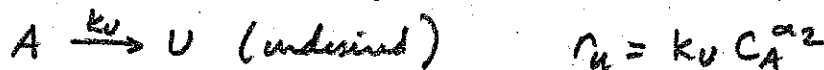1. For a series (parallel) reaction, what variables influence the amount of intermediate formed? How would you maximize the production of intermediate in a CSTR, PFR, or batch reactor?

For the case of parallel reactions

$$A \xrightarrow{k_D} D \text{ (desired)} \qquad r_D = k_D C_A^{\alpha_1}$$

$$A \xrightarrow{k_U} U \text{ (undesired)} \qquad r_U = k_U C_A^{\alpha_2}$$

$$-r_A = r_D + r_U = k_D C_A^{\alpha_1} + k_U C_A^{\alpha_2}$$

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

For $\alpha_1 > \alpha_2$, the reaction order desired is larger then that of undesired.

$$\alpha_1 - \alpha_2 = a$$

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

We want the concentration of A as high as possible. If gas phase, run it without inerts and at high pressures to keep C_A high. If liquid, use of diluents should be kept to a minimum.

A batch or plug flow reactor should be used in this case, because the conc. of A starts high and drops progressively throughout the reaction.

For $\alpha_2 > \alpha_1$, the concentration of A should be as low as possible. A CSTR should be used. A recycle reactor in which the product stream acts as diluent could be used to maintain entering A as low as possible.

Also we can look at

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

For $E_D > E_U$, the rate of reaction increases more rapidly with increasing temp. Keep temp. high.

For $E_U < E_D$, keep temp. low, but not so low as to preclude reaction.

For a series reaction, it is necessary to develop the equations for reactor design:

Batch reactor:

$$\frac{dN_A}{dt} = r_D V \qquad \text{for catalyst simply} \quad \frac{dN_A}{dt} = r_A' W$$

$$\frac{dC_A}{dt} = r_D$$

$$-r_D = k_D C_A$$

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

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

$$\ln\left(\frac{C_A}{C_{AO}}\right) = -k_D t$$

$$C_A = C_{AO}\, \exp\left(-k_D t\right)$$

$$\frac{dN_D}{dt} = -r_U + r_D$$

$$\frac{dC_D}{dt} = k_D C_A - k_U C_D = k_D C_{AO}\, \exp\left(-kt\right) - k_U C_D$$

$$\frac{dC_D}{dt} + k_U C_D = k_D C_{AO}\, \exp\left(-k_D t\right)$$

$$\frac{d}{dt}\left[C_D \exp\left(k_U t\right)\right] = k_D C_{AO}\, \exp\left[(k_U - k_D)t\right]$$

where integrating factor is $\exp\left(\int k_U dt\right)$.

$$C_D \exp\left(k_U t\right) = k_D C_{AO} \int_0^t \exp\left[(k_U - k_D)t\right] dt$$

$$= k_D C_{AO}\left[\frac{\exp(k_U - k_D)t - 1}{k_U - k_D}\right]$$

$$C_D = k_D C_{AO} \left[\frac{\exp(-k_D t) - \exp(-k_u t)}{k_u - k_D} \right]$$

We can solve for the optimum time when $\frac{dC_D}{dt} = 0$

$$\frac{dC_D}{dt} = \frac{k_D C_{AO}}{k_u - k_D} \left[-k_D \exp(-k_D t) + k_u \exp(-k_u t) \right] = 0$$

$$\exp(k_D - k_u) t = \frac{k_D}{k_u}$$

$$t = \frac{1}{k_D - k_u} \ln\left(\frac{k_D}{k_u} \right)$$

For a CSTR:

$$F_{AO} - F_A = -r_u V = k_D C_A V$$

$$v_o (C_{AO} - C_A) = k_D C_A V$$

$$C_A (1 + k_D \tau) = C_{AO} \quad \left(\text{where } \tau \equiv \frac{V}{v_o} \right)$$

$$C_A = \frac{C_{AO}}{1 + k_D \tau}$$

$$F_{DO}^{\;\;0} - F_D = -r_u V + r_D V$$

$$-v_o C_D = \left(k_u C_D - \frac{k_D C_{AO}}{1 + k_D \tau} \right) V$$

$$-C_D = \left(k_u C_D - \frac{k_D C_{AO}}{1 + k_D \tau} \right) \tau$$

$$C_D (1 + k_u \tau) = \frac{k_D C_{AO} \tau}{1 + k_D \tau}$$

$$C_D = \frac{k_D C_{AO} \tau}{(1 + k_u \tau)(1 + k_D \tau)} = \frac{k_D C_{AO}}{(\frac{1}{\tau} + k_u)(1 + k_D \tau)}$$

We can solve for the optimum when $\frac{dC_D}{d\tau} = 0$

$$\frac{dC_D}{d\tau} = k_D C_{AO} \left[-\left(\tfrac{1}{\tau} + k_u\right)^{-1} k_D (1 + k_D \tau)^{-2} + (1 + k_D \tau)^{-1} \tau^{-2} \left(\tfrac{1}{\tau} + k_u\right)^{-2} \right.$$

For a PFR:

$$\frac{dF_A}{dV} = r_D \qquad \text{for catalyst simply} \quad \frac{dF_A}{dW} = r_A'$$

$$v_0 \frac{dC_A}{dV} = -k_D C_A$$

$$\frac{dC_A}{d\tau} = -k_D C_A$$

$$\frac{dC_A}{C_A} = -k_D \, d\tau$$

$$C_A = C_{AO} \exp(-k_D \tau)$$

$$\frac{dF_D}{dV} = r_U - r_D = -k_U C_D + k_D C_{AO} \exp(-k_0 \tau)$$

$$\frac{dC_D}{d\tau} + k_U C_D = k_D C_{AO} \exp(-k_0 \tau)$$

$$\frac{d}{d\tau}\left[C_D \exp(k_U \tau) \right] = k_D C_{AO} \exp(k_U - k_D)$$

$$C_D = k_D C_{AO} \left[\frac{\exp(-k_D)\tau - \exp(-k_U)\tau}{k_U - k_D} \right]$$

We solve for the optimum time at $\frac{dC_D}{d\tau} = 0$

$$\frac{dC_D}{d\tau} = 0 = \frac{k_D C_{AO}}{k_U - k_D} \left[-k_D \exp(-k_D \tau) + k_U \exp(-k_U \tau) \right]$$

$$\tau = \frac{1}{k_D - k_U} \ln\left(\frac{k_D}{k_U} \right)$$

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

$$-r_A = -\frac{dC_A}{dt} = kC_A = A\exp\left(-\frac{E}{RT}\right)C_A$$

$$\frac{dC_A}{C_A} = -kdt$$

$$C_A = C_{AO}\exp(-kt) = C_{AO}\exp\left[-A\exp\left(-\frac{E}{RT}\right)t\right]$$

For an exothermic reaction, as the temperature increases the rate of the reaction and extent of reaction.

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

Whenever we have a reactive intermediate in our expression

$$A \xrightarrow{k_1} Q \xrightarrow{k_2} B$$

we can assume that the net formation of the intermediate is zero if:

① the active intermediate has a very short lifetime due to its high reactivity

② it is present in only low concentration

4. What is the chemical potential?

We define the chemical potential of a species i in solution as

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

where $d(nG) = (nV)dP - (nS)dT + \sum_i \mu dn_i$

The chemical potential μ_i is a measure (in solution) of the deviation of component i from thermodynamic equilibrium with the system.

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

Using calorimetry, we can determine ΔH_f & ΔS_f. We can use an adiabatic calorimeter to measure ΔH_f, and a constant volume calorimeter to determine ΔS_f. We can derive the equations

$$U = Q - W$$

$$dU = \delta Q - \delta W$$

$$= TdS - PdV$$

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

We measure ΔU in adiabatic bomb calorimeter process immersed inside constant volume container. We put this in a bath and measure the heat loss.
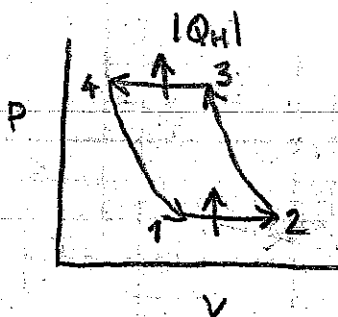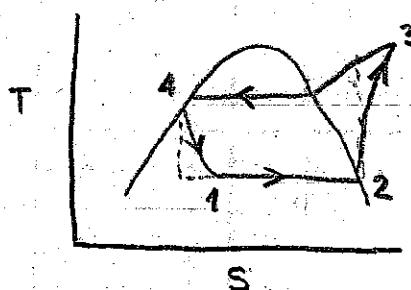
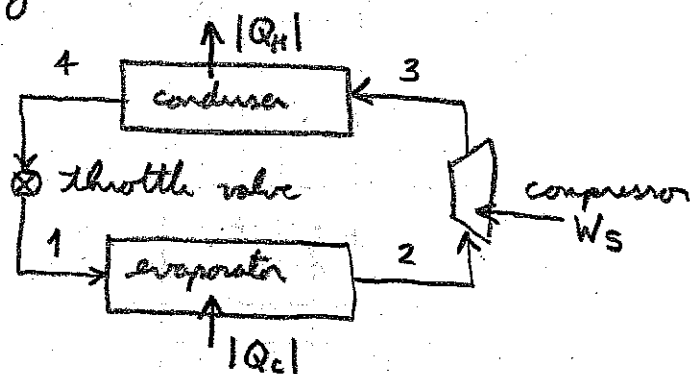$$q = U = C_V \Delta T$$

$$H \equiv U + PV$$

$$dH = dU + PdV + VdP$$

$$= TdS + VdP$$

We measure ΔH_f by monitoring physical or chemical change @ constant pressure (adiabatic flame calorimeter). We get ΔG_f from relation to the first two

$$G \equiv H - TS$$

$$dG = dH - TdS - SdT$$

$$= -SdT + VdP$$

6. How does a refrigerator work? Sketch T-S, P-V and/or P-H diagrams.
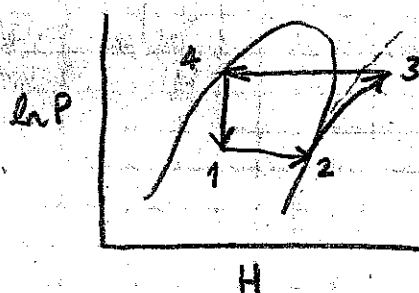
In a continuous refrigeration process, the heat absorbed at a low temperature is continuously rejected to the surroundings at a high temperature. We have a reversed heat engine.

$$W = |Q_H| - |Q_c|$$

$$w = \frac{\text{heat absorbed at low temp}}{W} = \frac{|Q_c|}{W}$$

$$= \frac{T_c}{T_H - T_c}$$

A liquid evaporates at constant pressure in the evaporator, removing heat as $|Q_c|$. The vapor travels through a compressor, where work W_S is performed on it. The vapor then condenses at constant pressure, rejecting heat $|Q_H|$. The liquid is then throttled isenthalpically to a lower pressure.

7. How does the rate constant vary with temperature?

We have for the rate constant

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

where $A \equiv$ preexponential factor or frequency factor
$E \equiv$ activation energy, J/mol or cal/mol
$R \equiv$ gas constant $= 8.314$ J/mol·K
$T \equiv$ absolute temperature, K

Activation energy is the min. energy that must be possessed by reacting molecules before reaction will occur. From kinetic theory of gases, factor $e^{-E/RT}$ gives fraction of collisions between molecules that together have min. energy E. Activation energy is avg. energy of those molecules that do react and the avg. energy of all reactant molecules.

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

CSTR:

$$IN - OUT + GEN = ACC$$

$$F_{Ao} - F_A + r_A V = 0 \quad (\text{mass balance})$$

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

$$0 = \dot{Q} - \dot{W}_S + \sum_{i=1}^{n} F_{io} H_{io} - \sum_{i=1}^{n} F_i H_i$$

$$0 = \dot{Q} - \dot{W}_S + F_{Ao} \sum \theta_i (H_{io} - H_i) - \Delta H_R(T) F_{Ao} X$$

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

$$\theta_i = \frac{F_{io}}{F_{Ao}} \quad , \quad \nu_i = \frac{\text{stoichiometric coeff}}{a}$$

$$0 = \dot{Q} - \dot{W}_S - F_{Ao} \sum \int_{T_{io}}^{T} \theta_i C_{p_i} dT - \left[\Delta H_R(T) + \int_{T_R}^{T} \Delta C_p dT \right] F_{Ao} X = 0$$

PFR:

$$IN - OUT + GEN = ACC$$

$$F_A|_z - F_A|_{z+\Delta z} + r_A A \Delta z = 0$$

$$\frac{dF_A}{} - -r_A A$$

$$\frac{dF_A}{dV} = r_A \quad (\text{mass balance})$$

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

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

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

$$0 = \dot{Q} - \dot{W} - F_{AO}\sum\int_{T_{io}}^{T}\theta_i c_{p_i}\,dT - \left[\Delta H_R^\circ(T_R) + \int_{T_R}^{T}\Delta C_p\,dT\right]F_{AO}X = 0$$

BATCH:

$$IN - OUT + GEN = ACC$$

$$r_A V = \frac{dN_A}{dt}$$

$$N_A = N_{AO}(1-X)$$

$$N_{AO}\frac{dX}{dt} = -r_A V$$

$$\frac{dE}{dt} = \dot{Q} - \dot{W}_s - \Delta H_R(T)(-r_A V)$$

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

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

Space time is the time necessary to process one reactor volume of fluid based on entrance conditions.

$$\tau \equiv \frac{V}{v_0} \quad \text{where } V \equiv \text{volume of reactor, } v_0 = \text{volumetric flowrate}$$

Space velocity is defined as

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

However the definition of space velocity is not always based on the entrance conditions. Often LHSV (liquid hourly space velocity) is defined at $60°$ or $70°F$ while GHSV is given at STP.

The mean residence time is the average time in which effluent molecules spend in the reactor. For an ideal reactor this simplifies to the space time t. We calculate the mean residence time as the first moment of an RTD function, $E(t)$

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

We can determine the variance of the distribution, σ, by taking the second moment about the mean residence time

$$\sigma^2 = \int_0^\infty (t - t_m)^2 E(t) dt$$

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

The Clapeyron equation states that the latent heat accompanying a phase change is a function of temperature only

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

where ΔH = latent heat of phase change
ΔV = volume change accompanying phase change
P_{sat} = vapor pressure

The Clausius-Clapeyron equation relates the latent heat of vaporization directly to the vapor pressure curve.

$$\Delta H_{lv} = -R \frac{d \ln P_{sat}}{d(1/T)}$$

We derive these relations by stating that at equilibrium two phases α and β are related

$$G^\alpha = G^\beta$$

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

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

Since at equilibrium

$$T^\alpha = T^\beta \quad \& \quad P^\alpha = P^\beta = P^{sat}$$

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

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

$$\Delta H^{\alpha\beta} = T\Delta S^{\alpha\beta} \quad (\text{at constant } T \text{ \& } P)$$

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

This is the Clapyron equation. For the particular case of when a liquid goes to a vapor

$$\Delta V^{\alpha\beta} = \Delta V^{\ell v} = V^v - V^\ell \approx V^v$$

$$\frac{dP^{sat}}{dT} = \frac{\Delta H^{\ell v}}{TV}$$

For the special case of an ideal gas

$$V = \frac{RT}{P}$$

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

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

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

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

This implies the empirical relation

$$\ln P^{sat} = A - \frac{B}{T}$$

The Antoine equation gives better results

$$\ln P^{sat} = A - \frac{B}{}$$

11. How do you calculate the adiabatic flame temperature?

The adiabatic flame temperature is the highest achievable temperature reached if the reactor is adiabatic. We can do an energy balance on our system

$$\Delta H = n_f \Delta \hat{H}_c^\circ + \sum_{output} n_i \hat{H}_i (T_{ad}) - \sum_{input} n_i \hat{H}_i (T_{feed}) = 0$$

where $\Delta \hat{H}_c^\circ$ = heat of combustion of fuel at 25°C

n_i = moles of ith component in feed or product

$\hat{H}_i$ = specific enthalpy of ith component relative to this component at 25°C in the state of aggregation for which $\Delta \hat{H}_c^\circ$ is specified

T_{ad} = product temperature, which by definition is the adiabatic flame temperature

We can solve for the adiabatic flame temperature

1. Integrate tabulated heat capacity formulas from 25°C to T_{ad} (trial and error using Newton's rule).

2. Use mean heat capacities and find T_{ad} by trial and error.

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

For a series reaction, the space time or actual time spent in the reactor (RTD) is most important. Reactive distillation of the desired product would be an intuitive process.

For a parallel reaction, the respective reaction orders and activation energies of the two reactions are of vital interest. If the order of the desired reaction is greater than that of the undesired, it is important to keep the concentration of reactants as high as possible (PFR, batch). Vice-versa, we want to keep the concentration of reactants as low as possible (CSTR or PFR with side streams). If the activation energy of the desired product is largest then keep temperature as high as possible and vice-

For an autocatalytic reaction, the choice of reactor is dependent on the properties of the reaction. For an exothermic reaction, it is important to keep the concentration as low as possible to avoid runaway. For this a CSTR or a PFR with side streams may work best. For an endothermic reaction, it is important to keep the concentration of reactant as high as possible. We use a PFR or batch reactor.

13. Give the three laws of thermodynamics.

0th law : If two bodies are in contact at thermodynamic equilibrium, they are also at the same temperature.

1st law : Conservation of energy. Although energy assumes many forms, the total quantity of energy is constant, and when energy disappears in one form it reappears in another.

$$U = Q - W$$

2nd law : No apparatus can operate in such a way that its only effect (in system and surroundings) is to convert heat absorbed by the system completely into work done by the system (perpetual motion machine of second kind). No process is possible which consists solely in the transfer of heat from one temperature level to a higher one.

Consider two heat reservoirs

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

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

Since $T_H > T_C$, the total entropy change is positive. Only when T_H is infinitesimally larger than T_C is entropy zero, which is reversible process
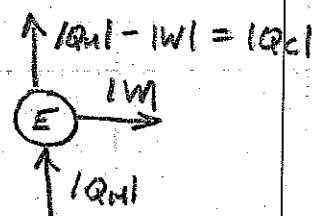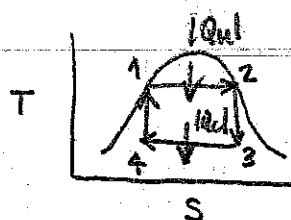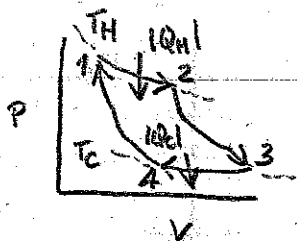
$$\Delta S_{\ldots} \geq 0$$

3rd law: The absolute entropy is zero for all perfect crystalline substances at absolute zero temperature.

$$S = \int_0^{T_f} \frac{(C_p)_s}{T} dT + \frac{\Delta H_f}{T_f} + \int_{T_f}^{T_v} \frac{(C_p)_\ell}{dT} dT + \frac{\Delta H_v}{T_v} + \int_{T_v}^{T} \frac{(C_p)_g}{T}$$

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 equation to describe each step. What is the efficiency?

Carnot cycle:

$1 \rightarrow 2$ System in contact with hot reservoir at T_H undergoes reversible isothermal process in which $|Q_H|$ is absorbed from the hot reservoir.

$2 \rightarrow 3$ System undergoes reversible adiabatic process to cause its temperature to lower to that of T_c.

$3 \rightarrow 4$ System in contact with cold reservoir at T_c undergoes reversible isothermal process to reject $|Q_c|$ to cold reservoir.

$4 \rightarrow 1$ System undergoes reversible adiabatic process to cause its temperature to increase to that of T_H.

$$\eta = \frac{\text{net work input}}{\text{heat input}} = \frac{|W|}{|Q_H|} = \frac{|Q_H| - |Q_c|}{|Q_H|}$$
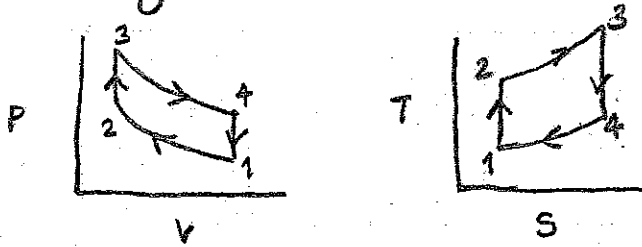
$$= 1 - \frac{|Q_c|}{|Q_H|} = 1 - \frac{T_c}{T_H}$$

This is due to adiabatic process

$$dU = dW = -PdV = C_V dT$$

$$\int_{T_c}^{T_H} \frac{C_V}{R} \frac{dT}{T} = \ln \frac{V_4}{V_1} = \ln \frac{V_3}{V_2}$$

Otto Cycle:

$1 \rightarrow 2$ Fuel-air mix is compressed adiabatically.

$2 \rightarrow 3$ Fuel is ignited, reaction occurs so fast that pressure increases isochorically (constant volume).

$3 \rightarrow 4$ High temperature, high pressure products expand adiabatically.

$4 \rightarrow 1$ Exhaust valve opens and pressure falls rapidly at constant volume.

$$\eta = \frac{-W_S \,(net)}{Q_{23}} = \frac{Q_{23} + Q_{41}}{Q_{23}} = 1 + \frac{Q_{41}}{Q_{23}}$$

$$Q_{23} = C_V (T_3 - T_2)$$
$$Q_{41} = C_V (T_1 - T_4)$$

$$\eta = 1 - \frac{T_1 - T_4}{T_3 - T_2}$$

$$T_1 = \frac{P_1 V_1}{R} = \frac{P_1 V_4}{R}$$

$$T_3 = \frac{P_2 V_2}{R} = \frac{P_2 V_3}{R}$$

$$\eta = 1 - \left(\frac{V_1}{V_2}\right)\left(\frac{P_1 - P_4}{P_2 - P_3}\right) = 1 - r\left(\frac{P_1 - P_4}{P_2 - P_3}\right)$$

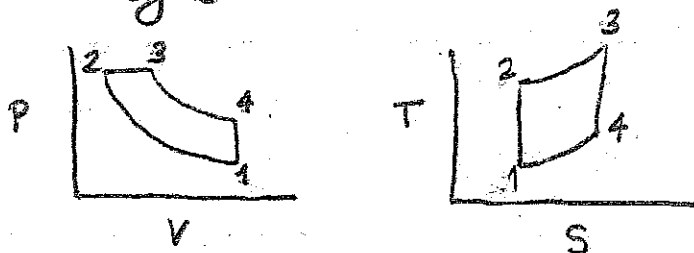$$P_1 V_1^{\gamma} = P_4 V_4^{\gamma} \qquad \left(\frac{P_1}{P_4}\right) = \left(\frac{V_4}{V_1}\right)^{\gamma}$$

$$P_2 V_2^{\gamma} = P_3 V_3^{\gamma} \qquad \left(\frac{P_2}{P_3}\right) = \left(\frac{V_3}{V_2}\right)^{\gamma}$$

$$\eta = 1 - r\left[\frac{(P_1/P_4) - 1}{(P_2/P_3) - 1}\right]\left(\frac{P_4}{P_3}\right)$$

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

Diesel Cycle:

1 → 2 Air is compressed adiabatically.

2 → 3 Fuel is injected slowly so that the combustion process proceeds at constant pressure.

3 → 4 High temperature, high pressure gases expand adiabatically.

4 → 1 Exhaust valve opens and pressure falls rapidly at constant volume.
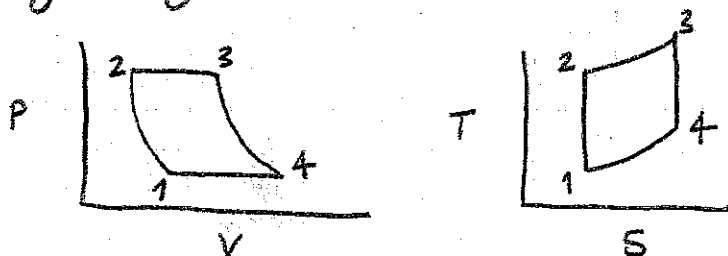
High temperature results from high compression ratio that carries compression step to a higher pressure.

$$\eta = \frac{-W_S(net)}{Q_{23}} = \frac{Q_{23} - Q_{41}}{Q_{23}} = 1 - \frac{Q_{41}}{Q_{23}}$$

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

where $T_D/T_A = V_D/V_A = \dfrac{V_D/V_C}{V_A/V_B} = \dfrac{r_e}{r}$

Brayton Cycle:

1 → 2 Entering air is compressed adiabatically.

2 → 3 Fuel is injected slowly so that combustion process proceeds at constant pressure.

3 → 4 High temperature, high pressure gases expand adiabatically across turbine to atmospheric.

4 → 1 Exhaust valve opens and exhaust gases are expelled.

$$\eta = \frac{-W_S(net)}{Q_{23}} = \frac{Q_{23} + Q_{41}}{Q_{23}} = 1 - \frac{T_D - T_A}{T_C - T_B}$$

$$= 1 - \left(\frac{P_A}{P_B}\right)^{\frac{\gamma-1}{\gamma}}$$
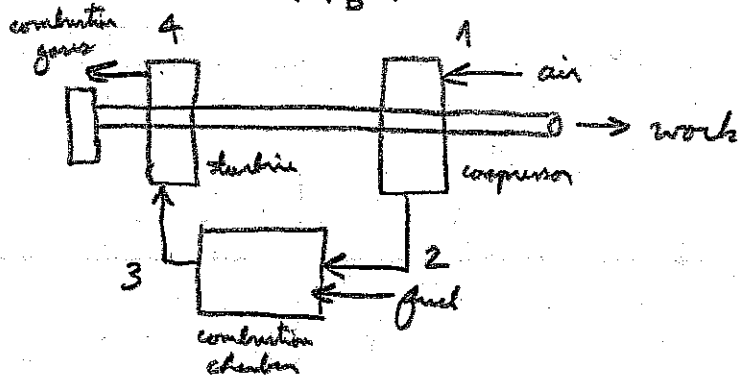
Otto & Diesel engines exemplify use of energy with high temperature, high pressure gases acting on piston within cylinder; no heat transfer with external source is needed. Turbines are more efficient in that advantages of internal combustion engine are combined with turbine in gas-turbine engine.
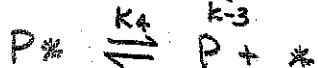
Rankine cycle:
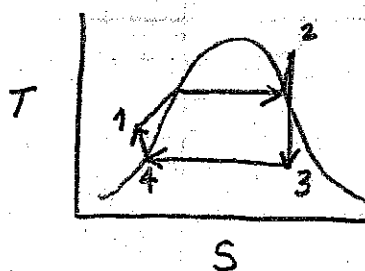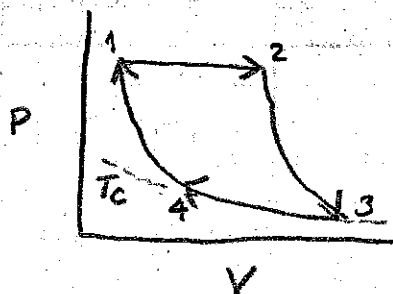
1→2 A constant-pressure heating process in a boiler.

2→3 Reversible, adiabatic expansion of vapor in a turbine to the pressure of the condenser.

3→4 A constant-pressure, constant-temperature process in a condenser to produce saturated liquid.

4→1 Reversible, adiabatic pumping of the saturated liquid to the pressure of the boiler.

$$\eta = \frac{|W_S(Rankine)|}{Q_{boiler}} = \frac{-Q_{boiler} - Q_{condenser}}{Q_{boiler}}$$

15. Derive a Langmuir-Hinshelwood expression for a solid catalyzed reaction

$$A + B \rightleftharpoons P$$

We propose a mechanism

$$A + * \overset{K_1}{\underset{K_2}{\rightleftharpoons}} A*$$

$$B + * \overset{}{\underset{K_2}{\rightleftharpoons}} B*$$

$$A* + B* \overset{k_3}{\underset{k_{-3}}{\rightleftharpoons}} P* + *$$

$$P* \overset{K_4}{\rightleftharpoons} P + *$$
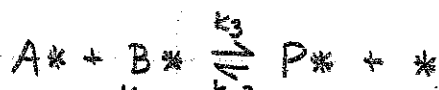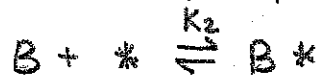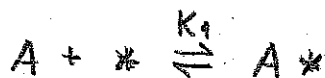
We assume that the surface reaction is rate limiting. Therefore we have

$$r_p = k_3 [A*][B*] - k_{-3} [P*][*]$$

$$K_1 = \frac{[A*]}{[A][*]}, \quad K_2 = \frac{[B*]}{[B][*]}, \quad K_4 = \frac{[P][*]}{[P*]}$$

$$[A*] = K_1 [A][*]$$

$$[B*] = K_2 [B][*]$$

$$[P*] = \frac{1}{K_4} [P][*]$$

$$r_p = K_1 K_2 k_3 [A][B][*]^2 - \frac{k_{-3}}{K_4} [P][*]^2$$

We do a site balance to obtain $[*]$ (using MARI)

$$[L] = [*] + [A*] + [B*] + [P*]$$
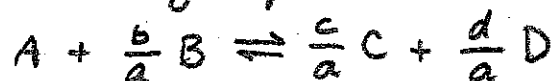
$$= [*] + K_1 [A][*] + K_2 [B][*] + \frac{1}{K_4} [P][*]$$

$$[*] = \frac{[L]}{1 + K_1 [A] + K_2 [B] + \frac{1}{K_4} [P]}$$

$$r_p = \frac{\left(K_1 K_2 k_3 [A][B] - \frac{k_{-3}}{K_4} [P] \right)[L]^2}{\left(1 + K_1 [A] + K_2 [B] + \frac{1}{K_4} [P] \right)^2}$$

$$r_p = \frac{\frac{1}{2} Z \left(K_1 K_2 k_3 [A][B] - \frac{k_{-3}}{K_4} [P] \right)[L]}{}$$

Remember your Thermodynamic Relationships Involving the Equilibrium Constant:

For the gas-phase reaction

$$A + \frac{b}{a}B \rightleftharpoons \frac{c}{a}C + \frac{d}{a}D$$

1. The pressure equilibrium constant K_P is

$$K_P = \frac{P_C^{c/a} P_D^{d/a}}{P_A P_B^{b/a}} \quad \text{where } P_i = \text{partial pressure of species } i$$

2. The concentration equilibrium constant is

$$K_C = \frac{C_C^{c/a} C_D^{d/a}}{C_A C_B^{b/a}}$$

3. For ideal gases, K_C and K_P are related

$$K_P = K_C (RT)^\delta \quad \text{where } \delta = \frac{c}{a} + \frac{d}{a} - \frac{b}{a} - 1$$

4. K_P is a function of temperature only, and the temperature is given by van't Hoff's equation

$$\frac{d \ln K_P}{dT} = \frac{\Delta H_{rxn}(T)}{RT^2} = \frac{\Delta H_{rxn}^\circ(T_R) + \Delta \hat{C}_P (T - T_R)}{RT^2}$$

5. If $\Delta \hat{C}_P = 0$ we can integrate to get

$$\ln \frac{K_{P_2}}{K_{P_1}} = \frac{\Delta H_{rxn}^\circ(T_R)}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

6. From Le Chatelier's principle we know that for exothermic reaction the equilibrium shifts to the left as temperature increases. For an endothermic reaction the equilibrium shifts to the right as temperature increases.

exothermic   endothermic
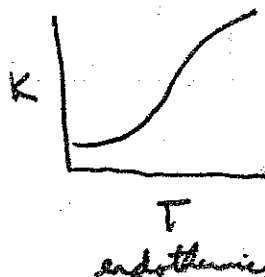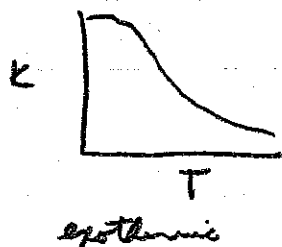
7. The equilibrium constant at temperature T can be found from the change in Gibbs free energy using

$$-RT \ln[K(T)] = \Delta G^{\circ}_{rxn}(T)$$

$$\Delta G^{\circ}_{rxn} = \frac{c}{a} G^{\circ}_{c} + \frac{d}{a} G^{\circ}_{D} - \frac{b}{a} G^{\circ}_{B} - G^{\circ}_{A}$$

8. Tables that list the standard Gibbs free energy of formation of a species G°_{i} are available in the literature.

9. The relationship between the change in Gibbs free energy and enthalpy, H, and entropy, S, is

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

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

We consider a system that is in thermal and mechanical contact with its surroundings at the same temperature. Because any change of state in the system is accompanying change in entropy dS, the total entropy of the system will change by the heat applied during the process

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

This inequality can be developed in two ways according to the process (constant T n constant P).

At constant V:

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

$$TdS \geq dU$$

$$dS_{U,V} \geq 0 \;,\; dU_{S,V} \leq 0$$

$$A \equiv U - TS$$

$$dA = dU - TdS$$

$$dA_{T,V} \leq 0$$

At constant P:

$$TdS \geq dH$$

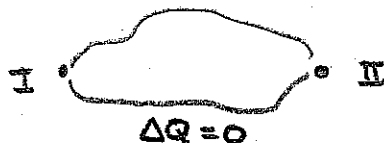$$dS_{H,P} \geq 0 \;,\; dH_{S,P} \leq 0$$

$$G = H - TS$$

$$dG = dH - TdS$$

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

These inequalities are the most important conclusions from thermodynamics

17. Prove that S tends toward a maximum.

We can define a closed system between points I & II which we have an adiabatic, irreversible path.

$\Delta Q = 0$

For a closed system
$$\Delta S_{sys} \geq 0$$

We can return to point I from point II using a reversible path in which the heat transfer between the system and surroundings all takes place during an isothermal step. The system has undergone a cycle so ΔU and $\Delta S = 0$. For the overall process the heat and work interactions must be equal and negative

$$W_{net} = Q_{net} = (-)$$

otherwise we have a perpetual motion machine. The heat interaction is negative, therefore the entropy in the second step is negative. The change in entropy in a closed system during an adiabatic process is positive. Thus the change in entropy of any closed system in an adiabatic process is positive. An isolated system is a special case of a closed adiabatic system so that the change of entropy in an isolated system for any process is greater than or equal to zero.

18. Gibbs mixing rule implies that $\Delta G_{mix} \leq 0$ for two substances to mix, $\Delta G_{mix} = n_A RT \ln\left(\frac{P_A}{P}\right) + n_B RT \ln\left(\frac{P_B}{P}\right)$

Gibbs – Duhem relation

$$U = TS - PV + \Sigma \mu N$$
$$dU = TdS - PdV + \Sigma \mu dN$$
$$0 = SdT - VdP + \Sigma N d\mu$$

By total Legendre transform

$$\underline{U} - T\underline{S} + P\underline{V} - \Sigma \mu_i N_i = 0$$
$$0 = -\underline{S}dT + \underline{V}dP - \Sigma N_i d\mu_i$$
$$d\mu = -SdT + VdP$$

Gibbs theorem: A total thermodynamic property of an ideal gas mixture is the sum of the total properties of individual species, each evaluated at the mixture temp but at its own partial pressure.

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 that of the first step, how would you adjust the temperature to maximize the production of B?

We use the selectivity ratio of the rate constants

$$S_A = \frac{k_1}{k_2} = \frac{A_1}{A_2} \exp\left(-\frac{(E_1 - E_2)}{RT}\right)$$

If the activation energy of the second step is higher we want to keep the system at low temperature.

20. How do you calculate the equilibrium constant at non standard temperature and pressure.

We use the van't Hoff equation to correct for non-standard temperature

$$\frac{d \ln K_p}{dT} = \frac{\Delta H_{rxn}(T)}{RT^2} = \frac{\Delta H_{rxn}^{\circ}(T_R) + \Delta \hat{C}_p (T - T_R)}{RT^2}$$

The equilibrium constant is independent of pressure.

21. Define U, H, S, G, and A.

$$U = Q - W$$
$$dU = TdS - PdV = \delta Q - W$$
$$H \equiv U + PV$$
$$A \equiv U - TdS$$
$$G \equiv H - TdS$$

$U \equiv$ Energy associated with matter, unrelated to position or velocity. It can be composed of translational, rotational, vibrational, atomic, and molecular interactions. This is a state property.

$S \equiv$ Measure of the change in ability of universe to produce work in the future, as a result of past or presently occuring transformations or processes.

$A \equiv$ Maximum work function, part of change in internal energy on which we are free to do work.

$G \equiv$ Maximum non-expansive work we can obtain from a process at constant P & T (good for electrical work)

$H \equiv$ Change in internal energy when system free to change its volume (when heat is supplied). E returning to surroundings as expansive work.

22. What is a Joule-Thompson liquefaction process?

A Joule-Thompson liquefaction process is a process by which a gas is expanded adiabatically through a valve to a lower temperature and pressure.

We define the Joule-Thompson coefficient as

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

$$dH = TdS + VdP$$

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

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

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

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

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

$$dH = C_p dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right] dP$$

For an isenthalpic process:

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

$$\mu = \left(\frac{\partial T}{\partial P} \right)_H = \frac{1}{C_p} \left[V - T \left(\frac{\partial V}{\partial T} \right)_P \right]$$

We could also apply the triple product rule

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

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

$$dH = TdS + VdP$$

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

$$dG = -SdT + VdP$$

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

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

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

We can use the van't Hoff equation

$$\frac{d \ln K_p}{dT} = \frac{\Delta H^\circ_{rxn} (T_R)}{RT^2} = \frac{\Delta H_{rxn} (T_R) + \Delta \hat{C}_p (T - T_R)}{RT^2}$$

If $\Delta \hat{C}_p$ is zero, we can integrate

$$\frac{d \ln K_p}{d \left(\frac{1}{T} \right)} = - \frac{\Delta H^\circ_{rxn} (T_R)}{R}$$

If $\Delta H_{rxn}^\circ > 0$, slope is negative. If $\Delta H_{rxn}^\circ < 0$, slope is positive.

We can derive the van't Hoff equation from the definition of the equilibrium constant

$$RT \ln K = -\Delta G_{rxn}$$

and the Gibbs-Helmholtz equation

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

$$\frac{d \ln K}{dT} = -\frac{1}{R} \frac{d}{dT} \left(\frac{\Delta G_{rxn}}{T} \right)$$

$$\frac{d \ln K}{dT} = -\frac{\Delta H_{rxn}}{RT^2}$$

$$\frac{d \ln K}{d\left(\frac{1}{T}\right)} = -\frac{\Delta H_{rxn}}{R}$$

We can also derive the van't Hoff equation for osmotic pressure

$$\pi = [B] RT$$

$$\mu_A^*(p) = \mu_A(x_A, p + \pi)$$

$$\mu_A(x_A, p + \pi) = \mu_A^*(p + \pi) + RT \ln x_A$$

$$\mu_A^*(p + \pi) = \mu_A^*(p) + \int_p^{p+\pi} V_m \, dp$$

$$-RT \ln x_A = \int_p^{p+\pi} V_m \, dp \underbrace{\qquad}_{\text{molar volume of solution}}$$

$$-RT \ln x_A = \pi V_m$$

We can approximate $\ln(x_A) = \ln(1 - x_B) \approx -x_B$

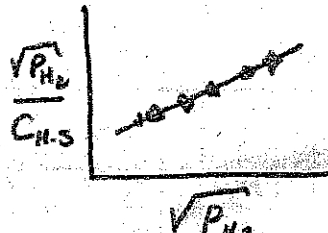$$RT x_B = \pi V_m$$

$$\pi = [B] RT$$

25. Give a physical interpretation of the activation energy.

The activation energy is the average energy of those molecules that do react and the average energy of all reactant molecules.

26. Where does the Langmuir isotherm come from?

The Langmuir isotherm plots the concentration of a given species bonded to the surface (catalyst) as a function of the concentration of species (or partial pressure). If you have proposed the correct mechanism for your surface reaction, the Langmuir isotherm will be linear.

For example $H_2 + 2S \rightleftharpoons 2HS$

$$C_{H \cdot S} = \frac{(K_A P_{H_2})^{1/2} C_t}{1 + (K_A P_{H_2})^{1/2}}$$

27. Why is entropy zero at $0K$?

We have the Third Law of Thermodynamics:
The absolute entropy is zero for all perfect crystalline substances at absolute zero temperature.

Because entropy is zero at $0K$, this implies perfect order according to Boltzmann. We define a quantity Ω as the number of ways that macroscopic particles can be distributed amongst the states available to them.

$$\Omega = \frac{n!}{(n_1!)(n_2!)(n_3!)\cdots}$$

The connection that Boltzmann made was that

$$S = k \ln \Omega$$

At $0K$, there is only one way to arrange the molecules in a system. Hence, $S = k \ln(1) = 0$.

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

We can use excess properties

$$V^E = V - \sum_i x_i V_i$$

$$\Delta V_{mix} = \sum_i x_i V_i \quad (\text{Amagat's law})$$

For an ideal solution

$$\Delta V_{mix}^{id} = 0$$

29. How would you calculate from first principles the heat capacity of two gases (e.g. H_2 & CH_3NCO).

We can use Kopp's rule, which allows you to estimate the heat capacity at or near 20°C by a sum of contributions of each atomic element.

ex. $(C_p)_{Cd(OH)_2} = (C_{pa})_{Ca} + 2(C_{pa})_O + 2(C_{pa})_H$

For a mixture of components, you can estimate the heat capacity by

$$C_{pm}(T) = \sum y_i C_{pi}(T)$$

This works well for similar liquids.

Also, using first principles we know that heat capacity is a measure of internal energy. For an ideal monatomic gas
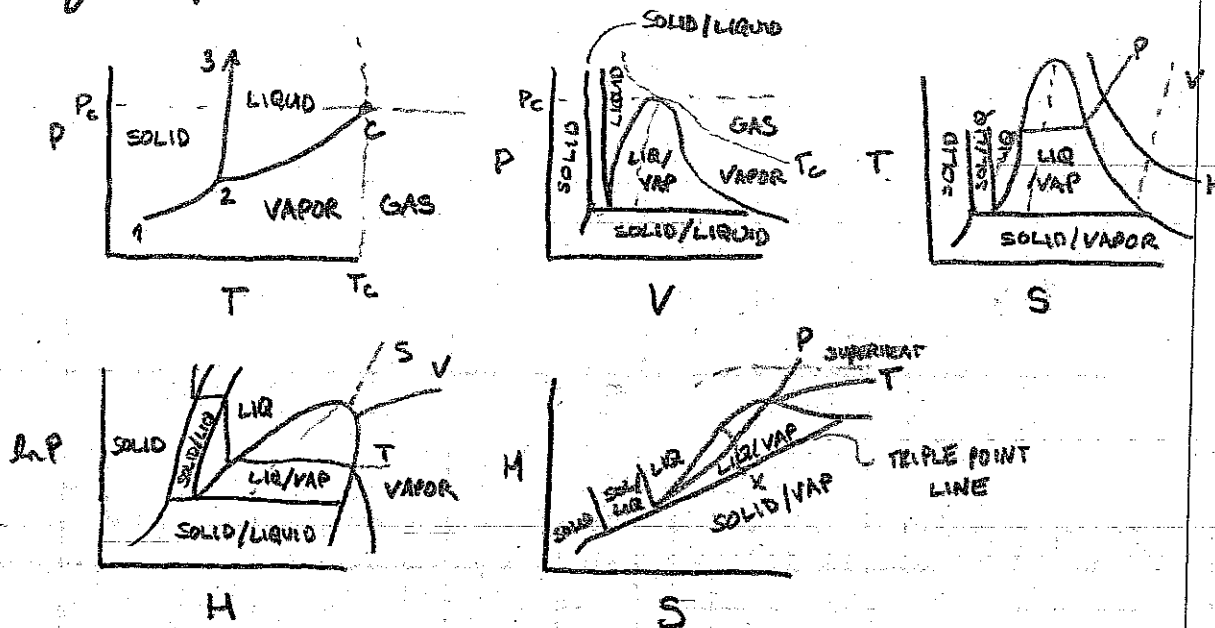
$$C_V = \frac{3}{2}R = \frac{1}{2}R \, (3° \text{ of freedom})$$

where three degrees of freedom are afforded by x, y, & z translational energy. For H_2, we have three additional degrees of freedom (2 in rotational, 1 in vibrational) and thus we estimate heat capacity by

$$C_V = \frac{1}{2}R \, (6° \text{ of freedom}) = 3R$$

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

32. What does polytropic mean?

The word isotropic means "same no matter how you look at it." If we are referring to a surface isotropic means same in x, y, and z coordinates.

A polytropic process is usually defined as one for which a relation is given by

$$PV^\delta = K$$

where K is a constant for a given process. For an ideal gas

$$\left(\frac{P_1}{P_2}\right) = \left(\frac{V_1}{V_2}\right)^\delta$$

$$\left(\frac{T_1}{T_2}\right) = \left(\frac{V_1}{V_2}\right)^{\delta-1}$$

$$W = -\int P \, dV \quad \text{(mechanically reversible nonflow process)}$$
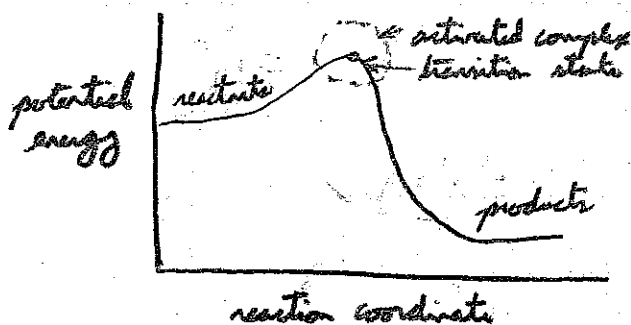
$$= \frac{R T_1}{\delta - 1}\left[\left(\frac{P_2}{P_1}\right)^{(\delta-1)/\delta} - 1\right]$$

$$Q = \frac{(\delta - \gamma) R T_1}{(\delta-1)(\gamma-1)}\left[\left(\frac{P_2}{P_1}\right)^{(\delta-1)/\delta} - 1\right]$$

$\delta = 0$ isobaric $\delta = \gamma$ adiabatic
$\delta = 1$ isothermal $\delta = \infty$ isochoric

33. How is the concept of reaction coordinate used?

Transition state theory is an attempt to identify the principal features governing the size of a rate constant in terms of a model of the events that take place during the reaction.

The reaction coordinate shows how the potential energy of reactants A and B change in the course of a bimolecular elementary reaction. Initially only A & B are present. As the reaction proceeds, A & B come into contact, distort, begin to exchange atoms. The potential energy rises to a max (activated complex) The climax occurs at the peak (transition state) in which closeness & distortion pushes toward products. Whether or not a colliding pair actually crosses the potential barrier depends on the kinetic energy the molecules have upon entering. An order of magnitude estimation of the lifetime at transition state is one period of vibration of breaking and forming bonds.

$$A + B \xrightarrow{1} C^{\ddagger} \xrightarrow{2} P \qquad r_2 = k^{\ddagger}[C^{\ddagger}]$$
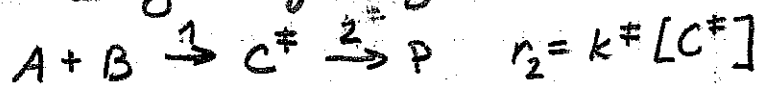
$$[C^{\ddagger}] = K^{\ddagger}[A][B]$$

$$r_{overall} = k_2[A][B] = k^{\ddagger}K^{\ddagger}[A][B]$$

Transition state theory pictures a reaction between A and B as proceeding through the formation of an activated complex $C^{\ddagger}$ that falls apart by unimolecular decay into products P with rate constant $k^{\ddagger}$

34. What is the phase rule when reactions are occuring?

For reacting systems, the phase rule is

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

The original phase rule says

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

$$F = \underbrace{[2 + (N-1)(\pi)]}_{\substack{T, P, \text{ and } N-1 \text{ var} \\ \text{in each phase}}} - \underbrace{[(\pi-1)(N) + r]}_{\substack{r \text{ independent chemical} \\ \text{reactions and } (\pi-1)(N)+r \\ \text{variables relating them}}}$$

$r \geq$ number of compounds present in the system — number of constituent elements not present as elements.

$$F = 2 - \pi + N - r - s$$

$s \equiv$ special constraints on system (azeotrope, requirement that system decompose by ...)

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

Absorption refrigeration is based on the idea of using heat as an energy source for refrigeration.
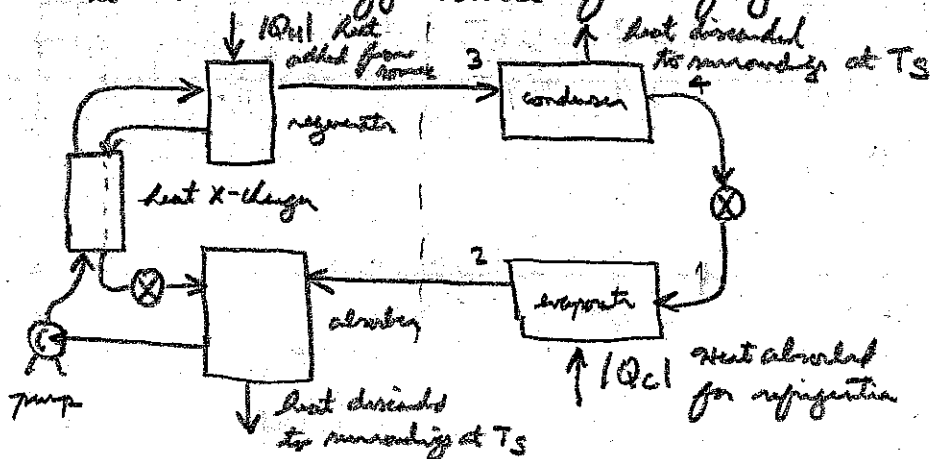
$$W = \frac{T_S - T_C}{T_C} |Q_C|$$

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

$$|Q_H| = |W| \frac{T_H}{T_H - T_S} = |Q_C| \frac{T_H}{T_H - T_S} \frac{T_S - T_C}{T_C}$$

The essential difference between a vapor-compression and an absorption refrigerator is in the different means employed for compression. Refrigerant as vapor from the evaporator is absorbed in a relatively nonvolatile solvent at the pressure of the evaporator and relatively low T. The liquid soln is pumped to pressure of condenser. Heat from surroundings is transferred to soln, raising T and evaporating refrigerant from solvent.

The most commonly used absorption-refrigeration system uses water as refrigerant and LiBr soln as absorbent. For lower T's usual system operates with ammonia as refrigerant and water as the solvent.

36. Give three methods of liquefying gases.

1. Isenthalpic expansion (Joule-Thompson) by expanding through a valve.

2. Isenthalpic expansion into a turbine or other engine.

3. Condensing through heat transfer.

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

A differential reactor is normally used to determine the rate of reaction as a function of concentration for heterogeneous systems. It consists of a tube containing a very small amount of catalyst usually arranged in the form of a thin wafer or disk. Because of the small amount of catalyst used, conversion is very small, as is change in reactant composition. Since reactant change is gradientless, reaction rate is considered to be spatially uniform in bed. The volumetric flowrate through the catalyst is modelled, as are the entering and exiting concentrations. If weight of catalyst is known, rate of reaction per unit mass catalyst is known. Since reactor is gradientless, design equation looks like CSTR.

$$-r_A' = \frac{F_{A0}X}{W} = \frac{F_P}{W} = \frac{v_0(C_{A0} - C_{Ae})}{W}$$

A little more on collection and analysis of rate data:

1. Differential method for constant volume systems:
$$-\frac{dC_A}{dt} = k C_A^{\alpha}$$

  a. Plot $\Delta C_A / \Delta t$ as a function of t

  b. Determine dC_A/dt from this plot.

  c. Taking $\ln$ of both sides
$$\ln\left(-\frac{dC_A}{dt}\right) = \ln k + \alpha \ln C_A$$

    Plot $\ln(-dC_A/dt)$ versus $\ln C_A$. This slope will be the reaction order α.

2. Integral method:

  a. Guess the reaction order and integrate the mole balance equation.

  b. Calculate resulting function of concentration for data and plot it as a function of time. If linear, probably have correct reaction order.

  c. If not linear, try it again.

3. Method of initial rates: Plot slope of $[\ln(-r_{A0})]$ versus $[\ln C_{A0}]$ will be reaction order.

4. Method of half-lives: Plot $\ln t_{1/2}$ as function of $\ln C_{A0}$. The reaction order will be 1 - slope.

5. Differential reactor

6. Least squares analysis

7. Laboratory reactors: Differential, fixed bed, stirred batch, stirred containing solids, continuous stirred tank, straight through transport, recirculating transport, pulse

8. Experimental planning

  a. Why?

  b. Within what limits?

  c. Are you choosing correct parameters?

  d. Standards!

  e. Can you do it again?

  f. Be careful, you can lie with statistics.

  g. We don't believe an experiment until its proven by theory.

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

The extent of reaction is defined as the conversion X_A

$$X_A = \frac{\text{moles of A reacted}}{\text{moles of A fed}}$$

Equilibrium conversion is the conversion reached when the reactants and products in a reversible reaction are in thermodynamic equilibrium.

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

Important characteristics of refrigerants include toxicity, flammability, cost, corrosion properties, and vapor pressure in relation to temperature. The vapor pressure must be higher than atmospheric to reduce air leaks. However vapor pressure shouldn't be too high for condenser (high cost of operating pressure equipment). Also, freon gives no freeze-ups, large latent heat (small volume required), T-S diagram gives steep sat'd vapor line (keeps average heat rejection small, more efficient).

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

The activity coefficient of a species in sol'n is simply the ratio of its actual fugacity to the value given by the Lewis Randall rule at the same T, P, and composition.

$$\gamma_i \equiv \frac{\hat{f}_i}{x_i f_i} = \frac{\hat{f}_i}{\hat{f}_i^{id}} = \frac{y_i P}{x_i f_i} = \frac{y_i P}{x_i P^{sat}}$$

The origin of the fugacity lies in the definition of the Gibbs free energy of a component i

$$G_i \equiv \Gamma_i(T) + RT \ln f_i$$

where $\Gamma_i(T)$ is an integration constant at constant T.

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

$$f_{ig} = P$$

Fugacity facilitates the application of equilibrium criteria, replacing μ_i but without the problems of μ_i.

41. What is the fugacity and how is it calculated?

The chemical potential, μ_i, is fundamental in formulation of criteria for phase equilibrium, chemical-reaction equilibrium. However, μ_i is defined in relation to internal energy and entropy, both primitive quantities which absolute values are unknown. We introduce fugacity as a replacement for μ_i

$$G_i \equiv \Gamma_i(T) + RT \ln f_i$$

from $G_{ig} = \Gamma_i(T) + RT \ln P$

$$G^E = G_i - G_i^{ig} = RT \ln \frac{f_i}{P} = RT \ln \phi_i$$

$$f_i^\nu = f_i^l = f_i^{sat}$$

$$\phi_i^\nu = \phi_i^l = \phi_i^{sat}$$

We calculate f_i for species i as a compressed liquid from saturated vapor

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

and evaluating for $P = P_i^{sat}$. Then we get

$$f_i^l = f_i^{sat} = \phi_i^{sat} P_i^{sat}$$

The definition of fugacity of a species in sol'n is analogous to pure species fugacity.

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

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

$$\bar{G}_R = \bar{G}_i - \bar{G}_i^{ig}$$

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

$$\hat{\phi}_i \equiv \frac{\hat{f}_i}{x_i P}$$

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

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

In Langmuir-Hinshelwood kinetics, if desorption controls, the initial rate of reaction is independent of pressure. If two adsorbed species participate in the rate controlling step, such as

$$A + S \rightleftharpoons A \cdot S$$

$$B + S \rightleftharpoons B \cdot S$$

$$A \cdot S + B \cdot S \rightleftharpoons C \cdot S + S$$

our rate will have the form

$$r = k_3 [A \cdot S][B \cdot S] = \frac{k_3 K_1 K_2 [A][B]}{(1 + K_1 [A] + K_2 [B])^2}$$

Since the denominator is squared, as pressure increases the rate will decrease.

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

We define an internal effectiveness factor

$$\eta = \frac{\text{actual overall reaction rate}}{\text{rate of reaction that would result if entire surface were exposed to external pellet concentration}}$$

For internal mass transfer limitation

$$-r_A' = \eta(-r_{As}') = \eta(k_n C_{As}^n)$$

We also define Thiele modulus ϕ

$$\phi^2 = \frac{k_n R^2 S_a \rho_p C_{As}^{n-1}}{D_e} = \frac{\text{"a" surface reaction rate}}{\text{"a" diffusion rate}}$$

For large $\phi > 30$

$$-r_A' = \frac{3}{\phi_n} \sqrt{\frac{2}{n+1}} k_n C_{As}^n = \frac{3}{R} \sqrt{\frac{2}{n+1}} \sqrt{\frac{D_e}{\rho_p S_a k_n C_{As}^{n-1}}} k_n C_{As}^n$$

$$\propto k_n^{1/2} C_{AS}^{(n+1)/2}$$

$$n' = \frac{1+n}{2} \quad \text{true and apparent} \qquad E_T = 2 E_{APP}$$
$$\text{reaction order}$$

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

The Third Law says that the absolute entropy is Zero for all perfect crystalline temperatures at absolute Zero temperature. This allows us to calculate absolute entropies based on

$$S = \int_0^{T_f} \frac{(c_p)_s}{T} dT + \frac{\Delta H_f}{T_f} + \int_{T_f}^{T_v} \frac{(c_p)_\ell}{T} dT + \frac{\Delta H_v}{T_v} + \int_{T_v}^{T} \frac{(c_p)_g}{T} dT$$

The second law tells us that a system in thermal and mechanical equilibrium with its surroundings

$$dS_{surr} = \frac{dQ_{surr}}{T_{surr}} = -\frac{dQ}{T}$$

$$dS^t + dS_{surr} \geq 0$$

where S^t is total entropy of system. Combining, we get

$$dQ \leq T dS^t$$

Application of the first law gives

$$dU^t = dQ + dW = dQ - P dV^t$$

$$dQ = dU^t + P dV^t$$

$$dU^t + P dV^t \leq T dS^t$$

$$\boxed{dU^t + P dV^t - T dS^t \leq 0}$$

Since this relation involves properties, it must be valid for any closed system. If constricted to constant T & P

$$dU^t_{T,P} + d(PV^t)_{T,P} - d(TS^t)_{T,P} \leq 0$$

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

$$G^t \equiv H^t - TS^t = U^t + PV^t - TS^t$$

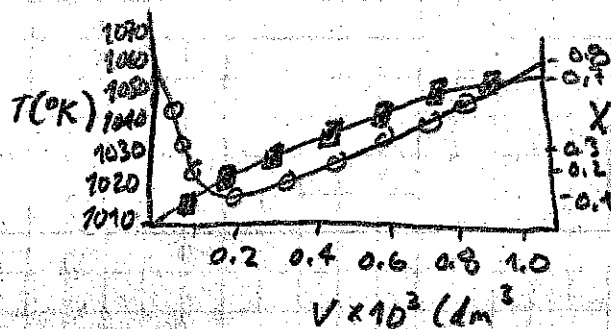$$\boxed{(dG^t)_{T,P} \leq 0}$$

The equilibrium state of a closed system is that state for which the total Gibbs energy is a minimum with respect to all possible changes at given T and P.

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

For an adiabatic, endothermic reaction
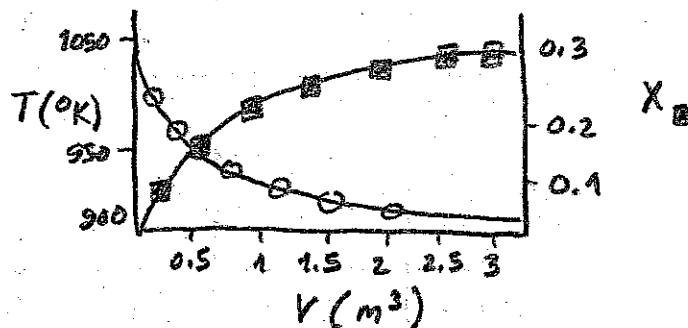
If we have heat exchange in the endothermic reaction

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

A fluidized bed consists of a bed of particles suspended in a liquid or gas. The suspension acts as a fluid as they are allowed to move and held up only by the drag on the individual particles as the fluid passes by. We can model the pressure drop using the Ergun equation:

$$\frac{\Delta p}{L} = \frac{150 \, \bar{v}_0 \, \mu}{g_c \, \phi_s^2 \, D_p^2} \frac{(1-\epsilon)}{\epsilon^3} + \frac{1.75 \, \rho \bar{v}_0^2}{g_c \, \phi_s \, D_p} \frac{1-\epsilon}{\epsilon^3}$$

The advantage of the fluidized bed lies in the contact time (residence time) between fluid and particle. The disadvantage is the pressure drop incurred in doing this.

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

$$\Delta U + \frac{\Delta u^2}{2} + g \Delta Z = Q + W$$

$$W = W_S + P_1 V_1 - P_2 V_2 = W_S - \Delta(PV)$$

$$\Delta U + \Delta(PV) + \frac{\Delta u^2}{2} + g \Delta Z = Q + W_S$$

$$\Delta H + \frac{\Delta u^2}{2} + g \Delta Z = Q + W_S$$

$$\Delta H + \frac{\Delta u^2}{2 g_c} + \frac{g}{g_c} \Delta Z = Q + W_S$$

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

We have a pressure equilibrium constant K_p

$$K_p = \frac{P_C}{P_A P_B}$$

We have a concentration equilibrium constant

$$K_c = \frac{C_C}{C_A C_B}$$

For ideal gases, the two are related by

$$K_p = K_c (RT)^{-1}$$

We can calculate this using van't Hoff's equation

$$\frac{d \ln K_p}{dT} = \frac{\Delta H_{rxn}(T)}{RT^2} = \frac{\Delta H_{rxn}^o(T_R) + \Delta \hat{C}_p (T - T_R)}{RT^2}$$

Or we can use Gibb's free energy

$$-RT \ln [K(T)] = \Delta G_{rxn}^o (T)$$

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

We derive an equation for the PFR:

$$IN - OUT + GEN = ACC$$

$$F_A|_z - F_A|_{z+\Delta z} + r_A A \Delta z = 0$$

$$-\frac{dF_A}{dz} = -r_A A$$

$$-\frac{dF_A}{dV} = k C_A$$

$$-v_0 \frac{dC_A}{dV} = k C_A$$

$$-\frac{dC_A}{d\tau} = k C_A$$

We can measure concentration at various lengths down the reactor and plot $(-dC_A/d\tau)$ versus C_A to get the rate constant, k, the slope.

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

For ideal gases

$$G^{id} = \sum_i x_i G_i + RT \sum_i x_i \ln x_i \qquad \Delta G_{mix} = RT \sum_i x_i \ln x_i$$

$$S^{id} = \sum_i x_i S_i - R \sum_i x_i \ln x_i \qquad \Delta S_{mix} = -R \sum_i x_i \ln x_i$$

$$V^{id} = \sum_i x_i V_i \qquad\qquad \Delta V_{mix} = 0$$

$$H^{id} = \sum_i x_i H_i \qquad\qquad \Delta H_{mix} = 0$$

Similarly for ideal solution

$$\Delta G^{id} = RT \sum_i x_i \ln x_i$$

$$\Delta S^{id} = -R \sum_i x_i \ln x_i$$

$$\Delta V^{id} = 0$$

$$\Delta H^{id} = 0$$

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

For a species i in a vapor mixture, we have

$$\hat{f}_i^v = y_i \hat{\Phi}_i P$$

and for species i in the liquid solution, we have

$$\hat{f}_i^l = x_i \gamma_i \hat{\Phi}_i^{sat} P_i^{sat} \underbrace{\exp \frac{V_i^l (P - P_i^{sat})}{RT}}$$

Poynting factor for high pressures

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

For ideal gases, $\Phi_i = 1$. For ideal solutions, $\gamma_i = 1$.

$$\boxed{y_i P = x_i P_i^{sat}} \quad \text{Raoult's Law}$$

In the limit of $x_i \to 0$, we have

$$\boxed{\hat{f}_i = x_i k_i} \quad \text{Henry's law}$$

where k_i is Henry's constant. We can use this for very dilute solutions.

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

No, Raoult's law is the simplest possible equation for VLE, and fails to represent real behavior for most systems.

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

The Lewis / Randall rule applies to each species in an ideal solution at all T, P, x_i

$$\hat{f}_{id} = x_i f_i$$

The Lewis fugacity rule applies to each species in an ideal mixture at fixed T, P, x_i

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

The fugacity of component i in a gas mixture can be related to the fugacity of pure component i in gas mix

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

Amagat's law states that at fixed T & P, the components mix isometrically.

$$V = \sum_i n_i v_i$$

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

A mixing rule is composition dependent, a combining rule is not.

EOS that are cubic in molar volume are capable of describing behavior of both liquid & vapor phase. The application of such equation to mixtures requires that EOS parameters be expressed as function of composition. No exact theory like that for the virial equation prescribes this composition dependence, which is instead imposed by mixing rules.

For Redlich Kwong

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

mixing rules are

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

$$b = \sum_i y_i b_i$$

The a_{ij} are of two types: pure-species parameters (like subscripts) and interaction parameters (unlike subscripts). We can calculate using combining rules

$$a_{ij} = (1 - l_{ij})(a_i a_j)^{1/2}$$

55. What is the maximum boiling azeotrope? Does it exhibit positive or negative deviation from Raoult's law? If a solution of this type is distilled will the azeotrope be recovered in the distillate or the bottoms?

An azeotrope exists in a two component system when $x_1 = y_1$, dewpoint and bubble point curves are tangent at same horizontal line. A boiling liquid of this composition produces a vapor of exactly the same composition, and the liquid therefore does not change as it evaporates.
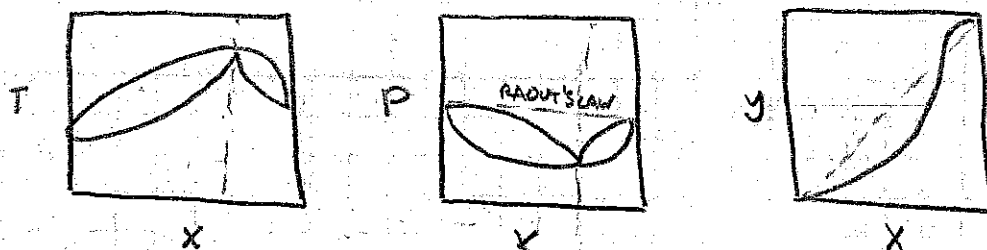
The maximum boiling azeotrope experiences negative deviation from Raoult's law. It will be recovered in the bottoms.

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

$$K_P = \frac{P_{NH_3}^2}{P_{N_2} P_{H_2}^3}$$

This shifts the equilibrium to the right.

57. Derive Maxwell's equations.

$$U = TdS - PdV$$

$$H \equiv U + PV$$

$$dH = dU + PdV + VdP$$

$$\quad = TdS + VdP$$

$$A \equiv U - TS$$

$$dA = dU - TdS - SdT$$

$$\quad = -SdT - PdV$$

$$G \equiv H - TS$$

$$dG = dH - TdS - SdT$$

$$= -SdT + VdP$$

We derive Maxwell's equations from the following relations:

$$dU = TdS - PdV$$

$$dH = TdS + VdP$$

$$dA = -SdT - PdV$$

$$dG = -SdT + VdP$$

These fundamental property relations are general equations for a homogeneous fluid of constant composition.

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

$$= Mdx + Ndy$$

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

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

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

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

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

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

These are Maxwell's equations.

58. Which liquid EOS allow for azeotrope? phase separation?

Wilson Equation

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

$$\ln \delta_1 = -\ln(x_1 + \Lambda_{12} x_2) + x_2 \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{\Lambda_{21} x_1 + x_2} \right]$$

$$\ln \delta_2 = -\ln(x_2 + \Lambda_{21} x_1) - x_1 \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{\Lambda_{21} + x_2} \right]$$

Wilson's equation has two adjustable parameters, Λ_{12} & Λ_{21}. Wilson's equation gives good representation of Gibbs energies for variety of miscible components. Particularly good for polar or associating compounds. Better than three-suffix Margules or Van Laar.

NRTL (non-random two liquid

$$\frac{g^E}{RT} = x_1 x_2 \left[\frac{\tau_{21} G_{21}}{x_1 + x_2 G_{21}} + \frac{\tau_{21} G_{12}}{x_2 + x_1 G_{12}} \right]$$

NRTL contains three parameters, good for strongly nonideal systems mixtures, especially for immiscible.

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Equation for g^E consists of two parts, a combinatorial part which attempts to describe dominant entropic contribution, and residual part which is due primarily to intermolecular forces.

59. What is the corresponding states theorem? What is its significance?

All fluids, when compared at the same reduced T & P, have approximately the same compressibility factor and deviate from ideal gas behavior to about the same degree.

All fluids having the same value of ω, when compared at the same T_r & P_r, have the same value of Z, and all deviate from ideal gas to about same degree.
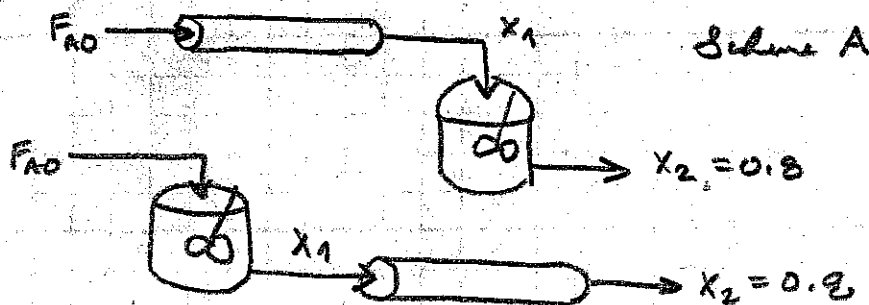
Correlation has advantage of allowing estimation of property values from very limited information.

$$Z = Z^0 + \omega Z^1$$
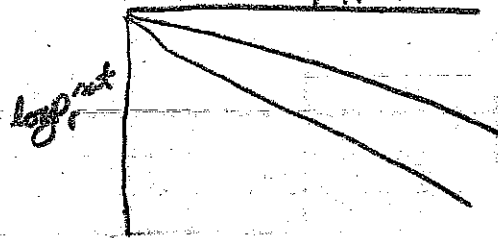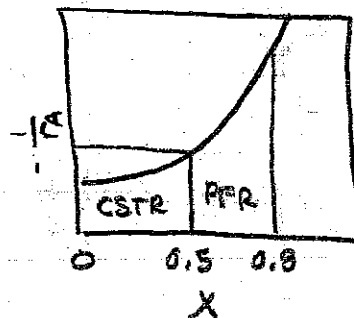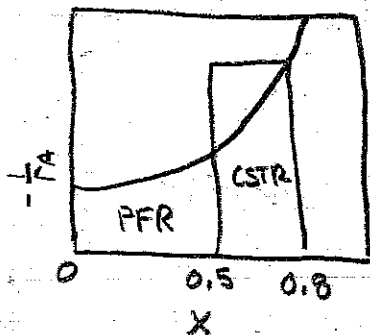

60. Describe the graphical approach to reactor design and analysis.
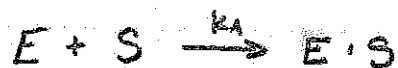
When comparing a sequence of reactors

Scheme A

$X_2 = 0.8$

$X_2 = 0.8$

We want to minimize the areas under the curves

$$\text{PFR}: \quad V = F_{AO} \int_1^2 \frac{dX}{-r_A} \qquad \text{CSTR}: \quad V = F_{AO} \frac{X_2 - X_1}{-r_A}$$

62. Derive the Michaelis - Menton rate equation.

$$E + S \xrightarrow{k_1} E \cdot S$$

$$E \cdot S \xrightarrow{k_2} E + S$$

$$E \cdot S + W \xrightarrow{k_3} P + E$$

$$-r_S = k_1 [E][S] - k_2 [E \cdot S]$$

$$r_{E \cdot S} = k_1 [E][S] - k_2 [E \cdot S] - k_3 [E \cdot S][W]$$

Using PSSH, we set $r_{E \cdot S} = 0$

$$0 = k_1 [E][S] - k_2 [E \cdot S] - k_3 [E \cdot S][W]$$

We redefine [E] by looking at total concentration of enzyme in the system

$$[E_t] = [E] + [E \cdot S]$$

$$0 = k_1 [E_t][S] - k_1 [E \cdot S][S] - k_2 [E \cdot S] - k_3 [E \cdot S][W]$$

$$[E \cdot S] = \frac{k_1 [E_t][S]}{k_1 [S] + k_2 + k_3 [W]}$$

$$-r_S = k_1 [E_t][S] - k_1 [E \cdot S][S] - k_2 [E \cdot S]$$

$$-r_S = k_3 [W][E \cdot S]$$

$$-r_S = \frac{k_3 [W][E_t][S]}{k_1 [S] + k_2 + k_3 [W]}$$

$$k_3' = k_3 [W] \quad , \quad K_m = \frac{k_3' + k_2}{k_1}$$

$$-r_S = \frac{k_3' [S][E_t]}{[S] + K_m}$$

If we let $V_{max} = k_3' [E_t]$

$$-r_S = \frac{V_{max} [S]}{K_m + [S]}$$

63. What is a Thiele parameter? What is its usefulness?

The Thiele modulus gives us an idea of the rate of the reaction versus the rate of diffusion.

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

$$= \frac{\text{"a" surface reaction rate}}{\text{"a" diffusion rate}}$$

When the Thiele modulus is large, diffusion usually limits the overall rate of reaction; when Φ_n is small, the surface reaction usually rate-limiting.

65. Give the van der Waals EOS. What is the significance of the constants a & b? How would you estimate them given critical T & P data? What does the PV diagram of a VdW gas look like? Where is it correct and where is it wrong? Where are its stable, unstable, and metastable regions?

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

$a \equiv$ accounts for attractive molecular forces

$b \equiv$ volume occupied by molecules

$$a = \frac{27 R^2 T_c^2}{64 P_c}, \quad b = \frac{RT_c}{8 P_c}$$

$T_1 > T_c$

T_c

$T_2 < T_c$

P

$V_{(liq)}^{sat}$ V $V_{(vap)}^{sat}$
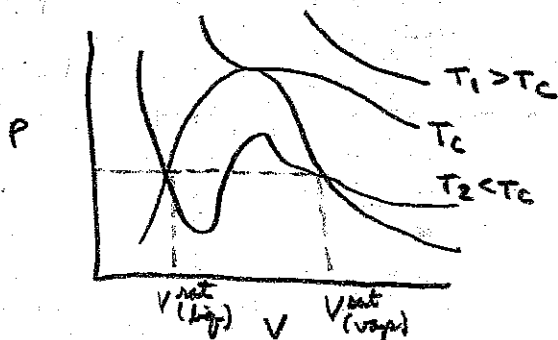
66. Given a closed drum of organic liquid which reacts exothermically with traces of water present in the drum, derive all the equations necessary to describe the temperature and pressure in the drum with Time.

We can write a mass balance on the batch reactor:

IN − OUT + GEN = ACC

$$\frac{dN_A}{dt} = r_D V$$

$$\frac{dC_A}{dt} = r_D$$

$$C_A = C_{AO}(1 - X_A)$$

$$- C_{AO}\frac{dX_A}{dt} = r_D$$

We can also write a corresponding energy balance

$$\dot{Q} - \dot{W}_S - N_{AO}\sum \Theta_i C_{p_i}(T - T_{io}) - N_{AO}X\left[\Delta H_R^\circ(\tau_R) + \Delta\hat{C}_p(T - T_R)\right] = 0$$

We can solve the equation simultaneously to find T as a function of X.

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

We write the mass balance on the CSTR:

IN − OUT + GEN = ACC

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

$$\frac{F_{AO} - F_A}{V} = -r_A$$

$$F_A = F_{AO}(1 - X_A)$$

$$\frac{F_{AO}X_A}{V} = r_A$$

We write the energy balance on the CSTR:

$$\dot{Q} - \dot{W}_s - [\Delta H_{Rx}^{\circ}(T_R) + \Delta C_p (T-T_R)]F_{A0} X = F_{A0} \sum_{i=1}^{n} \theta \hat{C}_{p_i} (T-T_i)$$

We can calculate ΔG_{Rxn}° based on equilibrium constant

$$-RT \ln [K(T)] = \Delta G_{Rxn}^{\circ}(T)$$

To shift equilibrium, change the temperature.

68. What is the Gibbs Helmholtz law?

$$G \equiv H - TS$$

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

$$\left(\frac{\partial}{\partial T}\left(\frac{G}{T}\right)\right)_p = -\frac{H}{T^2}$$

The Gibbs-Helmholtz law shows that if the enthalpy of the system is known, then the temperature dependence of G/T is also known.

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

$$\left(\frac{\partial}{\partial T}\left(\frac{G}{T}\right)_p\right) = \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_p + G\left(\frac{\partial}{\partial T}\left(\frac{1}{T}\right)\right)_p = \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_p - \frac{G}{T^2}$$

$$= \frac{1}{T}\left\{\left(\frac{\partial G}{\partial T}\right)_p - \frac{G}{T}\right\}$$

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

71. For the reaction $A \to P$ discuss the unimolecular reaction theory. What is the order of the reaction? For $r = k_{eff} C_A$, plot k_{eff} versus pressure. What is the effect of temperature on this plot? If the reaction took place in a CSTR, how would conversion depend on temperature?

Overall reaction has bimolecular as well as unimolecular steps.

$$A + A \to A^* + A$$

$$\frac{d[A^*]}{dt} = k_a [A]^2$$

$$A + A^* \to A + A$$

$$\frac{d[A^*]}{dt} = -k_a' [A^*][A]$$

$$A^* \to P$$

$$\frac{d[A^*]}{dt} = -k_b [A^*]$$

If unimolecular step is slow enough to be rate determining, overall reaction has first-order kinetics.

$$\frac{d[A^*]}{dt} = k_a [A]^2 - k_a' [A^*][A] - k_b [A^*] = 0 \quad \text{PSSH}$$

$$[A^*] = \frac{k_a [A]^2}{k_b + k_a' [A]}$$

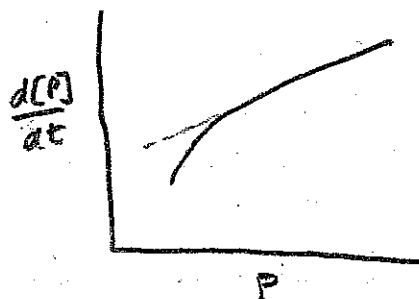$$\frac{d[P]}{dt} = k_b [A^*] = \frac{k_a k_b [A]^2}{k_b + k_a' [A]}$$

$$k_a' [A^*][A] \gg k_b [A^*] \quad , \quad k_a' [A] \gg k_b$$

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

If we decrease P (and therefore partial pressure, conc.) reaction switches to overall second-order kinetics.

$$k'[a] \ll k_b$$

$$\frac{d[P]}{dt} = k_a [A]^2$$

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

We use a batch reactor for small-scale operation, testing new products, manufacture of expensive products. Has advantage of high conversion from high residence time, disadvantage of high labor cost.

Semibatch has same disadvantages of batch, but good T control and capability of minimizing unwanted side reactions enables to minimize side reaction. Can maintain low concentration of one of components.

CSTR is used when intense agitation is required. Relatively easy to maintain good T control. Disadvantage is low conversion.

PFR is easy to maintain and produces high conversion per reactor volume. Disadvantage is ability to maintain T control and hot spots occur.

Also fixed bed, fluidized bed, etc.

74. What is the frequency factor?

One of Arrhenius parameters of reaction.

$$k = e^{-\Delta G \ddagger / RT} \quad \text{or} \quad -RT \ln k = \Delta G \ddagger$$

Measure of rate at which collisions occur irrespective of their energies. Gives rate of successful collisions.