

$$\Delta V_{mixing} = \left. \frac{\partial G}{\partial P} \right|_{T,x}$$

THERMODYNAMICS, KINETICS AND CHEMICAL FUNDAMENTALS PRELIM QUESTIONS

AM 1. For a series reaction, what variables influence the amount of intermediate formed? How would you maximize the production of intermediate in a CSTR, a PFR, or in a batch reactor?

AS 2. For an exothermic, first order reaction, plot the extent of reaction and the reaction rate as functions of temperature.

✓ ~~K 3.~~ When can the steady-state approximation be used?

AI 4. What is the chemical potential?

MA 5. Experimentally how would you determine ΔH_f , ΔG_f , ΔS_f ?

AS 6. How does a refrigerator work? Sketch T-S, P-V and/or P-H diagrams.

✓ ~~K 7.~~ How does the rate constant vary with temperature?

AI 8. Derive design equations for mass and energy for CSTR, PFR and batch reactors.

W 9. Define space time, space velocity and mean residence time.

AS 10. What are the Clapeyron and Clausius-Clapeyron equations?

✓ ~~K 11.~~ How would you calculate the adiabatic flame temperature?

~~AT 12.~~ Which type of reactor is best for a series reaction? a parallel? an autocatalytic?

1AM 13. Give the three laws of thermodynamics.

AS 14. Diagram the Carnot cycle, the Otto cycle, the Diesel cycle, the Brayton cycle, and the Rankine cycle. Draw TS and PV diagrams. Write the equations to describe each step. What is the efficiency?

✓ ~~K 15.~~ Derive a Langmuir-Hinshelwood expression for a solid catalyzed reaction, e.g. $A + B \rightarrow P$

AI 16. Prove that $dG < 0$ for any process.

W 17. Prove that S tends towards a maximum.

AS 18. What is the Gibbs mixture rule? Derive the Gibbs-Duhem relation.

~~✓~~ ~~K 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 for the first, how would you adjust the temperature to maximize the production of B?

~~✓~~ ~~AP 20.~~ How do you calculate the equilibrium constant at non standard temperature and pressure?

~~✓~~ ~~M 21.~~ Define U, H, S, G, F, and A.

~~✓~~ ~~AS 22.~~ What is a Joule-Thompson liquefaction process?

~~✓~~ ~~LC 23.~~ What is the slope of a $\ln K_{eq}$ vs. $1/T$ curve for an exo-endothermic reaction?

~~✓~~ ~~AI 24.~~ If $dG = 0$ at equilibrium, why isn't $dG_{rxn} = 0$ for any reaction?

~~✓~~ ~~M 25.~~ Give a physical interpretation of the activation energy.

~~✓~~ ~~AS 26.~~ Where does the Langmuir isotherm come from?

~~✓~~ ~~LC 27.~~ Why is entropy zero at 0 K?

~~✓~~ ~~AI 28.~~ How would you calculate the total volume when two equal volumes of different liquids are mixed?

~~✓~~ ~~M 29.~~ How would you calculate from first principles the heat capacity of two gases, e.g. H_2 and CH_3NCO ?

~~✓~~ ~~AS 30.~~ Analyze a complete problem, from determining the chemistry of the important reaction-step, to calculating the equilibrium conversion, transient response of the concentration and temperature, and its ultimate effect on a macroscopic variable in the system, such as pressure in a closed vessel.

~~✓~~ ~~LC 31.~~ Sketch H/S , T/S , $\ln P/H$, P/T , and P/V diagrams for a pure substance.

~~✓~~ ~~AI 32.~~ What does polytropic mean?

~~✓~~ ~~M 33.~~ How is the concept of reaction coordinate used?

~~✓~~ ~~AS 34.~~ What is the phase rule when reactions are occurring?

~~✓~~ ~~K 35.~~ How does absorption refrigeration work? What are suitable characteristics of a working fluid?

~~✓~~ ~~AI 36.~~ Give three methods of liquefying gases.

37. Why is it necessary to use differential reactors for kinetic studies?

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

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

40. What is the activity and why is it different from fugacity?

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

42. Considering Langmuir-Hinshelwood kinetics, why might the rate go down as the gas concentration goes up?

43. What would be the difference between activation energies determined in the regions where internal and external mass transfer dominate?

44. Why is the 3rd law important? What does it let us calculate in our everyday world? How does this relate to chemical equilibrium?

45. What does the temperature distribution in a PFR look like?

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

47. Find the enthalpy change for a pipe system consisting of a pump, a heat exchanger and a vertical step of height h in series.

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

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

50. For ideal gases what are ΔV_{mixing} , ΔH_{mixing} , ΔS_{mixing} , ΔG_{mixing} ? How do we express these quantities for ideal solutions?

51. What is Raoult's law? Henry's law? Where do they apply?

52. Can a Raoult's law solution have an azeotrope?

53. What is the Lewis fugacity rule? What is Amagat's law?

54. What is the difference between a mixing rule and a combining rule?

IC 158. What is a maximum boiling azeotrope? Does it exhibit 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?

AI 156. What is the effect of adding an inert gas on the equilibrium between N_2 , H_2 and NH_3 ?

M 157. Derive Maxwell's relations.

AJ 158. Which liquid phase equations of state allow for azeotropy? phase separation?

K 159. What is the corresponding states theorem? What is its significance?

AI 160. Describe the graphical approach to reactor design and analysis.

M 161. Derive an expression for the Joule-Thompson coefficient. What is the importance of its sign?

AJ 162. Derive the Michaelis-Menton rate equation.

K 163. What is a Thiele parameter? What is its usefulness?

AI 164. For the series reaction $A \rightarrow B \rightarrow C$ 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?

M 165. Give the van der Waals equation. What is the significance of the constants a and b ? How would you estimate them given critical temperature and pressure data? What does the P-V diagram of a VdW gas look like? Where is it "correct" and where is it "wrong?" Where are the stable, unstable, and metastable regions?

AJ 166. Given a closed drum of organic liquid which reacts exothermically with traces of water present in the drum, derive all the equations necessary to describe the temperature and pressure in the drum as a function of time.

K 167. Write the mass balance for a CSTR with a first order reaction. How does temperature effect equilibrium? How do you find ΔG° with limited data? How can you shift equilibrium in a CSTR with a first order reversible reaction?

AI 168. What is the Gibbs Helmholtz law?

M-69. How do you get the rate constant/non plug-flow experimental data for a first order reaction?

AS 70. From balanced reaction, how would calculate the adiabatic flame temperature? Write out the equation for heat of reaction for the reaction. How would you get ΔH_f if it was not tabulated?

L-71. For the reaction $\Delta \rightarrow \sim$ discuss the unimolecular reaction theory. What order is the reaction? For $r = K_{eff}C_A$, plot k_{eff} vs. pressure. What is the effect of temperature on this plot? If the reaction took place in a CSTR, how would conversion depend on temperature?

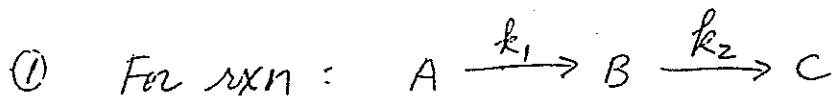
AI 72. How would one measure Gibbs free energy? enthalpy? entropy?

M-73. What are the important factors in choosing a reactor?

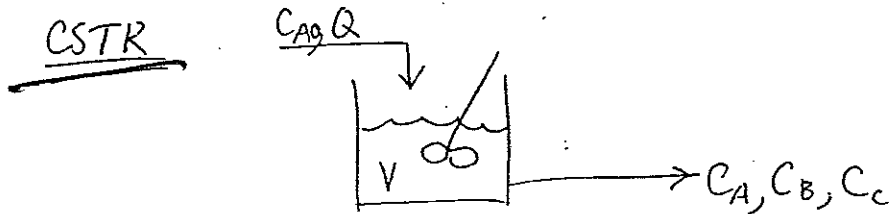
AS 74. What is the frequency factor?

Thermo / Kinetics

ls, 12



- ① mol balance on A
② mol balance on B



③ $\frac{dC_B}{dt} = 0$

rxn expression for A: $r_A = k_1 C_A$

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

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

$$C_{A0} = C_A(1 + k_1 \tau) \quad \text{where } \tau \equiv \frac{\text{space time}}{\text{time}} = \frac{V}{Q}$$

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

mole bal. for B: $k_1 C_A V - k_2 C_B V - C_B Q = 0$ assume no B in feed

$$V k_1 C_A = C_B (k_2 V + Q)$$

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

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

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

- Usually to maximize C_B , we change τ and not k_1 or k_2

$$\boxed{\frac{dC_B}{d\tau} = 0 \text{ for max. } C_B}$$

$$C_B = \frac{k_1 \tau C_{A0}}{(k_2 \tau + 1)(k_1 \tau + 1)} = \frac{k_1 \tau C_{A0}}{k_1 k_2 \tau^2 + (k_1 + k_2) \tau + 1}$$

$$\frac{dC_B}{d\tau} = \frac{(k_2 \tau + 1)(k_1 \tau + 1) k_1 C_{A0} - k_1 \tau C_{A0} (2k_1 k_2 \tau + k_1 + k_2)}{[(k_2 \tau + 1)(k_1 \tau + 1)]^2} = 0$$

Need computer to solve for τ such as to satisfy above eqn

Maybe not !!

$$(k_2 \tau + 1)(k_1 \tau + 1) - \tau (2k_1 k_2 \tau + k_1 + k_2) = 0$$

$$k_1 k_2 \tau^2 + \cancel{(k_1 + k_2)} \tau + 1 - 2k_1 k_2 \tau^2 - \cancel{(k_1 + k_2)} \tau = 0$$

$$1 - k_1 k_2 \tau^2 = 0$$

$$k_1 k_2 \tau^2 = 1$$

$$\boxed{\tau = \sqrt{\frac{1}{k_1 k_2}}}$$

Batch To maximize B in batch, we need to consider transient behavior.

$$\text{mole bal. on A: } -k_1 C_A = \frac{dC_A}{dt}$$

$$\text{mole bal. on B: } k_1 C_A - k_2 C_B = \frac{dC_B}{dt}$$

$$\int_{C_A}^{\frac{dC_A}{C_A}} = \int_0^t -k_1 dt$$

$$\ln C_A - \ln C_{A0} = -k_1 t$$

$$\ln \left(\frac{C_A}{C_{A0}} \right) = -k_1 t$$

$$\frac{C_A}{C_{A0}} = \exp(-k_1 t)$$

$$C_A = C_{A0} \exp(-k_1 t)$$

Substitute into mole bal for B:

$$k_1 C_{A0} \exp(-k_1 t) - k_2 C_B = \frac{dC_B}{dt}$$

$$\frac{dC_B}{dt} + k_2 C_B - k_1 C_{A0} \exp(-k_1 t) = 0$$

1st order
linear DFG

$$\text{let } C_B = u(t) v(t)$$

$$\frac{dC_B}{dt} = u \frac{dv}{dt} + v \frac{du}{dt} = k_1 C_{A0} \exp(-k_1 t) - k_2 u v$$

$$\text{let } \frac{dv}{dt} = -k_2 v$$

$$\frac{dv}{v} = -k_2 dt$$

$$\ln v = -k_2 t$$

$$v = \exp(-k_2 t)$$

~~Find u~~ Find u:

$$\therefore v \frac{du}{dt} = k_1 C_{A0} \exp(-k_1 t)$$

$$\exp(-k_2 t) \frac{du}{dt} = k_1 C_{A0} \exp(-k_1 t)$$

$$\frac{du}{dt} = k_1 C_{A0} \exp(k_2 t - k_1 t)$$

$$\int du = \int k_1 C_{A0} \exp[(k_2 - k_1)t] dt + C_1$$

$$u = k_1 C_{A0} \left(\frac{1}{k_2 - k_1} \right) e^{(k_2 - k_1)t} + C_1$$

$$\therefore C_B = uv = k_1 C_{A0} \left(\frac{1}{k_2 - k_1} \right) e^{-k_1 t} + C_1 e^{-k_2 t}$$

$$\text{at } t=0, C_B=0$$

$$0 = k_1 C_{A0} \left(\frac{1}{k_2 - k_1} \right) + C_1$$

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

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

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

$$\therefore \boxed{C_B = \left(\frac{k_1 C_{A0}}{k_2 - k_1} \right) \left[e^{-k_1 t} - e^{-k_2 t} \right]}$$

Find max. C_B by setting $\frac{dC_B}{dt} = 0$:

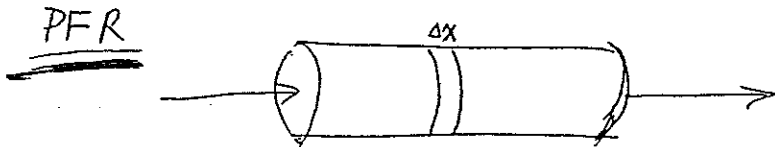
$$\frac{dC_B}{dt} = \left(\frac{k_1 C_{A0}}{k_2 - k_1} \right) \left[-k_1 e^{-k_1 t} + k_2 e^{-k_2 t} \right] = 0$$

$$k_2 e^{-k_2 t} = k_1 e^{-k_1 t}$$

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

$$\ln\left(\frac{k_2}{k_1}\right) = (k_2 - k_1)t$$

$$\boxed{t = \frac{\ln\left(\frac{k_2}{k_1}\right)}{k_2 - k_1}} \quad \text{for max } C_B !!$$



mole bal. on A: $QC_{A0} - QC_A - \int_0^V r_A dV = 0 @ SS$

$$QC_A|_x - QC_A|_{x+\Delta x} - k_1 C_A A \Delta x = 0 \quad \text{at SS}$$

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

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

$$\int_{C_{A0}}^{C_A} \frac{dC_A}{C_A} = \int_0^V -\frac{k_1}{Q} dV$$

$$\ln C_A - \ln C_{A0} = -\frac{k_1}{Q} V$$

$$\ln \frac{C_{A0}}{C_A} = \frac{k_1}{Q} V$$

$$C_A = C_{A0} \exp\left(-\frac{k_1}{Q} V\right)$$

$$\text{mole bal. on B: } Q C_B|_x - Q C_B|_{x+\Delta x} + k_1 C_A A \Delta x - k_2 C_B A \Delta x = 0$$

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

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

↓ substitute for C_A

$$-Q \frac{dC_B}{dV} + k_1 C_{A0} \exp(-k_1 \tau) - k_2 C_B = 0$$

$$-\frac{dC_B}{dV} - \frac{k_2}{Q} C_B + \frac{k_1 C_{A0}}{Q} \exp(-k_1 \tau) = 0$$

$$\frac{dC_B}{dV} + \frac{k_2}{Q} C_B = \frac{k_1 C_{A0}}{Q} \exp(-k_1 \tau)$$

~~let $A(V) = P(V)$~~

$$\frac{dC_B}{d\tau} + k_2 C_B = k_1 C_{A0} \exp(-k_1 \tau)$$

$$\text{let } C_B = u(\tau) v(\tau) \Rightarrow u \frac{dv}{d\tau} + v \frac{du}{d\tau} = k_1 C_{A0} e^{-k_1 \tau} - k_2 uv$$

$$\text{let } \frac{dv}{d\tau} = -k_2 v$$

$$\int \frac{dv}{v} = \int -k_2 d\tau$$

$$\ln v = -k_2 \tau$$

$$v = e^{-k_2 \tau}$$

$$\therefore \frac{du}{d\tau} k_1 C_{A0} \exp(-k_1 \tau) = v \frac{du}{d\tau}$$

$$e^{-k_2 \tau} \cdot \frac{du}{d\tau} = k_1 C_{A0} e^{-k_1 \tau}$$

$$\frac{du}{d\tau} = k_1 C_{A0} e^{(k_2 - k_1) \tau}$$

$$\int du = \int k_1 C_{A0} e^{(k_2 - k_1) \tau} d\tau + C_1$$

$$u = k_1 C_{A0} \left(\frac{1}{k_2 - k_1} \right) e^{(k_2 - k_1) \tau} + C_1$$

at $\tau = 0$, $u = 0$:

$$0 = k_1 C_{A0} \left(\frac{1}{k_2 - k_1} \right) + C_1$$

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

$$\therefore u = \left(\frac{k_1 C_{A0}}{k_2 - k_1} \right) \left[e^{(k_2 - k_1) \tau} - 1 \right]$$

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

Find $\max C_B$, $\frac{dC_B}{d\tau} = 0$:

$$\frac{dC_B}{d\tau} = \left(\frac{k_1 C_{A0}}{k_2 - k_1} \right) \left[-k_1 e^{-k_1 \tau} + k_2 e^{-k_2 \tau} \right]$$

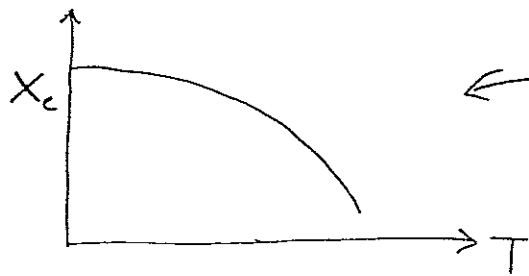
$$k_1 e^{-k_1 \tau} = k_2 e^{-k_2 \tau}$$

$$\frac{k_2}{k_1} = e^{(k_2 - k_1) \tau}$$

$$\ln \frac{k_2}{k_1} = (k_2 - k_1) \tau$$

$$\tau = \frac{\ln \frac{k_2}{k_1}}{k_2 - k_1} \quad \text{for } \max C_B$$

② Extent of rxn or conversion at equilibrium for exothermic rxn. as a function of temp.



← ? How to find it?

Van't Hoff

$$\left[\frac{\partial(G/T)}{\partial T} \right]_P = -\frac{H}{T^2}$$

Reaction rate as function of temp.

$$r_A = k C_A$$

$$\left[\frac{\partial(\Delta G^\circ/T)}{\partial T} \right]_P = -\frac{\Delta H^\circ}{T^2}$$

where k follows Arrhenius law: $R \left(\frac{\partial \ln k}{\partial T} \right)_P = \frac{\Delta H^\circ}{T^2}$

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

this is also a function of temp, although usually much weaker than the exponential depend.



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

$$K = \frac{k_f}{k_r} = \frac{X_A}{1-X_A}$$

res.
as $T \uparrow$,
 $\ln K \downarrow$
 $\rightarrow K \downarrow$
reactants
favored
 $X_A \downarrow$

? Is this correct?
Yes



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

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

$$X_A = \frac{e^{-\Delta H^\circ/RT}}{1 + e^{-\Delta H^\circ/RT}}$$

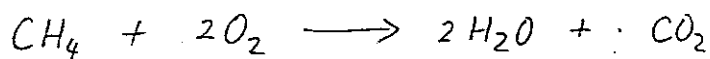
$$K = e^{-\Delta H^\circ/RT} = \frac{X_A}{1-X_A}$$

- ③ In general, we use the steady-state approximation when we deal with a reaction consisting of many steps. The SS approx. says that the net rate of formation or disappearance of an intermediate is zero. This approx. is valid if the conc. of the intermediate is very small and the steps consuming the intermediate are rapid.

④ $\mu_i \equiv \left(\frac{\partial U}{\partial n_i} \right)_{S, V, n_j} = \left(\frac{\partial G}{\partial n_i} \right)_{T, P, n_j} = \bar{g}_i$

Abstract concept introduced by Gibbs used in phase-equil. At equil, the chem. pot. is the same in all phases.

- ⑤ Determine H_f° calorimetrically.
For example, to find $H_{CH_4}^\circ$, measure heat of combustion:



Using an apparatus such as an adiabatic flame calorimeter, the change in enthalpy is equal to the heat given off by the combustion. The heat given off can be found by measuring the increase in temp from the inlet to the outlet.

Determine S_f° by:

$$S_{CH_4}^\circ = S_{CH_4} - S_C - 2S_{H_2}$$

where S_i can be found by:

$$ds = \left(\frac{\partial s}{\partial T}\right)_P dT + \left(\frac{\partial s}{\partial P}\right)_T dP$$
$$= \frac{C_P}{T} dT + \text{press. corrections}$$

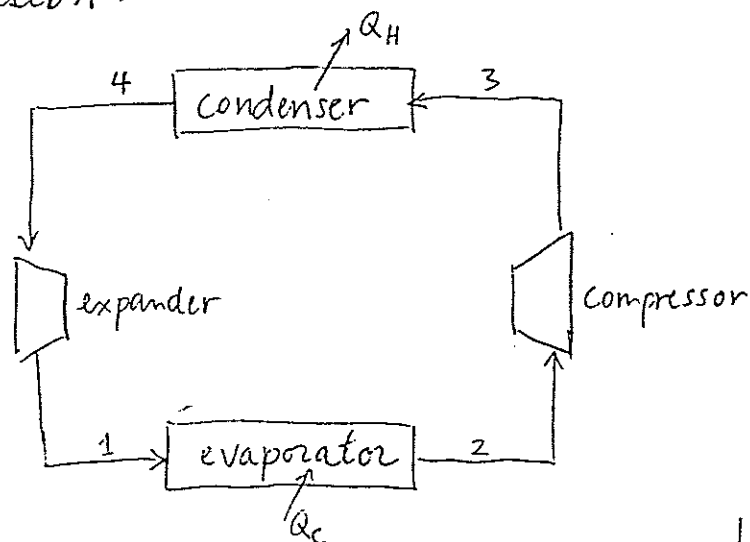
Using the fact that $S=0$ for all perfect crystalline solids at $0^\circ K$,

$$S = \int_0^{T_m} \frac{C_P^s}{T} dT + \frac{\Delta h^m}{T_m} + \int_{T_m}^{T_b} \frac{C_P^L}{T} dT + \frac{\Delta h^b}{T_b}$$
$$+ \int_{T_b}^T \frac{C_P^v}{T} dT + \text{pressure correct.}$$

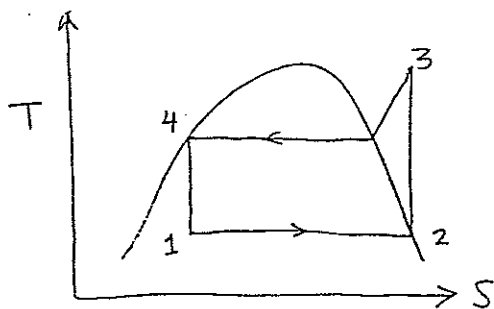
To find g^f , use:

$$g^f = h^f - T S^f$$

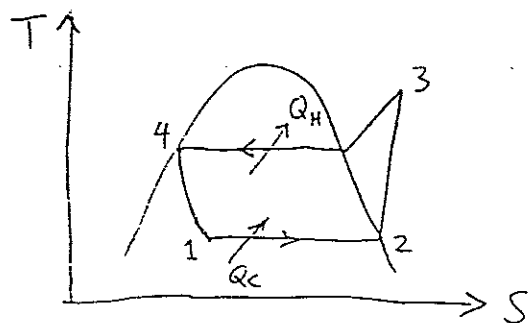
⑥ Refrigeration cycle with isentropic compression and expansion =



$$\text{COP} = \frac{|Q_C|}{|W_{\text{net}}|}$$



Refrigeration cycle with throttle valve (isenthalpic)



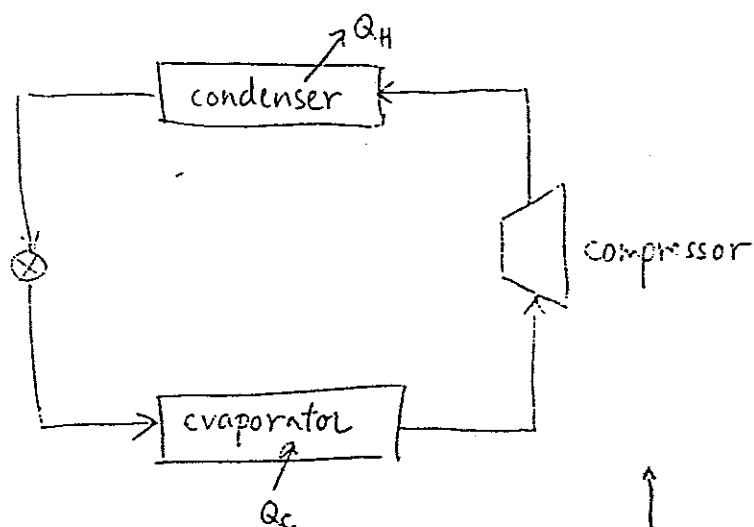
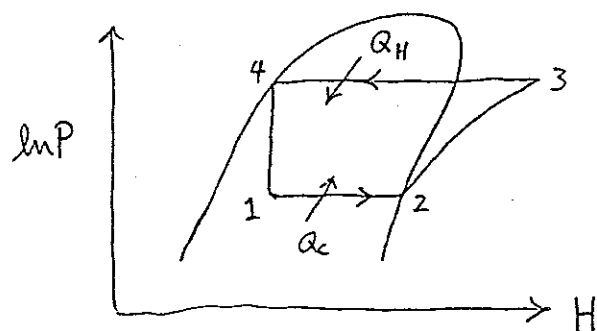
Note that 4-1 is isenthalpic and that 2-3 is no longer isentropic - in reality the compression step increases entropy a bit because it is irreversible.

1-2: evaporation which causes heat to be absorbed.

2-3: compress sat. vapor to superheated vapor

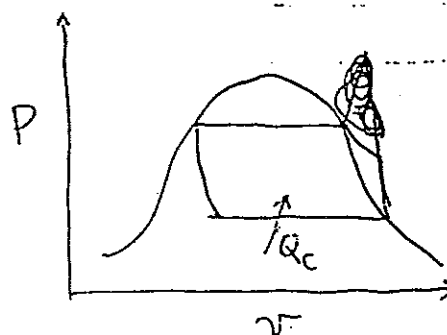
3-4: condensation to sat. liq. causes heat to be released

4-1: expansion and partial evaporation (isenthalpic)



Typical
refrigerator

[?] P-V diagrams?

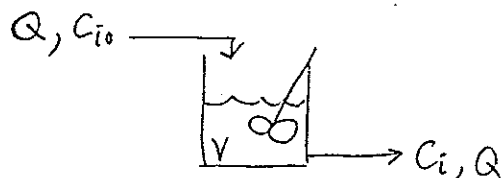


- ⑦ Rate constant varies with temp. according to empirically determined Arrhenius law:

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

↑
weak function
of temp.

⑧ CSTR



$$r_i [=] \frac{\text{mol}}{\text{volume} \cdot \text{sec}} = \text{production of } i$$

Mole balance

$$QC_{i0} - QC_i + r_i V = \frac{d\vec{e}_i}{dt} V \quad \text{at SS}$$

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

Assume tank is well-stirred

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

Energy balance

$$\frac{dE}{dt} = \overset{\substack{\text{total energy} \\ \text{of system}}}{\dot{Q} - \dot{W}} + \sum_i F_i e_i|_{in} - \sum_i F_i e_i|_{out}$$

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

$$= \sum F_i P v_i|_{out} - \sum F_i P v_i|_{in} + \dot{W}_s \rightarrow \text{negligible}$$

substituting

$$\frac{dE}{dt} = \dot{Q} - \sum F_i P v_i|_{out} + \sum F_i P v_i|_{in} + \sum F_i e_i|_{in} - \sum F_i e_i|_{out}$$

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

Often, above eqn. is expressed relative to species A =

$$F_i = F_{i0} + F_{A0} \overset{\substack{\text{conversion of A}}}{\gamma_i X} = F_{A0} (\underbrace{\theta_i}_{= \frac{C_{i0}}{C_{A0}}} + \gamma_i X)$$

$$\frac{dE}{dt} = \dot{Q} + F_{A0} \sum (\theta_i + \nu_i X) \dot{h}_i|_{in} - F_{A0} \sum (\theta_i + \nu_i X) \dot{h}_i|_{out}$$

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

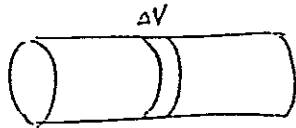
$$\frac{dE}{dt} = \int^A U(T_{surr} - T) dA + F_{A0} \sum \theta_i \dot{h}_i|_{in} - F_{A0} \sum (\theta_i + \nu_i X) \dot{h}_i|_{out}$$

$$\frac{dE}{dt} = \int^A U(T_{surr} - T) dA + F_{A0} \sum \theta_i (\dot{h}_{i0} - \dot{h}_i) - F_{A0} X \sum \nu_i \dot{h}_i$$

At SS, assuming no spatial variations of temp :

$$\boxed{0 = U \Delta T A + F_{A0} \sum \theta_i (\dot{h}_{i0} - \dot{h}_i) - F_{A0} X \sum \nu_i \dot{h}_i} \quad \text{where}$$

PFR



Mole bal

$$F_i|_V - F_i|_{V+\Delta V} + r_i \Delta V = 0 \quad \text{at SS.}$$

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

$$\boxed{\frac{dF_i}{dV} = r_i}$$

Energy bal

Same as CSTR except $X(V)$ - conversion varies !!

Batch

Mole bal

$$\boxed{\cancel{V} \frac{dc_i}{dt} = r_i \cancel{V}}$$

Energy bal

No flow in or out.

$$\frac{dE}{dt} = \dot{Q} - \dot{W}_s$$

$$\boxed{0 = \dot{Q} - \dot{W}_s} \quad \text{at SS}$$

- ⑨ Space time : $\tau = \frac{V}{Q_0}$ [s] sec ^{- 1 volume} Time necessary to process one reactor volume of fluid based on entrance conditions.

Space velocity : Reciprocal of space time.

Mean residence time : $t_m =$ average time the effluent molec. spend in reactor.

$$t_m = \frac{V}{\int_V dv}$$

$$H = U + PV$$

$$G = H - TS$$

$$du = Tds - p dv$$

$$dh = du + p dv + v dp$$

$$= T ds - p dv + p dv + v dp$$

$$dh = T ds + v dp$$

⑩ Clapeyron eqn : $\boxed{\frac{dp^{sat}}{dT} = \frac{\Delta h}{T \Delta v}}$

$$\mu^\alpha = \mu^\beta$$

for pure species coexisting in two phases at equil.

$$g^\alpha = g^\beta$$

$$dg^\alpha = dg^\beta$$

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

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

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

since $p = p^{sat}$ when V-L equil.

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

since $\Delta h^{\alpha\beta} = T \Delta s^{\alpha\beta}$

$$\frac{dp^{sat}}{dT} = \frac{\Delta h^{\alpha\beta}}{T \Delta v^{\alpha\beta}}$$

Clausius-Clapeyron eqn : $\boxed{\Delta h^{vap} = -R \frac{d \ln p^{sat}}{d(1/T)}}$

Assume V-L equil. with ideal gas vapor, assume $v^L \ll v^V$.

$$p v^V = RT \Rightarrow v^V = \frac{RT}{p} \approx \Delta v$$

$$\frac{dp^{sat}}{dT} = \frac{\Delta h^{vap} p^{sat}}{RT^2}$$

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

$$\frac{dp^{sat}/p^{sat}}{dT} = \frac{\Delta h^{vap}}{RT^2}$$

0.0585

$$\textcircled{11} \quad \frac{dE}{dt} = \dot{Q} - \dot{W}_s + \sum F_i h_{i0} - \sum F_i h_i$$

For adiabatic $\Rightarrow \dot{Q} = 0$

Assume no shaft work $\Rightarrow \dot{W}_s = 0$
 " SS

$$0 = \sum F_i (h_{i0} - h_i) = \sum F_i \Delta h_i = \Delta H = \Delta H_{rxn} + \Delta H_{heating}$$

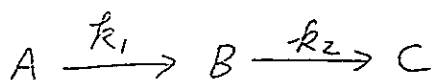
$$-\Delta H_{rxn} = \sum F_i C_{p,i} \Delta T$$

↑ can find this !!

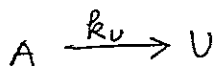
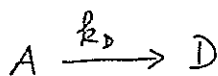
↑ I think it's a PFR

Series Reaction

If the desired product is an intermediate, then the best reactor is a CSTR. I found this by deriving C_B as function of space time and k_1, k_2 , and C_{A0} for the series rxn:



Parallel Reactions



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

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

We want to maximize C_D and minimize $C_U \Rightarrow$ maximize ratio $\frac{r_D}{r_U}$!!

$$\frac{r_D}{r_U} = \frac{k_D}{k_U} C_A^{\alpha_D - \alpha_U}$$

If $\alpha_D > \alpha_U$:

Then we want to keep C_A as high as possible.
This is done in a PFR or a batch reactor.

If $\alpha_D < \alpha_U$:

Then we want to keep C_A as low as possible.
This is done in a CSTR because C_A is at its
lowest value (that of the exit) since the CSTR is well
mixed.

Another factor to consider is the ratio of reaction
constants: $\frac{k_D}{k_U}$

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

If $E_U > E_D$:

Then we want the T as low as possible. Maybe
try cooling between reactors.

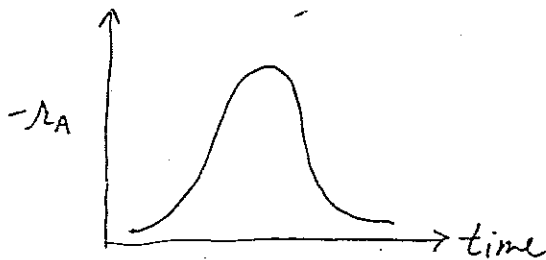
If $E_U < E_D$:

Then we want the T as high as possible. Limitations
are in the equipment.

Autocatalytic Reactions

Ex: $A + D \rightleftharpoons \cancel{A} + D$ is autocatalytic
where D acts as a catalyst for the rxn.

In this type of rxn, $-r_A$ is small initially, then it reaches a max., and finally decreases again.



In the beginning, $-r_A$ is small because there is not enough D around to serve as catalyst. Therefore, use CSTR because C_D is highest. Then use PFR because C_A starts to decrease as time goes on. PFR keeps C_A at highest level.

⑬ First Law : Conservation of energy

$$\left. \begin{array}{l} \text{Closed system : } dU = dQ - dW \\ \text{Open system : } dH = dQ - dW_s \end{array} \right\} \begin{array}{l} \text{neglecting KE} \\ \text{and PE} \end{array}$$

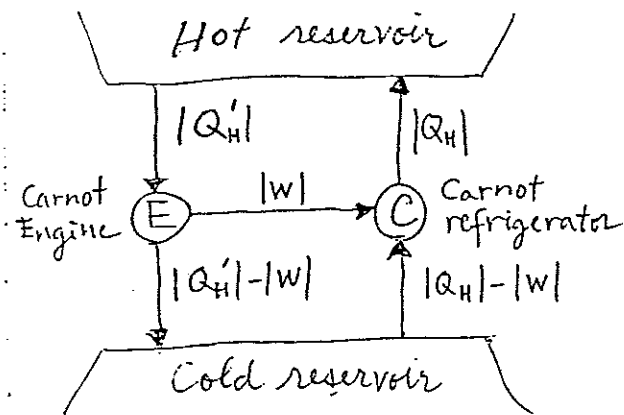
Second Law

- No apparatus can operate in such a way that its only effect is to convert heat absorbed completely into work
- No process is possible which consists of transferring heat from a lower temp. to a higher temp.
- $\Delta S_{TOT} \geq 0$ for all processes
 $\Delta S_{TOT} = 0$ only for reversible processes

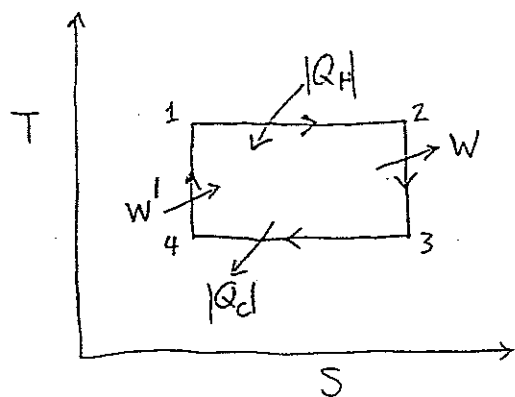
Third Law

The absolute entropy is zero for all perfectly crystalline substances at 0°K . Enables us to calculate absolute entropies of substances.

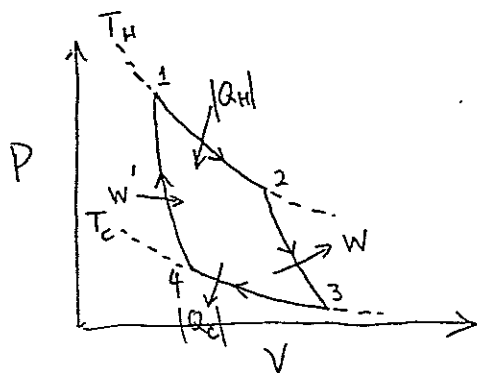
14) Carnot Cycle



Used for proof of Carnot theorem which states that no engine can have a higher thermal efficiency than a Carnot engine.



- 1-2 : Isothermal expansion. In equil. with hot reservoir (reversible)
- 2-3 : Adiabatic process where work is extracted (reversible)
- 3-4 : Isothermal compression. In equil. with cold reservoir (reversible)
- 4-1 : Adiabatic process where work is put in (reversible)

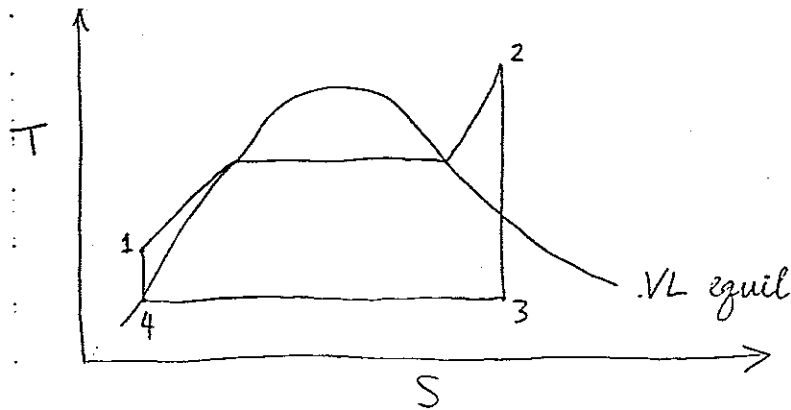


$$\text{Efficiency} = \eta = \frac{W - W'}{|Q_H|} = \frac{|Q_H| - |Q_C|}{|Q_H|} = 1 - \frac{|Q_C|}{|Q_H|}$$

$$\text{Entropy bal: } \Delta S = 0 = \frac{|Q_H|}{T_H} - \frac{|Q_C|}{T_C} + \cancel{S_{\text{gen}}} \rightarrow 0 \text{ if reversible}$$

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

Rankine cycle (fossil burning power plants)

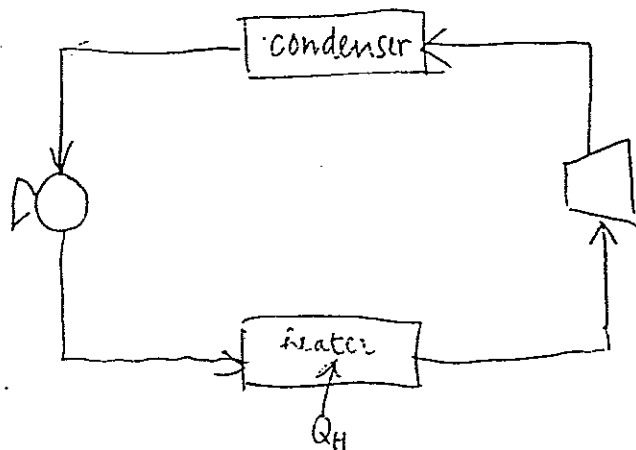


1-2 : heating at const. P . (along isobar)

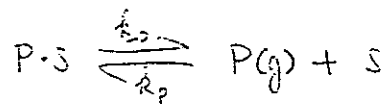
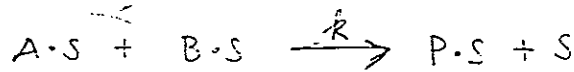
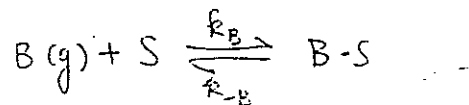
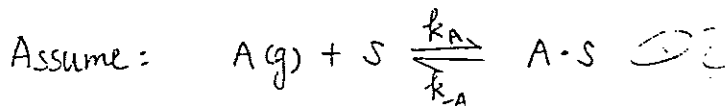
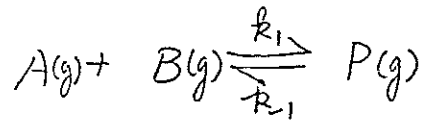
2-3 : Reversible, adiabatic expansion of the superheated steam. A little bit of condensation occurs.

3-4 : Condensation to sat. liq. Isothermal & isobaric

4-1 : Reversible, adiabatic (therefore isentropic) pumping of condensed liquid to the pressure of the boiler.



⑮ Langmuir-Hisshenwood expression for solid catalyzed reaction =



$$r = k \theta_A \theta_B$$

$$C_t = C_v + C_{A \cdot S} + C_{B \cdot S} + C_{P \cdot S}$$

$$r_{A \cdot S} = k_A p_A C_v - k_{-A} C_{A \cdot S} \approx 0$$

$$K_A = \frac{k_A}{k_{-A}} = \frac{C_{A \cdot S}}{p_A C_v} = \boxed{\frac{\theta_A}{p_A \theta_v} = K_A} \Rightarrow \theta_A = K_A p_A \theta_v$$

$$r_{B \cdot S} = k_B p_B C_v - k_{-B} C_{B \cdot S} \approx 0$$

$$K_B = \frac{k_B}{k_{-B}} = \frac{C_{B \cdot S}}{p_B C_v} = \boxed{\frac{\theta_B}{p_B \theta_v} = K_B} \Rightarrow \theta_B = K_B p_B \theta_v$$

$$r_{P \cdot S} = k_p p_P C_v - k_{-p} C_{P \cdot S} \approx 0$$

$$K_P = \frac{k_p}{k_{-p}} = \frac{C_{P \cdot S}}{p_P C_v} = \boxed{\frac{\theta_P}{p_P \theta_v} = K_P} \Rightarrow \theta_P = K_P p_P \theta_v$$

$$1 = \theta_v + \theta_A + \theta_B + \theta_P$$

$$1 = \theta_v + K_A p_A \theta_v + K_B p_B \theta_v + K_P p_P \theta_v$$

$$1 = \theta_v (1 + K_A p_A + K_B p_B + K_P p_P)$$

$$\theta_v = \frac{1}{(\dots\dots\dots)} = \frac{1}{\Phi}$$

$$\theta_A = \frac{K_A p_A}{\Phi}$$

$$\theta_B = \frac{K_B p_B}{\Phi}$$

$$\therefore \boxed{r = k \frac{K_A p_A K_B p_B}{\Phi^2}}$$

⑩ From 2nd law: $dS_{\text{TOT}} > 0$

$$dS + dS_{\text{surr}} > 0$$

$$dS + \frac{dQ_{\text{surr}}}{T} > 0$$

Since $dQ = -dQ_{\text{surr}}$,

$$dS \geq \frac{dQ}{T}$$

From 1st law for ~~closed~~^{open} system,

$$dU = dQ - dW + \sum \mu_i dn_i$$

$$\therefore dU \geq Tds - dW + \sum \mu_i dn_i \quad dU + PdV - Tds > 0$$

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

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

$$dG_{T,P} = dU + PdV - Tds$$

$$\therefore \boxed{dG_{T,P} \leq 0}$$

For open system, $dH = dQ - dW_s$ ^{assume no shaft work}

$$\therefore dH > Tds \Rightarrow dH - Tds > 0$$

$$G = H - TS \Rightarrow dG = dH - Tds - SdT$$

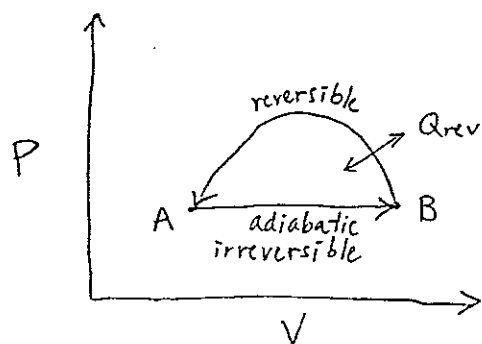
$$dG_{T,P} = dH - Tds > 0$$

$$\therefore \boxed{dG_{T,P} \leq 0}$$

?

(17) Prove S tends towards maximum.

Consider adiabatic, irreversible process $A \rightarrow B$:



For the cyclic process, $\Delta U = 0$

$$\therefore Q - W = 0$$

$$Q_{rev} = W = W_{rev} + W_{irrev}$$

Since $|W_{rev}| > |W_{irrev}|$ and W_{rev} is negative, $Q_{rev} < 0$

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

$$\therefore S_B - S_A > 0$$

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

⑮ Gibbs Mixture Rule \equiv Gibbs Theorem :

A total thermo property (U, H, C_p, S, A, G) of an ideal gas mixture is the sum of the total properties of the individual species, each evaluated at the mixture T but at its own partial P .

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

Derive Gibbs-Duhem Egn :

M = any extensive property ($U, H, G, \text{etc} \dots$)

$$dM = \left(\frac{\partial M}{\partial T} \right)_{P, n_T} dT + \left(\frac{\partial M}{\partial P} \right)_{T, n_T} dP + \sum \left(\frac{\partial M}{\partial n_i} \right)_{T, P, n_{j \neq i}} dn_i$$

\parallel
 \bar{m}_i

Euler's Theorem : $M = \sum_i \bar{m}_i n_i$

$$dM = \sum_i \bar{m}_i dn_i + \sum_i n_i d\bar{m}_i$$

$$\therefore \cancel{\sum_i \bar{m}_i dn_i} + \sum_i n_i d\bar{m}_i = \left(\frac{\partial M}{\partial T} \right)_{P, n_T} dT + \left(\frac{\partial M}{\partial P} \right)_{T, n_T} dP + \cancel{\sum_i \bar{m}_i dn_i}$$

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

Aside : Prove $\sum x_i d \ln x_i = 0$ at const. T, P .

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

$$\therefore \sum n_i d\mu_i = 0$$

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

? since $f_i = x_i \gamma_i f_i^\circ$

$$\mu_i - \mu_i^\circ = RT \ln x_i \gamma_i = RT [\ln x_i + \ln \gamma_i]$$

$$d\mu_i =$$

(20) $\Delta G^\circ = -RT \ln K_a$ Use Gibbs-Helmholtz Egn.

$$G = H - TS = \underbrace{U + PV}_H - TS$$

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

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

$$dH = dU + PdV + VdP$$

$$dH = TdS - PdV + PdV + VdP$$

$$\left(\frac{\partial H}{\partial T}\right)_P = T \left(\frac{\partial S}{\partial T}\right)_P$$

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

$$\text{Also, } \frac{\partial (\Delta G^\circ/T)}{\partial T} = - \frac{\Delta H^\circ}{T^2}$$

$$\therefore \boxed{\left(\frac{\partial \ln K_a}{\partial T}\right)_P = \frac{\Delta H^\circ}{RT^2}} \quad \text{How } K_a \text{ varies with } T$$

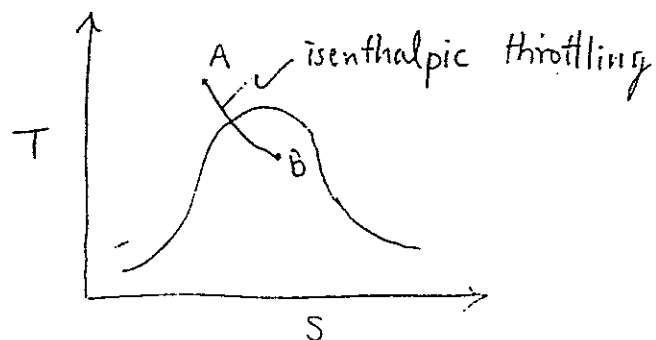
$$G = H - TS = U + PV - TS$$

$$dG = \cancel{TdS} - \cancel{PdV} + \cancel{PdV} + VdP - \cancel{TdS} - SdT$$

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

$$\boxed{\left(\frac{\partial \Delta G^\circ}{\partial P}\right)_T = \Delta V^\circ}$$

- (22) J-T liquefaction process is to take a gas at a low enough T and high enough P and expanding it through a throttle valve. Because of the \downarrow of T , some of the gas will condense.



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

G-H : $\frac{\partial (\Delta G/T)}{\partial T} = \frac{-\Delta H}{T^2}$

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

$$\frac{\partial (\Delta G/T)}{\partial (1/T)} = \Delta H$$

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

$\Delta G = -RT \ln K$

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

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

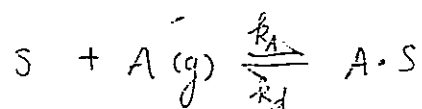
Exothermic : $\Delta H < 0 \Rightarrow$ slope = positive

Endothermic : $\Delta H > 0 \Rightarrow$ slope = negative

- ② Activation energy is the minimum energy that must be possessed by reacting molecules before the rxn will occur.

It's like a pass over a mountain range.

- ② Langmuir isotherm describes the surface conc. of adsorbed species in equil. with the gas.



$$r_{net} = k_a p_A C_v - k_d C_{A \cdot S} = 0 \quad \text{at equil.}$$

$$K = \frac{k_a}{k_d} = \frac{C_{A \cdot S}}{p_A C_v}$$

$$C_t = C_v + C_{A \cdot S}$$

$$C_{A \cdot S} = p_A K (C_t - C_{A \cdot S})$$

$$C_{A \cdot S} (1 + p_A K) = p_A K C_t$$

$$C_{A \cdot S} = \frac{p_A K C_t}{1 + p_A K}$$

- ② Entropy is zero at 0 K because a ^{pure} substance that is a perfect crystalline form has no other possible way to arrange the particles to obtain the lowest quantum state.

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

?

(28)

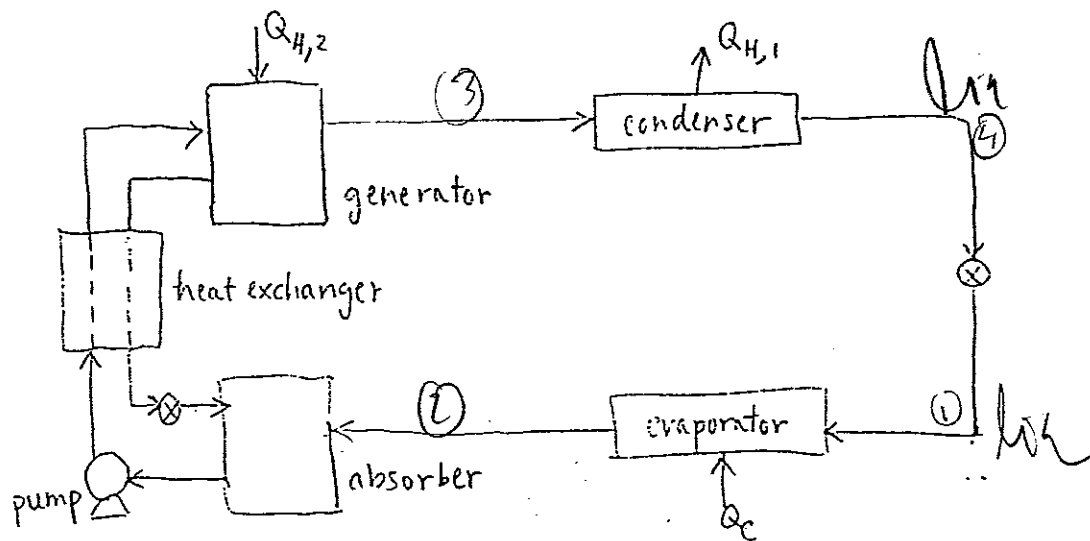
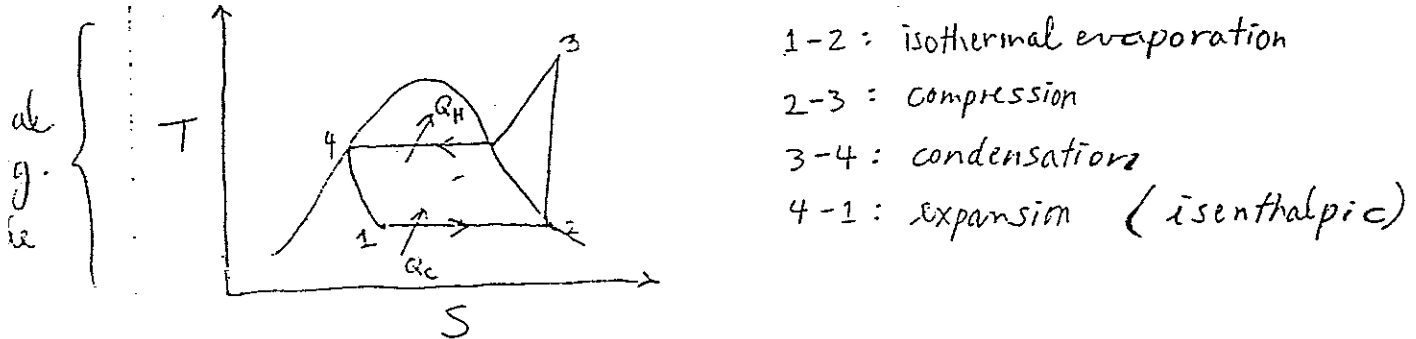
Calculate the total volume when two equal volumes of different liquids are mixed.

?

- (29) Calculate heat capacities of two gases H_2 and $CH_3 NCO$ from first principles.

35) Absorption refrigeration

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



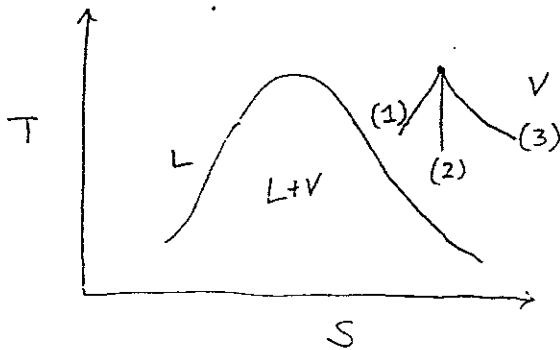
Some common systems :

(1) Refrigerant - H_2O
 Absorbent - LiBr soln

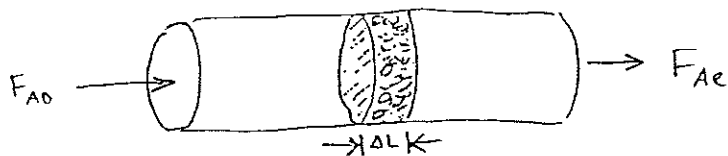
(2) Refrigerant - NH_3
 Absorbent - H_2O

③ Three methods of liquefying a gas

- (1) Heat exchange at const. P
- (2) Expansion in a turbine from which work is obtained (at const. S)
- (3) Throttling (at const. H)



③ Differential Reactors



Small amount of catalyst \Rightarrow reactant conc. essentially const. throughout. Also, since low conversion \Rightarrow small heat released, so nearly isothermal.

Differential reactors are normally used to determine the rate of rxn as a function of conc. for heterogeneous systems: $-r_A = -r_A(C_{Ao})$

③⑧ Difference between extent of rxn and equil. conversion

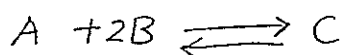
Equilibrium conversion:

$$X_e = \frac{C_{A0} - C_{Ae}}{C_{A0}} = \frac{\text{moles A reacted at equil}}{\text{initial moles of A}}$$

Extent of reaction

$$\varepsilon = \frac{n_{A0} - n_A}{\nu_A} = \frac{\text{moles A reacted}}{\text{stoch. coeff.}}$$

Ex



$$\varepsilon = \frac{n_{A0} - n_A}{\nu_A} = \frac{n_{B0} - n_B}{\nu_B} = \frac{n_{C0} - n_C}{\nu_C} \quad \left. \vphantom{\frac{n_{A0} - n_A}{\nu_A}} \right\} \text{ same for } A, B, C$$

$$\left. \begin{aligned} X_{A,e} &= \frac{C_{A0} - C_{Ae}}{C_{A0}} \\ X_{B,e} &= \frac{C_{B0} - C_{Be}}{C_{B0}} \end{aligned} \right\} X_{A,e} \neq X_{B,e}$$

(39) Why freon used instead of H_2O , air as refrigerant?

- 1) $P^{vap} > P_{atm}$ at temp. of evaporator to keep air out of system.
- 2) On the other hand, P^{vap} at T of condenser not too high since high-pressure equipment is expensive.

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

#2 rules out air \Rightarrow need too high P to condense air.

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

?
f diff.
n fugacity. Activity is an auxiliary function of chemical potential. It gives an indication of how "active" a substance is relative to its standard state since it provides a measure of the difference between the substance's chemical pot. at the state of interest and that of its std. state:

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

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

- ④ What is fugacity and how is it calculated?
What is it used for?

Fugacity is an auxiliary function of the chemical potential which is more easily identified with physical reality. It is a "corrected pressure" which for a component in a mixture of ideal gases is equal to the partial pressure of that component. The "corrections" are from deviations from ideality.

$$du_i = d\bar{g}_i \equiv RT d \ln f_i$$

where $\boxed{\frac{f_i}{y_i P} \rightarrow 1}$ as $P \rightarrow 0$ ^(ideal gas)

For a gas,

$$f_i = y_i \phi_i P$$

← corrections for non-ideality

← from volume explicit eos

$$\text{where } RT \ln \phi_i = \int_0^P \left[\bar{v}_i - \frac{RT}{P} \right] dP$$

For a liquid,

$$f_i^L = x_i \gamma_i f_i^*$$

← corrects for non-ideality

← std. state fugacity usually taken to be fugacity of pure i at T and P of solution.

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

$$RT \ln \gamma_i = \bar{g}_i^E = \left(\frac{\partial n_T g^E}{\partial n_i} \right)_{T, P, n_j}$$

postulate expressions for g^E based on experiment. It should satisfy BC's

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

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

for binary mixtures

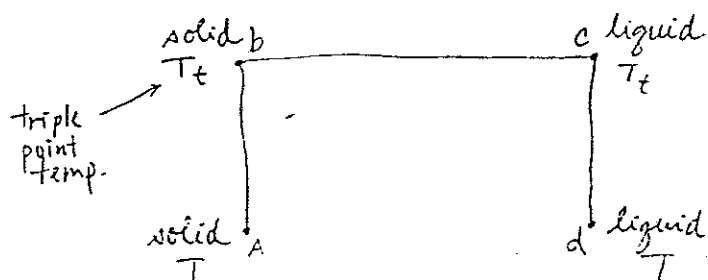
$$\text{where } g^E = g(\text{actual soln at } T, P, \text{ and } x) - g(\text{ideal soln at } T, P, \text{ and } x)$$

For a solid,

$$f_i^s = x_i \overset{1 \text{ (usually solid is pure } i)}{\cancel{x_i}} f_i^o = x_i f_i^i$$

↑
fugacity of pure subcooled liq.

Find $\frac{f_i^L}{f_i^S}$ by thermo cycle:



$$\Delta g_{A-D} = RT \ln \left(\frac{f_i^L}{f_i^S} \right)_{\text{pure } i}$$

$$du = Tds - Pdv$$

$$g = h - Ts = u + Pv - Ts$$

$$dg = du + Pdv + vdp - Tds - sdT$$

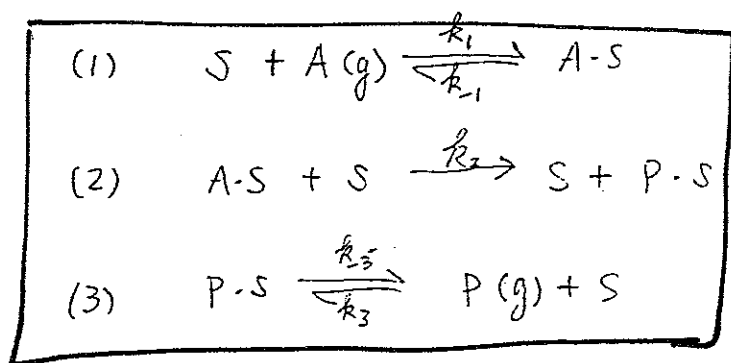
$$= \cancel{Tds} - \cancel{Pdv} + \cancel{Pdv} + vdp - \cancel{Tds} - sdT$$

$$= vdp - sdT$$

Fugacity is used for phase equilibria calculations !!

④② Considering Langmuir-Hinshelwood kinetics, why might the rate go down as the gas conc. goes up?

Consider the following rxn mechanism:



If rxn (2) is rate limiting, the overall rxn may go down as $p_A \uparrow$ because there will not be any vacant sites available.

$$r = k_2 C_{A \cdot S} C_v$$

$$k_1 C_v p_A = k_{-1} C_{A \cdot S} \Rightarrow C_{A \cdot S} = \left(\frac{k_1}{k_{-1}} \right) C_v p_A \quad // K_1$$

$$k_3 C_v p_P = k_5 C_{P \cdot S} \Rightarrow C_{P \cdot S} = K_2 C_v p_P$$

$$C_t = C_v + C_{A \cdot S} + C_{P \cdot S} = C_v + K_1 p_A C_v + K_2 p_P C_v$$

$$C_t = C_v (1 + K_1 p_A + K_2 p_P)$$

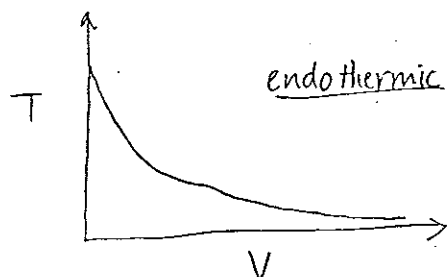
$$C_{A \cdot S} = K_1 p_A \frac{C_t}{1 + K_1 p_A + K_2 p_P}$$

$$\therefore r = k_2 K_1 p_A \frac{C_t^2}{(1 + K_1 p_A + K_2 p_P)^2} \quad \left. \vphantom{\frac{C_t^2}{(1 + K_1 p_A + K_2 p_P)^2}} \right\} \text{As } p_A \uparrow, r \downarrow$$

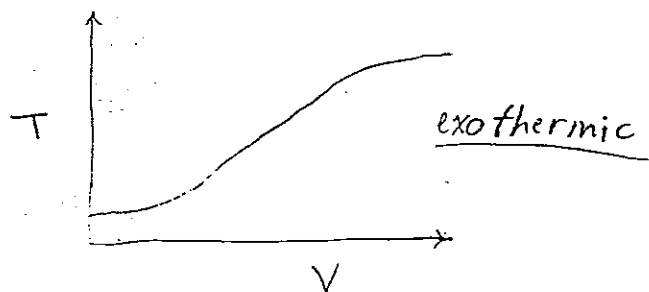
(13) Difference between activation energies determined in the regions where internal and external mass transfer dominate?

④⑤ What does the temp. distr. in PFR look like?

For adiabatic PFR,



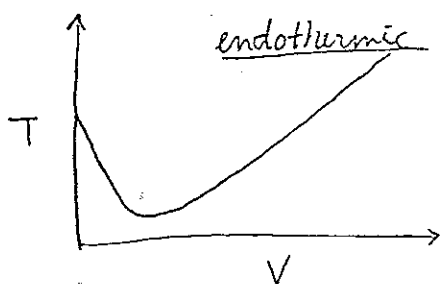
The reaction will die out after the T drops enough (slow down of kinetics).



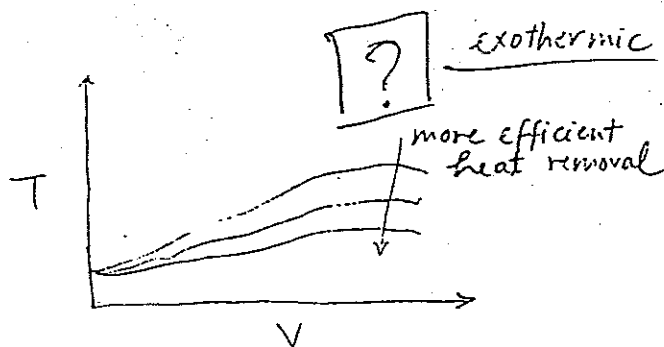
As $T \uparrow$, reaction rate \uparrow .

Near the end of reactor, $T \uparrow$ slowly because not much reactants left.

For PFR with heat exchange,



There's a minimum in T because rxn rate is largest there. As rxn rate decreases (due to depletion of reactants), T increases.

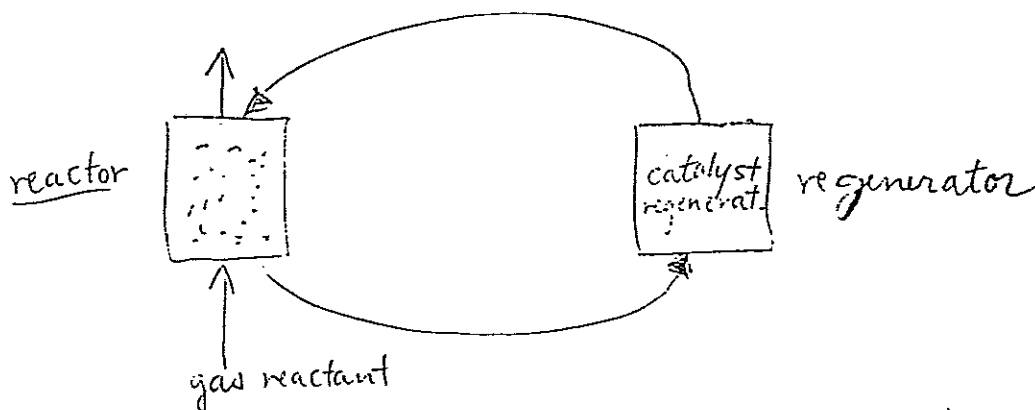


- ④⑥ What is a fluidized bed reactor? What are its advantages and disadvantages?

It is a reactor in which small particles of catalyst are suspended by upward motion of reacting fluid. Catalyst particles are in constant motion.
Particle diameter $\sim 100 \mu\text{m}$.

Advantages -

- (1) Allows continuous, automatically controlled operations using reactant-catalyst systems which require catalyst regeneration because catalyst deactivates quickly.



- (2) Because of turbulent mixing, less likely to be mass transfer limited.

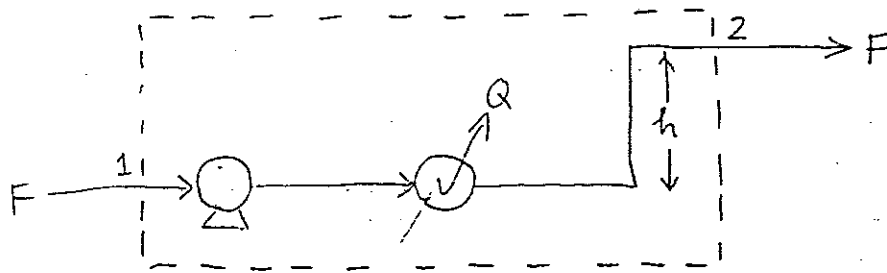
- (3) Very uniform T can be achieved throughout entire reactor because:

- (a) large $Re \Rightarrow$ good axial & radial mixing.
- (b) large C_p of solid catalyst relative to gas C_p together with large area for heat transfer \Rightarrow minimizes ΔT of reactant gas.

(4) Enhanced selectivity due to precise T

(5) Large scale operation possible

(47) Enthalpy change of pipe system consisting of a pump, a heat exchanger, and a vertical step of height h in series.



$$\frac{d(mu)}{dt} = \dot{m} \left[u_1 + \frac{1}{2}v_1^2 + z_1g - u_2 - \frac{1}{2}v_2^2 - z_2g \right] + \dot{Q} - \dot{W}$$

$$\begin{aligned} \text{where } \dot{W} &= \dot{W}_s + P_2 v_2 \dot{m} - P_1 v_1 \dot{m} & \frac{N}{m^2} \cdot \frac{m}{s} \cdot \frac{kg}{m^3} \\ &= \dot{W}_s + \dot{m} \Delta(Pv) & \frac{N \cdot kg}{m \cdot s^2} \cdot \frac{kg}{m^3} \end{aligned}$$

At SS, neglecting KE

$$0 = -\dot{m} \Delta[u + zg] + \dot{Q} - \dot{W}_s - \dot{m} \Delta(Pv)$$

$$\dot{m} \Delta[u + Pv + zg] = \dot{Q} - \dot{W}_s$$

$$\dot{m} \Delta[h + zg] = \dot{Q} - \dot{W}_s$$

$$\boxed{\dot{m} \Delta h = \dot{Q} + \frac{\dot{m}}{\rho} \Delta P - \dot{m} g \Delta h}$$

heat

loss in the pipe due to friction

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

By definition,

$$\Delta g^\circ = -RT \ln K_{eq}$$

depends only on T !!

$$\Delta g^\circ = \Delta h^\circ - T \Delta S^\circ$$

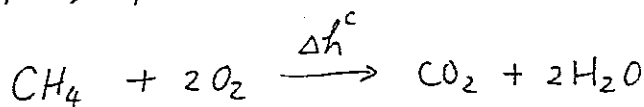
$$= \sum \nu_i h_i^{f,0} - T \sum \nu_i S_i^{f,0}$$

G-H:

$$\left[\frac{\partial (g/T)}{\partial T} \right]_P = -\frac{h}{T^2}$$

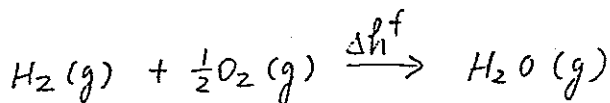
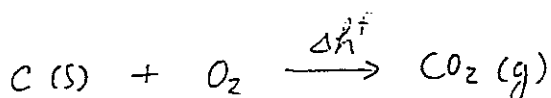
To find K_{eq} at diff. T

To find $h_i^{f,0}$, need to do calorimetry experiments.
For example, for $CH_4(g)$: combustion yields



$$\Delta h^c = h_{CO_2}^f + 2h_{H_2O}^f - h_{CH_4}^f - 2h_{O_2}^f$$

To find $h_{CO_2}^f$ and $h_{H_2O}^f$, perform following experiments:



If $h_{CO_2}^f$ was done at a T other than the desired T ,

$$\left(\frac{dH}{dT} \right)_P = C_p \Rightarrow \Delta h = \int_{T_{combustion}}^{T_{desired}} C_p dT$$

To find S_i^f , use 3rd law and low temp calorimetry
(for finding C_p^*):

$$S_i^f = \int_{T_m}^{T_m} \frac{C_p^* dT}{T} + \frac{\Delta h_m}{T} + \int_{T_m}^{T_b} \frac{C_p^L dT}{T} + \frac{\Delta h_b}{T} + \int_{T_b}^T \frac{C_p^V dT}{T}$$

(49)

Data

<u>Volume</u>	<u>C_A</u>
—	—
—	—
—	—

$$\frac{dF_i}{dV} = r_i \quad \text{for PFR}$$

$$v \frac{dC_A}{dV} = -k C_A$$

$$\int_{C_{A0}}^{C_A} \frac{dC_A}{C_A} = \int_0^V \frac{-k}{v} dV$$

$$\ln \frac{C_A}{C_{A0}} = \frac{-k}{v} V$$

$$k = \frac{v \ln \frac{C_A}{C_{A0}}}{V}$$

Or if using differential reactor,

$$r_A = -k C_A$$

$$\text{where } -r_A = \frac{(C_{A0} - C_A)v}{W} = \frac{\text{moles reacted/time}}{\text{mass catalyst}}$$

↑ mass of catalyst

$$\therefore k = \frac{-r_A}{C_A}$$

↑ this can be taken as average $\frac{C_{A0} + C_A}{2}$
 Little error involved since C. hardly changes!!

(50) For ideal gases,

$$\Delta T_{\text{mixing}} = 0$$

$$\Delta \bar{v}_{\text{mixing}} = 0$$

$$\Delta h_{\text{mixing}} = 0$$

$$\Delta S_{\text{mixing}} = -R \sum y_i \ln y_i$$

$$\Delta g_{\text{mixing}} = -T \Delta S_{\text{mixing}} = RT \sum y_i \ln y_i$$

$$\Delta a_{\text{mixing}} = \Delta \bar{u}_{\text{mixing}} - T \Delta S_{\text{mixing}} = RT \sum y_i \ln y_i$$

V_A	V_B
n_A	n_B

$$PV = nRT$$

For ideal solutions,

$$\Delta \bar{v}_{\text{mixing}} = 0$$

$$\Delta h_{\text{mixing}} = 0$$

$$\Delta S_{\text{mixing}} = -R \sum x_i \ln x_i$$

$$\Delta g_{\text{mixing}} = RT \sum x_i \ln x_i$$

$$dG = VdP - SdT$$

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

$$dS = -\frac{nR}{P} dP$$

$$\Delta S_A = -n_A R \ln \left[\frac{\frac{n_A R T}{V_T}}{\frac{n_A R T}{V_A}} \right]$$

$$\Delta S_A = -n_A R \ln y_A$$

$$\Delta S_B = -n_B R \ln y_B$$

$$\begin{aligned} \Delta S_{\text{mixing}} &= \Delta S_A + \Delta S_B \\ &= -n_A R \ln y_A - n_B R \ln y_B \end{aligned}$$

On molar basis,

$$\Delta S_{\text{mixing}} = -R \sum y_i \ln y_i$$

⑤1 What is Raoult's Law? Henry's Law? When do they apply?

Raoult's Law states that the fugacity is proportional to the fraction of the species in the mixture. The proportionality constant being the fugacity (at mixture T and P) of the pure species.

Raoult's Law $y_i P = x_i P_i^s \exp \left[\int_{P_i^s}^P \frac{v_i^c dP}{RT} \right]$

Assumptions :

- (1) vapor phase is ideal
- (2) liquid " " "
- (3) vapor phase above pure sat - i is ideal
- (4) neglect Poynting corr. factor

$$y_i P = x_i P_i^s$$

Applies when the mixture is nearly pure i.

Henry's Law (e.g. for binary)

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

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

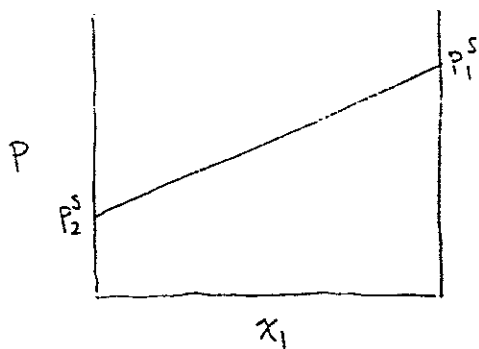
Applies when 2 is very dilute in 1.

52) Can Raoult's Law soln have 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 maxima or minima
to form azeotrope !!

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

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

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

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

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

53) Lewis fugacity rule

$$\boxed{f_i^V = y_i f_{\text{pure } i}^V \quad \text{and} \quad f_i^L = x_i f_{\text{pure } i}^L}$$

Lewis fugacity rule obtained from Amagat's Law =
 $V = \sum n_i \bar{v}_i$. Amagat's law implies that $\bar{v}_i = v$.

From Chp. 3 of Praeger's book,

$$RT \ln \frac{f_i}{y_i P} = \int_0^P \left(\bar{v}_i - \frac{RT}{P} \right) dP$$

For pure i ,

$$RT \ln \left(\frac{f_{\text{pure } i}}{P} \right) = \int_0^P \left(\bar{v}_i - \frac{RT}{P} \right) dP$$

If Amagat's law holds,

$$RT \ln \frac{f_i}{y_i P} = \int_0^P \left(\bar{v}_i - \frac{RT}{P} \right) dP = RT \ln \frac{f_{\text{pure } i}}{P}$$

$$\therefore \boxed{f_i = y_i f_{\text{pure } i}}$$

⑤④ Difference between mixing and combining rule?

Mixing rule dictates how the mixture property is obtained from composition. It is based on probability and has basis theoretically.

$\boxed{E_x}$: VdW parameter for binary mixture

$$a = \sum_i \sum_j y_i y_j a_{ij} = y_1^2 a_{11} + 2 y_1 y_2 a_{12} + y_2^2 a_{22}$$

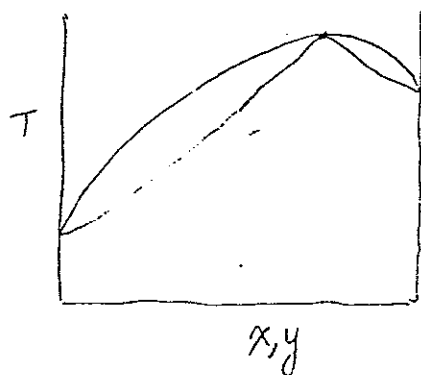
Combining rules state how "cross" parameters depend on pure component parameters. It has little theoretical basis.

$\boxed{E_x}$: VdW energy interaction parameter a_{12} for binary

$$a_{12} = \sqrt{a_{11} a_{22}}$$

- ⑤⑤. What is a maximum boiling azeotrope? Does it exhibit 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 bottoms?

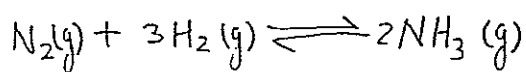
Exhibits a maximum saturation temp. This also means



that it is hardest to boil \Rightarrow which means easiest to condense, thus there's a minimum in the P vs. x diagram

It exhibits negative deviations from Raoult's law. The azeotrope will be recovered in the bottoms.

- ⑤⑥. Effect of adding an inert gas on the equilibrium between N_2 , H_2 , and NH_3 ?



Since K_{eq} depends only on T , adding inert will not affect K_{eq} .

$$K_{eq} = \frac{a_{NH_3}^2}{a_{N_2} a_{H_2}^3} = \frac{y_{NH_3}^2 P^2}{y_{N_2} P y_{H_2}^3 P^3} = \frac{y_{NH_3}^2}{y_{N_2} y_{H_2}^3 P^2} \quad \left. \vphantom{\frac{y_{NH_3}^2}{y_{N_2} y_{H_2}^3 P^2}} \right\} \text{assuming ideal gas}$$

However, adding will change the extent of reaction (how much reactants reacted). In this case, conversion decreases because less reactants have to react to produce the same K_{eq} since the conc. in the denominator

57) Derive Maxwell's relations

$$du = Tds - Pdv \Rightarrow \left(\frac{\partial T}{\partial v} \right)_s = - \left(\frac{\partial P}{\partial s} \right)_v$$

$$\begin{aligned} h &= u + Pv \\ dh &= du + Pdv + v dP \\ &= Tds + v dP \Rightarrow \left(\frac{\partial T}{\partial P} \right)_s = \left(\frac{\partial v}{\partial s} \right)_P \end{aligned}$$

$$\begin{aligned} g &= h - Ts \\ dg &= dh - Tds - s dT \\ &= \cancel{Tds} + v dP - \cancel{Tds} - s dT \Rightarrow \left(\frac{\partial v}{\partial T} \right)_P = - \left(\frac{\partial s}{\partial P} \right)_T \end{aligned}$$

$$\begin{aligned} a &= u - Ts \\ da &= du - Tds - s dT \\ &= \cancel{Tds} - Pdv - \cancel{Tds} - s dT \Rightarrow \left(\frac{\partial P}{\partial T} \right)_v = \left(\frac{\partial s}{\partial v} \right)_T \end{aligned}$$

[?] Why does azeotropy occur when γ goes from $<$ to > 1 or vice versa?
And how can you tell if γ can switch from $>$ to < 1 ?

(58) Which liquid phase eos allow for azeotropy?
For phase separation?

<u>Models</u>	<u>Azeotropy</u> (γ switches from $>$ to < 1)	<u>Phase separ.</u>	<u>Comments</u>
2-suffix Margules	<u>no ?</u>	yes	good for simple liq. mixtures of similar size, shape, structure.
3-suffix Margules	yes	yes	good for chemically dissimilar molec. whose sizes are similar
van Laar	yes	yes	good for molec. that are chemically similar but of different sizes
Wilson	yes	<u>no</u>	good for solns of polar or associating components in non-polar solvents
NRTL	yes	yes	strongly non-ideal solns. especially partially immiscible systems
Uniquac	yes	yes	anything

⑥⑩ Describe the graphical approach to reactor design and analysis.

For isothermal reactors

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

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

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

$$\frac{d}{dV} F_{A0}(1-X) = r_A$$

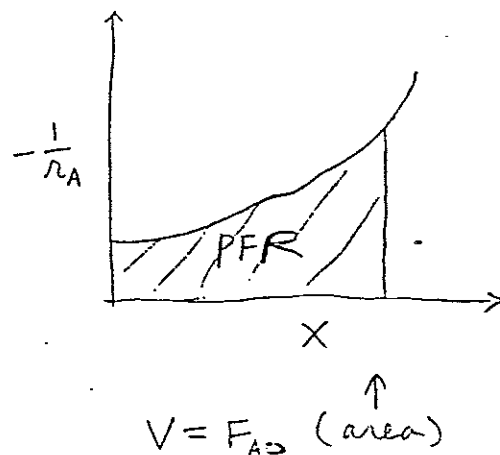
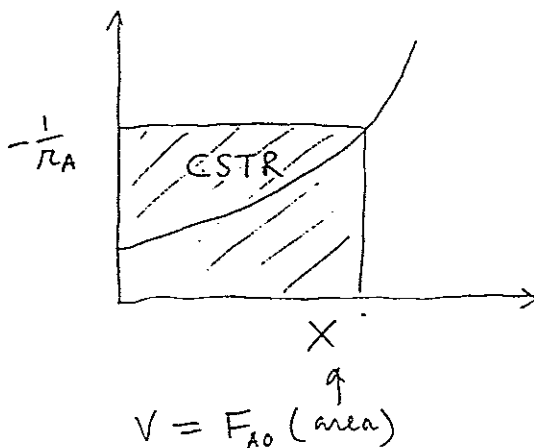
$$-F_{A0} \frac{dX}{dV} = r_A$$

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

For rxn: $nA \longrightarrow mB$

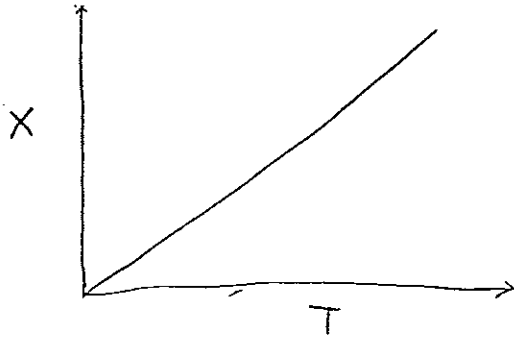
$$-r_A = k C_A^n = k [C_{A0}(1-X)]^n$$

For a given T of rxn, can get r_A 's for various X's :



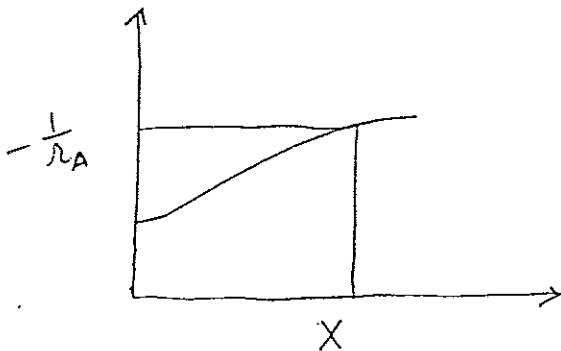
For non-isothermal reactors

(1) Make an energy balance and plot X vs. T



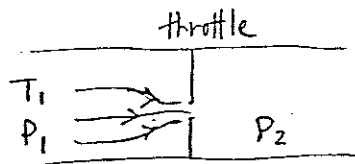
$$\text{Now, } -r_A = k [C_{A0}(1-X)]^n = A e^{\left(\frac{E_a}{RT}\right)} [C_{A0}(1-X)]^n$$

Pick X 's \Rightarrow get T 's from graph \Rightarrow calculate $-r_A$
Can plot $-\frac{1}{r_A}$ vs. X graph:



Can get volume for
CSTR or PFR !!

- ⑥ Derive expression for Joule-Thompson ^(μ) coeff. What is significance of its sign?



$$\mu_{J.T} \equiv \left(\frac{T_2 - T_1}{P_2 - P_1} \right)_h$$

↓ $\Delta's \rightarrow 0$

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

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

$$0 = C_P dT + \left[v - T \left(\frac{\partial v}{\partial T} \right)_P \right] dP$$

$$\boxed{\mu = \left(\frac{\partial T}{\partial P} \right)_h = - \frac{\left[v - T \left(\frac{\partial v}{\partial T} \right)_P \right]}{C_P}}$$

Alternately,

$$\left(\frac{\partial h}{\partial P} \right)_T \left(\frac{\partial P}{\partial T} \right)_h \underbrace{\left(\frac{\partial T}{\partial h} \right)_P}_{= \frac{1}{C_P}} = -1$$

$$dh = T ds + v dP$$

$$\left(\frac{\partial h}{\partial P} \right)_T = \left(\frac{\partial s}{\partial P} \right)_T + v = -T \left(\frac{\partial v}{\partial T} \right)_P + v$$

$$\therefore \boxed{\mu = \frac{- \left[v - T \left(\frac{\partial v}{\partial T} \right)_P \right]}{C_P}}$$

For ideal gases,

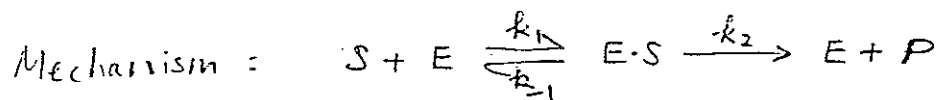
$$Pv = RT$$

$$\left(\frac{\partial v}{\partial T}\right)_P = \frac{R}{P} \Rightarrow v - \frac{TR}{P} = 0 \Rightarrow \mu = 0 !!$$

When $\mu = 0$, $T = T_{\text{inversion}}$

The sign of μ indicates the effect that changing P will bring in T . For most gases, $\mu > 0 \Rightarrow$ when $P \downarrow$, $T \downarrow$.

⑥② Derive Michaelis-Menten rate equation.



$$r = \frac{dP}{dt} = k_2 [E \cdot S]$$

M-M assumed that first step is in equilibrium !!

$$\Rightarrow K_s = \frac{k_{-1}}{k_1} = \frac{[S][E]}{[E \cdot S]}$$

$$[E]_0 = [E] + [E \cdot S] \Rightarrow [E] = [E]_0 - [E \cdot S]$$

$$K_s = \frac{[S] \{ [E]_0 - [E \cdot S] \}}{[E \cdot S]}$$

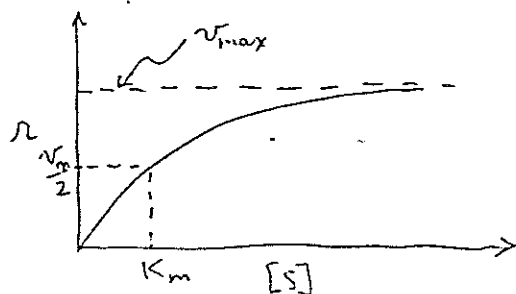
$$[E \cdot S] K_s = [S][E]_0 - [S][E \cdot S]$$

$$[E \cdot S] (K_s + [S]) = [S][E]_0$$

$$[E \cdot S] = \frac{[S][E]_0}{K_s + [S]}$$

$$\therefore r = \frac{k_2 [S][E]_0}{K_s + [S]} = \frac{[S] v_{\max}}{K_m + [S]}$$

In this case $K_s = \text{dissociation const.} = K_m$!!



63. What is the Thiele parameter? Its usefulness?

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

$$= \frac{k_n C_{AS}^n (\rho_p S_a R)}{D_e [(C_{AS} - 0)/R]} = \frac{k_n C_{AS}^{n-1} R^2}{D_e} \quad \frac{\frac{1}{s \cdot m^2} \cdot m^2}{m^2/s}$$

k_n = n^{th} order rxn. rate

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

Small $\Phi \rightarrow$ surface rxn limited; significant amount of reactant diffuses well inside the pellet without reacting.

Large $\Phi \rightarrow$ diffusion limited; most reactants consumed near the pellet surface.

(64) For series rxn $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ where $k_2 \gg k_1$,
how to maximize selectivity of B over C?

$$r_B = k_1 C_A$$

$$r_C = k_2 C_B$$

$$\text{Maximize } \frac{r_1}{r_2} = \frac{k_1}{k_2} \frac{C_A}{C_B} !!$$

Use PFR or batch because we want to maintain C_A as high as possible.

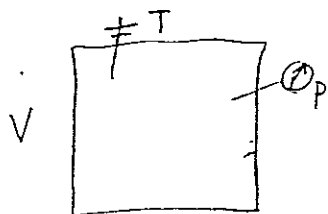
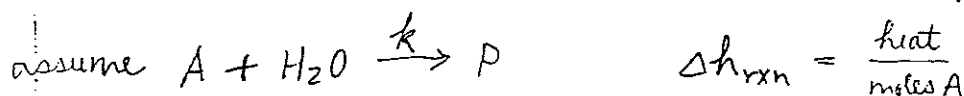
Since $k_2 \gg k_1$ and $k = A \exp\left(\frac{-E}{RT}\right)$, we suspect that:
 $E_2 < E_1$.

$$\text{So, } \frac{r_1}{r_2} = \frac{A_1}{A_2} \exp\left[\frac{(E_2 - E_1)}{RT}\right] \frac{C_A}{C_B}$$

Therefore, run at as high a T as possible !!

Also, the τ (space time) is very important.
Find τ such that $[B]$ is maximum. See #1.

- ⑥⑥ Given a closed drum of organic liquid which reacts isothermally with traces of water present in the drum, derive all the equations necessary to describe the temp. and P in the drum as function of time.



$$-r_A = k[A][H_2O]$$

rate of heat produced by rxn = $k[A][H_2O]V\Delta h_{rxn}$

Energy balance :

$$\left\{ \begin{array}{l} \text{rate of} \\ \text{change of} \\ \text{energy of} \\ \text{system} \end{array} \right\} = \frac{d}{dt} [u] \rho V$$

$$\frac{du}{dt} \rho V = \dot{Q} - \dot{V} + k[A][H_2O]V\Delta h_{rxn}$$

$[A] \approx \text{constant}$ since there is a lot of organic liquid

Need to find $[H_2O]$ as function of time :

$$\frac{d[H_2O]}{dt} = -k[A][H_2O]$$

$$\int_{[H_2O]_0}^{[H_2O]} \frac{d[H_2O]}{[H_2O]} = -k[A] \int_0^t dt$$

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

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

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

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

Assuming $C_v \approx$ constant since only trace of water and mostly organic.

$$du = C_v dT$$

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

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

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

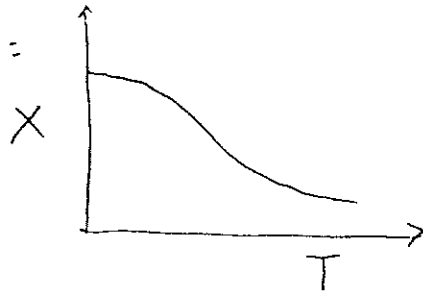
(67) Write the mass balance for CSTR with first order reaction. $A \xrightarrow{k} B$

At SS, $F_{A0} - F_A + k C_A V = 0$

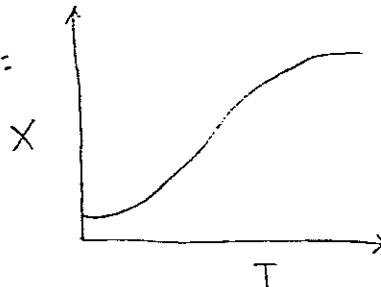
$$F_{A0} - F_{A0}(1-X) + k C_A V = 0$$

How does T affect equilibrium?

For reversible exothermic rxn =



For reversible endothermic rxn =



(68) Gibbs-Helmholtz Law: $\left(\frac{\partial (g/T)}{\partial T} \right)_P = \frac{-h}{T^2}$

$$g = h - Ts$$

$$\frac{g}{T} = \frac{h}{T} - s$$

$$\left[\frac{\partial (g/T)}{\partial T} \right]_P = \frac{h \cdot \left(\frac{\partial h}{\partial T} \right)_P}{T^2} - \frac{h}{T^2} - \left(\frac{\partial s}{\partial T} \right)_P$$

$$\left(\frac{\partial (g/T)}{\partial T} \right)_P = \frac{-h}{T^2}$$

(61) How to get rate constant from non-plug flow experimental data for 1st order rxn?