

THERMODYNAMICS, KINETICS AND CHEMICAL
FUNDAMENTALS PRELIM QUESTIONS

- ✓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?
- ✓2. For an exothermic, first order reaction, plot the extent of reaction and the reaction rate as functions of temperature.
- ✓3. When can the steady-state approximation be used?
- ✓4. What is the chemical potential?
- NEED TO ANSWER YET! 5. Experimentally how would you determine ΔH_f , ΔG_f , ΔS_f ? $\Delta H_f = C_p - T \Delta S_f$
 $C_{102} \rightarrow CO_2$
 $C_{102} \rightarrow CO_2$
 $C_{102} \rightarrow CO_2$
- ✓6. How does a refrigerator work? Sketch T-S, P-V and/or P-H diagrams. $C_{102} \rightarrow CO_2$
 $C_{102} \rightarrow CO_2$
- ✓7. How does the rate constant vary with temperature? $C_{102} \rightarrow CO_2$
 $C_{102} \rightarrow CO_2$
- OKAY... 8. Derive design equations for mass and energy for CSTR, PFR and batch reactors. $C_{102} \rightarrow CO_2$
 $C_{102} \rightarrow CO_2$
- ✓9. Define space time, space velocity and mean residence time.
- ✓10. What are the Clapeyron and Clausius-Clapeyron equations?
- ✓11. How would you calculate the adiabatic flame temperature?
12. Which type of reactor is best for a series reaction? a parallel? an autocatalytic?
- ✓13. Give the three laws of thermodynamics.
- ✓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?
- ✓15. Derive a Langmuir-Hinshelwood expression for a solid catalyzed reaction, e.g. $A + B = P$
- ✓16. Prove that $dG < 0$ for any process.
- ✓17. Prove that S tends towards a maximum.
- ✓18. What is the Gibbs mixture rule? Derive the Gibbs-Duhem relation.

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

- ✓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?
- ✓20. How do you calculate the equilibrium constant at non standard temperature and pressure?
- ✓21. Define U, H, S, G, F, and A.
- ✓22. What is a Joule-Thompson liquefaction process?
- ✓23. What is the slope of a $\ln K_{eq}$ vs. $1/T$ curve for an exo-
endothermic reaction?
- ✓24. If $dG = 0$ at equilibrium, why isn't $dG_{rxn} = 0$ for any reaction?
- ✓25. Give a physical interpretation of the activation energy.
- ✓26. Where does the Langmuir isotherm come from?
- ✓27. Why is entropy zero at 0 K?
- ✓28. How would you calculate the total volume when two equal
volumes of different liquids are mixed?
- ✓29. How would you calculate from first principles the heat capacity
of two gases, e.g. H_2 and CH_3NCO ?
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.
- ✓31. Sketch H/S, T/S, $\ln P/H$, P/T, and P/V diagrams for a pure
substance.
- ✓32. What does polytropic mean?
- ✓33. How is the concept of reaction coordinate used?
- ✓34. What is the phase rule when reactions are occurring?
- ✓35. How does absorption refrigeration work? What are suitable
characteristics of a working fluid?
- ✓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?
- Q... 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 $A + B = C$?
- ✓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?

- ✓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 the bottoms?
- ✓56. What is the effect of adding an inert gas on the equilibrium between N_2 , H_2 and NH_3 ?
- ✓57. Derive Maxwell's relations.
- ✓58. Which liquid phase equations of state allow for azeotropy? phase separation?
- ✓59. What is the corresponding states theorem? What is its significance?
- ✓60. Describe the graphical approach to reactor design and analysis.
- ✓61. Derive an expression for the Joule-Thompson coefficient. What is the importance of its sign?
- ✓62. Derive the Michaelis-Menton rate equation.
- ✓63. What is a Thiele parameter? What is its usefulness?
- ✓64. 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?
- ✓65. 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?
- Q... • 66. 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.
- Q... • 67. 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?
- ✓68. What is the Gibbs Helmholtz law? **DERIVE IT!**

- 69. How do you get the rate constant/non plug-flow experimental data for a first order reaction?
- ✓ 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?
- 71. For the reaction $A \rightarrow B$ 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?
- ✓ 72. How would one measure Gibbs free energy? enthalpy? entropy?
- ✓ 73. What are the important factors in choosing a reactor?
- ✓ 74. What is the frequency factor? A
pre-exponential factor

THERMO, KINETICS PRELIM QUESTIONS

1. series reaction - $A \xrightarrow{k_1} B \xrightarrow{k_2} P$

Amount of B determined by:

- 1) relationship between k_1 and k_2 - their dependence on T
- 2) initial concentrations of A and B
- 3) extent of mixing

maximize production of B

$$\frac{dA}{dt} = -k_1 A \Rightarrow \frac{A}{A_0} = e^{-k_1 t}$$

$$\frac{dB}{dt} = k_1 A - k_2 B = k_1 A_0 e^{-k_1 t} - k_2 B$$

$$\frac{dB}{dt} + k_2 B = k_1 A_0 e^{-k_1 t} \quad B = B_0 e^{-k_2 t}$$

$$B = e^{-k_2 t} \int e^{k_2 t} k_1 A_0 e^{-k_1 t} dt = \frac{e^{-k_2 t}}{k_2 - k_1} k_1 A_0 e^{k_2 t} e^{-k_1 t} + C$$

$$B = \frac{k_1 A_0}{k_2 - k_1} e^{-k_1 t} - C e^{-k_2 t} \quad C = \frac{-k_1 A_0}{k_2 - k_1}$$

$$B = \cancel{B_0 e^{-k_2 t}} + A_0 \frac{k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t})$$

$$\Rightarrow \frac{B}{A_0} = \frac{k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t})$$

$$\max B : \frac{\partial B/A_0}{\partial t} = 0 = \frac{k_1}{k_2 - k_1} (-k_1 e^{-k_1 t} + k_2 e^{-k_2 t})$$

$$\frac{k_1 k_2 e^{-k_1 t}}{k_2 - k_1} = \frac{k_1 e^{-k_2 t}}{1 - k_1/k_2} \quad \frac{k_1}{k_2} = e^{-(k_2 - k_1)t_{opt}}$$

$$t_0 = \frac{\ln(k_1/k_2)}{k_1 - k_2}$$

Batch and PFR

CSTR

$$A_0 V = A V + k_1 A V_R$$

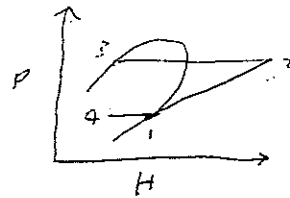
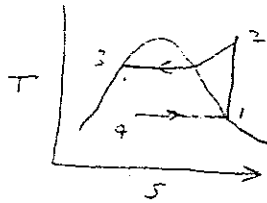
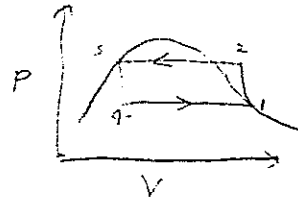
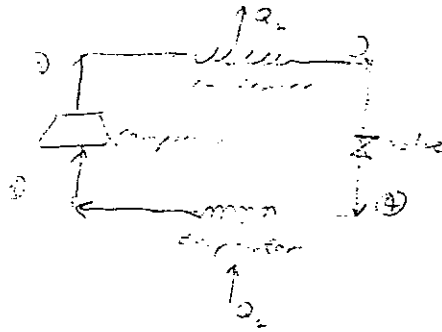
$$\frac{A}{A_0} = \frac{1}{1 + k_1 \frac{V_R}{V}} = \frac{1}{1 + k_1 \tau} \quad \tau = space \text{ time}$$

$$0 = B V + (k_2 B - k_1 A) V_R \quad B = \frac{k_1 A V_R}{V + k_2 V_R} = \frac{k_1 A \tau}{1 + k_2 \tau} = \frac{k_1 A_0 \tau}{(1 + k_2 \tau)(1 + k_1 \tau)}$$

$$\frac{B}{A_0} = \frac{k_1 \tau}{(1 + k_2 \tau)(1 + k_1 \tau)}$$

$$\frac{d}{d\tau} \left(\frac{B}{A_0} \right) = 0 \Rightarrow \tau_0 = \frac{1}{\sqrt{k_1 k_2}} \quad \checkmark$$

6. Refrigerant is compressed ($1 \rightarrow 2$), then condensed by rejecting heat to the atmosphere ($2 \rightarrow 3$). Next the liquid is expanded through a valve ($3 \rightarrow 4$) and then evaporated, pulling heat from the air we want to refrigerate.



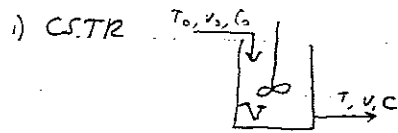
7. Rate constant $k = k(T)$

Arrhenius $k = k_0 e^{-E/RT}$

Collision theory $k = k_1 T^{1/2} e^{-E/RT}$

Transition state theory $k = k_2 T e^{-E/RT}$

8. Reactor Design equations.



Mass balance

$$I_n = O_{ut} + R_{xn} + A_{ccum}$$

$$v_0 C_0 = v C + R V + 0$$

$$V = \frac{v_0 C_0 - v C}{R}$$

Heat balance

$$v_0 (C_p) \cdot T_0 = v C_p T + R V (-\Delta H') + V C_p \frac{dT}{dt}$$

9. Space time - time required to process one reactor volume of feed

Space velocity - inverse of space time

Residence time - amount of time during which individual portions of mixture stay in the reactor

10. Clapeyron equation - latent heat of phase change related to properties

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

derivation: $dG^L = dG^V$

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

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

Clausius-Clapeyron eqn - latent heat of vaporization related to

vapor pressure curve - assumes ideal gas and $\Delta V^{LR} = V^V$

$$\Delta V^{LR} = \frac{RT}{P^{sat}}$$

$$\Delta H = \frac{RT^2}{P^{sat}} \frac{dP^{sat}}{dT}$$

$$\frac{dP^{sat}}{P^{sat}} = d \ln P^{sat}$$

$$\frac{dT}{T^2} = -d(1/T)$$

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

11. adiabatic flame T

1) guess T

2) solve for composition of products

3) heat liberated = $\sum y_i \Delta H_{f,i}^{\circ}(\text{prod}) + (-\Delta H_{f,i}^{\circ})_{\text{fuel}} \times n_{\text{fuel}} - \sum y_i \Delta H_{f,i}^{\circ}(\text{reactants})$

4) compare w/ heat reqd to heat products to T

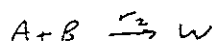
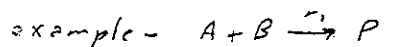
5) If heat lib > heat req then $T_2 > T$

If heat lib < heat req then $T_2 < T$

12. Optimal reactors

Series reaction: PFR or Batch - keeps lower concentration of intermediates because of low mixing - can cut off reaction at peak intermediate concentration, keeps high conc. of initial reagent

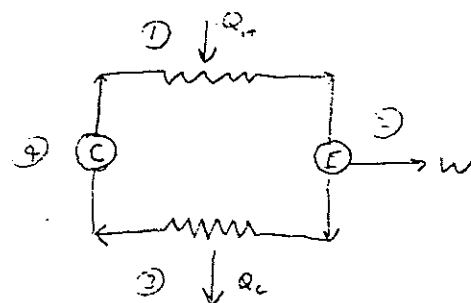
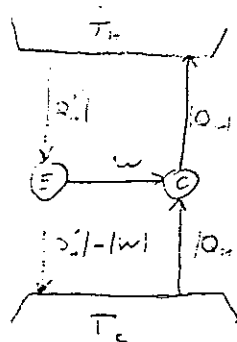
Parallel reaction: depends on reaction kinetics



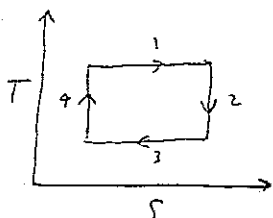
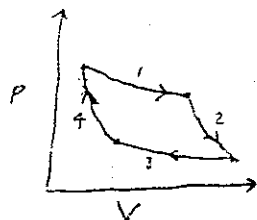
if $E_1 > E_2$ use high T

if $E_2 > E_1$ use low T

14. Heat engine



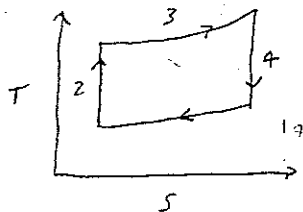
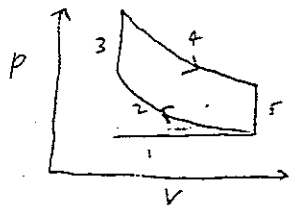
- Carnot
- ① Isothermal expansion with absorption of Q_H
 - ② Adiabatic expansion from $T_H \rightarrow T_C$
 - ③ Isothermal compression with rejection of Q_C
 - ④ Adiabatic compression from $T_C \rightarrow T_H$



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

Otto

- ① Intake at constant P
- ② ~ Adiabatic compression
- ③ Rapid, constant V compression - combustion
- ④ ~ Adiabatic expansion - produce W
- ⑤ Rapid, constant V expansion

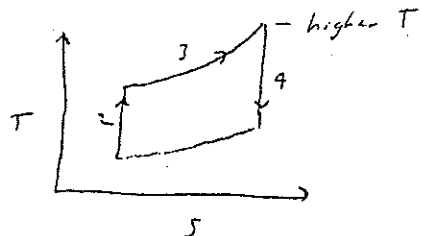
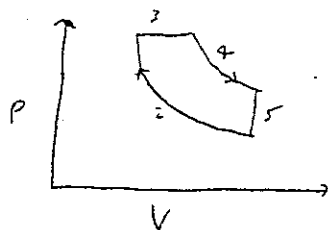


$$\eta = 1 - \left(\frac{1}{r}\right)^{\gamma-1}$$

r = compression ratio (step 2)

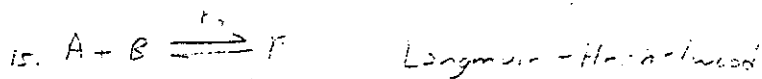
Diesel

Combustion step occurs at constant P



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

r_c = expansion ratio (step 4)



- monolayer coverage
- all sites equivalent
- one molecule per site
- same energy of adsorption at each site

mass balances; \underline{A} $k_{1A} P_A (1 - \theta_A - \theta_B) = k_{-1A} \theta_A + k_{-2} \theta_A \theta_B$

\underline{B} $k_{1B} P_B (1 - \theta_A - \theta_B) = k_{-1B} \theta_B + k_{-2} \theta_A \theta_B$

rate of \downarrow = rate of \downarrow + rate of rxn

assume $\theta_A \theta_B \ll \theta_A$ or θ_B

$$\theta_B = \frac{k_{1B} P_B (1 - \theta_A)}{k_{-1B} + k_{-2} P_A}$$

$$k_{1A} P_A (1 - \theta_A) \left(1 - \frac{k_{1B} P_B}{k_{-1B} + k_{-2} P_A} \right) = k_{-1A} \theta_A$$

$$K_A = \frac{k_{1A}}{k_{-1A}} \quad K_B = \frac{k_{1B}}{k_{-1B}}$$

$$K_A P_A (1 - \theta_A) \left(1 - \frac{K_B P_B}{1 + K_B P_B} \right) = \theta_A$$

$$\theta_A = \frac{K_A P_A}{1 + K_A P_A + K_B P_B}$$

$$\theta_B = \frac{K_B P_B (1 + K_A P_A + K_B P_B - K_A P_A)}{(1 + K_A P_A + K_B P_B) (1 + K_B P_B)}$$

$$\theta_B = \frac{K_B P_B}{1 + K_A P_A + K_B P_B}$$

$$\text{rate} = k_2 \theta_A \theta_B = \frac{k_2 K_A K_B P_A P_B}{(1 + K_A P_A + K_B P_B)^2}$$

16. $dS_{\text{sur}} = \frac{dQ_{\text{sur}}}{T_{\text{sur}}} = -\frac{dQ}{T}$

$2^{\text{nd}} \text{ law } dS + dS_{\text{sur}} \geq 0$

$dS - \frac{dQ}{T} \geq 0$

$dQ \leq T dS$

$1^{\text{st}} \text{ law } dU = dQ - P dV$

$dQ = dU + P dV \leq T dS$

$dU + P dV - T dS \leq 0$

at const T, P $(dU)_{T,P} + d(PV)_{T,P} - d(TS)_{T,P} = d(\overbrace{U + PV - TS}^G)_{T,P} \leq 0$

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

17. Prove 2nd law of thermo.

consider 2 heat reservoirs w/ transfer of $|Q|$ between them

$$\Delta S_H = \frac{-|Q|}{T_H} \quad \Delta S_C = \frac{|Q|}{T_C}$$

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

$$T_H > T_C \Rightarrow \Delta S_T > 0$$

this a proof by example; any example would give the same result

18. Gibbs mixture rule (phase rule)

$$F = C - P + 2$$

F = Deg. of freedom
 C = # constituents

P = phases

Gibbs/Duhem Eqn

extensive property M

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

$$\bar{m}_i = \left(\frac{\partial M}{\partial n_i} \right)_{T,P,n_j}$$

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

$$n \left(dM - \left(\frac{\partial M}{\partial T} \right)_{P,n} dT - \left(\frac{\partial M}{\partial P} \right)_{T,n} dP - \sum \bar{m}_i dx_i \right) + \underbrace{(M - \sum \bar{m}_i x_i)}_0 dn = 0$$

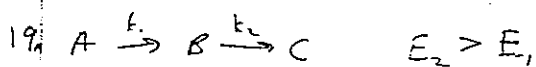
$$M = \sum x_i \bar{m}_i$$

$$dM = \sum (x_i d\bar{m}_i + \bar{m}_i dx_i)$$

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

@ const T, P

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



maximize production of B

want $\frac{k_1}{k_2}$ to be max

$$\frac{k_1}{k_2} = \frac{k_1^0 e^{-E_1/RT}}{k_2^0 e^{-E_2/RT}} = \frac{k_1^0 \exp[(E_2 - E_1)/RT]}{k_2^0}$$

$(E_2 - E_1) > 0$, thus we need low T to increase $\frac{k_1}{k_2}$

so low T would maximize the production of B

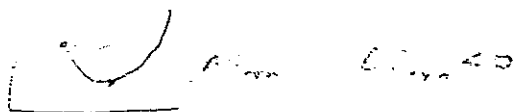
23. $\frac{\partial \ln K}{\partial T} = \frac{\Delta H}{T^2}$ $\frac{\partial \ln K}{\partial (1/T)} = -\Delta H$

slope negative for exothermic ($\Delta H < 0$)

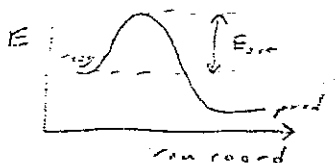
slope positive for endothermic ($\Delta H > 0$)

24. $\Delta G_m = 0$ because the process tends to be at a minimum

ΔG_m is the change in free energy per mole of substance from reactants to products

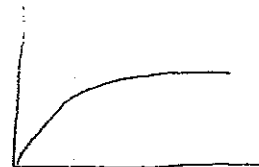


25. Activation energy - height of potential barrier which the reactants must overcome to react



26. Langmuir adsorption isotherm

- 1) Molecules are adsorbed at discrete sites
- 2) Monolayer coverage - max
- 3) Energy of adsorption depends on some organization on surface
- 4) Adsorption occurs by collision of gas phase molecules with vacant sites
- 5) desorption rate depends on amount of material on surface



27. Entropy is zero at 0K by definition from the 3rd law of thermo.

This is only true for pure crystalline solids.

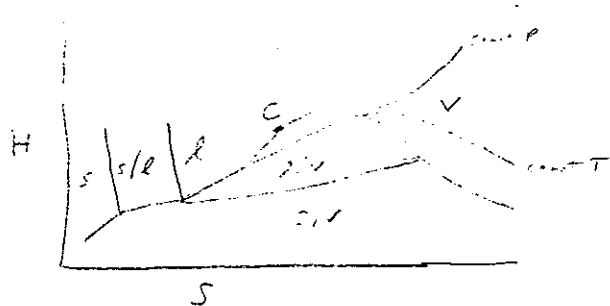
28. $V = \sum n_i \bar{V}_i = n_1 \bar{V}_1 + n_2 \bar{V}_2 - (n_1 + n_2) \Delta \bar{V}_{mix}$

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

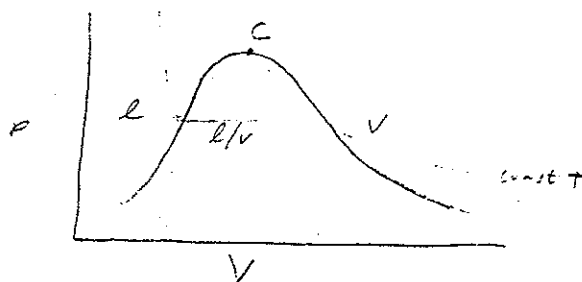
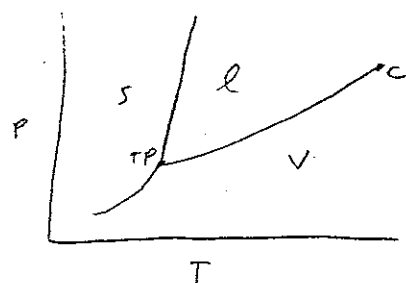
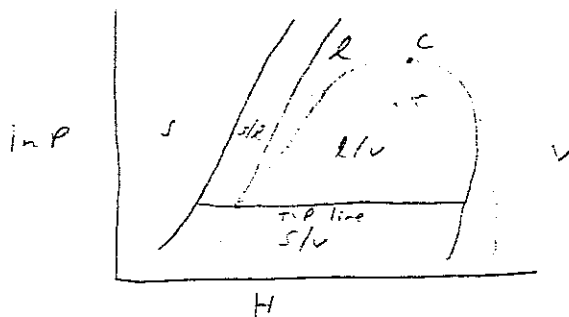
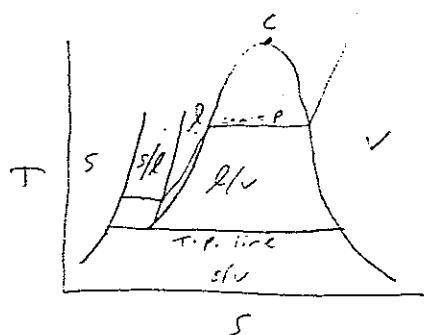
29. Calculate heat capacity from 1st principles

$C_p = C_v + R$ $C_v = \frac{1}{2} R f$ $f = \# \text{ degrees of freedom} = 3 \times \# \text{ atoms} -$

31.



(Mollier Diagram)



32. only mechanical equilibrium is important

only the general equations applying to an ideal gas apply
multidimensional

33. Reaction coordinate - expresses how far a reaction has progressed.
for example, it is used to plot the energy of reaction over the
progression of the reaction

34. Phase rule w/ reaction:

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

$$R = \# \text{ rxns}$$

38. Extent of reaction is not tied to a particular species

$$\xi = \frac{n_i - n_{i,0}}{\nu_i}$$

Conversion - $f = \frac{r_i - n_{i,0}}{r_{i,0}}$

39. Freon as refrigerant

- 1) large latent heat; need smaller fluid flow
- 2) want steep saturated vapor line on T-S diagram to keep avg. T of heat rejection small
- 3) low pressure not too low } pressure levels
high pressure not too high
- 4) Non-toxic, non-corrosive, non-flammable
- 5) No freeze-ups (evaporator T above freezing pt @ condenser operating P)

40. Activity $a = \frac{f_i}{f_i^\circ}$ is the fugacity relative to standard state fugacity. For ideal gases, $f_i^\circ = P$

$$K = \prod (a_i)^{\nu_i}$$

41. Fugacity: has dimensions of pressure (corrected pressure)

defines Gibbs energy $dG \equiv RT \ln f$

Calculation of fugacity of species i , f_i :

gas: $RT \ln \frac{f_i}{y_i P} = \int_0^P (\bar{V}_i - \frac{RT}{P}) dP$

liquid: $f_i = x_i \gamma_i P_i^\circ \phi_i^\circ (P, C)$

42. Remember Langmuir-Hinshelwood rate expression derived in

15.

$$r = \frac{k_2 K_A P_A K_B P_B}{(1 + K_A P_A + K_B P_B)^2} \quad \text{if } K_B P_B \gg 1 + K_A P_A$$

$$\Rightarrow r = \frac{k_2 K_A P_A}{K_B P_B}$$

as P_B goes up, rate goes down!

46. Fluidized bed reactors

gas reacts with solid particles suspended in a fluidized bed

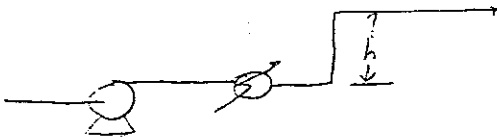
advantages

- no hot spots
- good heat transfer
- fluid like, no transfer of solids from one bed to another
- high burning rates
- uniform temperature
- easy replacement of catalyst in reactor
- good contact of gas and solid

disadvantages

- can't use catalysts which agglomerate or don't flow freely
- need extensive solid collection system
- larger pressure drop
- erosion of internals more likely
- fluid flow deviates from plug flow

47.



Enthalpy changes:

pump - $\Delta H = V\Delta P$

HX - $\Delta H = Q$

step h - $\Delta H = -\rho gh$

48. Find K_p for $A + B \rightleftharpoons C$ w/out experiment

find $\Delta H_{rxn}(T)$ from tables

$$\frac{2 \ln K}{2T} = \frac{\Delta H}{2T^2} \Rightarrow \boxed{K(T)} \quad \text{Van't Hoff eqn.}$$

49.

50. Property changes of mixing

$$\Delta V_{mix}$$

$$\Delta H_{mix}$$

$$\Delta S_{mix}$$

$$\Delta G_{mix}$$

ideal gas

$$0$$

$$0$$

$$-R \sum y_i \ln x_i$$

$$RT \sum y_i \ln y_i$$

ideal solution

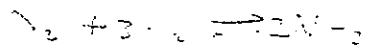
$$0$$

$$0$$

$$-R \sum x_i \ln x_i$$

$$RT \sum x_i \ln x_i$$

55. Add more N_2 to the system



add inert, will push the equilibrium toward NH_3 because total moles decrease

$$K_p = \frac{P_{NH_3}^2}{P_{N_2} P_{H_2}^3} = \frac{y_{NH_3}^2}{y_{N_2} y_{H_2}^3} P^{-2} \quad \text{if } P \text{ is constant, } K_p \text{ is constant}$$

57. Thermodynamic Relations

$$dU = TdS - PdV \Rightarrow dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

$$\frac{\partial U}{\partial S} = T \quad \frac{\partial U}{\partial V} = -P$$

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

$$dG = -SdT + VdP \Rightarrow \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

$$dH = TdS + VdP \Rightarrow \left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S$$

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

58. Binary liquid equations of state

1) Ideal liq. mixture $G^E = 0$, $\gamma_i = 1$ No entropy or immiscibility

2) 2-suffix Margules: $G^E = AX_1X_2$ $\ln \gamma_i = \frac{A}{RT} X_j^2$

entropy immisc

suitable for similar size, shape, chemical nature

3) Van Laar $\frac{G^E}{RT} = \frac{2\alpha_{12} X_1 X_2 q_1 q_2}{X_1 q_1 + X_2 q_2}$ $\ln \gamma_i = \frac{A_i}{\left(1 + \frac{A_i X_i}{C X_j}\right)^2}$

entropy immisc

4) 3-suffix Margules $\ln \gamma_i = AX_2^2 + BX_2^3$ entropy immisc

5) Wilson entropy no immisc esp. for polar in non-polar soln.

6) Scatchard-Hildebrand (regular soln) entropy immisc

$$\text{anything non-polar} \quad RT \ln \gamma_i = V_i \Phi_2^2 (\delta_i - \delta_2)^2$$

7) Flory-Huggins entropy immisc soln of molecules that differ greatly in size

$$\mu_{T-} = \left(\frac{\partial \mu}{\partial T} \right)_P = - \frac{\partial H}{\partial T} = - \frac{\partial H}{\partial T} = -$$

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

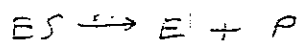
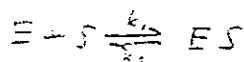
$$\mu_{T-} = - \frac{1}{T} \left(\frac{\partial H}{\partial T} \right)_P = - \frac{C_P}{T} \quad \text{if } \mu = -kT \ln S$$

$$\mu_{T-} = - \frac{1}{T} \left(V + T \left(\frac{\partial S}{\partial T} \right)_P \right) \quad \frac{\partial \mu}{\partial T} = - \left(\frac{\partial \mu}{\partial T} \right)_P$$

$$\mu_{T-} = - \frac{1}{T} \left(V - T \left(\frac{\partial S}{\partial T} \right)_P \right)$$

Sign of J-T coeff tells how fluid changes w/ expansion or comp.

62. Michaelis-Menton \rightarrow enzyme catalysis



$$\frac{d[P]}{dt} = k_2 [ES]$$

$$\frac{d[ES]}{dt} = k_1 [E][S] - k_{-1} [ES] - k_2 [ES] = 0$$

$$[ES] = \frac{k_1 [E][S]}{k_{-1} + k_2}$$

$$V = \frac{k_2 [ES]}{k_{-1} + k_2}$$

$$[E]_0 = [E] + [ES] \quad [S]_0 = [S] + [ES]$$

$$[E]_0 \ll [S]_0 \Rightarrow [ES] \ll [S] \Rightarrow [S] = [S]_0$$

$$\frac{d[ES]}{dt} = k_1 ([E]_0 - [ES]) [S]_0 - k_{-1} [ES] - k_2 [ES] = 0$$

$$[ES] = \frac{k_1 [E]_0 [S]_0}{k_{-1} [S]_0 + k_2 + k_1}$$

$$V_0 = \frac{k_2 [ES]}{k_{-1} [S]_0 + k_2 + k_1}$$

$$k_2 [E]_0 = V_{max}$$

$$\frac{k_{-1} + k_2}{k_1} = K$$

$$V_0 = \frac{V_{max} [S]_0}{K + [S]_0}$$

63. Thiele modulus \rightarrow 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

67. CSTR - first order

$$F_{A0} (1 - f_{Ain}) = F_{A0} (1 - f_{Aout}) - (-r_A) V_R$$

$$F_{A0} (f_{Aout} - f_{Ain}) = k C_A V_R$$

$$k = k_0 e^{-E/RT} \leftarrow T\text{-effect}$$

$$\tau = \frac{V_R}{v_0} = \frac{C_{A0} - C_A}{k f_{Aout}}$$

$$C_{Aout} = \frac{C_{A0}}{1 + k\tau}$$

Le Chatelier's principle

$T \uparrow$ conv \uparrow for endo

$T \uparrow$ conv \downarrow for exo

for endo
 $\uparrow T$, $C_{Aout} \uparrow$, \therefore shift of reaction position
 for exo
 $\uparrow T$, $C_{Aout} \downarrow$, increase conv.

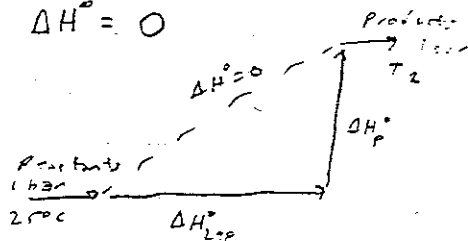
68. Gibbs-Helmholtz law

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

69.

70. Adiabatic flame T

$$\Delta H^\circ = 0$$



$$\Delta H_{298}^\circ + \Delta H_p^\circ = \Delta H^\circ = 0$$

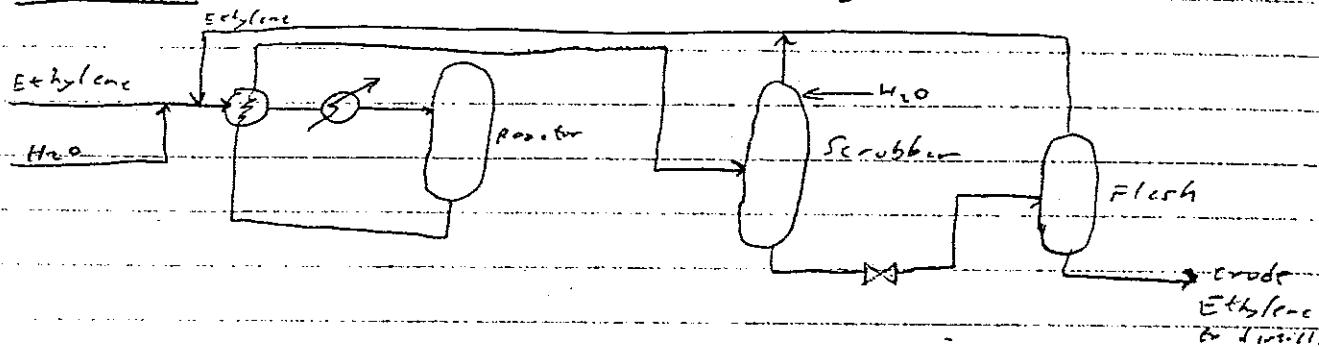
$$\Delta H_p^\circ = (\sum n_i C_{p,i}^\circ) (T_2 - 298.15) = -\Delta H_{298}^\circ$$

use iteration scheme since $C_{p,i}$ depends on T_2

$$T_2 = \frac{-\Delta H_{298}^\circ}{\sum n_i C_{p,i}^\circ} + 298.15$$

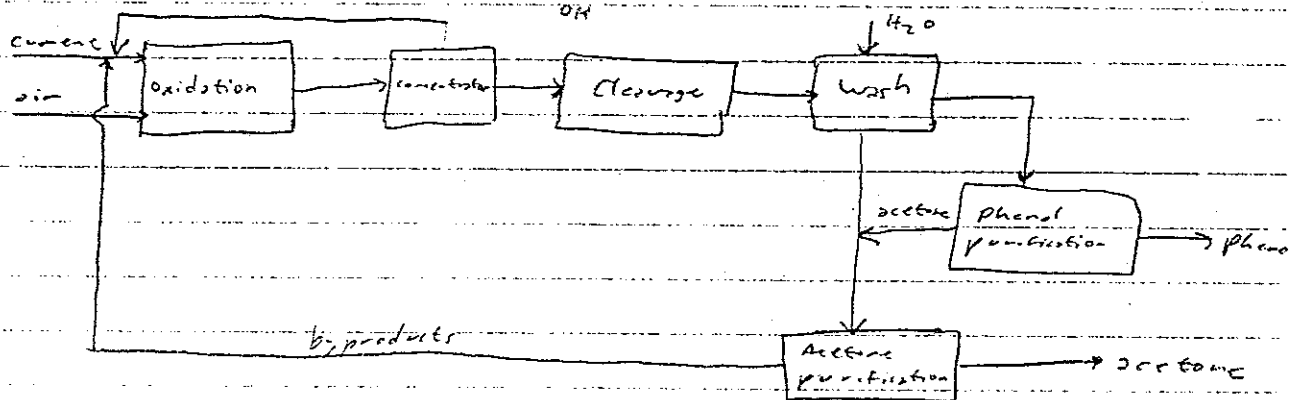
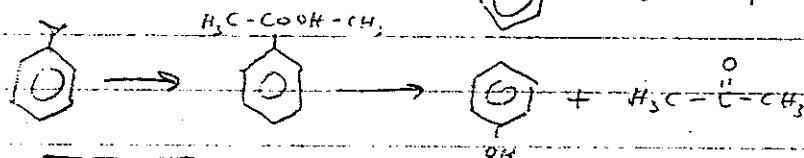


g) $\text{CH}_2\text{CH}_2\text{OH}$: hydration or fermentation of ethylene



r) acetone: $\text{CH}_3 - \overset{\text{O}}{\parallel} - \text{CH}_3$

oxidation of cumene get phenol and acetone

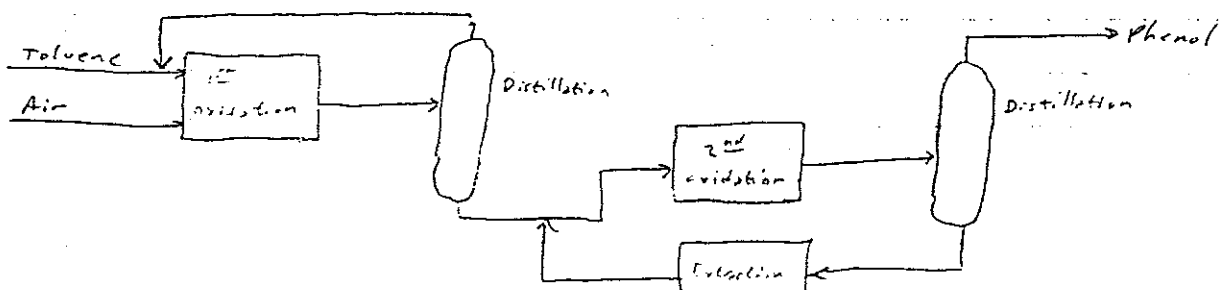
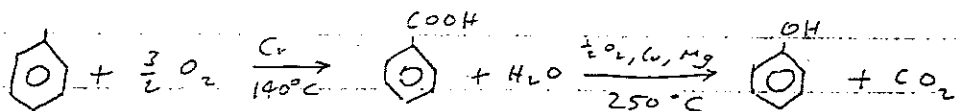


s) benzene: i) separated from aromatic streams from refineries

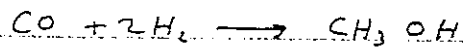
ii) dealkylation of toluene

t) phenol: i) oxidation of cumene, see acetone

ii) oxidation of toluene

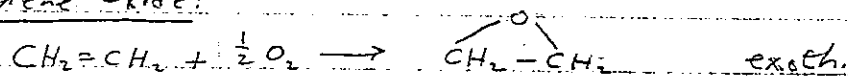


j) CH₃OH: syn gas products reacted over methanol catalyst (V)

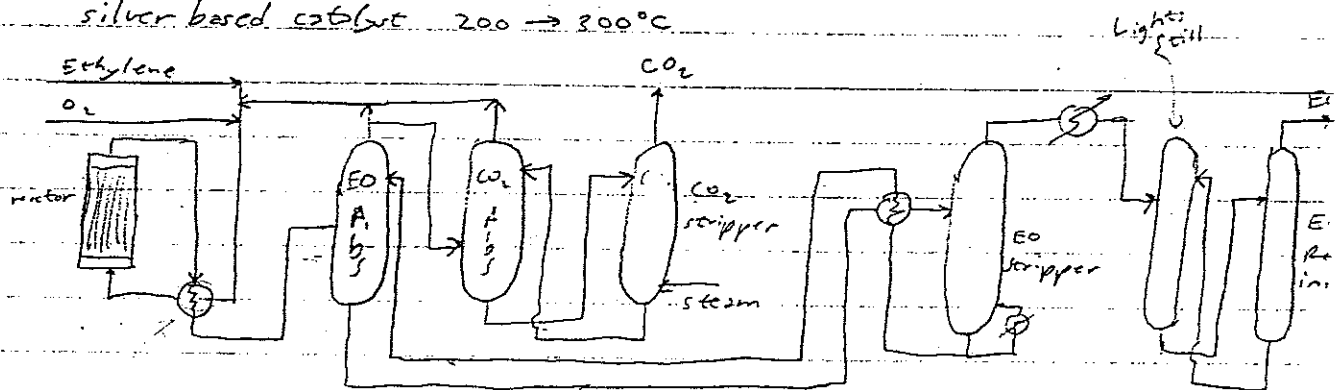


k) H₃PO₄: react phosphate rock with H₃PO₄/H₂SO₄ mixture

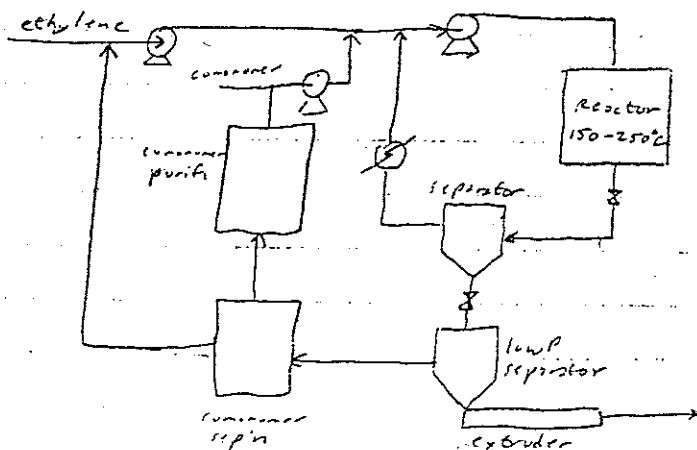
l) Ethylene Oxide:

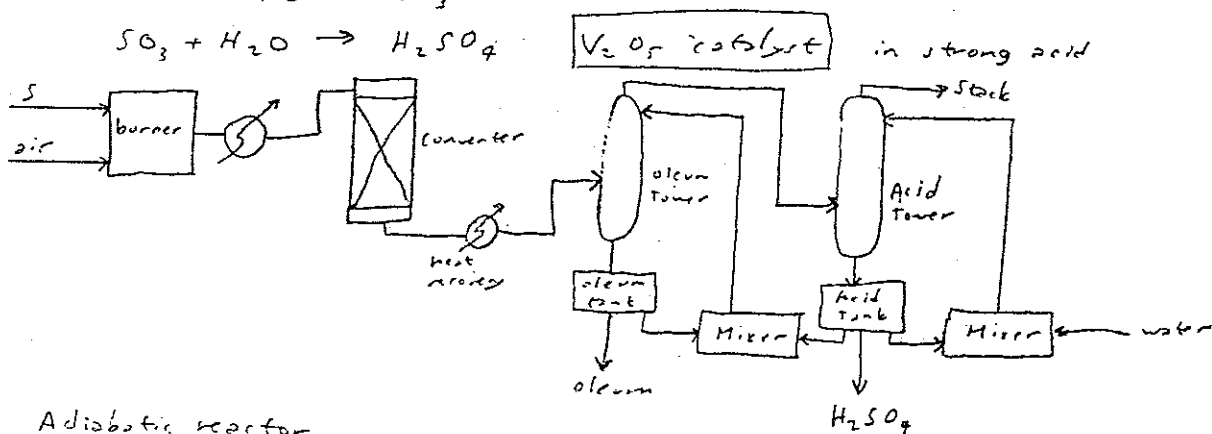
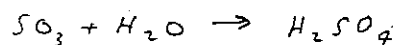
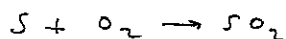
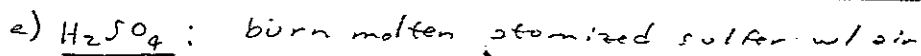
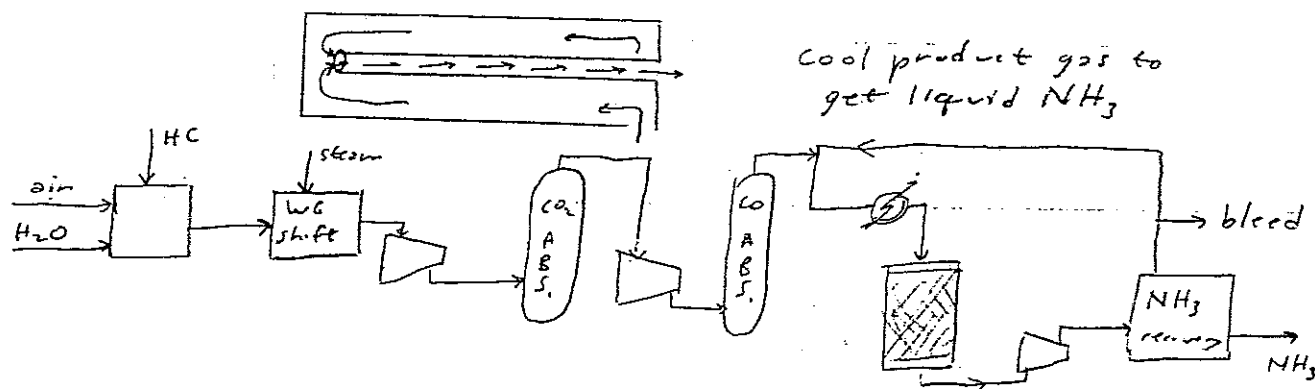
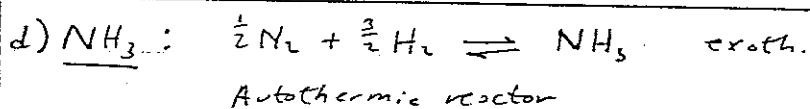
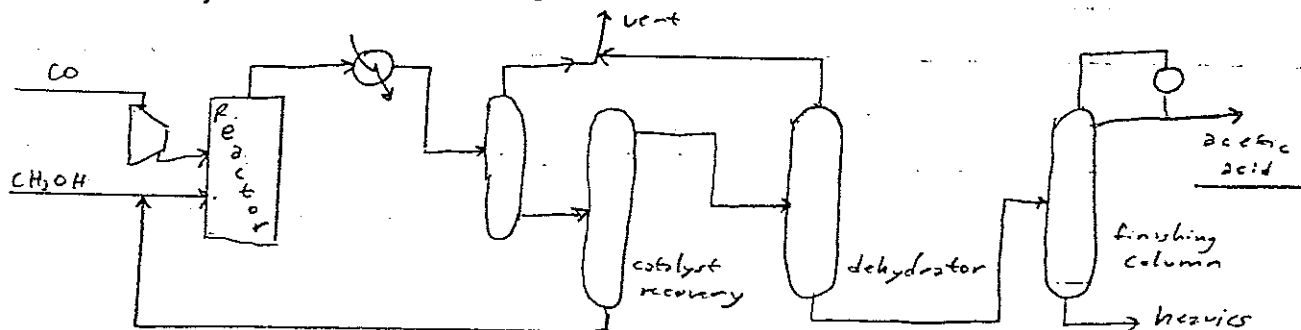
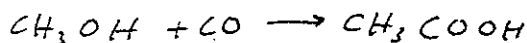
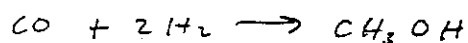
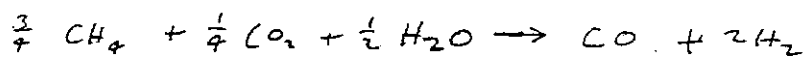


silver based catalyst 200 → 300°C



m) Polyethylene Ziegler Natta Catalysts





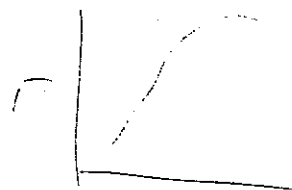
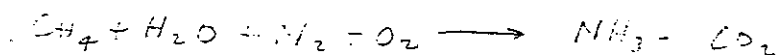
Adiabatic reactor

Feed @ $410^\circ\text{F} \rightarrow 600^\circ\text{F}$ 60-70% conv.

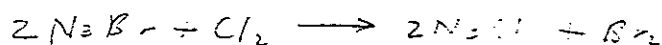
Cooled to $\sim 430^\circ\text{F}$ and then reheat.

77-98% conv.

1. water gas shift followed by reaction with nitrogen over iron oxide catalyst



3. Bubble Cl_2 through solution to reduce NaBr



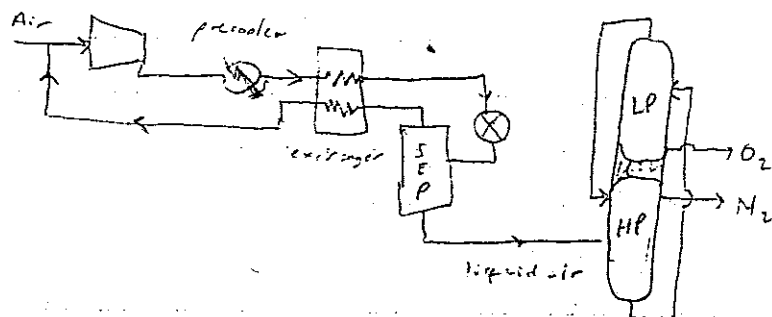
Cl^- is more e-negative so it prefers to be in ionic form

4. Iodine comes from seaweed or kelp.

5. Use a turbine to recover mechanical work from geothermal steam. T & P - must not be low enough T to allow condensation; don't want to run too far into vacuum region.

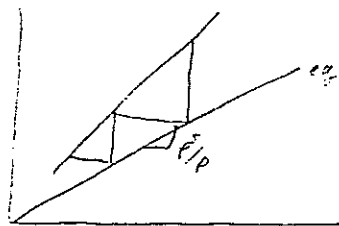
The CO_2 can be left in the system; it won't harm the turbine.

6. Cryogenic distillation

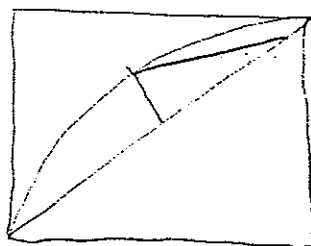


7. non-volatile organic oil
absorption

8. Raoult's Law $p_i = x_i P_i^{\text{sat}}$



9.



$$\left(\frac{L}{V}\right)_{\min} = R_{\min}$$

$$R = 1.4 R_{\min}$$

10. Height of absorption column

$$Z = (NTU)(HTU) = \frac{V/S}{k_y a} \int_0^b \frac{dy}{y - y^*}$$

S = cross section

V = molar flow rate

$k_y a$ = overall mass transfer coefficient

$$\frac{1}{k_y a} = \frac{1}{k_{y,i} a} + \frac{m}{k_{x,i} a}$$

m = slope of equil. line

a = contact area factor

11. Gas and liquid resistances

$$\frac{1}{K_{y,i} a} = \frac{1}{k_{y,i} a} + \frac{m}{k_{x,i} a}$$

$$\frac{1}{K_{x,i} a} = \frac{1}{k_{x,i} a} + \frac{1}{m k_{y,i} a}$$

12. Distill CH_3Br -oil mixture

Use extractive distillation with steam as extractant

13. bubble through water to remove CO_2 from air

14. refrigerate air to liquefy $\text{O}_2 + \text{N}_2$, get H_2 (+ Ar)

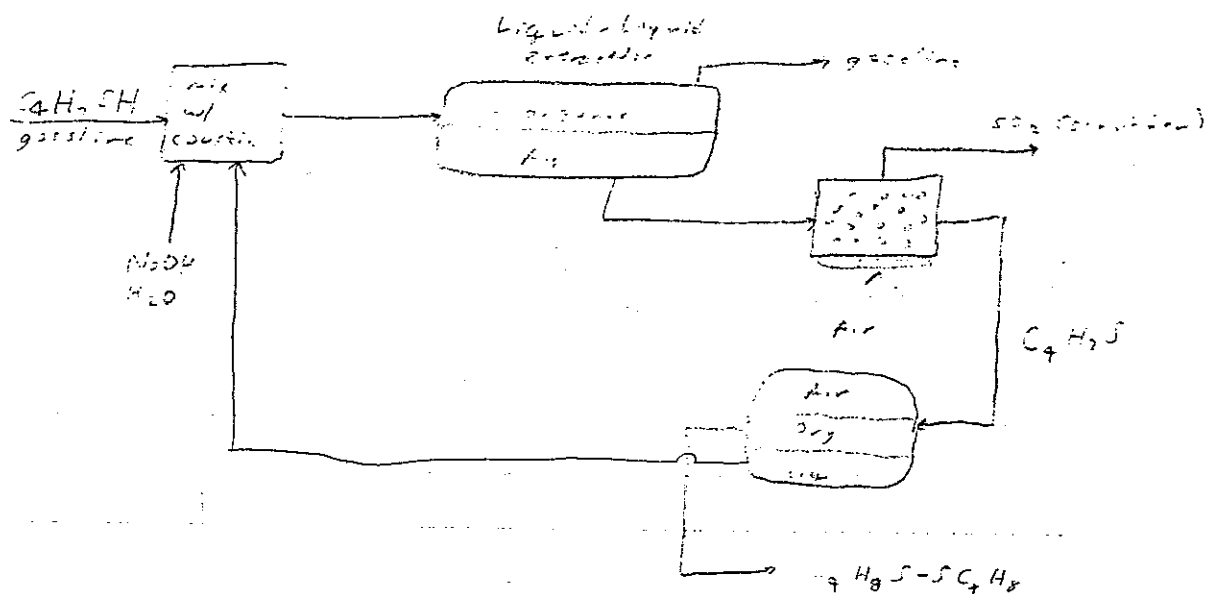
15. steam reforming of natural gas
partial oxidation of hydrocarbons

18. mercaptans C_4H_9SH

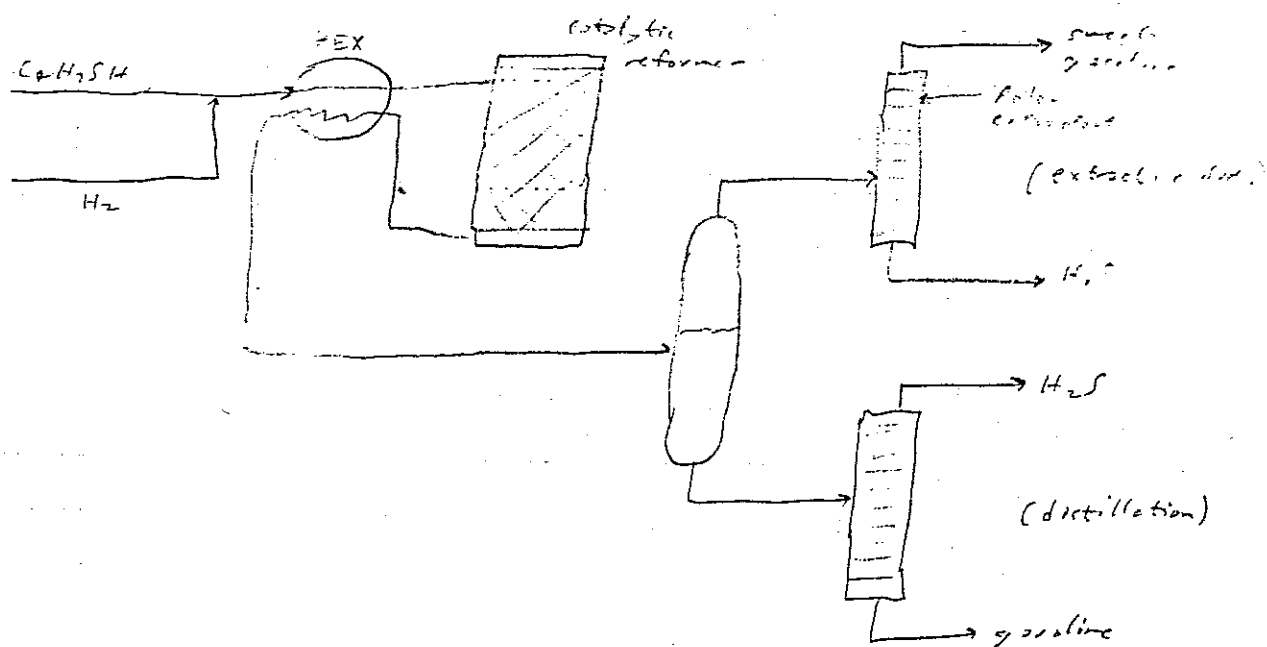
used to give gasoline its odor
(easy to smell)

to separate from light hydrocarbons

①

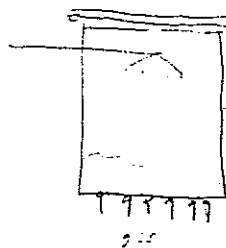


② Convert sulfur to H_2S



Peter's Questions

- 16) \exists a positive ΔT
to wet bulb T in countercurrent cooling tower
still need to cool further



Serrouni principle: lowers P in tower, allowing more evaporation

$$P_A \approx \gamma P$$

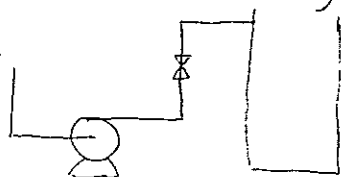
(Raoult's law)

$$P_A(T) \text{ const. w/ } P$$

- 20) use solid lubricant - graphite, teflon

21)

$$22) \quad \frac{1}{2}(V_2^2 - V_1^2) + \frac{P_2 - P_1}{\rho} + g(h_2 - h_1) = W - l_v$$



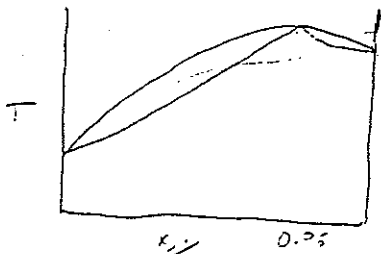
$$\frac{1}{2}(V_2^2 - V_1^2) + C = W$$

as downstream velocity V_2 decreases,
work must increase to keep up the pressure
drop and overcome some viscous losses

\therefore power consumption would increase

Don't put valve at inlet because pressure might decrease enough to
vaporize the feed and thus cause cavitation in the pump

24.



Azeotrope at $\sim 96\%$

add benzene to do extractive distillation