = \dot{W}_{\text{flow}} + \dot{W}_{\text{shaft}}$$

$$= \sum F_i P v_i / \text{out} - \sum F_i P v_i / \text{in} + \dot{W}_s \quad \text{negligible}$$

$$\rightarrow \frac{dE}{dt} = \dot{Q} + \sum F_i h_{i, \text{in}} - \sum F_i h_{i, \text{out}}$$

neglect KE, PE in E,

$$e \approx u,$$

$$u + p v = h.$$

$$F_i = F_{i0} (\theta_i + \nu_i X)$$

$$\dot{Q} = \int_A U (T_{\text{surr}} - T) dA \approx U A T A$$

$$\frac{dE}{dt} = U A T A + F_{A0} \sum \theta_i (h_{i0} - h_i) - F_{A0} X \sum \nu_i h_i = 0 \quad \text{at SS}$$

$$U A T A - F_{A0} \sum \int_{T_{i0}}^T \theta_i C_{p,i} dT - F_{A0} X \left(C_{h20} (T_{\text{ref}}) + \int_{T_{\text{ref}}}^T \Delta C_p dT \right) = 0$$

Simplifying:

$$U \Delta T A - F_{A0} \sum_i \theta_i \bar{C}_{p,i} (T - T_{i0}) - F_{A0} X [\Delta \hat{h}_{rxn}^o + \Delta \bar{C}_p (T - T_{ref})] = 0$$

• PFR:

- mass $F_i|_V - F_i|_{V_{ref}} + r_i \Delta V = 0 \quad \text{at s.s.}$

$$-\frac{dF_i}{dV} + r_i = 0 \rightarrow \frac{dF_i}{dV} = r_i$$

$$F_A = F_{A0} (1 - X)$$

$$F_{A0} \frac{dX}{dV} = -r_A$$

- energy

$$U \Delta T A - F_{A0} \sum_i \theta_i \bar{C}_{p,i} (T - T_{i0}) - F_{A0} X [\Delta \hat{h}_{rxn}(T)] = 0$$

• Batch:

- mass $V \frac{dc_i}{dt} = r_i V$

$$\left[\frac{dc_A}{dt} = -r_A \right]$$

- energy

$$\frac{dE}{dt} = \dot{Q} - \dot{W} + \sum F_i u_i|_{in} - \sum F_i u_i|_{out}$$

$$\left[\frac{dE}{dt} = \dot{Q} - \dot{W} \right]$$

9. DEFINE SPACE TIME, SPACE VELOCITY, AND MEAN RESIDENCE TIME.

- Space time is defined as:

$$\tau = \frac{V}{v_0}$$

V \equiv reactor volume

v_0 \equiv volumetric flow rate entering reactor.

- it is the time necessary to process one reactor volume of stuff based on entrance conditions

- Space velocity is defined as:

$$SV \equiv \frac{v_0}{V} \quad \text{or} \quad SV = \frac{1}{\tau}$$

- however, in industry, often v_0 not used in definition of space velocity

liquid hourly space velocity $\equiv LHSV = \frac{v_0 \text{ at } 60^\circ \text{ or } 70^\circ \text{ F}}{V}$

gas hourly space velocity $\equiv GHSV = \frac{v_0 \text{ (at STP)}}{V}$

- Mean residence time:

$$t_m = \frac{V}{\int_V dt} = \frac{V}{\frac{1}{V} \int_V v dt} = \frac{V}{\langle v \rangle}$$

when $\langle v \rangle = v_0$, then $t_m = \tau$.

$$t_m = \frac{\int_0^\infty t E(t) dt}{\int_0^\infty E(t) dt} = \int_0^\infty t F(t) dt$$

10. WHAT ARE THE CLAPEYRON & CLAUSIUS CLAPEYRON EQUATIONS ?

• Clapeyron eqn:

$$\frac{dp^{sat}}{dT} = \frac{\Delta \hat{h}^{vap}}{T \Delta v^{vap}}$$

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

pure species in a phase equilibrium

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

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

$$dg = v dp - s dT$$

$$v^{\alpha} dp - s^{\alpha} dT = v^{\beta} dp - s^{\beta} dT$$

$$(v^{\alpha} - v^{\beta}) dp = (s^{\alpha} - s^{\beta}) dT$$

$$\Delta v^{vap} dp^{sat} = \Delta s^{vap} dT$$

$p = p^{sat}$ in v-L equil

$$\frac{dp^{sat}}{dT} = \frac{\Delta s^{vap}}{\Delta v^{vap}}$$

$$\Delta \hat{h}^{vap} = T \Delta s^{vap}$$

$$\frac{dp^{sat}}{dT} = \frac{\Delta \hat{h}^{vap}}{T \Delta v^{vap}}$$

• Clausius-Clapeyron eqn:

$$\Delta \hat{h}^{vap} = -R \frac{d \ln p^{sat}}{d \left(\frac{1}{T} \right)}$$

$v^L \ll v^V$, ideal vapor, v-L equilibrium, $\Delta \hat{h}^{vap}$ is constant

$$v^L - v^V = \Delta v^{vap} \approx v^V = \frac{RT}{p}$$

$$\frac{dp^{sat}}{dT} = \frac{\Delta \hat{h}^{vap} p^{sat}}{RT^2} \Rightarrow \frac{d \ln p^{sat}}{d \left(\frac{1}{T} \right)} = - \frac{\Delta \hat{h}^{vap}}{R}$$

$$\ln \frac{p^{sat}(T_2)}{p^{sat}(T_1)} = - \frac{\Delta \hat{h}^{vap}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

⑩

Clapeyron

$$\frac{dP^{sat}}{dT} = \frac{\Delta H^{AB}}{T\Delta V^{AB}}$$

exact thermodynamic relation

Clausius Clapeyron

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

assumptions :

- ① vapour is ideal gas
- ② $V^v \gg V^l$
- ③ ΔH^{ev} is constant

$$\text{①) } \Delta H^{ev} \approx \Delta H^{AB}$$

product is constant

relation to equilibrium

highest T limit

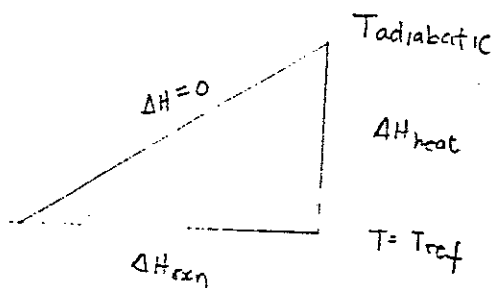
11. HOW WOULD YOU CALCULATE THE ADIABATIC FLAME TEMPERATURE?

$$\frac{dE}{dt} = \dot{Q} - \dot{W}_s + \sum F_i h_{i0} - \sum F_i h_i$$

adiabatic no shaft work s.s.

$$\sum F_i (h_{i0} - h_i) = 0 \Rightarrow \Delta \hat{h} = 0$$

$$\Delta \hat{h} = \Delta \hat{h}_{rxn} + \Delta \hat{h}_{heating} \Rightarrow -\Delta H_{rxn} = \sum F_i \int_{T_0}^{T_{adib}} C_p dT$$

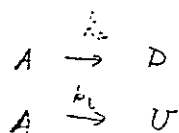


$$\Delta H_{rxn}(T_{ref}) + \sum F_i \int_{T_0}^{T_{ad}} C_p dT = 0$$

$$\Delta H_{rxn}(T_{ref}) + \sum F_i C_{pmh} \Delta T = 0$$

$$C_{pmh} = \frac{\int_{T_1}^{T_2} C_p}{T_2 - T_1}$$

12 WHICH TYPE OF REACTOR IS BEST FOR A PARALLEL REACTION?



D = desired product

U = Undesired product

- want to minimize U and maximize D

$$r_D = k_D C_A^{\alpha_1}$$

$$r_U = k_U C_A^{\alpha_2}$$

$$S_{DU} = \frac{r_D}{r_U} = \frac{k_D}{k_U} C_A^{\alpha_1 - \alpha_2}$$

- for $(\alpha_1 > \alpha_2)$ $\alpha_1 - \alpha_2 = a$

$$S_{DU} = \frac{k_D}{k_U} C_A^a$$

- to keep this ratio as high as possible, we want to keep C_A as high as possible during rxn. So if the rxn is in the gas phase, run w/o inerts at high P. If rxn is in liquid phase, diluents should be kept to minimum.

- BSTR & PFR should be used, since C_A starts out high, then drops in CSTR, C_A always at minimum concentration that of the outlet.

- for $(\alpha_1 < \alpha_2)$ $\alpha_2 - \alpha_1 = a$

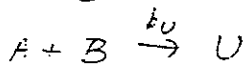
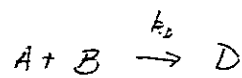
$$S_{DU} = \frac{k_D}{k_U} \frac{1}{C_A^a}$$

- to keep high ratio \Rightarrow low C_A , which can be accomplished w/ the addition of inerts or running reactor at low C_A .
Recycle reactor where product stream act as diluent could work CSTR is best.

- we don't know the activation energies, we don't know whether to run rxn at high or low T 's.

$$\frac{k_D}{k_U} = \frac{A_D}{A_U} \exp \left[-\frac{(E_D - E_U)}{RT} \right]$$

- if $E_D > E_U$, $k_D \uparrow$ faster than k_U w/ $\uparrow T$, so reaction should be operated at high T .
- if $E_U > E_D$, should carry reaction out at low T



$$r_D = k_D C_A^{\alpha_1} C_B^{\beta_1}$$

$$r_U = k_U C_A^{\alpha_2} C_B^{\beta_2}$$

$$S_{DU} = \frac{r_D}{r_U} = \frac{k_D}{k_U} C_A^{\alpha_1 - \alpha_2} C_B^{\beta_1 - \beta_2}$$

- for $(\alpha_1 > \alpha_2; \beta_1 > \beta_2)$

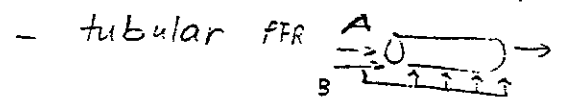
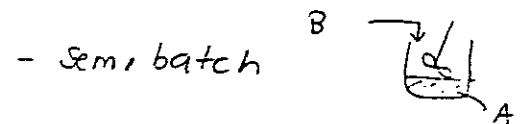
$$S_{DU} = \frac{k_D}{k_U} C_A^a C_B^b$$

PFR's	BSTR
high	P

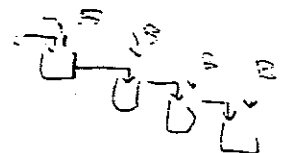


- for $(\alpha_1 > \alpha_2, \beta_1 < \beta_2)$

$$S_{DU} = \frac{k_D}{k_U} \frac{C_A^a}{C_B^b}$$



- series of CSTR's



- for $(\alpha_1 < \alpha_2, \beta_1 > \beta_2)$

$$S_{DU} = \frac{k_D}{k_U} \frac{C_U^b}{C_A^a}$$

reverse of above

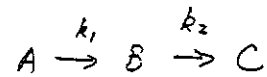
- for $(\alpha_1 < \alpha_2, \beta_1 < \beta_2)$

$$S_{DU} = \frac{k_D}{k_U} \frac{1}{C_A^a C_B^b}$$

CSTR

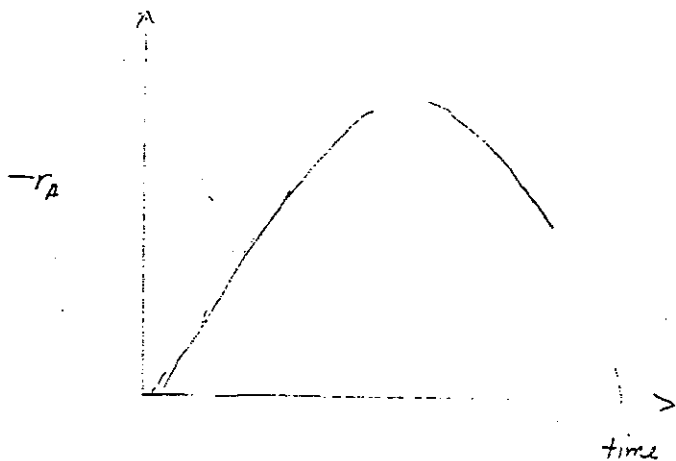
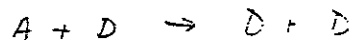
PFR w/ large recycle is

— Series reactions.



• for maximizing B, use BATCH or PFR

— autocatalytic reactions



In such reactions, there is a maximum in the rate. In the beginning, $-r_A$ is small because C_D is small so use CSTR to make it the highest, then use a PFR because PFR keeps it at the highest.

13. GIVE THE THREE LAWS OF THERMODYNAMICS.

First Law: conservation of energy

closed $[dU = dQ - dW]$ or $\Delta U = Q - W$

open $dU = dQ - dW + dE_{\text{in}}$ \rightarrow reflects KE & PE

Second Law: Irreversibilities of systems, increase in entropy

$$\Delta S_{\text{total}} \geq 0$$

equality holds for
reversible processes

THIRD LAW: Crystalline entropy, definition of entropy

$$S = 0 \text{ for perfect crystals}$$

$$S = \int_0^{T_f} \frac{C_p^s}{T} dT + \frac{\Delta H_f}{T_f} + \int_{T_f}^{T_v} \frac{C_p^l}{T} dT + \frac{\Delta H_v}{T_v} + \int_{T_v}^T \frac{C_p^g}{T} dT$$

$$S = k \ln \Omega$$

(13)

1st law

$$dU = \delta Q - \delta W \quad (\text{closed system})$$

$$\Delta \left[\left(H + \frac{1}{2} W^2 + gZ \right) dm \right]_{\text{flowing streams}} = \delta Q - \delta W_s \quad \text{steady flow processes}$$

- the change in internal energy of a closed system is equal to the energy that passes thru its boundary as heat or work

- the internal energy of an isolated system is constant

2nd law - the entropy of an isolated system increases in the course of a spontaneous change: $\Delta S_{\text{tot}} > 0$ where S_{tot} is the total entropy of the isolated system that contains the system of interest

Kelvin Planck statement

also . no cyclic process is possible whose only result is to transfer an amount of heat Q from a source at a single temperature totally into work W (so $W=Q$)

Clausius statement

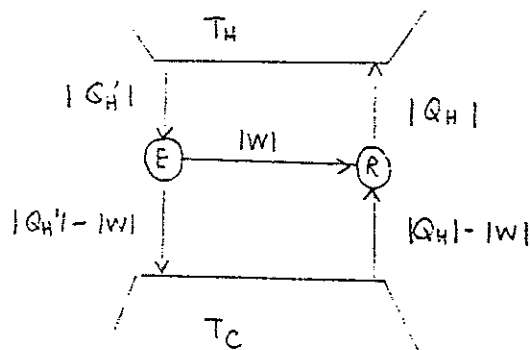
- no cyclic process is possible whose only result is a flow of heat out of a system at one temperature and an equal magnitude flow of heat into a second system at a higher temperature
i.e. no perfect heat engine, no perfect refrigerator

3rd law

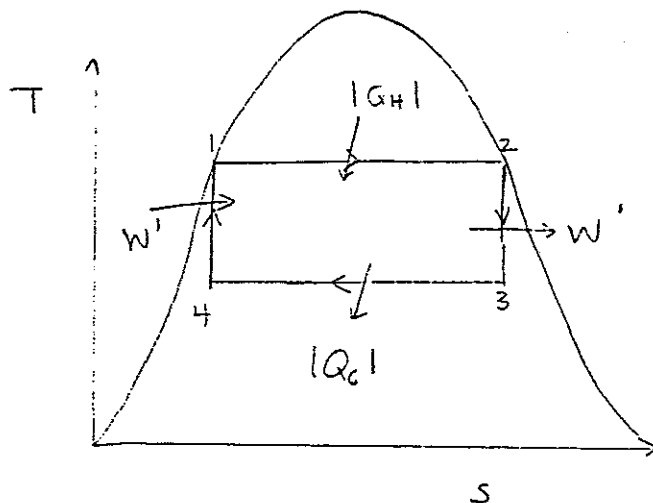
- if the entropy of every element in its most stable state at $T=0$ is taken as zero, then every substance has a positive entropy which at $T=0$ may become zero and which does become zero for all perfect crystalline substances

4. DIAGRAM THE CARNOT CYCLE, THE OTTO CYCLE, THE DIESEL CYCLE, THE BRAYTON CYCLE, AND THE RANKINE CYCLE. DRAW TS & PV DIAGRAMS. WRITE THE EQUATIONS TO DESCRIBE EACH STEP. WHAT IS THE EFFICIENCY?

Carnot Cycle



used to show that no engine can have a higher thermal efficiency than a Carnot engine: Carnot theorem.

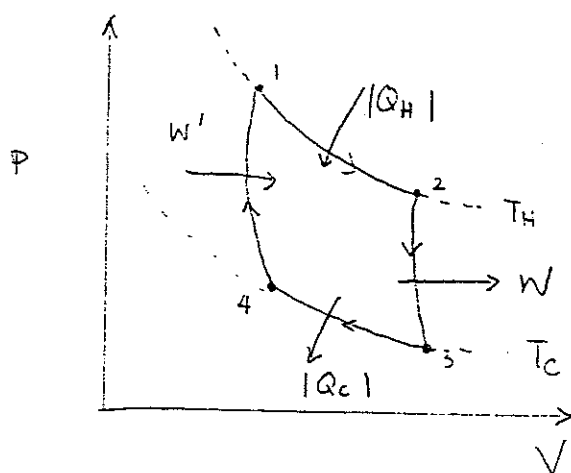


1-2: Isothermal expansion. In equil w/ hot reservoir (reversible).

2-3: Adiabatic, work is extracted (reversible).

3-4: Isothermal compression. In equil w/ cold reservoir. (reversible).

4-1: adiabatic, work input (reversible).



Ideal gas

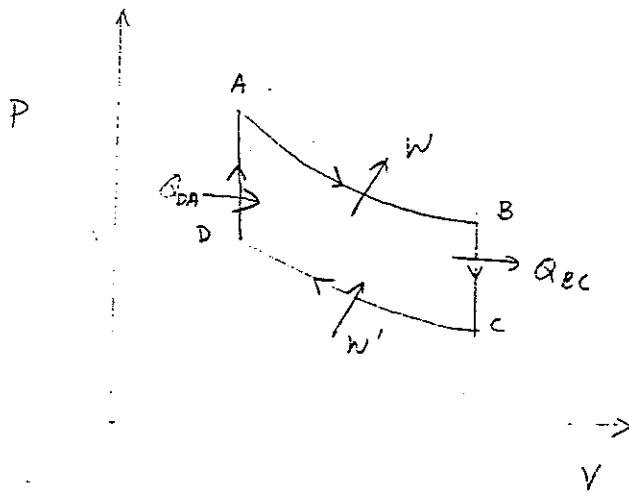
$$\text{efficiency} = \eta = \frac{W - W'}{|Q_H|} = \frac{|Q_H| - |Q_C|}{|Q_H|}$$

$$\eta = 1 - \frac{|Q_C|}{|Q_H|}$$

$$dS = 0 = \frac{|Q_H|}{T_H} - \frac{|Q_C|}{T_C} + \frac{S_{gen}}{T_0}$$

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

• Otto Cycle (Engine)



D-A: heat absorbed due to combustion (const. volume)

A-B: adiabatic expansion
Work done against piston (reversible)

B-C: const volume cooling.

C-D: adiabatic compression of gases (reversible)

- air standard otto cycle (ideal)
- internal combustion engine

$$\eta = \frac{W - W'}{|Q_{DA}|} = \frac{|Q_{DA}| - |Q_{BC}|}{|Q_{DA}|} = 1 - \frac{|Q_{BC}|}{|Q_{DA}|} = 1 - \frac{C_V(T_B - T_C)}{C_V(T_A - T_D)}$$

$$\frac{P_A}{P_D} = \frac{P_B}{P_C} \rightarrow \frac{P_C}{P_D} = \left(\frac{V_D}{V_C}\right)^\gamma = \left(\frac{1}{r}\right)^\gamma$$

$$\eta = 1 - \frac{T_B - T_C}{T_A - T_D} = 1 - \frac{P_B V_B - P_C V_C}{P_A V_A - P_D V_D} = 1 - \frac{V_C}{V_D} \left(\frac{P_B - P_C}{P_A - P_D}\right)$$

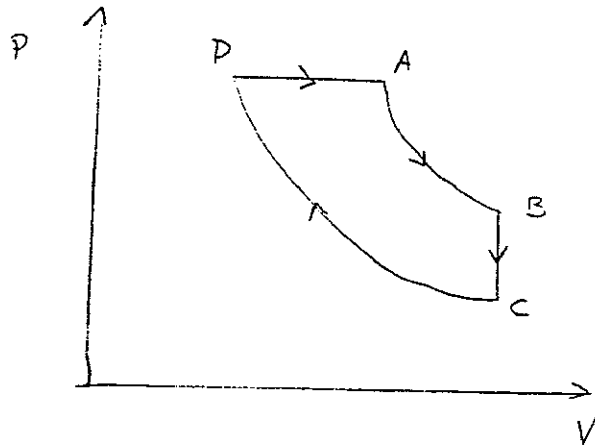
$$\eta = 1 - r \frac{P_C}{P_D} = 1 - \left(\frac{1}{r}\right)^{\gamma-1}$$

$$r \equiv \frac{V_C}{V_D}$$

larger the compression ratio, the greater the η .

DIESEL Engine

- main difference w/ Otto cycle in that compression ratio large enough s.t. ignition occurs w/o any firing device.

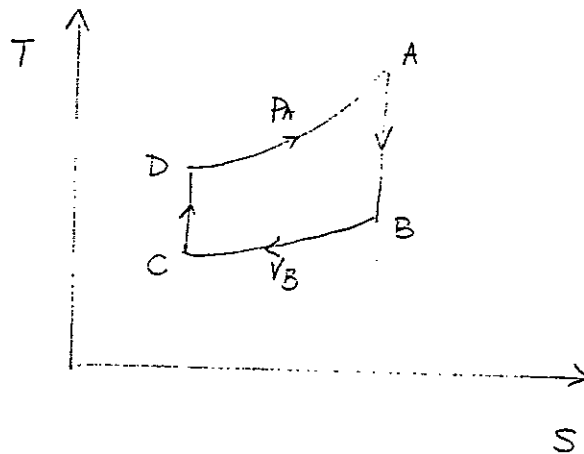


D-A: Isobaric heating, slow addition of fuel

A-B: Isentropic expansion

B-C: cooling at const V. due to opening of exhaust valve

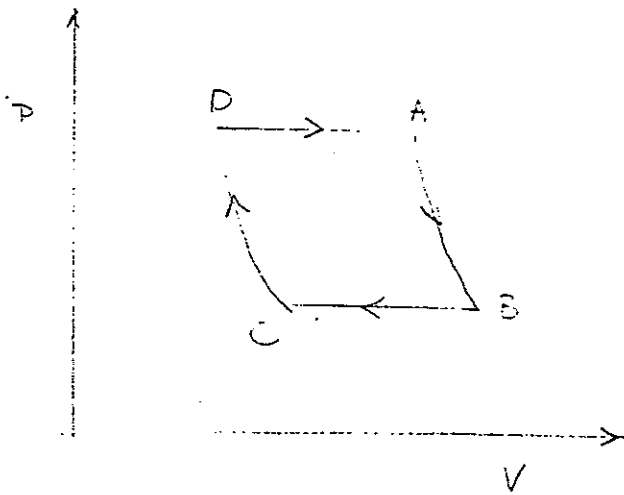
C-D: adiabatic compression



$$Q_{DA} = C_p (T_A - T_D)$$

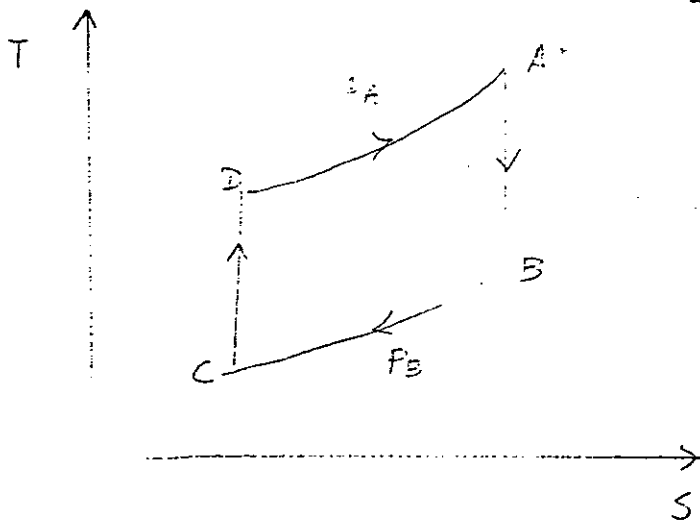
$$\therefore \eta = 1 - \frac{C_v}{C_p} \left(\frac{T_B - T_C}{T_A - T_D} \right) = 1 - \frac{1}{\gamma} \left(\frac{T_B - T_C}{T_A - T_D} \right)$$

Brayton Engine



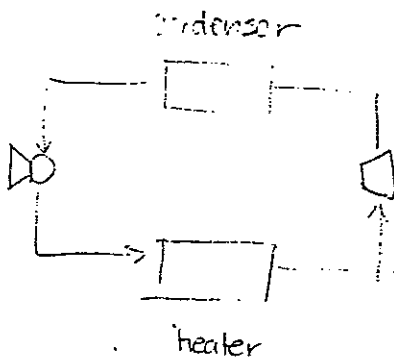
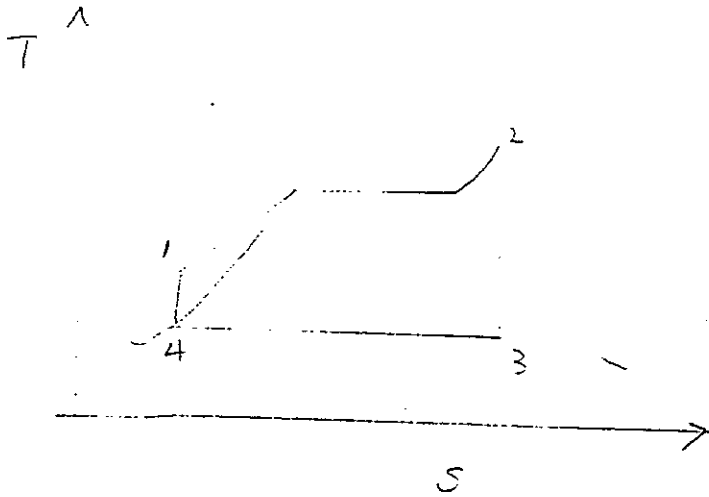
- B-C · Isobaric heating
- C-D · Isentropic expansion
- D-A · Isobaric compression
- A-B · Isentropic compression

these are
totally wrong!



$$\eta = 1 - \frac{T_B - T_C}{T_A - T_D}$$

• Rankine cycle (fossil burning power plants)

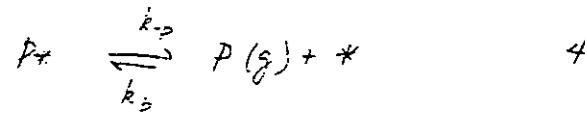
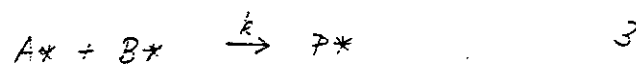
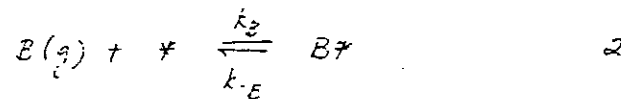
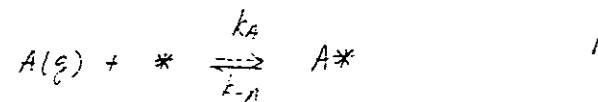


- 1-2: heating at const P
- 2-3: reversible, adiabatic expansion of superheated steam
- 3-4: Condensation to sat liq
isothermal $\hat{=}$ isobaric
- 4-1: reversible, adiabatic pumping of condensed liquid to pressure of boiler

15. DERIVE A LANGMUIR-HINSHELWOOD EXPRESSION FOR A SOLID CATALYZED REACTION



Mechanism:



$$-r = k \theta_A \theta_B \quad C_L = C_* + C_{A*} + C_{B*} + C_{P*}$$

PSSH. $-r_1 = k_A P_A C_* - k_{-1} C_{A*} \approx 0$

$$K_A = \frac{k_A}{k_{-1}} = \frac{C_{A*}}{P_A C_*} = \frac{\theta_A}{P_A \theta_*} \rightarrow \theta_A = K_A P_A \theta_*$$

$$-r_2 = k_B P_B C_* - k_{-2} C_{B*} \approx 0 \rightarrow \theta_B = K_B P_B \theta_*$$

$$-r_4 = k_P P_P C_* - k_{-3} C_{P*} \approx 0 \rightarrow \theta_P = K_P P_P \theta_*$$

$$1 = \theta_* + \theta_A + \theta_B + \theta_P$$

$$= \theta_* + K_A P_A \theta_* + K_B P_B \theta_* + K_P P_P \theta_*$$

$$\rightarrow \theta_* = \frac{1}{(1 + K_A P_A + K_B P_B + K_P P_P)} = \frac{1}{Q}$$

$$-r = k \frac{K_A K_B P_A P_B}{Q^2}$$

16. PROVE THAT $dG < 0$ FOR ANY PROCESS

- 2nd Law. $ds^{tot} > 0$ for any process

$$ds + ds^{sur} > 0$$

$$ds + \frac{dq_{sur}}{T} > 0$$

$$\text{but } dq = -dq_{sur}$$

$$ds > \frac{dq}{T}$$

- 1st law, closed system.



$$dU = dq - dw$$

$$dU < Tds - dw$$

$$dU + PdV - Tds < 0$$

$$G = H - TS$$

$$H = U + PV$$

$$G = U + PV - TS$$

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

$$dG|_{T,P} = dU + PdV - Tds$$

$$dG|_{T,P} < 0$$

- 1st law, open system

$$dH = dU + PdV + VdP$$

$$dH = dq - dw_s \quad \text{0 assumed}$$

$$dH < Tds \rightarrow dH - Tds < 0$$

$$dU + PdV + VdP - Tds < 0$$

$$dG|_{T,P} = dU + PdV - Tds < 0$$

$$dG|_{T,P} < 0$$

(16)

$$\Delta S + \Delta S_R \geq 0$$

since reservoir is in an eqbm state, it undergoes a reversible process, so that

$$\Delta S_R = \frac{Q_R}{T} \quad (1)$$

$$W_R = P \Delta V_R$$

heat, work and volume change for the reservoir are the negatives of the quantities for the system

$$Q_R = -Q \quad (2)$$

$$W_R = -W$$

$$\Delta V_R = -\Delta V$$

first law $\Delta U = Q - W$

but $W = -W_R = -P \Delta V_R = P \Delta V$

$$Q = \Delta U + P \Delta V \quad (3)$$

combining (1) and (2)

$$\Delta S_R = -\frac{Q}{T} \quad (4)$$

we now combine (3) and (4) to obtain

$$\Delta S_R = -\frac{(\Delta U + P \Delta V)}{T}$$

and insert into $\Delta S + \Delta S_R \geq 0$ to obtain

$$\Delta S - \left(\frac{\Delta U + P \Delta V}{T} \right) \geq 0 \quad (5)$$

from def'n of enthalpy

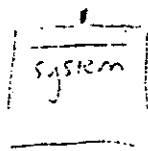
$$\Delta H = \Delta U + P \Delta V$$

and @ const P

$$\Delta H = \Delta U + P \Delta V$$

so for a constant T, P process (5) becomes

$$\Delta S - \frac{\Delta H}{T} \geq 0 \quad (6)$$



T, P

consider a closed system in thermal and mechanical communication with a large reservoir @ const T and P

16 cont'd

the Gibbs Exn (Gibbs free enrg) is defined as

$$G = H - TS$$

$$\text{so } \Delta G_{T,P} = \Delta H - T\Delta S$$

so since T (absolute) is a const. we rewrite (6) as

$$\Delta G \leq 0 \quad (T, P, n \text{ fixed})$$

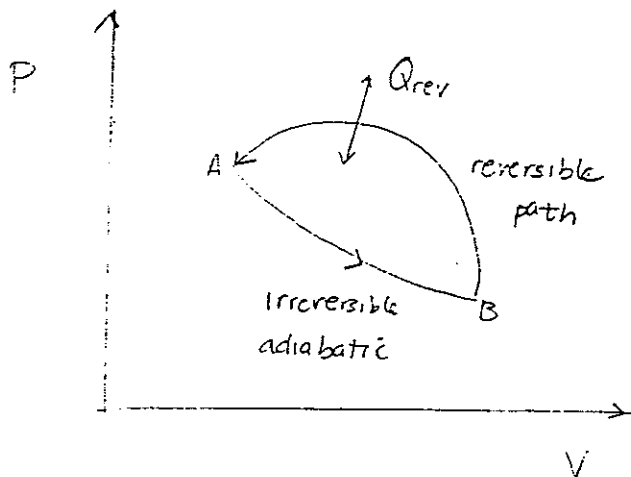
i.e. multiply (6) by T

how do I do it when it is not closed?

$$dH = dQ$$

$$dH > TdS$$

17. PROVE THAT S TENDS TOWARD A MAXIMUM



• cyclic process: $\Delta U = 0$

$$Q - W = 0$$

$$Q_{rev} - W = W_{rev} + W_{irr}$$

• $|W_{rev}| > |W_{irr}|$ and W_{rev} is < 0 , then $Q_{rev} < 0$

$$\Delta S_{B \rightarrow A} = \int_B^A \frac{dQ_{rev}}{T} < 0 = S_A - S_B$$

$$S_B - S_A > 0$$

$$\Delta S_{A \rightarrow B} > 0$$

S increases for
any process

16. WHAT IS THE GIBBS MIXTURE RULE? DERIVE GIBBS DUREN RELATION.

- Gibbs mixture rule is the Gibbs theorem

A total thermodynamic property; ($U, H, C_p, S, A, G, \text{etc}$) of an ideal mixture is the sum of the total properties of the individual species, each, evaluated at the mixture T but at its own partial P

$$M^{\text{IG}}(T, P) = \sum_i n_i m_i^{\text{IG}}(T, P_i)$$

M = any extensive property (U, H, G, A, etc)

$$nm = m(T, P, n_i)$$

$$d(M) = \left. \frac{\partial(M)}{\partial T} \right|_{P, n_i} dT + \left. \frac{\partial(M)}{\partial P} \right|_{T, n_i} dP + \sum_i \left. \frac{\partial(M)}{\partial n_i} \right|_{T, P} dn_i$$

$$= n \left. \frac{\partial m}{\partial T} \right|_{P, n_i} dT + n \left. \frac{\partial m}{\partial P} \right|_{T, n_i} dP + \sum_i \bar{m}_i dn_i$$

$$d(nm) = ndm + m dn$$

$$dn_i = d(x_i n) = x_i dn + n dx_i$$

\vdots

$$\left(dm - \left(\frac{\partial m}{\partial P} \right)_{T, x_i} dP - \left(\frac{\partial m}{\partial T} \right)_{P, x_i} dT - \sum \bar{m}_i dx_i \right) n + \left(m - \sum x_i \bar{m}_i \right) n$$

- to derive G-D normally:

$$d(nm) = \left. \frac{\partial(nm)}{\partial P} \right|_{T, n_i} dP + \left. \frac{\partial(nm)}{\partial T} \right|_{P, n_i} dT + \sum \bar{m}_i dn_i$$

$$-nm = \sum_i \bar{m}_i n_i \quad (\text{Euler})$$

equate

$$d(nm) = \sum_i \bar{m}_i dn_i + \sum_i n_i d\bar{m}_i$$

$$\left. \frac{\partial(nm)}{\partial P} \right|_{T, n_i} dP + \left. \frac{\partial(nm)}{\partial T} \right|_{P, n_i} dT - \sum_i n_i d\bar{m}_i = 0$$

GISS DUTHERI !

- for $M = G$

$$\left. \frac{\partial G}{\partial T} \right|_{P, n} = -S$$

$$\left. \frac{\partial G}{\partial P} \right|_{T, n} = V$$

$$\left. \frac{\partial G}{\partial n_i} \right|_{T, P, n_j} = \mu_i$$

$$SdT - VdP + \sum_i n_i d\mu_i = 0$$

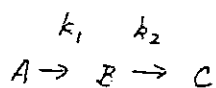
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$$S^E dT - v^E dP + \sum_i x_i d\mu_i^E = 0$$

$$\mu_i^E = RT \ln \gamma_i$$

at const T, P : $\sum_i x_i d \ln \gamma_i = 0$

- 19 FOR THE REACTION $A \rightarrow B \rightarrow C$, WITH RATE CONSTANTS k_1 AND k_2 IN WHICH THE ACTIVATION ENERGY FOR THE SECOND STEP IS GREATER THAN THE FIRST, HOW WOULD YOU ADJUST THE T TO MAXIMIZE THE PRODUCTION OF B



$$E_2 > E_1$$

$$k = A \exp\left(-\frac{E_a}{RT}\right)$$

$$\text{as } E_a \uparrow, k \downarrow$$

$$T \uparrow, k \uparrow$$

$$\frac{k_2}{k_1} = A \exp\left[-\frac{(E_2 - E_1)}{RT}\right]$$

We want to $\downarrow k_2$ but increase k_1 , so decrease T

19) want $\frac{k_2}{k_1}$ small (see ①)

$$\frac{k_2}{k_1} = \frac{\exp\left(-\frac{E_{a,2}}{RT}\right)}{\exp\left(-\frac{E_{a,1}}{RT}\right)} = \exp\left[\underbrace{-\frac{1}{RT}(E_{a,2} - E_{a,1})}_{\substack{\text{so } -ve \\ \text{is } +ve}}\right]$$

\Rightarrow lower T is better

$$\ln \frac{k}{A} = \frac{\Delta H^\ddagger}{RT}$$

20. HOW DO YOU CALCULATE THE EQUILIBRIUM CONSTANT AT NON-STANDARD TEMPERATURE & PRESSURE?

Gibbs - Helmholtz $\rightarrow \frac{\partial \frac{\Delta G^\circ}{T}}{\partial \frac{1}{T}} = \Delta H^\circ$

$$\Delta G^\circ = -RT \ln K_a \rightarrow \frac{\partial \ln K_a}{\partial \frac{1}{T}} = - \frac{\Delta H^\circ}{R}$$

$$\frac{\partial \ln K_a}{\partial T} = \frac{\Delta H^\circ}{RT^2}$$

$$\therefore \ln \frac{K_a(T_2)}{K_a(T_1)} = \frac{\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

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

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

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

$$\frac{\partial G}{\partial P} \Big|_T = V \rightarrow \frac{\partial \Delta G}{\partial P} \Big|_T = \Delta V^\circ \rightarrow \boxed{\frac{\partial \ln K_a}{\partial P} = - \frac{\Delta V^\circ}{RT}}$$

21. DEFINE U , H , S , G , F , and A

$U \equiv$ internal energy

$$dU = TdS - PdV$$

$$U = \int_0^P \left[V - T \left(\frac{\partial V}{\partial T} \right)_{P, n_T} \right] dP - PV + \sum_i n_i h_i^\circ$$

$$U = \int_V^\infty \left[P - T \left(\frac{\partial P}{\partial T} \right)_{V, n_T} \right] dV + PV + \sum_i n_i u_i^\circ$$

$H \equiv$ enthalpy

$$dH = TdS + VdP$$

$$H = \int_0^P \left[V - T \left(\frac{\partial V}{\partial T} \right)_{P, n_T} \right] dP + \sum_i n_i h_i^\circ$$

$$H = \int_V^\infty \left[P - T \left(\frac{\partial P}{\partial T} \right)_{V, n_T} \right] dV + PV + \sum_i n_i u_i^\circ$$

$A \equiv$ Helmholtz energy

$$dA = -SdT - PdV$$

$$A = \int_0^P \left[V - \frac{nRT}{P} \right] dP + RT \sum_i n_i \ln y_i P - PV + \sum_i n_i (h_i^\circ - TS_i^\circ)$$

$$A = \int_V^\infty \left[P - \frac{nRT}{V} \right] dV - RT \sum_i n_i \ln \frac{V}{n_i RT} + PV + \sum_i n_i (u_i^\circ - TS_i^\circ)$$

$G \equiv$ Gibbs free energy

$$dG = -SdT + VdP$$

$$G = \int_0^P \left[V - \frac{nRT}{P} \right] dP + RT \sum_i n_i \ln y_i P + \sum_i n_i (h_i^\circ - TS_i^\circ)$$

$$G = \int_V^\infty \left[P - \frac{nRT}{V} \right] dV - RT \sum_i n_i \ln \frac{V}{n_i RT} + PV + \sum_i n_i (u_i^\circ - TS_i^\circ)$$

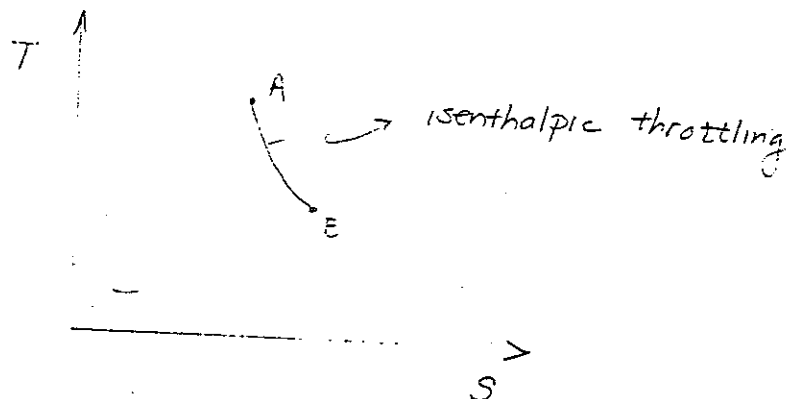
$S \equiv$ entropy

$$S = \int_0^P \left[\frac{nR}{P} - \left(\frac{\partial V}{\partial T} \right)_{P, n_T} \right] dP - R \sum_i n_i \ln y_i P + \sum_i n_i s_i^\circ$$

$$S = \int_V^\infty \left[\frac{nR}{V} - \left(\frac{\partial P}{\partial T} \right)_{V, n_T} \right] dV + PV + \sum_i n_i u_i^\circ$$

22. WHAT IS A JONLE-THOMPSON LIQUEFACTION PROCESS ?

- J-T liquefaction process is to take a gas at a low enough T and high enough P and expanding it through a throat the valve such that some gas to condense.



23. WHAT IS THE SLOPE OF A $\ln K_{eq}$ VS. $\frac{1}{T}$ CURVE FOR AN EXOTHERMIC AND ENDOTHERMIC RXN ?

$$\Delta G = -RT \ln K_{eq}$$

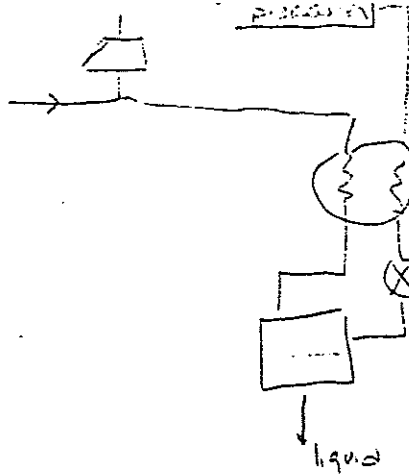
$$G-H: \quad \frac{\partial \left(\frac{\Delta G}{T} \right)}{\partial \left(\frac{1}{T} \right)} = \Delta H$$

$$\frac{\partial \ln K_{eq}}{\partial \frac{1}{T}} = -\frac{\Delta H}{R}$$

\therefore exothermic $\Delta H < 0 \rightarrow \text{slope} > 0$

endothermic $\Delta H > 0 \rightarrow \text{slope} < 0$

22



Joule Thomson = Linde

gas fed by

throttling valve

→ use Joule-Thomson expansion to lower T

24. IF $\Delta G = 0$ AT EQUILIBRIUM, WHY ISN'T $\Delta G_{rxn} = 0$ FOR ANY REACTI

$$\Delta G_{rxn} = \Delta G_{rxn}^{\circ} + RT \ln K_{eq}$$

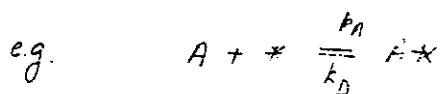
- $\Delta G_{rxn} \neq 0$ if rxn is not at equilibrium. For irreversible reactions, $\Delta G \neq 0$. In particular, $\Delta G < 0 \Rightarrow$ forward reaction happens spontaneously

25. GIVE A PHYSICAL INTERPRETATION OF THE ACTIVATION ENERGY?

- Activation energy is the minimum energy that must be possessed by reacting molecules before rxn would occur. Like passing over a mountain range

26. WHERE DOES THE LANGMUIR ISOTHERM COME FROM?

- Langmuir isotherm describes the surface conc. of adsorbed species in equilibrium w/ gas.



$$r_{net} = k_A P_A C_* - k_D C_{A*} = 0$$

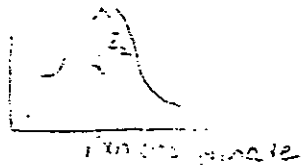
$$K = \frac{k_A}{k_D} = \frac{C_{A*}}{P_A C_*}$$

$$C_t = C_* + C_{A*}$$

$$C_{A*} = \frac{P_A K C_t}{1 + P_A K}$$

35

PE



E_a = energy barrier

= minimum energy that reactants must have
in order to form products

27. WHY IS ENTROPY ZERO AT 0K?

Entropy is zero at 0K because a pure substance that is a perfect crystalline form has no other possible way to arrange the particles to obtain lowest quantum state

$$S = k \ln W = k \ln 1 = 0 !$$

EE HOW WOULD YOU CALCULATE THE TOTAL VOLUME WHEN TWO EQUAL VOLUMES OF DIFFERENT LIQUIDS ARE MIXED?

$$\Delta v_{mix} = v^E = v_{mix} - x_1 v_1 - x_2 v_2$$

$$V_{mix} = n_T v^E + n_1 v_1 + n_2 v_2 = V^E + V_1 + V_2$$

- assume V_1, V_2 known

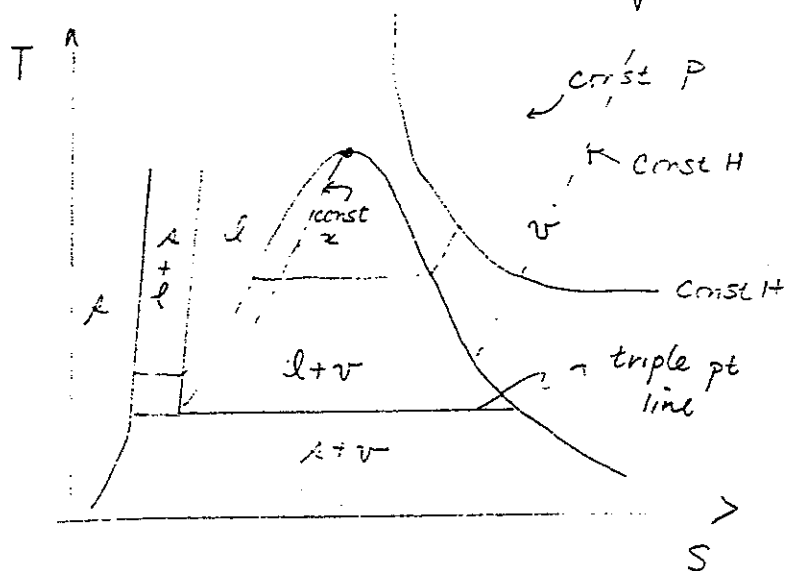
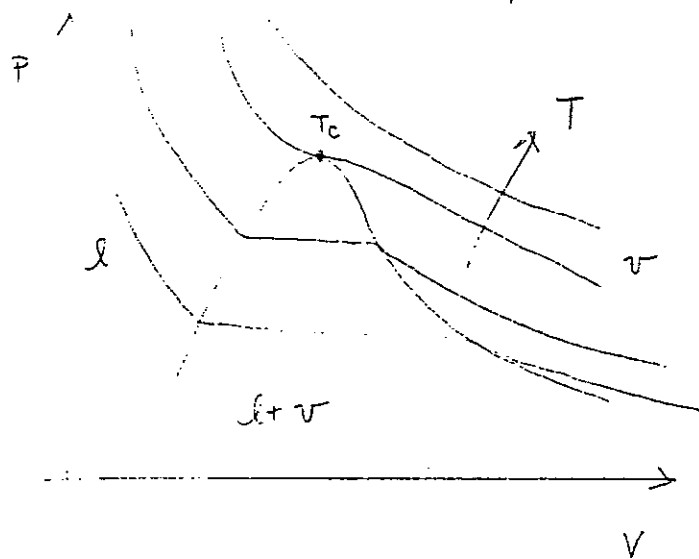
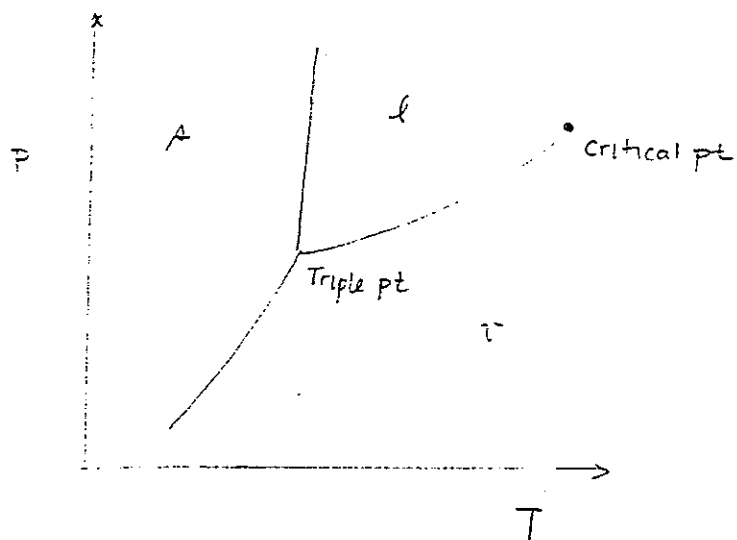
$$\frac{\partial G^E}{\partial P} \bigg|_{T,x} = V^E$$

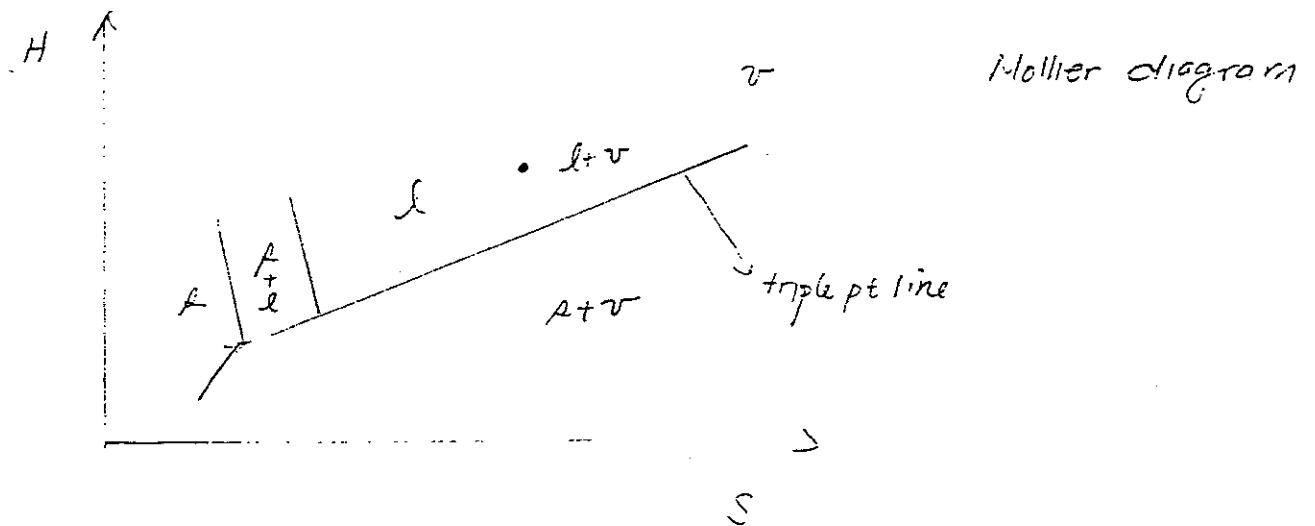
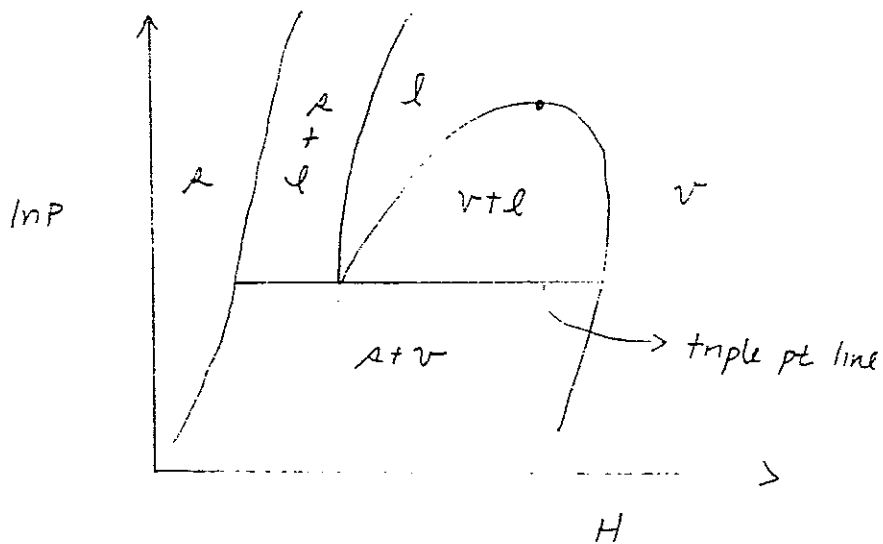
29. How would you calculate from first principles the heat capacity of two gases. EG H_2 & CH_3NCO ?

$$C_p = \frac{\partial h}{\partial T} \bigg|_p \quad C_v = \frac{\partial u}{\partial T} \bigg|_p \quad h = u + Pv$$

$$C_p = \frac{\partial (u + Pv)}{\partial T} \bigg|_p = \frac{\partial u}{\partial T} \bigg|_p + \frac{\partial (Pv)}{\partial T} \bigg|_p = C_v + \dots$$

31. SKETCH $H-S$, $T-S$, $lnP-H$, $P-T$, and $P-V$ DIAGRAMS FOR A PURE SUBSTANCE





32. WHAT DOES POLYTROPIC MEAN?

A process that follows the eqn $Pv^\gamma = \text{const}$. Applies for a reversible process for ideal gas. Also can be written as:

$$Tv^{\gamma-1} = \text{const} \quad \& \quad TP^{-\frac{\gamma-1}{\gamma}} = \text{const}$$

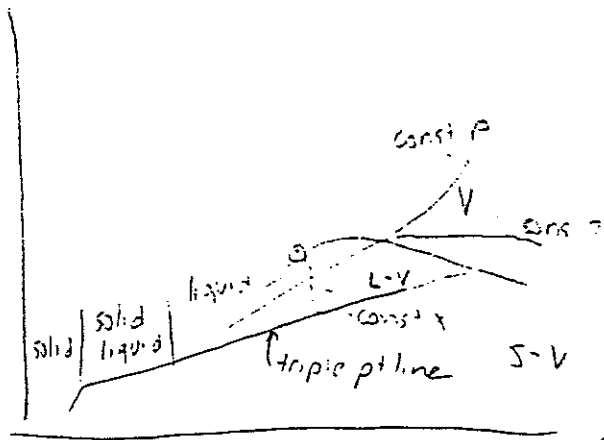
$\gamma=0$ isobaric

$\gamma=1$ isothermal

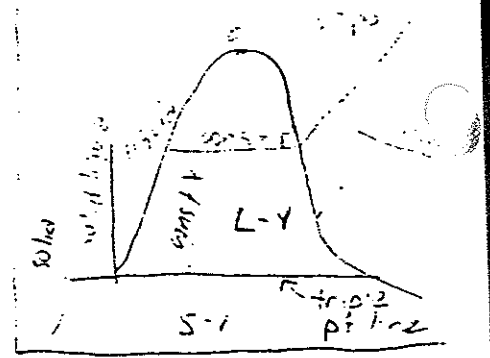
$\gamma=\infty$ const volume $\left(TP^{-\frac{\gamma-1}{\gamma}} = T \frac{1}{P} = \frac{\gamma}{R} = \text{const} \right)$

31)

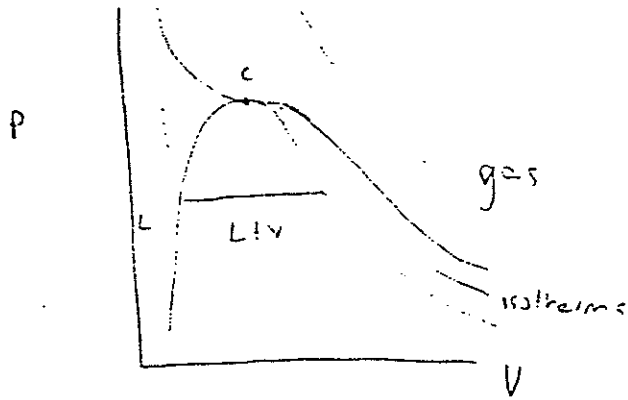
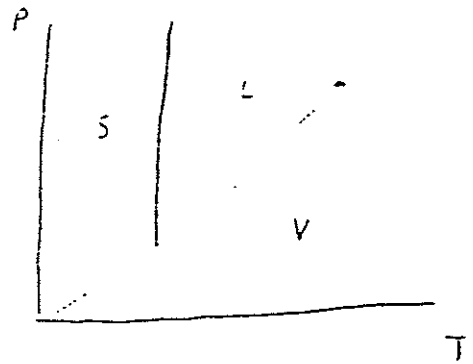
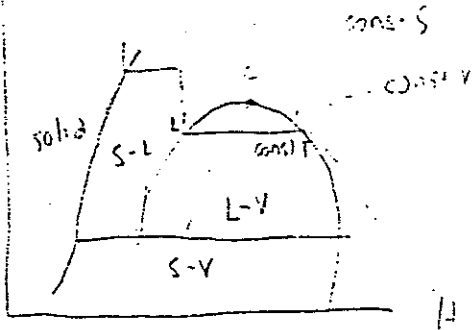
11



12



21P



General mole balance:

$$\underline{F_{i0} - F_i + r_i V = \frac{d}{dt} (C_i V)} \quad \text{no spatial variations}$$

$$\underline{-\frac{\partial F_i}{\partial V} + r_i = \frac{\partial C_i}{\partial t}} \quad \text{spatial variations}$$

General energy balance:

$$\underline{\frac{\partial E_{sys}}{\partial t} = \dot{Q} - \dot{W}_s + \sum_i F_i \hat{h}_i|_{in} - \sum_i F_i \hat{h}_i|_{out}}$$

$$\begin{aligned} \frac{\partial}{\partial t} E_{sys} &= \frac{\partial}{\partial t} \left(\sum_i n_i e_i \right) = \frac{\partial}{\partial t} \left(\sum_i n_i \left(u_i + \frac{1}{2} v_i^2 + g \hat{h}_i \right) \right) \\ &= \frac{\partial}{\partial t} \left(\sum_i n_i (\hat{h}_i - P v_i) \right) + \frac{\partial}{\partial t} \left(\sum_i n_i \left(\frac{1}{2} v_i^2 + g \hat{h}_i \right) \right) \end{aligned}$$

$$\therefore \sum_i n_i \frac{\partial \hat{h}_i}{\partial t} + \sum_i \hat{h}_i \frac{\partial n_i}{\partial t} - \frac{\partial}{\partial t} (P \sum_i n_i v_i) = \dot{Q} - \dot{W}_s + \sum_i F_i \hat{h}_i|_{in} - \sum_i F_i \hat{h}_i|_{out}$$

PFR:

$$n_i = C_i dV$$

$$T = f(t, V), \quad C_i = f(t, V)$$

$$\sum_i C_i \frac{\partial \hat{h}_i}{\partial t} + \sum_i \hat{h}_i \frac{\partial C_i}{\partial t} - \frac{\partial}{\partial t} (P \sum_i C_i v_i) = \frac{\partial \dot{Q}}{\partial V} - \frac{\partial \dot{W}_s}{\partial V} - \frac{\partial}{\partial V} (\sum_i F_i \hat{h}_i)$$

$$\sum_i C_i \frac{\partial \hat{h}_i}{\partial t} - \frac{\partial P}{\partial t} = \frac{\partial \dot{Q}}{\partial V} - \frac{\partial \dot{W}_s}{\partial V} - \sum_i F_i \frac{\partial \hat{h}_i}{\partial V} - \sum_i \hat{h}_i \left(\frac{\partial F_i}{\partial V} + \frac{\partial C_i}{\partial t} \right)$$

$= r_i$

$$\underline{\sum_i C_i C_p \frac{\partial T}{\partial t} - \frac{\partial P}{\partial t} = Ua(T_a - T) - \frac{\partial \dot{W}_s}{\partial V} + (-r_A)(-\Delta H_R(T)) - \left(\sum_i F_i C_{pi} \frac{\partial T}{\partial V} \right)}$$

CSTR:

$$n_i = C_i V$$

$$T = f(t), \quad C_i = f(t)$$

$$\sum C_i V C_{p_i} \frac{dT}{dt} + \sum h_i V \frac{dC_i}{dt} - V \frac{dP}{dt} = \dot{Q} - \dot{W}_s + \sum F_i h_i|_{in} - \sum F_i h_i|_{out}$$

$$F_{i0} - F_i - \nu_i r_A V = V \frac{dC_i}{dt}$$

$$V \sum_i C_{p_i} C_i \frac{dT}{dt} = UA(T_a - T) - \dot{W}_s - F_{A0} \sum_i \theta_i \int_{T_0}^T C_{p_i} dT - \Delta H_R(T)(-r_A V)$$

Batch:

$$n_i = n_{A0}(\theta_i + \nu_i X)$$

$$n_{A0} \left(\sum \theta_i C_{p_i} + \Delta C_p X \right) \frac{dT}{dt} = UA(T_a - T) - \dot{W}_s - \Delta H_R(T)(-r_A V)$$

34. WHAT IS THE PHASE RULE WHEN RXNS ARE OCCURRING?

Phase rule, non reacting.

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

\uparrow \uparrow \uparrow
 degrees # of # of
 of phase species
 freedom

Phase rule, reacting.

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

↑
of chem
reactor
equl

less deg of freedom since
chemical eq of librx
relates species

34

$$F = N - P + 2 - R$$

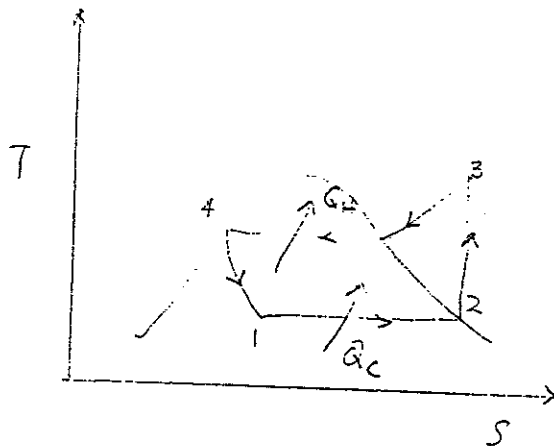
(phases (

spaces

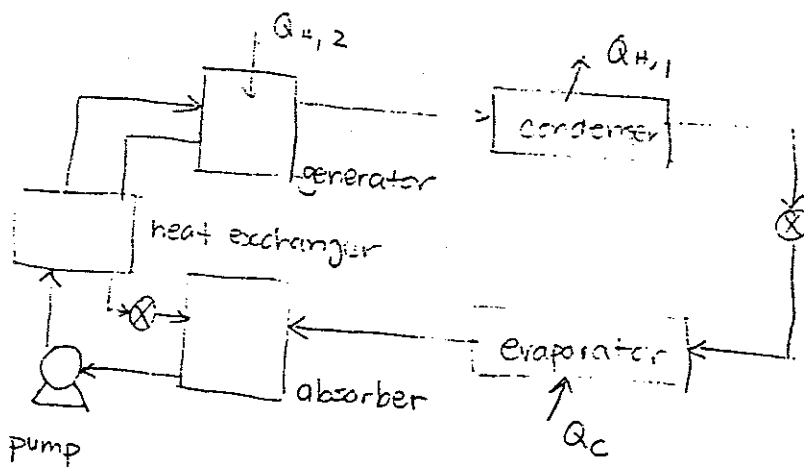
#rxns

35. HOW DOES ABSORPTION REFRIGERATION WORK? WHAT ARE SUITABLE CHARACTERISTICS OF A WORKING FLUID?

- Work of compression supplied by heat at high temp. (heat engine) instead of an electric motor (as in normal vapor compression refrigeration)



- 1-2: Isothermal evaporation
- 2-3: compression
- 3-4: condensation
- 4-1: expansion (isenthalpic)



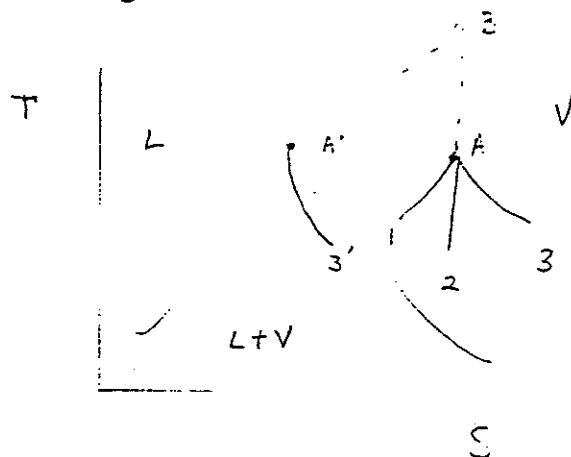
dissolving gas into liquid

Some common systems:

- (1) refrigerant - H_2O
absorbent - LiBr soln
- (2) refrigerant - NH_3
Absorbent - H_2O

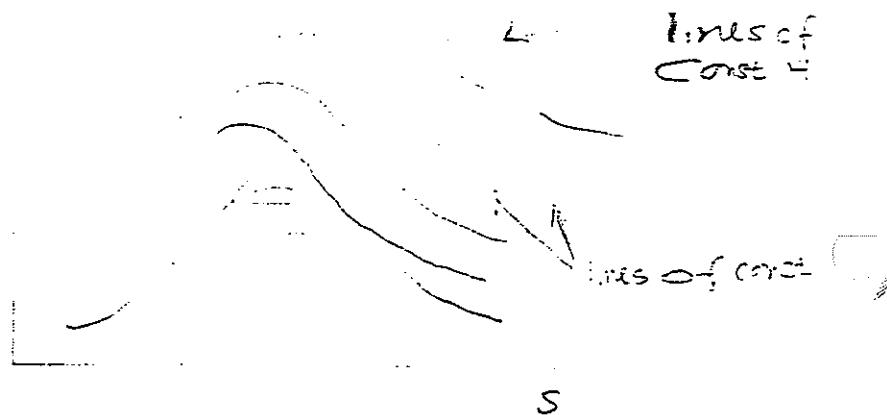
36. GIVE THREE METHODS OF LIQUEFYING GASES.

1. heat exchange at constant P
2. expansion in a turbine from which work is obtained
3. throttling (at const H)



- usually a heat sink used to precool via method 1, then the other two methods used.
 - for method 3, must be at low enough T and high enough P such that the isenthalpic path goes into the $L+V$ region (3')
- This accomplished by compression to B then const P cooling to A' .

on T-S diagram:



39. WHY IS FREON USED IN REFRIGERATORS INSTEAD OF H_2O or air, etc.?

- 1) $p^{vap}(T_c) > p^{atm}$ so that air does not leak into system
at T_c of evaporator
- 2) $p^{vap}(T_H)$ should not be too high, high P equipment expensive

∴ #1 rules out H_2O for $T_{evap} < 100^\circ C$

#2 rules out air, need high P to condense air

40

$$a_i \equiv \frac{f_i}{f_i^\circ}$$

\sim standard state (density)

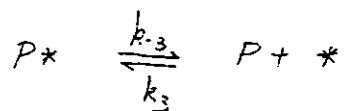
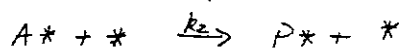
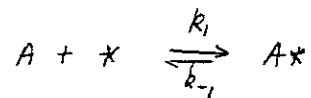
you have divided by a standard state, so different from f_i°

important for chem eqm calcs

$$\prod (a_i)^{\nu_i} = \exp - \frac{\sum \nu_i G_i^\circ}{RT} = K$$

42. CONSIDER LANGMUIR-HINSHELWOOD KINETICS, WHY MIGHT RATE GO DOWN AS GAS CONCENTRATIONS RISE UP?

for $A \rightarrow P$:



$$-r = k_2 \theta_{A^*} \cdot \frac{1}{2} z \theta_*$$

PSSH :

$$K_1 = \frac{C_{A^*}}{P_A C_*}$$

$$K_3 = \frac{C_{P^*}}{P_P C_*}$$

$$\theta_{A^*} = K_1 P_A \theta_*$$

$$\theta_{P^*} = K_3 P_P \theta_*$$

$$C_T = C_* + C_{A^*} + C_{P^*} \rightarrow$$

$$1 = \theta_* + \theta_{A^*} + \theta_{P^*}$$

$$1 = \theta_* (1 + K_1 P_A + K_3 P_P)$$

$$\therefore -r = \frac{k_2 K_1 P_A \cdot \frac{1}{2} z}{(1 + K_1 P_A + K_3 P_P)^2}$$

$$\therefore \text{as } P_A, P_P \uparrow$$

$$-r \downarrow$$

less vacant sites available, so $-r \downarrow$

43

internal

$$\eta \rightarrow \frac{1}{\phi}$$

$$\phi \propto \sqrt{k} \Rightarrow k_{app} = k_{true}^{1/2}$$

$$b/c -r_n = \frac{1}{\phi} r_n$$

$$E_{transition} = \frac{E_a}{2}$$

external?

$$-r_n = k_g C$$

$$k_g \approx \frac{D_{AB}}{\delta}$$

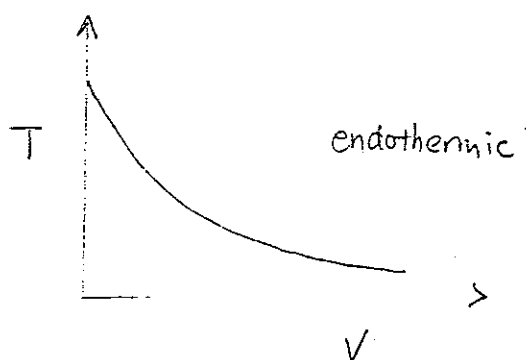
$$D_{AB} \propto T^{1.75}$$

$$D_{AB} = D_{AB,0} \exp\left(-\frac{E^*}{RT}\right)$$

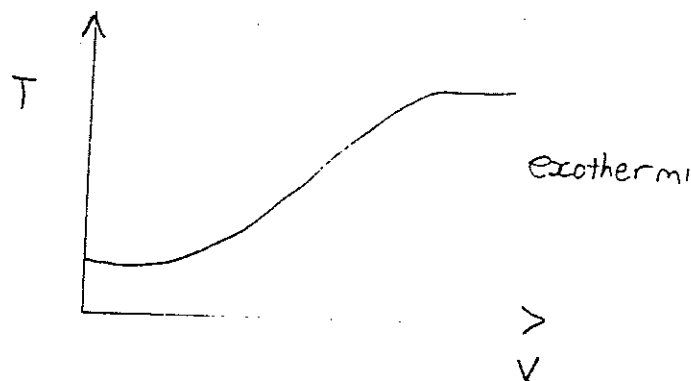
E^* completely different

45 WHAT DOES THE TEMPERATURE DISTRIBUTION IN A PFR LOOK LIKE

- For adiabatic PFR

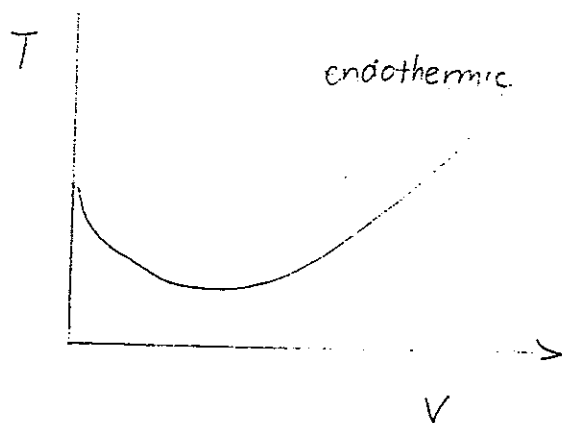


Reaction dies out as $T \downarrow$
enough (slow down the kinetics)

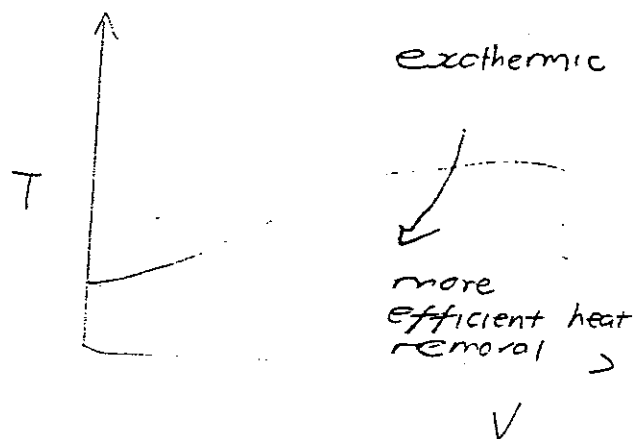


Reaction rate \uparrow as $T \uparrow$,
but T tapers off as
reaction slows due to
consumption of reactants

- For PFR w/ heat exchange



minimum in T due to
the largest rxn rate,
but depletion of reactants
cause T to increase



(45)

Fluidized bed reactor - solid material in the form of fine particles is held in suspension by upward flow of reacting fluid

- adv - uniform T, avoiding hot spots
- can handle large amounts of feed
- good T control
- ease of catalyst replacement/regeneration
- high surface area
- disadv - high cost of reactor
- catalyst regeneration equipment
- larger pressure drop than fixed bed → high operating costs
- abrasion (erosion of materials)
- can't be used w/ some catalysts which will not flow readily or will agglomerate easily
- catalyst fines are carried out and foul heat exchanger

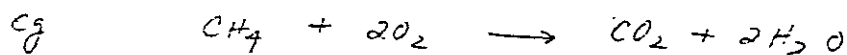
48. How do you find K_{eq} for $A + B \rightleftharpoons C$

$$\Delta G_{rxn}^{\circ} = -RT \ln K_{eq} \rightarrow K_{eq} = \exp\left(-\frac{\Delta G_{rxn}^{\circ}}{RT}\right)$$

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

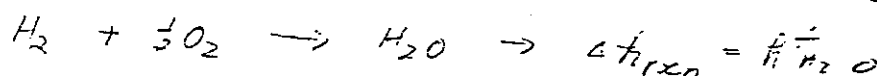
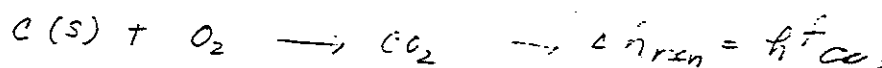
$$= \sum \nu_i h_i^{\circ} - T \sum \nu_i S_i^{\circ}$$

- to find h_i° , need calorimetry experiments:



$$\Delta h_{rxn} = h_{CO_2}^{\circ} + 2h_{H_2O}^{\circ} - h_{CH_4}^{\circ}$$

to get $h_{CH_4}^{\circ}$



for h at various T : $h(T) = h(T_0) + \int_{T_0}^T C_p dT$

- to find S_i° , use 3rd law and low T calorimetry

$$S_i^{\circ} = \int_0^{T_m} \frac{C_p^s dT}{T} + \frac{\Delta h_{fm}}{T_m} + \int_{T_m}^{T_b} \frac{C_p^L dT}{T} + \frac{\Delta h_{fb}}{T_b} + \int_{T_b}^T \frac{C_p^v dT}{T}$$

G-H $\rightarrow \frac{\partial(\frac{G}{T})}{\partial(\frac{1}{T})} = h$ to get K_{eq} at different T .

51. WHAT IS RAOULT'S LAW? HENRY'S LAW? WHERE DO THEY APPLY?

(for V-L equilibrium)

$$f_i^V = f_i^L$$

$$y_i \phi_i P = x_i \gamma_i f_i^0$$

$$y_i \phi_i P = x_i \gamma_i \phi_i^s P_i^s \exp \left[\int_{P_i^s}^P \frac{\bar{v}_i dP}{RT} \right]$$

$$y_i P = x_i P_i^s$$

Raoult's Law

- 1) Low P, vapor phase ideal
- 2) liquid phase ideal
- 3) vapor above pure sat. is ideal
- 4) low P neglects Poynting correction

when mixture nearly pure i at low P

→ Henry's Law, binary systems.

$$f_2 = H_{2,1} \cdot x_2$$

$$H_{2,1} = \lim_{x_2 \rightarrow 0} \frac{f_2}{x_2}$$

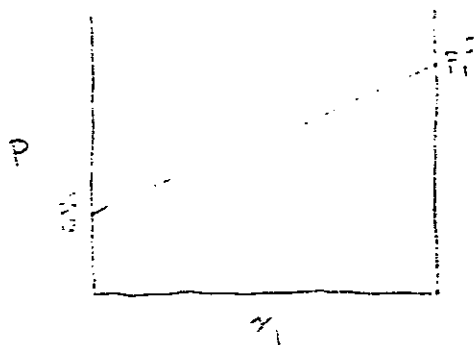
when dilute x_2 in 1

Can Raoult's Law solve for an azeotrope?

$$y_1 P = x_1 P_1^S \quad y_2 P = x_2 P_2^S$$

$$P = x_1 P_1^S + x_2 P_2^S = x_1 P_1^S + (1-x_1) P_2^S$$

$$P = x_1 (P_1^S - P_2^S) + P_2^S$$



No azeotrope is formed
because

$$1 = \frac{y_1 P}{P_1^S} + \frac{y_2 P}{P_2^S}$$

$$1 = \left(\frac{y_1}{P_1^S} + \frac{y_2}{P_2^S} \right) P$$

$$1 = \left[\frac{y_1}{P_1^S} + \frac{1-y_1}{P_2^S} \right] P$$

$$= \frac{y_1 P_2^S + P_2^S - y_1 P_1^S}{P_1^S P_2^S} P$$

$$P = \frac{P_1^S P_2^S}{y_1 (P_2^S - P_1^S) + P_1^S}$$

53)

$$y_i P = x_i P_i^s$$

azeotrope $\Rightarrow y_i = x_i$

$$P = P_i^s$$

\rightarrow pure i , a trivial azeotrope

34. WHAT IS THE DIFFERENCE BETWEEN A MIXING RULE AND A COMBINING RULE?

- Mixing rule dictates how mixture property is obtained from composition. Based on probability and has theoretical basis

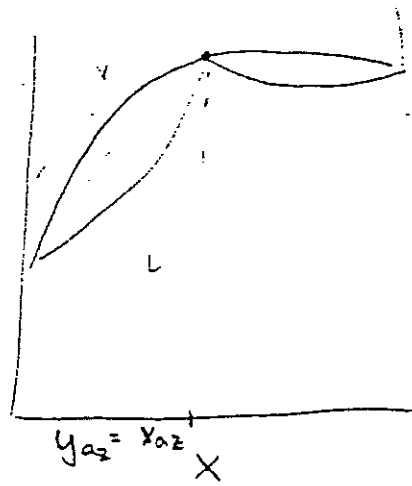
eg
$$a = \sum_i \sum_j y_i y_j a_{ij}$$

- Combining rule states how "cross terms" can be related to pure component parameters. It has little theoretical basis.

eg
$$a_{12} = (a_{11} a_{22})^{1/2}$$

55

T

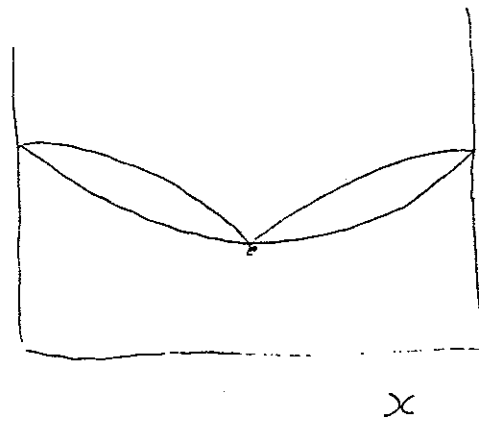


-ve deviations from Raoult's law

- recovered in bottoms where there is the highest T

maximum boiling azeotrope.

T



- recovered in distillate where T lowest

minimum boiling azeotrope

57. DERIVE MAXWELL'S RELATIONS

$$\bullet \quad du = Tds - Pdv \rightarrow \quad \left. \frac{\partial T}{\partial v} \right|_s = - \left. \frac{\partial P}{\partial s} \right|_v$$

$$\bullet \quad h = u + Pv \quad \left(\frac{\partial T}{\partial P} \right)_s = \left(\frac{\partial v}{\partial s} \right)_P$$

$$dh = du + Pdv + vdp$$

$$= Tds - Pdv + Pdv + vdp$$

$$= Tds + vdp$$

$$\rightarrow \quad \left. \frac{\partial T}{\partial v} \right|_s = \left. \frac{\partial v}{\partial s} \right|_P$$

$$\bullet \quad g = h - Ts$$

$$dg = dh - Tds - sdT$$

$$= Tds + vdp - sdT - Tds$$

$$= vdp - sdT$$

$$\rightarrow \quad \left. \frac{\partial v}{\partial T} \right|_P = - \left. \frac{\partial s}{\partial P} \right|_T$$

$$\bullet \quad a = u - Ts$$

$$da = du - Tds - sdT$$

$$= Tds - Pdv - Tds - sdT$$

$$= -Pdv - sdT$$

$$\rightarrow \quad \left. \frac{\partial P}{\partial T} \right|_v = \left. \frac{\partial s}{\partial v} \right|_T$$

60. DESCRIBE THE GRAPHICAL APPROACH TO REACTOR DESIGN AND ANALYSIS.

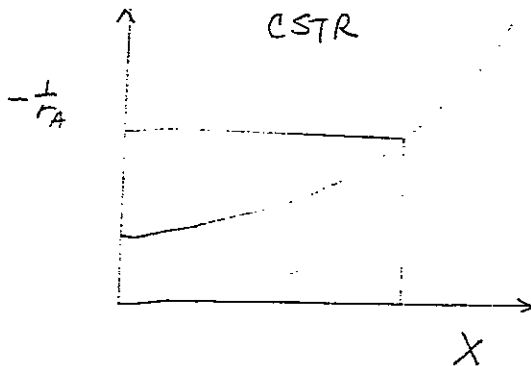
- Isothermal reactors

$$\text{CSTR: } F_{A0} - F_{A0}(1-X) + r_A V = 0$$

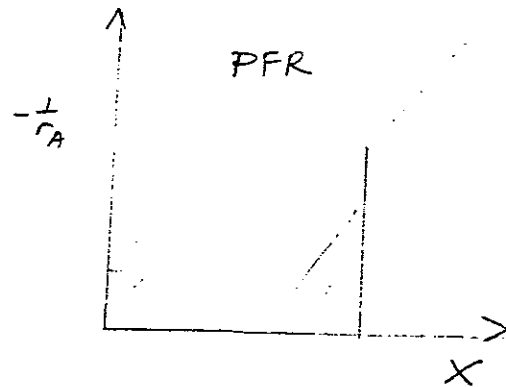
$$V = \frac{F_{A0} X}{-r_A}$$

$$\text{PFR: } \frac{dF_A}{dV} = r_A$$

$$V = F_{A0} \int_0^X \frac{dX}{-r_A}$$



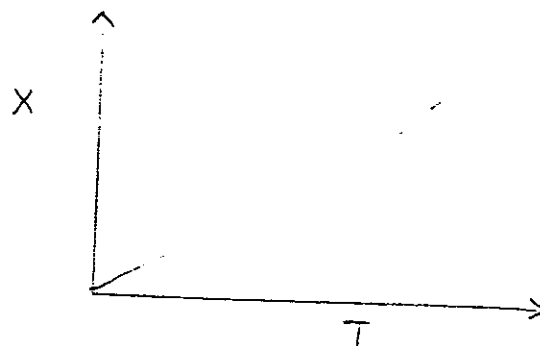
$$V = F_{A0} \cdot \text{area}$$



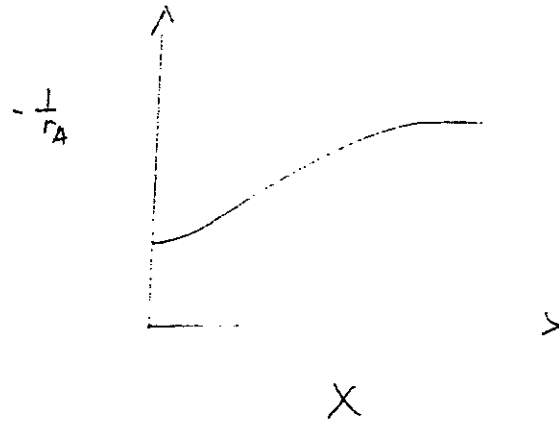
$$V = F_{A0} \cdot \text{area}$$

- Non isothermal reactors

— use energy balance to plot X vs T .



- pick X to get T from energy balance graph, get $-r_A$ and plot $-\frac{1}{r_A}$ vs X graph



now get volume like before.

(61)

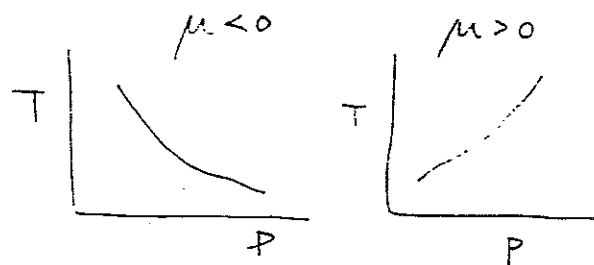
$$\mu = \left(\frac{\partial T}{\partial P} \right)_H$$

change in T per unit P change
when a gas expands under adiabatic
conditions

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

Joule-Thomson 0 = $\left(\frac{\partial H}{\partial P} \right)_T dP + C_p dT$

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



$\mu > 0 \Rightarrow$ gas cools upon isenthalpic expansion

$\mu < 0 \Rightarrow$ gas heats upon isenthalpic expansion

- gases show cooling effect when $T < \underline{\text{inversion temp}}$

63. WHAT IS THE THIELE PARAMETER? WHAT IS ITS USEFULNESS

$$\Phi_n^2 = (\text{Thiele modulus or parameter})^2 = \frac{\text{surface rxn rate}}{\text{rate of intraparticle diffusion}}$$

$$\Phi_n^2 = \frac{k_n C_{As}^n (\rho_p S_a R)}{D_e [(C_{As} - 0)/R]} = \frac{k_n C_{As}^{n-1} R^2}{D_e}$$

k_n = n^{th} order rate constant

ρ_p = density of particle

R = radius of particle

S_a = surface area / mass catalyst

C_{As} = conc. of A at surface of spherical pellet

D_e = effective diffusivity

generalized:

$$\Phi_{i,n} = f_i \left[\frac{(n+1)}{2} \frac{k_n \rho_p C_{As}^{n-1}}{D_e} \right]^{1/2}$$

f_i = shape factor

$$f_i = \frac{V}{S}$$

$$= \frac{R}{3} \text{ sphere.}$$

$$= \frac{R}{2} \text{ cylinder}$$

$$= L \text{ slab}$$

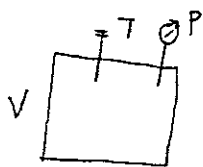
Small $\Phi \rightarrow$ Surface rxn limited, significant amt of reactant diffuses into pellet w/o reacting

large $\Phi \rightarrow$ transport limited, most reactant consumed at pellet surface.

(64)

- perform rxn in a plugflow or batch reactor for exact optimum τ for every molecule
- minimize $\frac{k_2}{k_1}$ using appropriate T
see previous questions on this topic

66. GIVEN A CLOSED DRUM OF ORGANIC LIQUID WHICH REACTS EXOTHERMICALLY WITH TRACES OF WATER PRESENT IN THE DRUM, DERIVE ALL EQNS NECESSARY TO DESCRIBE THE TEMPERATURE AND PRESSURE IN THE DRUM AS A FUNCTION OF TIME.



$$-r_A = k C_A C_{H_2O}$$

- rate of heat production: $k C_A C_{H_2O} V \Delta H_{rxn}$

$$\frac{d}{dt} [u] \rho V = \dot{Q} - \dot{W} + k C_A C_{H_2O} V \Delta H_{rxn}$$

- pseudo 1st order, since trace of C_{H_2O} .

$$\frac{dC_{H_2O}}{dt} = -k C_A C_{H_2O}$$

$$C_{H_2O} = C_{H_2O}^0 \exp[-k C_A t]$$

$$\left. \frac{\partial u}{\partial T} \right|_V = C_V \approx \text{const. mostly organic.}$$

$$du = C_V dT$$

$$C_V \rho V \frac{dT}{dt} = \dot{Q} + k C_A V \Delta H_{rxn} C_{H_2O}^0 \exp(-k C_A t)$$

- use EOS to find $P(t)$

⑦

$$F_{A1} - F_A + \int r_a dV = \frac{dN_A}{dt} \quad \text{mole balance}$$

Ass

$$F_{A1} - F_A + \int r_a dV = 0 \quad \text{steady state}$$

r_a is the same everywhere in reactor (well-stirred)

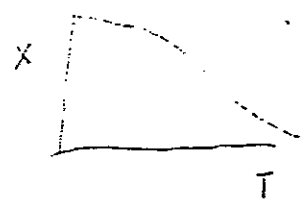
$$F_{A1} - F_A + r_a V = 0$$

$$r_a = -kC_A \quad 1^{st} \text{ order}$$

$$F_{A1} - F_A - kC_A V = 0$$

exothermic rxn $k \downarrow T \uparrow$

endothermic $k \uparrow T \downarrow$



... do you have ΔG° or thermo data?

$$\Delta G_R^\circ = \sum \Delta G_{f, \text{products}}^\circ - \sum \Delta G_{f, \text{reactants}}^\circ$$

if $A \rightleftharpoons B$ in above mass balance and in elementary

$$r_a = -k_1 C_A + k_{-1} C_B$$

$$-r_a = k_1 C_A - k_{-1} C_B$$

$$-r_a = k_1 \left(C_A - \frac{k_{-1}}{k_1} C_B \right)$$

$$-r_a = k_1 \left(C_A - \frac{C_B}{K} \right)$$

what eqn?

- change inlet T or Q

- add diluent (inerts) // in equal no of moles on each side

69.

How Do YOU GET THE RATE CONSTANT / NON PLUG-FLOW
EXPERIMENTAL DATA FOR 1st ORDER REACTION?

Batch reactor:

$$\frac{dn_i}{dt} = r_i V$$

$$\frac{dC_A}{dt} = -k C_A$$

$$\frac{dC_A}{dt} + k C_A = 0$$

$$C_A = C_{A0} e^{-kt}$$

plot $\ln \frac{C_A}{C_{A0}}$ vs t

$$\ln \frac{C_A}{C_{A0}} = -kt$$

slope = $-k$

CSTR:

$$V = \frac{F_{A0} - F_A}{-r_A} = \frac{F_{A0} - F_A}{k C_A}$$

$$\text{const } v: V = \frac{C_{A0} - C_A}{k C_A} \cdot v_0$$

$$V = \frac{v_0}{k} \cdot \left(\frac{C_{A0}}{C_A} - 1 \right)$$

$$k = \tau \left(\frac{C_{A0}}{C_A} - 1 \right)$$

$$\ln \tau = \ln k - \ln \left(\frac{C_{A0}}{C_A} - 1 \right)$$

Plot $\ln \left(\frac{C_{A0}}{C_A} - 1 \right)$
vs. τ .

Intercept = $\ln k$

70

$$T = T_0 + \frac{(-\Delta H_r) C_{A0}}{\rho_r C_p}$$

$$\Delta H_r^\circ = \sum \Delta H_{f, \text{products}} - \sum \Delta H_{f, \text{reactants}}$$

assume doesn't ch. much w/ T

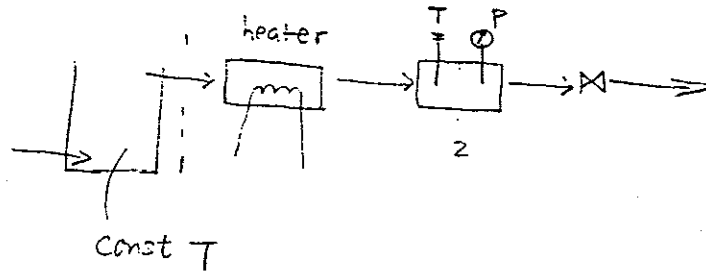
otherwise what do you do?

72.

How would one measure G , H , and S ?

• H , enthalpy:

- Flow calorimeter



$$\Delta H = H_2 - H_1 = Q \quad \text{1st law}$$

cannot measure absolute values, can only have references.

73

- phase (heterogeneous / homogeneous rxn) catalyst → fixed & fluidize
- T (exothermic or endothermic) e.g. runaway
- side rxns (series or II) i.e. selectivity
- stability, control e.g. mass loss, runaway
- pressure
- frequency of use (continuous or batch)
- value of product e.g. high value added product → batch
- scale of production
- labour requirements
- eqbm limitations (membrane reactive distillation)
- controlling regime i.e. mass transfer or rxn
- RTD variation

$$\ln \frac{[H_2O]}{[H_2O]_0} = -k[A]t$$

$$[H_2O] = [H_2O]_0 \exp(-k[A]t)$$

Also, system will change its internal energy by raising in temp.

$$\left(\frac{\partial u}{\partial T}\right)_v = C_v$$

Assuming C_v = constant since only trace of water and mostly organic.

$$du = C_v dT$$

$$C_v V \frac{dT}{dt} = \dot{Q} + k[A]V \Delta H_{rxn} [H_2O]_0 \exp(-k[A]t)$$

Use above equation for $T(t)$!!

Now if we have an eos describing the organic, we can find $P(t)$!!

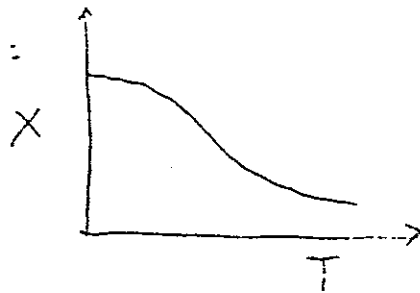
(67) Write the mass balance for CSTR with first order reaction. $A \xrightarrow{k} B$

At SS, $F_{A0} - \bar{F}_A + k C_A V = 0$

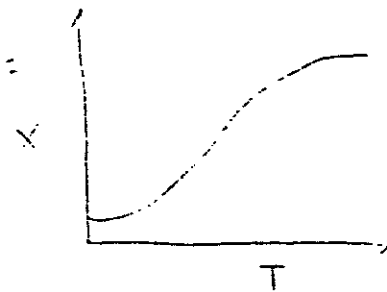
$$F_{A0} - F_{A0}(1-X) + k C_A V = 0$$

How does T affect equilibrium?

Reversible
for exothermic rxn:



Reversible
for endothermic rxn:



Max Helmholtz Law: $\left(\frac{\partial(\frac{G}{T})}{\partial T} \right)_P = -\frac{h}{T^2}$

$$G = H - TS$$

$$\frac{G}{T} = \frac{H}{T} - S$$

$$\frac{\partial(\frac{G}{T})}{\partial T} = \frac{1}{T} \frac{\partial H}{\partial T} - \frac{h}{T^2} - \left(\frac{\partial S}{\partial T} \right)_P$$

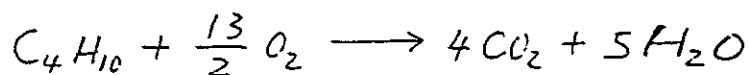
$$= \frac{1}{T} - \frac{h}{T^2} - \frac{1}{T}$$

⑥ How to get rate constant from non-flow experimental data for 1st order rxn?

70. See #11 for calculation of adiabatic flame temperature and equation for heat of reaction.

h^f can be found calorimetrically.

For example to find h^f of C_4H_{10} ,
measure the heat of combustion:



$$\Delta h^c = 5h_{H_2O}^f + 4h_{CO_2}^f - h_{C_4H_{10}}^f - \frac{13}{2}h_{O_2}^f$$

measure from experiment

from heat of formation experiment

74. The frequency factor is also known as the Arrhenius prefactor or pre-exponential factor.

It is a measure of the rate at which collisions occur.

Thus, it depends on the velocity of the molecules, which in turn depends on the temperature, mass, and volume of the molecules.

$$k = A e^{-E_a/RT}$$

reaction rate const. \nearrow k \nwarrow frequency factor \nwarrow A \nwarrow fraction of collisions with sufficient energy to lead to reaction \nwarrow $e^{-E_a/RT}$