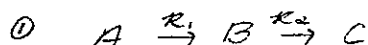1. Find: [1] for a series reaction, what variables influence the amount of intermediate formed? [2] How would you maximize the production of intermediate in a CSTR, a PFR, or in a batch reactor?

[1] $A \xrightarrow{k_1} B \xrightarrow{k_2} C$

$\tau = \dfrac{V}{v_0}$ space or residence time

$V = \dfrac{v_0}{V}$ space velocity

The variables that influence the amount of intermediate formed are →

[1] reaction conditions → e.g. concentrations
[2] residence time $= \tau = \dfrac{V}{v_0}$ for a flow reactor or real time for a batch reactor.

Reaction time is most important, because if $A \to B$ is slow, more time will be required in the reactor but if $A \to B$ is fast and the space time is too long, B will be converted to C.

[2] To maximize production of B, it is the best if the conversion from $A \to B$ is fast and from $B \to C$ is slow.

CSTR → $\dfrac{d(C_A V)}{dt}^{0} = F_{A0} - F_A + r_A V$

More Balance → $r_A V = F_{A0} - F_A$

assume 1st order → $-r_A = k_1 C_A$

Assuming $v = c\tau$ → $F_A = C_A v_0$

OR → $-k_1 C_A V = C_{A0} v_0 - C_A v_0$

$\dfrac{V}{v_0} = \tau = \dfrac{1}{k_1} - \dfrac{C_{A0}}{k_1 C_A}$ → $\dfrac{1}{k_1} - \tau = \dfrac{C_{A0}}{k_1 C_A}$ solve for C_A $\dfrac{1}{C_{A0}} - \dfrac{\tau k_1}{C_{A0}} = \dfrac{1}{C_A}$

$C_A = \left(\dfrac{1}{C_{A0}} - \dfrac{\tau k_1}{C_{A0}} \right)^{-1}$

FOR B → $\dfrac{d(C_B V)}{dt} = F_{B0}^{0} - F_B + r_B V$ $r_B = R_1 C_A - R_2 C_B$

$$r_B V = F_B \qquad F_B = C_B v_0$$

$$(R_1 C_A - R_2 C_B) V = C_B v_0$$

$$\tau = \dfrac{C_B}{(R_1 C_A - R_2 C_B)}$$

PLUG IN FOR
C_A as a function
of τ. Solve for
$C_B = f(\tau)$

Find $\dfrac{d C_B}{d \tau}$ + set equal
to zero,
maximize

Ⓐ

PFR → Mole Balance → $0 = F_A|_x - F_A|_{x+\Delta x} + r_A V_{\Delta x}$

$$\dfrac{d F_A}{dx} = r_A V$$

rate expression → $r_A = -R_1 C_A$
Stoichiometry → $v = v_0$ $F_A = C_A v_0$

hence → $\dfrac{d C_A v_0}{dx} = -R_1 C_A V$

$$-\dfrac{1}{R_1 C_A} \dfrac{d C_A}{dx} = \dfrac{V}{v_0} = \tau$$

integrate to get
C_A

Ⓑ Do the same as above.

HENCE, the overall sequence of things to do →
① Find Mole Balance for A
② Find Rate Expression for A
③ Find stoichiometry for A
④ Combine, get $C_A = f(\tau, others)$
⑤ Do 1-4 for B
⑥ Plug C_A into B
⑦ find $C_B = f(\tau)$
⑧ find $\dfrac{d C_B}{d \tau}$, set equal to ...

2. Find: for an exothermic, first order reaction, plot the extent of reaction and the reaction rates as functions of temperature.

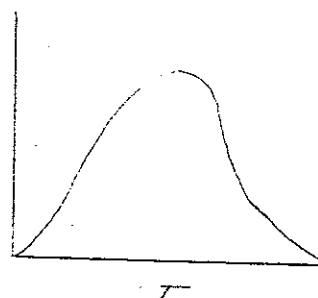$$A \rightarrow B \qquad -r_A = R_1 C_A$$

EXOTHERMIC

If the inlet T increases, the equilibrium conversion decreases
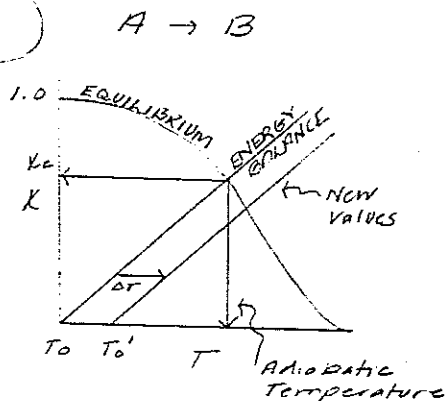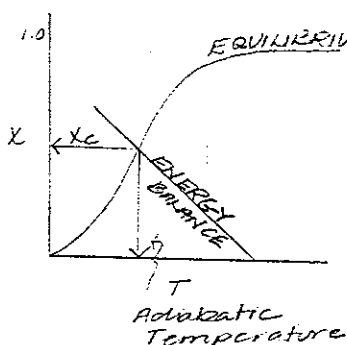

$$-r_A = R_1(T) C_A - R_2 (T)$$
$$R_1 = A e^{-\frac{E_a}{RT}}$$

$A \rightleftarrows B + \Delta$, by LeChatlier's principle, the addition of heat by the increase in temperature forces the reaction in the reverse at high T.

ENDOTHERMIC

If the inlet T increases, the equilibrium conversion increases

USE INTERSTAGE
HEATING TO OBTAIN
A BETTER CONVERSION

---

3. Find: when can the steady-state approximation be used?

FAST
REACTIONS
ARE IN
FAST
EQUILIBRIUM!
NET RATE = 0 !

The steady-state approximation or the Pseudo-steady-state Hypothesis (PSSH) can be used when an active intermediate molecule has →

① a very short lifetime due to high reactivity
② intermediate is present only in very low concentrations.

HENCE → Rate of Formation of an active intermediate = Rate of disappearance of active inter- mediate. Thus, the net rate of production of intermediate

4. Find: what is the chemical potential?

The Chemical potential of a species is defined as follows →

$$\mu_i = \left[\frac{\partial(nG)}{\partial n_i}\right]_{T,P,n_j}$$

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

Hence, the Chemical potential of species i is the partial derivative of the Gibb's energy with respect to the number of moles of species i, at constant P, T and n_j. To minimize the energy of a system, the Chemical potential will want to be minimized.

5. Find: experimentally how would you determine ΔH_f, ΔS_f and ΔG_f?

$$\Delta G_f = \Delta H_f - T\Delta S_f$$

ΔH_f → use a calorimeter

     MEASURE Q FOR FORMATION @ $25°C$ & 1 atm

$$\left(\frac{\partial \frac{\Delta G_f}{T}}{\partial T}\right)_P = \frac{-H}{T^2}$$

$$\Delta S_p = \frac{\Delta H_p - \Delta G_f}{T}$$

6. Find: how does a refrigerator work? sketch T-S, P-V and/or P-H diagrams.

Refrigeration → the maintenance of a temperature below that of the surroundings.

Heat is transferred from a low temp. to a higher one, according to the second law this can't be accomplished w/o the input of energy.
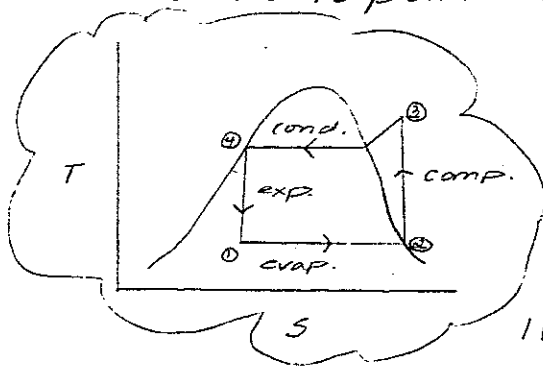
This is done in the following steps →

energy from fridge which cools it.

① liquid/vapor mixture at $T = T_1$ is evaporated at $T = P \overset{\rightarrow}{<} CT$ to all vapor.

② the vapor is then compressed at constant entropy to a higher $T = T_3$.

③ the vapor is then condensed and a new $T = T_2$ is reached.

④ the liquid is expanded isentropically back to point ①.

adsorbed in evap.

$|Q_c| = \Delta H = H_2 - H_1$

$|Q_H| = \Delta H = H_3 - H_4$

↑ rejected in condenser

$|W| = |Q_H| - |Q_c|$
$= (H_3 - H_4) - (H_2 - H_1)$

coeff. of perf. $\omega = \dfrac{|Q_c|}{|W|} = \dfrac{H_2 - H_1}{(H_3 - H_4) - (H_2 - H_1)}$

The other and probably more used type of
refrigerator is as follows →

① liquid/vapor mixture is evaporated
at $T = T_1$, with $P = T = CT$ to all vapor.

refrigerant used ② vapor is compressed to $T = T_3$ to a higher
point. (superheated)

TO atmos. ③ vapor is then condensed to a liquid.
($P = CT$)

MUCH LOWER COST. ④ liquid goes through a constant enthalpy
throttling valve back to point ①.

KNOW THIS!

$|Q_c| = H_2 - H_1$ $|W| = |Q_H| - |Q_c|$ $H_1 = H_4$
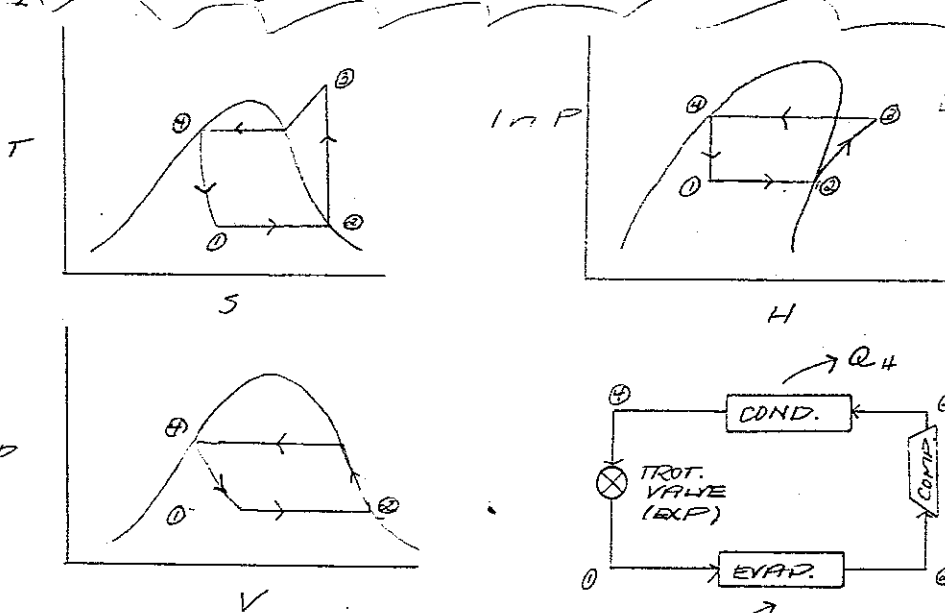
$|Q_H| = H_3 - H_4$ $= H_3 - H_4 - (H_2 - H_1)$

$= H_3 - H_2$

$$W = \frac{|Q_c|}{W} = \frac{H_2 - H_1}{H_3 - H_2}$$

7. Find: how does the rate constant vary with T?

$$-r_A = -k_1 C_A^n$$

↗ rate constant

The rate constant is a function of T and the relationship is Arrhenius, that is →

$$k_1(T) = A e^{-\frac{E_a}{RT}}$$

A = preexponential factor ⎫ Determined from
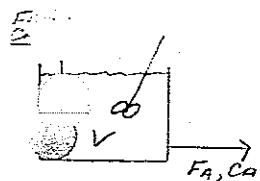E_a = activation energy   ⎭ Experiments

OR → other relationships →

Collusion Theory → $k_1(T) = A_2 T^{1/2} e^{-E/RT}$
Transition State Theory → $k_1(T) = A_3 T e^{-E/RT}$

8. Find: derive design equations for mass and energy for CSTR, PFR and batch reactors.

CSTR   Mass Balance

| Rate of Mass Accum. | = | Rate of Mass in | − | Rate of Mass out | + | Rate of Mass Generation |

$$\frac{d C_A V}{dt} = F_{A0} - F_A + \int_0^V r_A \, dV$$

$V = CT$
$$V \frac{d C_A}{dt} = F_{A0} - F_A + r_A V$$
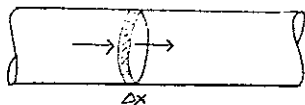
At S.S.

$$0 = F_{A0} - F_A + r_A V$$

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

$F_{A0} = C_{A0} V_0$
$F_A = C_A V$

PFR   Mass Balance

$$\frac{d C_A}{dt} \pi r^2 \Delta x = F_A |_x - F_A |_{x+\Delta x} + \int r_A V$$

ASSUME S.S. →

$$F_A |_x - F_A |_{x+\Delta x} + r_A \Delta V = 0 \qquad \Delta V = \Delta x A_c$$

$$F_A|_x - F_A|_{x+\Delta x} + r_A A_c \Delta x = 0$$

$$r_A A_c - \frac{(F_A|_{x+\Delta x} - F_A|_x)}{\Delta x} = 0 \quad \rightarrow \quad r_A A_c = \frac{dF_A}{dx}$$

$$\boxed{r_A = \frac{dF_A}{dV}}$$

$$(dV = A_c \, dx)$$

BATCH Mass Balance

$$\frac{dC_A V}{dt} = 0 - 0 + \int_0^V r_A \, dV$$

$$\frac{dC_A V}{dt} = r_A V \rightarrow \quad \text{assumes density change is small}$$

$$\boxed{\frac{dC_A}{dt} = r_A} \qquad \text{or} \qquad \boxed{\frac{dN_A}{dt} = r_A V} \quad \text{this does not account for V change}$$

CSTR Energy Balance

$\dot{Q} = U_A \Delta T_{lm}$

Rate of Energy Accum.	=	Rate of Energy in	−	Rate of Energy out	+	Rate of Energy generation

$$\frac{dE}{dt} \xrightarrow{\text{s.s.}} = F_{in} E_{in} - F_{out} E_{out} + \dot{Q} - \dot{W}$$

← work done by the system (is +)

↗ Heat put into the system

IN GENERAL AT S.S. →

Plugging in for work, conversion, etc...

$$\dot{Q} - \dot{W}_s - F_{A0} \sum_i \int_{T_{i0}}^T \theta_i C_{p_i} \, dT + \Delta H_R(T) F_{A0} X = 0$$

$$= V \sum C_{p_i} C_i \frac{dT}{dt}$$

$$\Delta H_R(T) = \Delta H_R^0(T_R) + \Delta C_p (T - T_R)$$

FOR A CSTR →

$Q = U_A \Delta T_{lm}$

$$\boxed{\frac{\dot{Q} - \dot{W}_s}{F_{A0}} - \sum_i \int_{T_{i0}}^T \theta_i C_{p_i} \, dT + X \Delta H_R(T) = 0}$$

$T_a =$ ambient temperature

ADIABATICALLY →

$$\dot{Q} = 0$$
$$\dot{W}_s = 0$$

HENCE → $$\boxed{-X \Delta H_R(T) = \sum_i \int_{T_{i0}}^T \theta_i C_{p_i} \, dT}$$

$\dot{Q} = \int^A U(T_a - T) dA$

$\int^V U_a(T_a - T) dV$

FOR A PFR →

$$\boxed{\int_0^V U_a(T_a - T) dV - \dot{W}_s^0 - F_{A0} \sum_i \int_{T_{i0}}^T \theta_i C_{p_i} \, dT + X \Delta H_R(T) = 0}$$

ADIABATICALLY →

$$\boxed{-X \Delta H_R(T) = \sum_i \int_{T_{i0}}^T \theta_i C_{p_i} \, dT}$$

FOR A BATCH REACTOR → $\qquad N_A = N_{A0}(\theta_A + \nu_A X)$

$$\dot{Q} = UA(T_a - T)$$

$$UA(T_a - T) - \dot{W}_s - \Delta H_R(T)(-r_A V) = V \sum C_{p_i} C_i \frac{dT}{dt}$$

$$= \sum C_{p_i} N_i \frac{dT}{dt}$$

$$UA(T_a - T) - \dot{W}_s - \Delta H_R(T)(-r_A V) = \sum C_{p_i} N_i \frac{dT}{dt}$$

9. Find: space time, space velocity, mean residence time.

time required to
process one
reactor volume

$\tau = $ space time = mean res. time $= \dfrac{V}{v_0}$ (=) s

V = reactor volume
v_0 = flow rate, volumetric
into reactor.

# of time reactor
volume is replaced
per time.

$SV = $ space velocity $= \dfrac{v_0}{V} = \dfrac{1}{\tau}$ (=) $\dfrac{1}{s}$

MEAN RESIDENCE TIME ~ AVERAGE LENGTH OF TIME THAT A MOLECULE STAYS IN THE REACTOR $\dfrac{V}{F}$

10. Find: what are the Clapeyron and the Clausius-Clapeyron Equations?

CLAPEYRON →

$$\frac{dP^{sat}}{dT} = \frac{\Delta H^{\alpha\beta}}{T \Delta V^{\alpha\beta}}$$ KNOW THIS!

CLAUSIUS-CLAPEYRON →

Assume for $\alpha\beta = \ell v$
that $V^v \gg V^\ell \to \Delta V^{\ell v} = V^v = \dfrac{RT}{P^{sat}}$

$$\frac{dP^{sat}}{dT} = \frac{\Delta H^{\ell v}}{T^2 R / P^{sat}}$$

$$\Delta H^{\ell v} = R\left(\frac{dP^{sat}/P^{sat}}{dT/T^2}\right) = -R \frac{d\ln P^{sat}}{d(1/T)}$$

$$\Delta H^{\ell v} = -R \frac{d\ln P^{sat}}{d(1/T)}$$ KNOW THIS!

11. Find: how would you calculate the adiabatic flame temperature?

No heat leaves,
since this is
the highest
temperature.

ADIABATIC FLAME TEMPERATURE = the temperature achieved if the fuel is burned completely in a perfectly insulated container.

Energy Balance →   ENTHALPY
 Steady state   BALANCE!
 $\dot{Q} = 0$
 $\dot{W}_s = 0$ $0 = IN - OUT + GEN.$

$$\Delta H = \sum_i n_i \hat{H}_i(T_{feed})\Big|_{IN} - \sum_i n_i \hat{H}_i(T_{ad})\Big|_{out} + n_f \Delta \hat{H}_c^\circ$$

Moles of fuel burned

$\Delta \hat{H} = \overline{C_p} \Delta T$ is must be at correct T!

$$\boxed{\sum_i n_i \hat{H}_i(T_{ad})\Big|_{OUT} = \sum_i n_i \hat{H}_i(T_{feed})_{IN} - n_f \Delta \hat{H}_c^\circ}$$

① Know right hand side of equation
② Must guess left and side, get equal to right hand side.   (GUESS T_{ad})

NOTE: Must calculate C_p for all specirs in product stream, then have to integrate $\int_{as}^{T_{ad}} (\sum_i n_i C_{p_i}) dT$.

OR → ① Guess T_{ad}
② Solve for composition of product stream (Mass Balance)
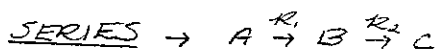③ heat liberated $= \sum_i y_i \Delta H_f^{\circ 298}|_{prod} + (-\Delta H_f^\circ)_{fuel} \times n_f$
$- \sum_i y_i \Delta H_f^{\circ 298}|_{free\ radicals}$

④ Compare with heat required to heat products to T.
⑤ if heat lib. > heat req. $T_a > T$
⑥ if heat lib. < heat req. $T_a < T$

2. Find: which type of reactor is best for a series reaction? A parallel? An auto-catalytic?

SERIES → $A \xrightarrow{R_1} B \xrightarrow{R_2} C$

A PFR or Batch reactor → these type of reactors allow for the reaction to be controlled better. That is, it keeps a lower concentration of intermediate because of low mixing. Can stop reaction at peak intermediate concentration, can keep high concentration of initial reagent (PFR).

PARALLEL REACTION $A \xrightarrow{k_1} B$ $\xrightarrow{R_2} C$
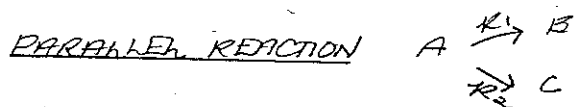
This depends on the reaction order

1).
○ GUESS T_{out}
○ DETERMINE CONVERSION ie. COMPOSITION OF PRODUCS
$$F(T) = \sum_i n_i \int_{T_R}^{T_{in}} C_{p_i} dT - \sum_i n_i \int_{T_r}^{T_{out}} C_{p_i} dT - \sum \Delta H_R = 0$$

○ IF $F(T) > 0 \Rightarrow$ GUESS $T\uparrow$
IF $F(T) < 0 \Rightarrow$ GUESS $T\downarrow$

13. Find: give the three laws of thermodynamics

① Conservation of Energy → that is energy is neither created or destroyed.

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

$$\Delta E_k^0 + \Delta E_p^0 + \Delta U = Q - W$$

CLOSED SYSTEMS
$$\Delta U = Q - W \qquad \text{Finite changes}$$
$$dU = dQ - dW \qquad \text{Differential changes}$$

OPEN SYSTEMS
$$\Delta H + \frac{\Delta u^2}{2} + g\Delta z = Q - W_s$$

② ① No Apparatus can operate in such a way that its only effect (in system and surroundings) is to convert heat adsorbed completely into work.

② No process is possible which consists solely in the transfer of heat from one T level to a higher one.

②a It is impossible by a cyclic process to convert the heat adsorbed by a system completely into work.

MOST GENERALLY → All spontaneous processes in nature tend to occur with an increase in entropy and the direction of change is such as to increase the entropy of the system.

$$\Delta S \geq 0 \qquad \oint \frac{dQ}{T} \leq 0$$
$$dS_i \geq 0$$

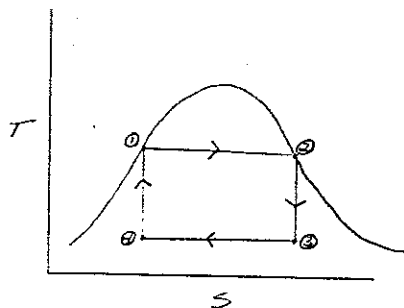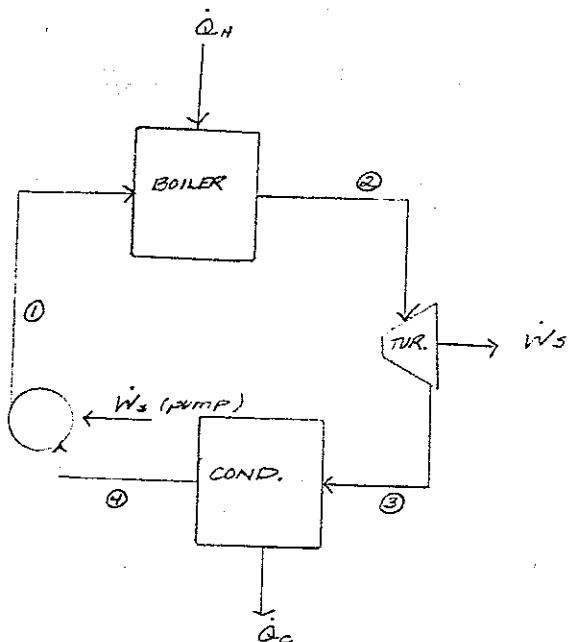③ The entropy of all pure crystalline solids may be taken to be zero at the absolute zero of temperature.

$S_T = \int_0^T C_p \, d\ln T$ (for pure substances)

L R ln Ω
s = k ln Ω

OR →

$$S = \int_0^{T_f} \frac{(C_p)_s}{T} dT + \frac{\Delta H_f}{T_f} + \int_{T_f}^{T_v} \frac{(C_p)_l}{T} dT + \frac{\Delta H_v}{T_v} + \int_{T_v}^{T} \frac{(C_p)_g}{T} dT$$
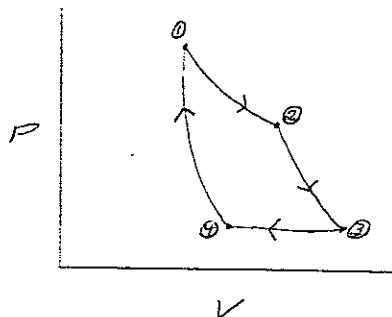
THE CARNOT CYCLE

$1-2 \rightarrow$ isothermal expansion

$2-3 \rightarrow$ adiabatic (reversible) expansion

$3-4 \rightarrow$ isothermal compression

$4-1 \rightarrow$ adiabatic (reversible) compression

$$\eta = 1 - \frac{T_c}{T_H}$$
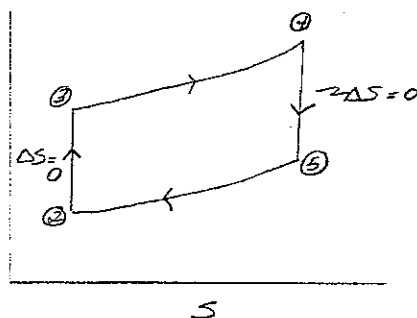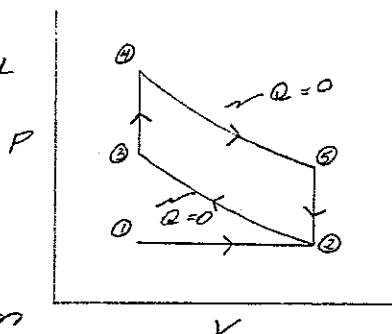
$$|W| = |Q_H| - |Q_c|$$

The OTTO CYCLE $\rightarrow$ TS and PV

$1-2 \rightarrow$ intake of fuel/air mixture at constant pressure

$2-3 \rightarrow$ adiabatic compression

$3-4 \rightarrow$ rapid, constant volume compression combustion
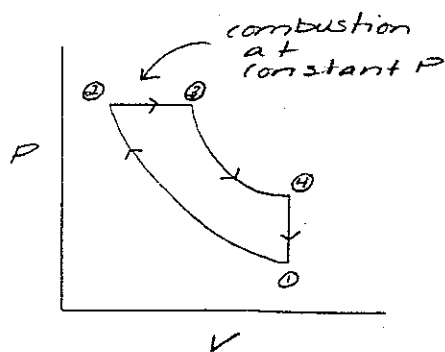
$4-5 \rightarrow$ Adiabatic expansion, produce W

$5-2 \rightarrow$ rapid, constant V expansion

The DIESEL CYCLE

Spontaneous combustion

combustion at constant P

THE RANKINE CYCLE
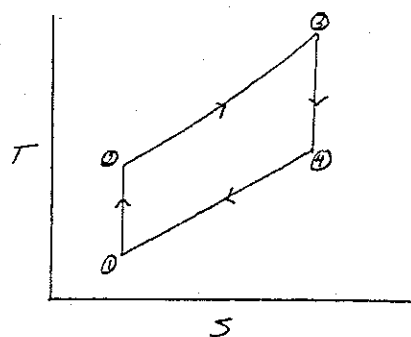
this is the carnot
cycle but for pratical
use!

A STEAM POWER
PLANT!

$$A + B \rightarrow P$$

$$A + S \underset{R_{d1}}{\overset{R_{a1}}{\rightleftharpoons}} AS$$

$$B + S \underset{R_{da}}{\overset{R_{a2}}{\rightleftharpoons}} BS$$

$$AS + BS \overset{R}{\rightarrow} P + S$$

$$\theta_A + \theta_B + \theta_V = 1$$

$$R_{a1}\, \theta_V\, P_A - R_{d1}\, \theta_A = 0$$

$$R_{a2}\, \theta_V\, P_B - R_{d2}\, \theta_B = 0$$

$$r_P = R\, \theta_A\, \theta_B$$

$$\theta_A = \frac{R_{a1}\, P_A\, \theta_V}{R_{d1}}$$

$$\theta_B = \frac{R_{a2}\, P_B\, \theta_V}{R_{d2}}$$

$$\theta_V = 1 - \theta_A - \theta_B = 1 - \frac{R_{a1}\, P_A\, \theta_V}{R_{d1}} - \frac{R_{a2}\, P_B\, \theta_V}{R_{a2}}$$

$$\theta_V \left(1 + \frac{R_{a1}\, P_A}{R_{d1}} + \frac{R_{a2}\, P_B}{R_{d2}}\right) = 1 \qquad \theta_V = \left(1 + \frac{R_{a1}\, P_A}{R_{d1}} + \frac{R_{a2}\, P_B}{R_{d2}}\right)^{-}$$

$$r_P = \frac{R\left(\frac{R_{a1}\, R_{a2}}{R_{d1}\, R_{d2}}\right) P_A\, P_B}{\left(1 + \frac{R_{a1}\, P_A}{R_{d1}} + \frac{R_{a2}\, P_B}{R_{d2}}\right)^2}$$

(16) Prove $dG < 0$ for any process →

$$\text{KNOW} \rightarrow dS_{SURR} = \frac{dQ_{SURR}}{T_{SURR}} = -\frac{dQ}{T}$$

$$2^{nd} \text{ Law} \rightarrow dS + dS_{SURR} \geq 0 \qquad dS - \frac{dQ}{T} \geq 0$$

$$\text{HENCE} \rightarrow \frac{dQ}{T} \leq dS$$

$$1^{st} \text{ Law} \rightarrow dU = dQ - PdV \qquad dQ = dU + PdV$$

$$dU + PdV \leq TdS$$

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

$$\text{THEN, FOR } T = CT$$
$$P = CT$$

$$d(U)_{T,P} + d(PV)_{T,P} \quad d(TS)_{T,P} \leq 0$$

$$d\underbrace{(U + PV - TS)}_{G}{}_{T,P} \leq 0$$

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

(17) Prove that S tends toward a maximum
(THAT IS, PROVE THE SECOND LAW
OF THERMODYNAMICS)

Consider 2 heat reservoirs with transfer of $|Q|$ between them →

$$dS = \frac{dQ}{T} \qquad \Delta S_H = \frac{-|Q|}{T_H}$$

$$\Delta S_C = \frac{|Q|}{T_C}$$

$$\text{HENCE} \quad \Delta S_T = \frac{-|Q|}{T_H} + \frac{|Q|}{T_C} = |Q|\left(\frac{1}{T_C} - \frac{1}{T_H}\right)$$

$$= |Q|\left(\frac{T_H - T_C}{T_H T_C}\right)$$

$$T_H > T_C \quad \text{HENCE} \quad \boxed{\Delta S_T \geq 0}$$

$$\boxed{\begin{array}{l} \text{D.O.F.} \\ \text{in a} \quad = 2 + m - \pi \\ \text{mixture} \end{array}}$$

$m = \#$ of components
$\pi = \#$ of phases

GIBBS - DUHEM EQUATION $\rightarrow$

$$\left(\frac{\partial M}{\partial P}\right)_{T,x} dP + \left(\frac{\partial M}{\partial T}\right)_{P,x} dT - \sum x_i d\bar{M}_i = 0$$

$T, P = \text{CONSTANT}$

$$\sum x_i d\bar{M}_i = 0$$

DERIVATION $\rightarrow$

For an open system $\rightarrow$

① $dU = TdS - PdV + \sum \mu_i dn_i$

$$\left\{ \begin{array}{l} \text{Integrate from} \\ \text{0 Mass } (U = S = V = n_i = 0) \\ \text{to a finite mass} \\ (U, S, V, n_i) \end{array} \right\} \begin{array}{l} \text{CONSTANT} \\ T, P \end{array}$$

$$U = TS - PV + \sum \mu_i n_i$$

TAKE TOTAL
DIFFERENTIAL $\rightarrow$

② $dU = Td\cancel{S} + SdT - P\cancel{dV} - VdP + \sum \mu_i dn_i + \sum n_i d\mu_i$

COMPARING ① and ② $\rightarrow$

$$\boxed{0 = SdT - VdP + \sum n_i d\mu_i}$$

which the activation energy for the second step is greater than the 1st, how would you adjust the temperature to maximize the production of B?

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \qquad E_{B \to C} > E_{A \to B}$$

$$r_B = k_1 C_A - k_2 C_B$$
$$= k_1^\circ e^{-E_1/RT} C_A$$
$$\quad - k_2^\circ e^{-E_2/RT} C_B$$

$T \uparrow K \uparrow$
$T \downarrow K \downarrow$
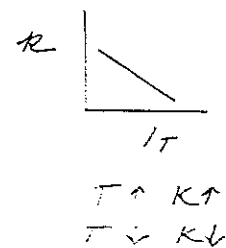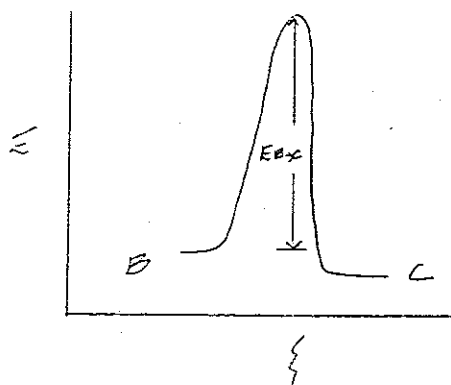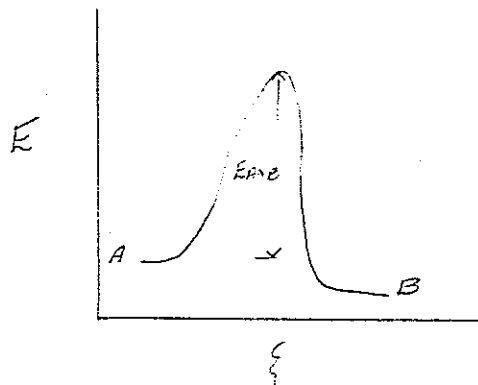
Don't want second reaction to occur, it requires a higher T to get the same K, thus you would want to keep some middle T which made the K high for rxn ① but kept it low for rxn ②.

Maximize $\dfrac{k_1}{k_2} \rightarrow \dfrac{k_1^\circ e^{-E_1/RT}}{k_2^\circ e^{-E_2/RT}} = \dfrac{k_1^\circ}{k_2^\circ} e^{\frac{(E_2 - E_1)}{RT}}$

$(E_2 - E_1) > 0$
hence need to decrease T to make $\dfrac{k_1}{k_2}$ greater

(20) How do [...] [...] the equilibrium constant at non-standard temperature and pressure?

Use the Vant-Hoff Equation →

$$\frac{d \ln K_a}{\partial T} = \frac{\Delta H_{rxn}}{RT^2}$$

$$\ln\left(\frac{K}{K_{ref}}\right) = -\frac{\Delta H_{rxn}}{R}\left[\frac{1}{T} - \frac{1}{T_{ref}}\right] \quad \left(\begin{array}{l}K_a \text{ is not a}\\ \text{strong function}\\ \text{of pressure}\end{array}\right)$$

FROM Gibbs-Helmholtz →

$$\frac{\partial(G/T)}{\partial T} = -\frac{H}{T^2} \quad \rightarrow \quad \frac{\partial \Delta G^\circ / T}{\partial T} = -\frac{\Delta H_{rxn}}{T^2}$$

$$\Delta G^\circ = -RT\ln K$$

$$\frac{\partial(R\ln K)}{\partial T} = \frac{\Delta H_{rxn}}{T^2}$$

$$R\ln K\Big|_{K_1}^{K_2} = \Delta H_{rxn}\left(-\frac{1}{T}\right)\Big|_{T_1}^{T_2}$$

$$\boxed{R\ln(K_2/K_1) = \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\Delta H_{rxn}} \quad \longrightarrow \quad \text{SOLVE FOR } K_2!$$

(21) Define U, H, S, G, A

$$dU = TdS - PdV \qquad U = H - PV$$
$$dH = TdS + VdP \qquad H = U + PV$$
$$dA = -SdT - PdV \qquad A = U - TS$$
$$dG = -SdT + VdP \qquad G = H - TS = U + PV - TS$$

U = internal energy
H = enthalpy
A = Helmholtz energy
G = Gibbs Energy
S = entropy $dS \geq 0$ always

f – FUGACITY

$$d\,G = VdP = RTd\ln f \quad \text{AS DEFINED BY G.N. LEWIS}$$

$$\frac{d(G - G^{ig})}{\partial T} = d\ln\left(\frac{f}{P}\right)$$

Liquify in → ① heat exchange at constant P

3 ways ② By expansion in a turbine where work is obtained

③ By throttling process

(Claude / Linde)

Throttle a gas to decrease the P, hence the T, which will cause condensation →

LINDE~ THROTTLE VALVE

Drop into T-S curve under saturation curve

CLAUDE~ EXPANSION ENGINE

Want to cut into the two phase region of a T-S diagram

② what is the slope of a $\ln K_{eq}$ vs. $1/T$ curve for an exo-endothermic reaction?

Gibbs-Helmholz

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

$$\frac{\partial(G/T)}{\partial T} = \frac{\partial\left(\frac{H}{T}\right)}{} - \frac{\partial S}{\partial T}$$

$$\frac{\partial(G/T)}{\partial T} = \frac{1}{T}\frac{\partial H}{\partial T} - \frac{1}{T^2}H - \frac{\partial S}{\partial T} \qquad \frac{dH}{dT} = T\frac{dS}{dT} + V\frac{dP}{dT}^0$$

$$\frac{d(G/T)}{d(T)} = -\frac{H}{T^2}$$

$$\frac{d(\Delta G/T)}{dT} = -\frac{\Delta H}{T^2} \qquad \Delta G = -RT\ln K$$
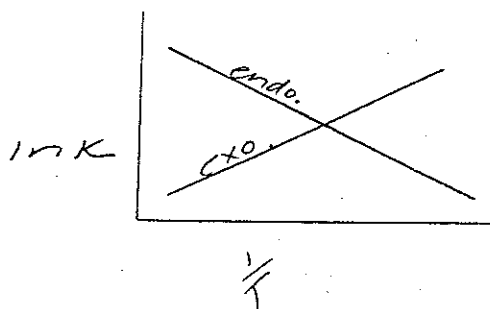
$$\frac{d(-R\ln K)}{dT} = -\frac{\Delta H}{T^2}$$

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

$$\frac{d\ln K}{dT/T^2} = \frac{\Delta H}{R} \qquad \Delta H < 0 \ \text{exo.}$$
$$\Delta H > 0 \ \text{endo.}$$

$$\frac{d\ln K}{d(1/T)} = -\frac{\Delta H}{R}$$

DERIVE THE CLAUSIUS EQUATION
Clapeyron

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

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

$$-S^\alpha dT + V^\alpha dP = -S^\beta dT + V^\beta dP$$

$$(-S^\alpha + S^\beta)dT = (V^\beta - V^\alpha)dP$$

$$\Delta S^{\alpha\beta} dT = \Delta V^{\alpha\beta} dP$$

Also, for a phase
change →

$$\Delta G^{\alpha\beta} = 0 = \Delta H^{\alpha\beta} - T\Delta S^{\alpha\beta}$$

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

HENCE →

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

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

DERIVE THE CLAUSIUS-CLAPEYRON EQUATION

Assume $\alpha\beta \rightarrow \ell v$
then assume $V^v \gg V^\ell$

$$\frac{dP^{sat}}{dT} = \frac{\Delta H^{\ell v}}{T\Delta V^v} \qquad i.e. \quad V^v = \frac{RT}{P^{sat}}$$

$$\frac{dP^{sat}}{dT} = \frac{\Delta H^{\ell v} P^{sat}}{T^2 R}$$

$$\frac{(d\ln P^{sat})}{(dT/T^2)} = \frac{\Delta H^{\ell v}}{R} \qquad -\frac{d\ln P^{sat}}{d(1/T)} = \frac{\Delta H^{\ell v}}{R}$$

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

reaction? IF $\Delta G_{eq} = 0$, WHY DOESN'T $\Delta G_{rxn} = EQ$

$\Delta G_{eq} = 0$ because the process seeks to be at a minimum, at equilibrium
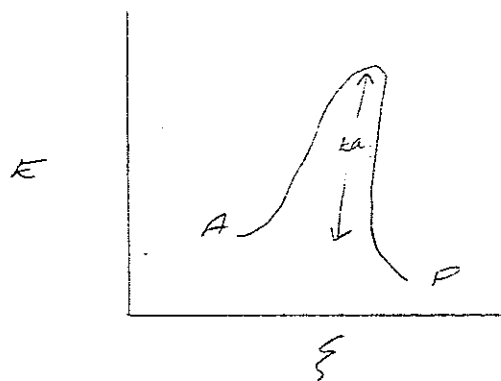
ΔG_{rxn} is the change in gibbs energy necessary to reach a minimum from reactant states.

dG

dG_1 dG_{rxn} ΔG_{rxn} dG_2 $dG=0$ here

ξ
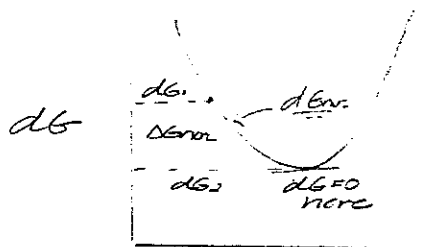
$\Delta G_{rxn} < 0$ can see this here

$\Delta G_{rxn} = dG_2 - dG_1$

⑳ Give a physical interpreation of the activation energy.


k

A E_a P

ξ

$A \rightarrow B$

height of the potential barrier which the reactants must overcome to react

㉑ where does the Langmuir isotherm come from?

① Molecules are adsorbed at discrete sites
② Monolayer corerage — Max. cov. $\theta = 1$
③ Energy of adsorbed species same anywhere on a surface
④ Adsorption occurs by collision of gas phase molecules with vacant sites.
⑤ Desorption rate depends on amount of material on surface

θ_{AS}

P_A
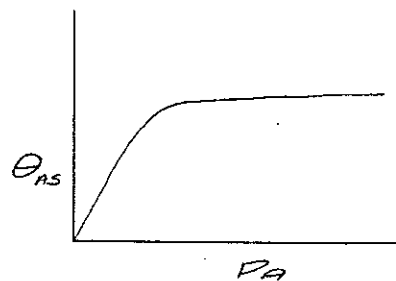
$\theta_{AS} = \dfrac{KP_A}{1 + KP_A}$

∴ Entropy is zero at 0K by the third law of thermodynamics. This is only true for pure crystalline substances.

$$S = K \ln W$$

↑ orientation

(28) How would you calculation the total volume when two equal volumes of different liquids are mixed?

$$V_T = n_A V_A + n_B Y_B \quad \text{for an ideal mixture}$$

$$\Delta M^{mix} = M - \sum n_i M_i$$

$$V = \sum n_i v_i + \Delta V^{mix}$$

$$V_T = \sum n_i \bar{v}_i = n_1 v_1 + n_2 v_2 - (n_1 + n_2) \Delta V^{mix}$$

(29) How would you calculate from 1st principles the heat capacity of two gases, e.g. H_2 and CH_3NCO?

$$\Delta M^{mix} = \sum n_i \overline{\Delta M_i}$$

$$C_p = C_v + R$$

$$C_v = \frac{1}{2} RF \qquad F = \# \text{ of degrees of freedom}$$

$$F = 3 \text{ for an atom} \quad \rightarrow \quad C_v = \frac{3}{2} R \quad \text{Monoatomic}$$

$$O-O \quad F = 2 + 2 + 1 = 6 \qquad C_v = \frac{1}{2} R(5) = \frac{5}{2} R \quad \text{Diatomic}$$

↑ ↑ ↑
trans. rot. vib. ?

(30) YEAH, Right!

(31) Sketch H/S, T/S, $\ln P/H$, P/T and P/v diagrams for a pure substance.
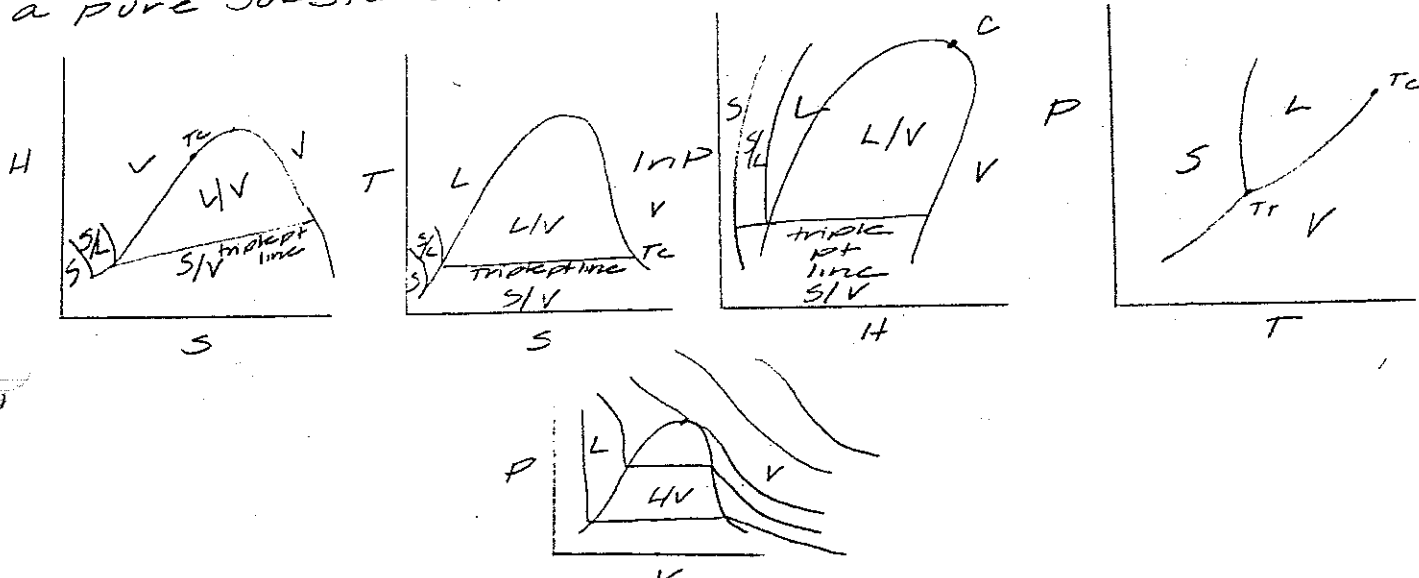
<u>Polytropic</u> → changes can be measured in more than one direction

no specific conditions other than mechanical reversibility are imposed.

$$PV^\delta = K$$

(33) How is the concept of the reaction coordinate used?

It is used to define how far a reaction has progressed from reactants to products.

$$\xi = \frac{n_i - n_{io}}{\nu_i}$$

CHARACTERIZES THE EXTENT TO WHICH A REACTION HAS TAKEN PLACE

$$dn_i = \nu d\varepsilon$$

(34) What is the phase rule when reactions are occurring?
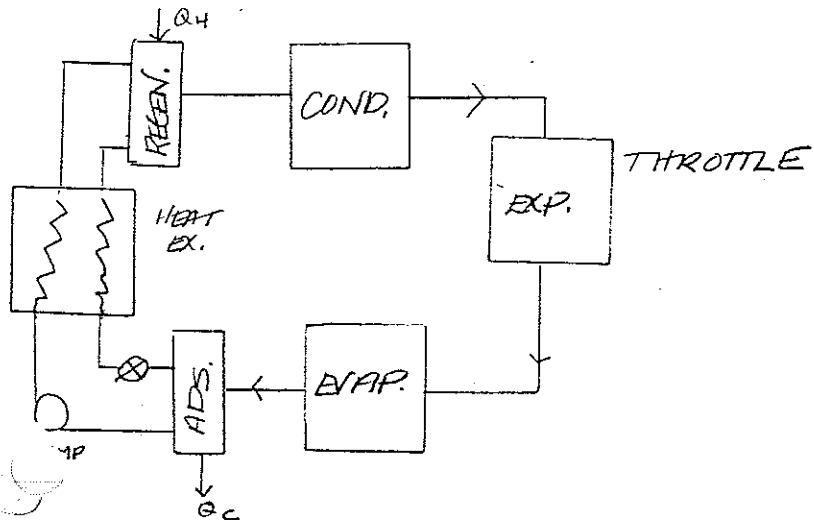
$$DOF = 2 + N - \pi - R$$

NO RXN →

UNKNOWNS	EQUATIONS
$2 + (N-1)\pi$	$+ (\pi - 1)N$
	$+ R$

UNKNOWNS − EQUATIONS = D.O.F.

$$2 + N\pi - \pi - N\pi + N - R$$

(35) How does adsorption refrigeration work? What are the suitable characteristics of a working fluid?

Q_H REGEN. COND. THROTTLE EXP. HEAT EX. ADS. EVAP. Q_c

want high ΔH_ref
high solubility in solvent
no freeze-ups
positive ρ

(36) Give three methods of liquifying gases →
① heat exchange − P=CT
② J-T throttling
③ EXPAND IN TURBINE

kinetics studies?

Want to calculated the rate at a known concentration → a PFR's concentration varies with distance down a PFR and batch reactors concentration varies with time. CSTR isn't useful for catalytic studies, so a PFR w/high recycle is used.

---

38) What is the difference between extent of reaction and equilibrium conversion?

$$\xi = \frac{n_i - n_{io}}{\nu_i}$$

$$X = \frac{n_{io} - n_i}{n_{io}}$$

39) Why is freon used in refrigerators instead of water, air, etc?

No freeze ups → evap. temp > freezing pt. at condenser operating pressure

Large latent heat → requires small fluid volume

and on...

40) What is activity and why is it different from fugacity?

$$a = \frac{f_i}{f_i^\circ} \qquad f_i^\circ = \text{fugacity in it's standard state} \qquad a = x_i \gamma_i \qquad f_i = x_i \gamma_i f_i^\circ$$

41) What is fugacity and how is it calculated? What is it used for?

Used to correct for non-idealities

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

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

$$\frac{f}{P} \to 1 \text{ as } P \to 0$$

42) Consider L-H kinetics, why might the rate go down as the gas concentration goes up?

$$\text{rate} = \frac{R_2 k_1 k_2 P_1 P_2}{(1 + K_1 P_1 + K_2 P_2)^2} \qquad \text{LANGMUIR-HINSHELWOOD} = L-H$$

-energics determined in the regions where external
and internal mass transfer dominates?
    HMMM...

Why is the third law important? What does it let
us calculate in our everyday world? How does this
relate to chemical equilibrium?

Because it allows for
calculation of S and
any $T, P \rightarrow$ Establishes
absolute entropy
and a T scale.

$\Delta H \rightarrow$ cal
$\Delta S \rightarrow$ 3rd law
$\Delta G \rightarrow \Delta H - T\Delta S$
$\rightarrow K \rightarrow$ chemical
         equilibrium.

⑮ What does the T distribution in a PFR look like?
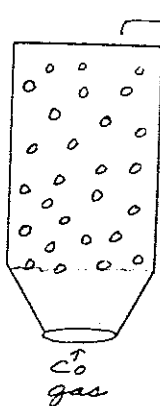
This would depend
if exothermic or
endothermic...
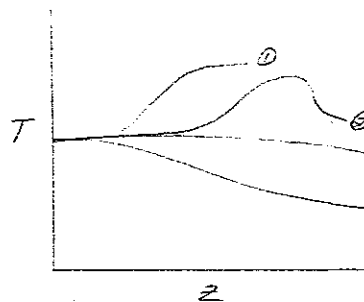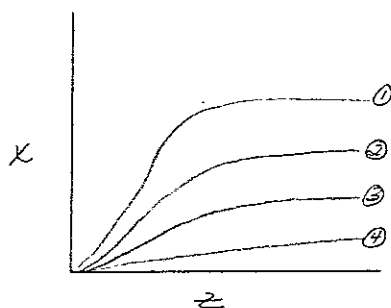
① Adiabatic runaway
   reaction → reactor
   heats up
   EXOTHERMIC
② low heat removal cap.
③ Intermediate heat
   removal
④ Efficient heat removal

X vs z curves labeled ①②③④; T vs z curves labeled ①②③④

⑯ What is a fluidized bed reactor and what are its
   advantages and disadvantages?

Vertical
bed of
fine
particles

Operates slightly
above fluid velocity
at which particle
movement is
observed.

ADVANTAGES	DISADVANTAGES
① Good heat and mass transfer	① Hard to control
② No hot spots	② Bypassing (bubbling) jets!
③ Fluid like, so you can transfer solids from one bed to another (regen.)	④ ΔP can be high
	④ Erosion of internals can occur
	⑤ Scale up is difficult
	⑥ Difficult to model
	⑦ High Capital Investment

ΔP and agitated
bed height will
become constant
at velocity values
big and that at
which initiation of   } particle
                         mvmt.
                         is observed

... a pump, a heat exchanger and a vertical drop ... in series.

Mechanical Energy Balance

$$\frac{d(mU)}{dt} + \Delta\left[\left(U + \tfrac{1}{2}u^2 + g\,z\right)\dot{m}\right] = \dot{Q} - \dot{W}$$

$$\dot{W} = \dot{W}_S + \Delta[(PV)\dot{m}]$$

$$\frac{d(mU)}{dt} + \Delta\left[\left(U + PV + \tfrac{1}{2}u^2 + g\,z\right)\dot{m}\right] = \dot{Q} - \dot{W}_S \quad \underset{\frac{dG}{dt}\;\frac{dW_S}{dt}}{\downarrow\;\downarrow}$$

$$\underbrace{U + PV}_{H}$$

$$\overset{\text{steady}}{\underset{\text{state}}{\nearrow}}$$

$$\cancel{\frac{d(mU)}{dt}} + \Delta\left[\left(H + \tfrac{1}{2}u^2 + g\,z\right)\dot{m}\right] = \dot{Q} - \dot{W}_S$$

$$\Delta H + \tfrac{1}{2}\Delta u^2 + g\Delta z = \frac{\dot{Q}}{\dot{m}} - \frac{\dot{W}_S}{\dot{m}} = Q - W_S \quad \overset{\text{on a}}{\underset{\text{basis}}{\text{per mass}}}$$

KNOW → $dH = TdS + VdP$

for a reversible
process → $dS = \dfrac{dQ}{T}$

Hence → $dH = dQ + VdP$

$$\Delta H = Q + \int VdP$$

$$Q = \Delta H - \int VdP = \Delta H - \int \frac{dP}{\rho}$$

$$\cancel{\Delta H} + \tfrac{1}{2}\Delta u^2 + g\Delta z = \cancel{\Delta H} - \int\frac{dP}{\rho} - W_S$$

$$W_S + \tfrac{1}{2}\Delta u^2 + g\Delta z + \int\frac{dP}{\rho} = 0$$

TO CORRECT
FOR IRREV.
ADD
F

$$\cancel{W_S}^0 + \cancel{F_{EL}}^0 + \tfrac{1}{2}u^2 + g\Delta z + \int_{P_1}^{P_2}\frac{dP}{\rho} = 0$$

&

BERNOULLI'S EQUATION →

$$\tfrac{1}{2}u^2 + g\Delta z + \frac{\Delta P}{\rho} = 0$$

Heat Exchange →

$$\Delta H = Q = mC_{pc}(T_2 - T_1)$$

Pump →

$\Delta S = 0$
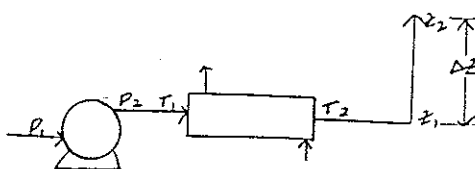$dH = TdS + VdP$ $\Delta H = H_2 - H_1$
$\boxed{\Delta H = VdP}$ $-W_S = \Delta H$

height →

$$\Delta H = \rho g \Delta z$$

HENCE, for the problem
at hand →

without experimental data...

$$K_{eq} = \frac{[C]}{[A][B]}$$
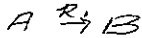
$$\Delta H_{RXN}^\circ = \sum_i Y_i \Delta H_f^\circ$$

THEN →

$$\Delta H_{RXN}(T) = \Delta H_{RXN}^\circ - \int_{T_R}^{T} C_p \, dT$$

Using the
Vant Hoff
Equation →

$$\frac{d \ln K}{dT} = \frac{\Delta H_{RXN}(T)}{RT^2}$$

49) How do you get the rate constant from plug flow experimental data for a first order experiment?

$$A \xrightarrow{R} B$$

$$-r_A = k C_A$$

PFR → $\left(r_A = \frac{dF_A}{dV} \right)$ → $V = \int \frac{dF_A}{r_A}$

BATCH → $\left(\frac{dN_A}{dt} = \int r_A \, dV \right)$

CSTR → $\left(V = \frac{F_{A0} - F_A}{-r_A} \right)$

$$\tau = \frac{V}{V_0} = C_{A0} \int_0^{X_{Af}} \frac{-dX_A}{-r_A} \qquad C_A = C_{A0}(1 - X_A)$$
$$-r_A = k C_{A0}(1 - X_A)$$

$$\tau = -C_{A0} \int_0^{X_{Af}} \frac{dX_A}{k C_{A0}(1-X_A)} = -\int_0^{X_{Af}} \frac{dX_A}{k(1-X_A)} \longrightarrow \left(\text{get } X_A \text{ at different } \tau, \text{ integrate and find } k \right)$$

$$F_A = C_A v$$
$$F_A = F_A^0(1 - X_A) = C_A v$$
$$F_A = C_{A0} v_0 (1 - X_A) = C_A v$$

$$V = \int \frac{d(C_{A0} v_0 (1-X_A))}{-r_A} = C_{A0} v_0 \int \frac{d(1-X_A)}{-r_A} = -C_{A0} v_0 \int \frac{dX_A}{-r_A}$$

$$\tau = \frac{V}{V_0} = C_{A0} \int \frac{-dX_A}{-r_A}$$

and ΔG_{mix}?

Ideal Gas

$\Delta V_{mix} = 0$

$\Delta H_{mix} = 0$

$\Delta G_{mix} = RT \Sigma y_i \ln y_i$

$\Delta S_{mix} = R \Sigma y_i \ln \frac{1}{y_i}$

$\Delta U_{mix} = 0$

Ideal solution

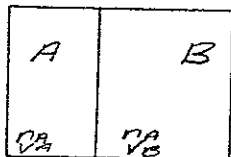$\Delta V_{mix} = 0$

$\Delta H_{mix} = 0$

$\Delta G_{mix} = RT \Sigma x_i \ln x_i$

$\Delta S_{mix} = R \Sigma x_i \ln \frac{1}{x_i}$

$\Delta U_{mix} = 0$

$$\Delta G_{mix} = -T \Delta S_{mix}$$

A	B
$\frac{n_A}{V_A}$	$\frac{n_B}{V_B}$

EXAMPLE →

$$dU = TdS - PdV = 0$$

$$TdS = PdV$$

$$S = \frac{P}{T} dV$$

$$PV = nRT$$

$$\frac{P}{T} = \frac{nR}{V}$$

$$S = \frac{nR}{V} dV = nR \frac{dV}{V}$$

$$\Delta S_{mix} = nR \int_{V_i}^{V_f} \frac{dV}{V}$$

$$\Delta S_{mix} = nR \ln(V_f / V_i)$$

$$\Delta S_{mix} = n_A R \ln\left(\frac{V_A + V_B}{V_A}\right) + n_B R \ln\left(\frac{V_A + V_B}{V_B}\right)$$

$$V_A = \frac{n_A RT}{P} \qquad V_B = \frac{n_B RT}{P}$$

$$\left(\frac{V_A + V_B}{V_A}\right) = \frac{n_A + n_B}{n_A} = \frac{1}{y_A}$$

$$\left(\frac{V_A + V_B}{V_B}\right) = \frac{n_A + n_B}{n_B} = \frac{1}{y_B}$$

$$\Delta S_{mix} = y_A n_T R \ln\left(\frac{1}{y_A}\right) + y_B n_T R \ln\left(\frac{1}{y_B}\right)$$

WHAT IS KNOWN ?

$$f_1^v = f_1^L \quad \longleftarrow \quad \text{EQUILIBRIUM EQUATION FOR A COMPONENT}$$

ASSUME

① $f_1^v = y_1 f_{pure_1}^v$

② $f_1^L = x_1 f_{pure_1}^L$

ALL ASSUMPTIONS ARE AT CONSTANT T AND P

HENCE →

$$f_1^L = f_1^v \rightarrow y_1 f_{pure_1}^v = x_1 f_{pure_1}^L \qquad y_1 \phi_1 P = \gamma_1 x_1 P_1^{sat} \phi_1^{sat}$$

③ $f_{pure_1}^v \rightarrow$ ideal gas

$\rightarrow f_{pure_1}^v = P$

④ $f_{pure_1}^L = P_1^s$

HENCE →

$$\boxed{y_1 P = x_1 P_1^{sat}} \quad \text{RAOULT'S LAW} \qquad \boxed{\text{Raoult's Law as } x_1 \rightarrow 1}$$

$$x_1 \rightarrow 1$$

WHAT IS HENRY'S LAW?

If partial pressure in the gas phase is not large →

$$P_1 = y_1 P = H x_1$$

$$f_1^L = f_1^v$$

$$f_1^v = y_1 P = H x_1$$

$$f_1^L = \gamma_1 x_1 f_1^\circ$$

HENCE → $\gamma_1 x_1 f_1^\circ = H x_1 \rightarrow \boxed{H = \gamma_1 f_1^\circ}$

$$\boxed{\text{Henry's Law AS } x_1 \rightarrow 0}$$

$$f_1^L = x_1 H$$

㊾ CAN A RAOULT'S LAW SOLUTION HAVE AN AZEOTROPE?

No, it can not because Raoult's law assumes that $\gamma_1 = 1$

For a minimum boiling azeotrope $\gamma_1 > 1$
For a maximum boiling azeotrope $\gamma_1 < 1$

$\gamma = 1$ is neither

↑
want to stay together as T is raised

$$f_i = y_i f_{i \, pure}$$

LEWIS - RANDALL RULE

AMAGAT'S LAW → at a fixed Temperature and pressure, the volume of a mixture is a linear function of mole numbers.

$$V = \sum n_i v_i$$

The components mix isometrically that is, with no change in the total volume.

64) The Difference between a mixing rule and a combining rule →

A MIXING RULE IS COMPOSITION DEPENDENT →
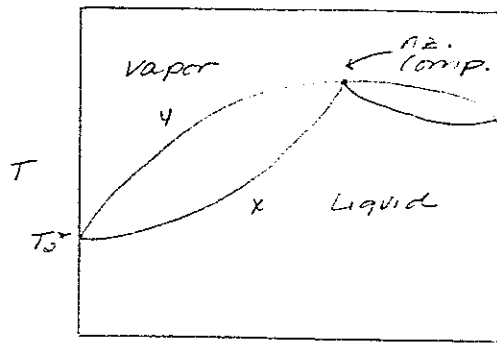$$a = \sum_i \sum_j x_i x_j \, a_{ij}$$
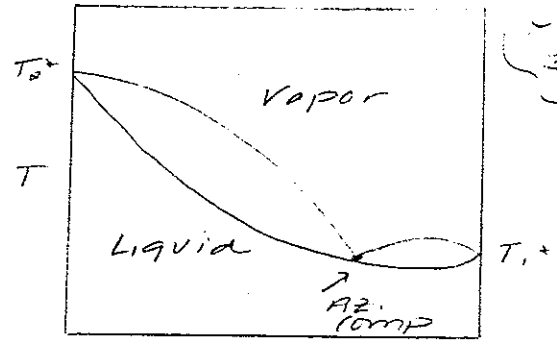
A COMBINING RULE IS INDEPENDENT OF COMPOSITION →
$$a_{ij} = \sqrt{a_i a_j}$$

positive or negative deviations from Raoult's law? If a solution of this type is distilled will the azeotrope be recovered in the distillate or the bottoms?
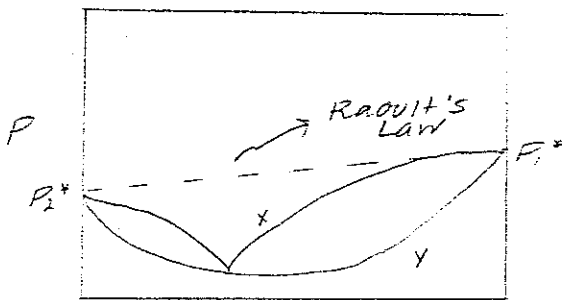

① Shows negative
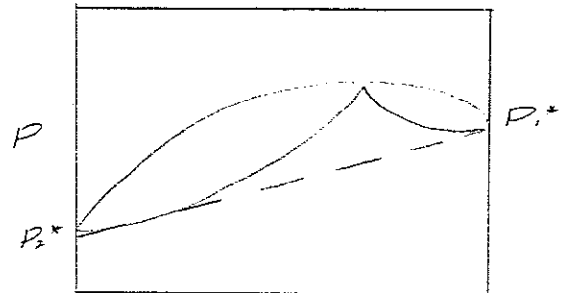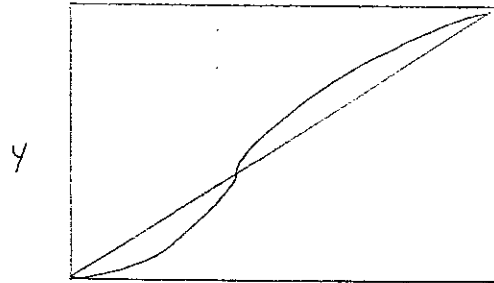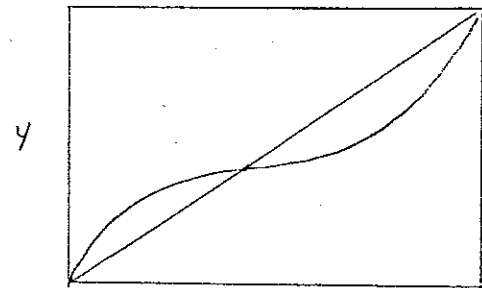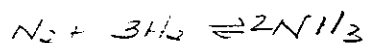 dev. from Raoult's
  Law

② if $x_{feed} > x_{azeotrope}$
  recovered in dist

  if $x_{feed} < x_{azeotrope}$
  recovered in bottoms

① Shows positive
  dev. from Raoult's
  Law

what is the effect of adding an inert gas on the equilibrium between N_2, H_2 and NH_3?

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

Add an inert gas,
pressure increases,
hence right side
will be favored →

$$Ka = \frac{a_{NH_3}^2}{a_{N_2} a_{H_2}^3} = \frac{y_{NH_3}^2}{y_{N_2} y_{H_2}^3} \left(\frac{\phi_{NH_3}}{\phi_{N_2} \phi_{H_2}^3} \right) \left(\frac{1}{P^2} \right)$$

Increase $P \rightarrow$ Increase y_{NH_3}
Because Ka is not
a function of
pressure (will
be constant)

---

53 which liquid phase equations of state allow for azeotropy? phase separation?

Here are some BINARY
LIQUID E.O.S. →

① Ideal liquid mixture → $G^E = 0$ (No azeotropy
$\gamma_i = 1$ or immiscibility)

② 2-Suffix Margules Equation → $G^E = A x_1 x_2$
$\ln \gamma_i = \frac{A}{RT} x^2$

Azeotropy
Immiscability

Suitable for
similar size,
shape, chemical
nature

③ Van Laar → $\frac{G^E}{RT} = \frac{2 a_{12} x_1 x_2 q_1 q_2}{x_1 q_1 + x_2 q_2}$

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

Azeotropy
Immiscability

④ 3-Suffix Margules Equation → $\ln \gamma_i = A x_2^2 + B x_2^3$

Azeotropy
Immiscability

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

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

$$dF = M\,dx + N\,dy$$

$$M = \left(\frac{\partial F}{\partial x}\right)_y \qquad N = \left(\frac{\partial F}{\partial y}\right)_x$$

diff.

$$\left(\frac{\partial M}{\partial y}\right)_x = \frac{\partial^2 F}{\partial x \partial y} \qquad \left(\frac{\partial N}{\partial x}\right)_y = \frac{\partial^2 F}{\partial x \partial y}$$

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

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

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

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

⑥ ... azeotropy
     -ne immiscibility   (... for polar molecules) in non-polar solvents

⑥ Scatchard-Hildebrand
     (regular solution)   (azeotropy immiscibility)

Anything non-polar

$$\rightarrow RT \ln \gamma_1 = V_1 \, \Phi_2^2 \, (\delta_1 - \delta_2)^2$$

⑦ Florey-Huggins → solution of molecules that differ greatly in size
     (azeotropy immiscibility)

㊸ What is the corresponding states theorem? What is its significance?

    <u>The C.S.T. says</u> → All gases, when compared to the same reduced T_R and P_R have approximately the same compressibility factor, and all deviate from ideal-gas behavior to about the same degree.

    → The C.S.T. allows for the ability to find the P, V, T relation for a gas given only it's critical temperature and pressure.

㊿ Describe the graphical approach to reactor design and analysis.

    Can design CSTR'S and PFR'S using a plot of $-\frac{1}{r_A}$ vs. X.

      CSTR → the total area $\left(-\frac{1}{r_A}\right)(X)$ is the volume of the reactor.

      PFR → the area under the curve $-\int \frac{dX}{r_A}$ is the volume of the reactor.

what is the importance of its sign?

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

JOULE-THOMPSON COEFFICIENT

$$dH = f(T,P) = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP = 0$$

$$\Rightarrow dT\left(\frac{\partial H}{\partial T}\right)_P = -dP\left(\frac{\partial H}{\partial P}\right)$$

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

MAXWELL'S EQUATIONS →

$$dF = Mdx + Ndy$$

$$y = CT$$

$$M = \left(\frac{dF}{dx}\right)_y$$

$$x = CT$$

$$N = \left(\frac{dF}{dy}\right)_x$$

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

ACTUALLY → $dH = TdS + VdP$ $\left(\frac{\partial H}{\partial T}\right)_P = C_P$

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

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \rightarrow \text{FROM MAXWELL'S RELATIONS}$$

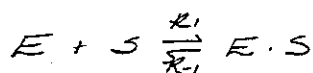$$\left(\frac{\partial H}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P + V$$

$$C_P - T\left(\frac{\partial V}{\partial T}\right)_P + V = 0$$

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H = \frac{\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right]}{C_P}$$

$\mu > 0$ fluid heats upon expansion

$\mu < 0$ fluid cools upon expansion

② Derive the Michaelis-Menten rate equation →

$$E + S \underset{R_{-1}}{\overset{R_1}{\rightleftharpoons}} E\cdot S$$

$$E\cdot S \overset{R_2}{\rightarrow} P + E$$

need this

$$r_p = R_2[ES]$$

$$r_{ES} = \frac{d[ES]}{dt} = R_1[E][S] - R_{-1}[ES] - R_2[ES]$$
$$= R_1[E][S] - [ES](R_{-1} + R_2)$$
$$= 0$$

$$[ES] = \frac{R_1}{(R_1 + R_2)} [E][S]$$

$$[E]_{TOT} = [ES] + [E]$$

$$[S]_{TOT} = [S] + [ES]$$

$$[S_0] = [S]$$

$$r_p = \frac{R_1 R_3 [E][S]}{(R_1 + R_2)}$$

$$[E] = [E]_{TOT} - [ES]$$

$$[S] = [S]_{TOT} - [ES]$$

$$\boxed{\begin{array}{c} [E_0] << [S_0] \\ \Rightarrow [S] >> [ES] \end{array}}$$

THIS IS VERY
IMPORTANT
TO REMEMBER!

$$[ES] = \frac{R_1}{(R_1 + R_2)} ([E_0] - [ES])[S_0]$$

SOLVE FOR $[ES]$ →

$$[ES]\left(1 + \frac{R_1}{R_{-1} + R_2}[S_0]\right) = \frac{R_1}{(R_{-1} + R_2)}[E_0][S_0]$$

$$\boxed{[ES] = \frac{R_1 [E_0][S_0]}{[(R_{-1} + R_2) + R_1 [S_0]]}}$$

$$r_p = \frac{R_3 R_1 [E_0][S_0]}{[(R_{-1} + R_2) + R_1 [S_0]]} = \frac{R_3 [E_0][S_0]}{\left[\frac{(R_{-1} + R_2)}{R_1} + [S_0]\right]}$$

$$V_{MAX} = R_3 [E_0]$$

$$K = \frac{(R_{-1} + R_2)}{R_1}$$

$$\boxed{r_p = \frac{V_{MAX}[S_0]}{K + [S_0]}}$$

③ What is a Thicle parameter, what is its usefulness?

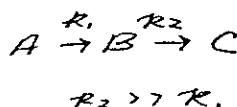$$\phi^2 = \text{Thicle parameter} = \frac{R^2 R}{D} \text{ for a sphere!}$$

ϵ = effectiveness
= $\dfrac{\text{actual rate}}{\text{theoretical rate}}$

$$\boxed{\phi^2 = \frac{R^2 R}{D}} \qquad \phi = R\sqrt{\frac{R}{D}}$$

This is a dimensionless group which plays a key role in determining the limitations that intraparticle diffusion places on observed reaction rates and the effectiveness with which the catalyst surface area is utilized

④ For the series reaction $A \to B \to C$ where the rate of the second reaction is much greater than that of the first how would you maximize the selectivity of B over C?

$$S = \frac{Y_B}{Y_C}$$

$$A \xrightarrow{R_1} B \xrightarrow{R_2} C$$

$$R_2 >> R_1$$

$r_1 = k_1 [A] = k_1' A_1 c^{\frac{-E_1}{RT}} [A]$ $\begin{matrix} \text{(rosmy)} \\ E_1 > E_2 \end{matrix}$

$r_2 = k_2 [B] = k_2' A_2 c^{\frac{-E_2}{RT}} [B]$

$r_B = k_1 [A] - k_2 [B] = k_1' A_1 c^{\frac{-E_1}{RT}} [A] - k_2' A_2 c^{\frac{-E_2}{RT}} [B] = \dfrac{d[B]}{dt}$

$r_C = k_2' A_2 c^{\frac{-E_1}{RT}} [B] = \dfrac{d[C]}{dt}$

WANT TO MAXIMIZE

$\dfrac{d[B]}{d[C]} \rightarrow \dfrac{d[B]}{d[C]} = \dfrac{k_1' A_1 c^{\frac{-E_1}{RT}} [A]}{k_2' A_2 c^{\frac{-E_2}{RT}} [B]} - 1$

$= \dfrac{k_1' A_1}{k_2' A_2} e^{\left(\frac{E_2 - E_1}{RT}\right)} \dfrac{[A]}{[B]} - 1$

$\underset{c^{\frac{\Delta E}{RT}}}{\underbrace{\qquad}}$

increase
T, exp ↓

$\dfrac{dB}{dC} \uparrow$

$\boxed{\text{INCREASE } T}$

(63) Give the van der waals Equation →
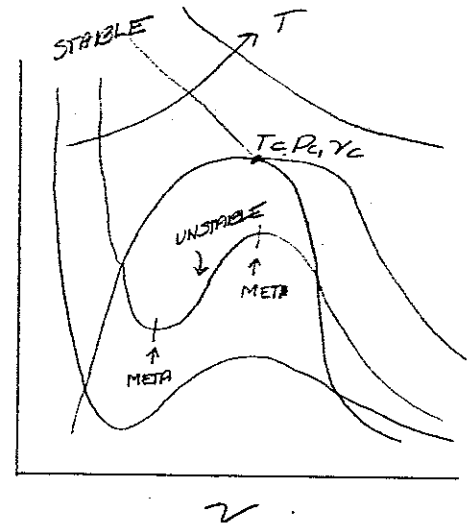
① $\boxed{P = \dfrac{RT}{v - b} + \dfrac{a}{v^2}}$

b accts. for volume taken
up by molecules

a accts. for 2 bodied
interactions

ESTIMATE b, a given
critical data →

Know ② $\left(\dfrac{\partial P}{\partial v}\right) = 0$ } 3 EQUATIONS
③ $\left(\dfrac{\partial^2 P}{\partial v^2}\right) = 0$ 3 UNKNOWNS

(a, b, v_C)

↗ At the critical
point

STABLE

$T_C P_C, v_C$

UNSTABLE

META

META

P

v

CORRECT OUTSIDE OF
THE L-V CURVE,
WRONG INSIDE

(68) What is the Gibbs-Helmholz Law? Derive it!

$\dfrac{\partial (G/T)}{\partial T} = -\dfrac{H}{T^2}$ $G = H - TS$ $\dfrac{G}{T} = \dfrac{H}{T} - S$

$\left[\dfrac{\partial (G/T)}{\partial T}\right]_{P,X} = -\dfrac{H}{T^2} + \dfrac{1}{T}\left(\dfrac{\partial H}{\partial T}\right)_P - \left(\dfrac{\partial S}{\partial T}\right)_P$ & $\left(\dfrac{\partial H}{\partial T}\right)_P = C_p$ $\left(\dfrac{\partial S}{\partial T}\right)_r = \dfrac{C_p}{T}$

$\left[\dfrac{\partial (G/T)}{\partial T}\right]_{P,X} = \dfrac{-H}{T^2}$

exothermically with traces of H_2O present in the drum, derive all equations necessary to describe the T and P in the drum as functions of time.

⑥ Write the mass balance for a CSTR with a first order reaction. How does T affect equilibrium? How do you find $\Delta G°$ with limited data? Can you shift equilibrium in a CSTR with a first order reversible reaction?

$$A \rightarrow B$$
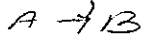
$$V = \frac{F_{A0} - F_A}{-r_A} \qquad\qquad F_A = F_{A0}(1 - x_A)$$

$$V = \frac{F_{A0} - F_{A0} + F_{A0} x_A}{-r_A} = \frac{F_{A0} x_A}{-r_A} = \frac{F_{A0} x_A}{R \, C_A}$$

$$\tau = \frac{V}{v_0} = \frac{C_{A0}}{C_A} \frac{x_A}{R}$$

INCREASE T →

$$\frac{E_a}{RT} \downarrow$$

$$\frac{1}{e^{\frac{E_a}{RT}}} \qquad R\uparrow$$

$$\tau \downarrow$$

equilibrium
will shift
to the right

$$R = A e^{-\frac{E_a}{RT}}$$

$\Delta G°$
(Use Vant Hoff)