

Thermodynamics

→ Laws.

1. E neither created/destroyed - appears instantaneously.

$$\Delta U = \Delta Q - \Delta W$$

2. No < complete conversion of heat → energy
transfer of heat from hotter to colder

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

$$\text{Combined Statement 1/2: } dU \leq dQ - dW \\ \leq TdS - PdV$$

3. Entropy of a perfect crystalline material at 0K is zero.

• (Nernst's Law states this trend)

• $S = k \ln W$; at 0K no other choices; $W=1 \Rightarrow S=0$.

→ Basics. ∴ $dU = dQ - dW$ (irreversible).

$$= TdS - PdV; dQ_{\text{rev}} = TdS, dW_{\text{rev}} = PdV$$

$$H = U + PV$$

$$G = H - TS$$

$$A = U - TS$$

So using above: $dH = dU + PdV + VdP$

$$\therefore dH = TdS + VdP$$

$$dG = dH - TdS - SdT$$

$$\therefore dG = VdP - SdT$$

$$dA = dU - TdS - SdT$$

$$\therefore dA = -SdT - PdV$$

→ Maxwell's Relations:

$$dU = TdS - PdV \Rightarrow \left(\frac{\partial U}{\partial S}\right)_V = T, \left(\frac{\partial U}{\partial V}\right)_S = -P \Rightarrow \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

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

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

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

Heat Capacity Relations

$$\left(\frac{\partial U}{\partial T}\right)_V = C_V \quad \left(\frac{\partial H}{\partial T}\right)_P = C_P \quad \left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T} \quad \left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T}$$

→ Adiabatic Ideal Gas.

$$du = d\phi - dw = -PdV$$

$$C_v dT = -PdV \xrightarrow{IG} C_v dT = -\frac{RT}{V} dV \Rightarrow C_v \frac{dT}{T} = -R \frac{dV}{V}$$

$$\therefore \ln\left(\frac{T_2}{T_1}\right) = -\frac{R}{C_v} \ln\left(\frac{V_2}{V_1}\right); \quad \frac{C_p}{C_v} = \frac{C_v + R}{C_v} = 1 + \frac{R}{C_v} \Rightarrow \frac{R}{C_v} = \frac{C_p}{C_v} - 1 = \gamma - 1$$

$$\Rightarrow \frac{T_2}{T_1} = \frac{V_2^{1-\gamma}}{V_1^{1-\gamma}}$$

$$= \left(\frac{P_1}{P_2}\right)^{1-\gamma} \left(\frac{T_2}{T_1}\right)^{1-\gamma} \Rightarrow \frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}} \Rightarrow \frac{P_2}{P_1} = \frac{V_1^\gamma}{V_2^\gamma} \Rightarrow P_1 V_1^\gamma = P_2 V_2^\gamma$$

$$W = \int PdV$$

$$= \int \frac{k}{V^\gamma} dV = k \int \frac{dV}{V^\gamma} = -\frac{k}{\gamma-1} \left(V_2^{-(\gamma-1)} - V_1^{-(\gamma-1)} \right)$$

$$= \frac{k}{1-\gamma} \left(\frac{V_2}{V_2^\gamma} - \frac{V_1}{V_1^\gamma} \right) = \frac{1}{1-\gamma} (P_2 V_2 - P_1 V_1) = \frac{1}{\gamma-1} (P_1 V_1 - P_2 V_2)$$

$$= \frac{P_1 V_1}{\gamma-1} \left(1 - \frac{P_2 V_2}{P_1 V_1} \right) = \frac{P_1 V_1}{\gamma-1} \left(1 - \frac{T_2}{T_1} \right) = \frac{P_1 V_1}{\gamma-1} \left(1 - \left(\frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}} \right)$$

$$= \frac{RT_1}{\gamma-1} \left(1 - \left(\frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}} \right)$$

→ Heat Capacities

$$dS = \left(\frac{\partial S}{\partial T} \right)_V dT + \left(\frac{\partial S}{\partial V} \right)_T dV$$

$$= \frac{C_v}{T} dT + \left(\frac{\partial P}{\partial T} \right)_V dV \quad \text{where} \quad \left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial V}{\partial P} \right)_T \left(\frac{\partial T}{\partial V} \right)_P = -1$$

$$\left(\frac{\partial S}{\partial T} \right)_P = \frac{C_v}{T} + \left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial V}{\partial T} \right)_P = \frac{C_v}{T} + \left(\frac{\partial V}{\partial T} \right)_P^2 \left(\frac{\partial P}{\partial V} \right)_T$$

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \quad \text{Thermal expansion} \quad IG \rightarrow \frac{1}{T}$$

$$K_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \quad \text{Compressibility} \quad IG \rightarrow 1/P$$

$$C_p = C_v + VT \frac{\alpha^2}{K_T} \xrightarrow{IG} C_p = C_v + R$$

→ Joule-Thompson Coefficient

$$\mu = \left(\frac{T_2 - T_1}{P_2 - P_1} \right)_H \quad \text{in limit of } \Delta S \rightarrow 0 \quad \mu = \left(\frac{\partial T}{\partial P} \right)_H$$

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

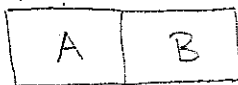
$$\therefore \mu = \left(\frac{\partial T}{\partial P} \right)_H = \frac{V - T \left(\frac{\partial V}{\partial T} \right)_P}{C_p}$$

$$IG: \mu = \frac{V - \frac{RT}{P}}{C_p} = 0 \quad \text{Real: } \begin{matrix} \text{hi } T & \mu < 0 \\ \text{lo } T & \mu > 0 \end{matrix}$$

Inversion T; $\mu = 0$

→ Prove S tends toward a maximum.

Heat transfer from $A \rightarrow B$



Entropy Balance $\frac{dS}{dt} = \sum m_k s_k + \frac{\dot{Q}}{T} + \dot{S}_g$

Assume reversible heat transfer

$$\frac{dS_A}{dt} = \frac{\dot{Q}_A}{T_A} = -h \frac{(T_A - T_B)}{T_A} \quad \frac{dS_B}{dt} = \frac{\dot{Q}_B}{T_B} = +h \frac{(T_B - T_A)}{T_B}$$

For overall system

$$\dot{S}_g = -h \frac{(T_A - T_B)}{T_A} + h \frac{(T_B - T_A)}{T_B} \quad \dot{Q} = 0 \quad \text{so} \quad \frac{dS_{tot}}{dt} = \dot{S}_g = \frac{dS_A}{dt} + \frac{dS_B}{dt}$$

$$\dot{S}_g = \frac{h \Delta T^2}{T_A T_B} \geq 0$$

→ Prove $\Delta G_{T,P} < 0$ for any process

2nd Law sez $\Delta S_{tot} > 0$ (all processes irreversible to some extent)

$$dS_{tot} = dS_{sys} + dS_{surr} > 0$$

$$dS_{sys} - \frac{dQ_{surr}}{T} > 0 \Rightarrow dS_{sys} > \frac{dQ_{surr}}{dT}$$

↑
heat transfer to
system

For closed system

$$dU < dQ - dW \Rightarrow dU < TdS - PdV$$

$$G = U + PV - TS$$

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

$$dG_{T,P} = dU + PdV - TdS \quad \text{from above} \quad dG_{T,P} < 0$$

→ Gibbs Duhem Equation

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

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

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

or more spec: $SdT + VdP + \sum_i n_i du_i = 0$

→ Clapeyron + Clausius Clapeyron Equations

$$g' = g''$$

$$dg' = dg''$$

$$v'dp - s'dt = v''dp - s''dt$$

$$\frac{dp}{dt} = \frac{s'' - s'}{v'' - v'} = \frac{\Delta s}{\Delta v}$$

$$dq' = dq''$$

$$h' - ts' = h'' - ts''$$

$$\Delta s = \frac{\Delta h}{T}$$

$$\therefore \frac{dp}{dt} = \frac{\Delta h}{T \Delta v} \Rightarrow \left(\frac{dp^*}{dt} \right) = \frac{\Delta h}{T \Delta v}$$

$$VLE \Rightarrow p^* = p^{vap} \quad \Delta h = \Delta h^{vap} \quad \Delta v = v^v - v^l \sim v^v = \frac{RT}{p}$$

$$\therefore \left(\frac{dp^{vap}}{dt} \right) = \frac{p^{vap} \Delta h^{vap}}{RT^2} \Rightarrow \ln \left(\frac{p_2^{vap}}{p_1^{vap}} \right) = -\frac{\Delta h^{vap}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

→ Gibbs Helmholtz Law.

$$G = H - TS$$

$$\frac{G}{T} = \frac{H}{T} - S \Rightarrow \frac{\partial(G/T)}{\partial T} = \frac{1}{T} \frac{\partial H}{\partial T} - \frac{H}{T^2} - \frac{\partial S}{\partial T}$$

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

→ Chemical Potential

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

→ Gibbs Phase Rule

$$U: \pi \text{ phases}, (m-1) \text{ mole frac.} + T, P \Rightarrow U = \pi(m-1) + 2$$

$$K: \mu_i' = \mu_i'' \text{ each species: } m(\pi-1)$$

$$\sum \nu_i dn_i = 0 \text{ each reaction: } r$$

additional constraints s:

$$\therefore F = 2 + \pi(m-1) - m(\pi-1) - r - s = 2 + m + \pi - r - s = F$$

→ Corresponding States

Microscopic.

- Reduced pressure is a universal function of reduced temperature and reduced volume. Function is valid for all fluids given 2 unique parameters ϵ, σ .

$$P^R = \mathcal{F}(T^R, V^R)$$

$$; P^R = \frac{P\sigma^3}{\epsilon}, T^R = \frac{KT}{\epsilon}, V^R = \frac{V}{N\sigma^3}$$

Macroscopic.

- Same deal but now reducing parameters are macroscopic - the critical properties.

$$\frac{P}{P_c} = \mathcal{F}\left(\frac{T}{T_c}, \frac{V}{V_c}\right)$$

→ Van der Waals EOS.

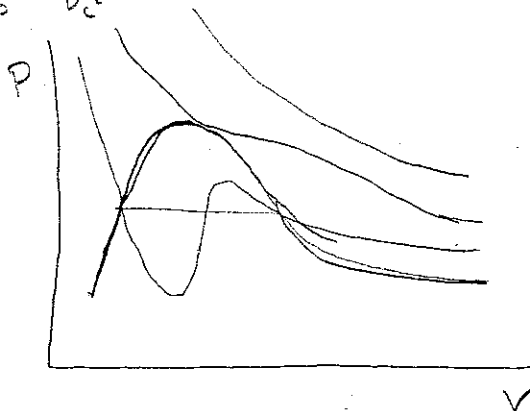
$$P = \frac{RT}{v-b} - \frac{a}{v^2} \quad b \rightarrow \text{finite size of gas particles - free vol is now } v-b \text{ in } v$$

- Can get a, b from critical data, P_c, T_c .

$$\left(\frac{\partial P}{\partial v}\right)_{cp} = \left(\frac{\partial^2 P}{\partial^2 v}\right)_{cp} = 0 \text{ with } P_c = \frac{RT_c}{v_c-b} - \frac{a}{v_c^2} \text{ solve for } a, b, v_c.$$

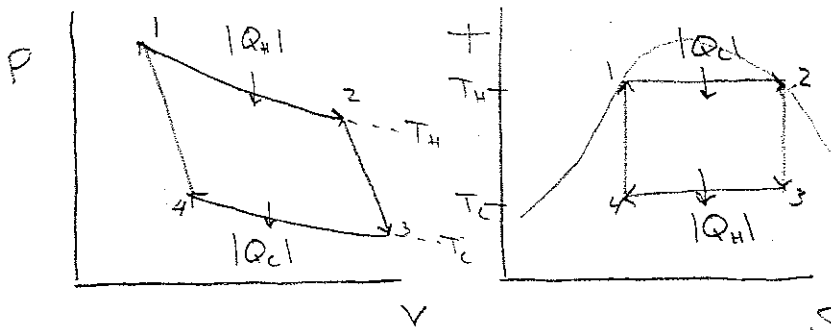
$$\therefore a = \frac{27R^2T_c^2}{64P_c} \quad b = \frac{RT_c}{8P_c}$$

- VdW correct outside VLE curve
incorrect inside curve (dashed lines).



Carnot Cycle.

- > 1-2 Isothermal Exp
- > 2-3 Adiabatic Exp
- > 3-4 Isothermal Comp
- > 4-1 Adiabatic Comp



• Net Work $W = |Q_H| - |Q_C|$

• Efficiency $\eta = \frac{\text{network}}{\text{heat input}} = \frac{|Q_H| - |Q_C|}{|Q_H|} = 1 - \frac{|Q_C|}{|Q_H|} = 1 - \frac{T_C}{T_H} = \eta$

• Isothermal Steps: $dU = dQ - dW \Rightarrow \text{const } T \Rightarrow Q = W$

$$Q = W = \int P dV = \int RT \frac{dV}{V} = RT \ln \frac{V_2}{V_1} \quad (1GL)$$

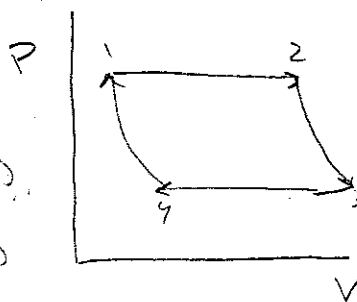
$$Q = W = RT \ln \frac{V_2}{V_1} = RT \ln \frac{P_1}{P_2}$$

• Adiabatic Steps: $dU = dQ - dW \Rightarrow \left. \begin{array}{l} dU = C_V dT \\ dW = P dV \end{array} \right\} C_V dT = P dV$

$$P_1 V_1^\gamma = P_2 V_2^\gamma \quad (\text{as before})$$

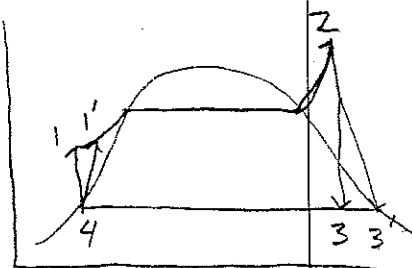
Rankine Cycle.

- > 1-2 Const+P heating (superh vap.)
- > 2-3 Adiabatic Exp (wet vap)
- > 3-4. Const+P, T Cond (sat liquid)
- > 4-1 Rev, Adiabatic compression.



Diff Between Carnot/Rankine.

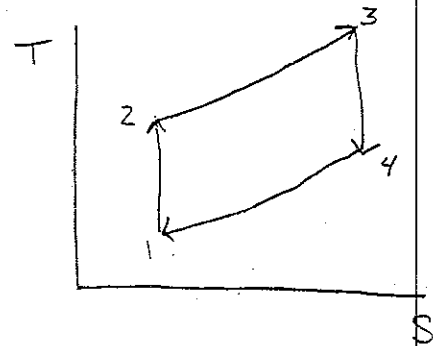
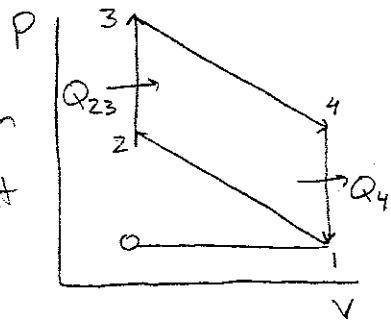
- Heating past vaporization 1-2
- Complete condensation 3-4.



• Reality: 2-3, 4-1 not reversible so look at line shifts toward increasing entropy.

Otto Cycle. - Ideal Cycle for Internal Combustion Engine.

- > 0-1 volume expansion
- 1-2 adiabatic compression
- 2-3 const vol heat addition
- 3-4 adiabatic expansion
- 4-1 const vol ejection of heat



Thermal Efficiency $\eta = \frac{Q_{23} + Q_{41}}{Q_{23}}$

CV steps: Use $Q = C_v \Delta T \Rightarrow \eta = 1 + \frac{Q_{41}}{Q_{23}} = 1 - \frac{T_4 - T_1}{T_3 - T_2} = \eta$.

Compression Ratio: $r = \frac{V_1}{V_2}$

IGL $\Rightarrow T = \frac{PV}{R} \quad \eta = 1 - \frac{V_1(P_4 - P_1)}{V_2(P_3 - P_2)} = 1 - r \frac{P_4 - P_1}{P_3 - P_2}$

Adiabatic Comp/Exp

$$P_3 V_2^\gamma = P_4 V_1^\gamma \quad P_2 V_2^\gamma = P_1 V_1^\gamma \Rightarrow \frac{P_1}{P_2} = \left(\frac{1}{r}\right)^\gamma$$

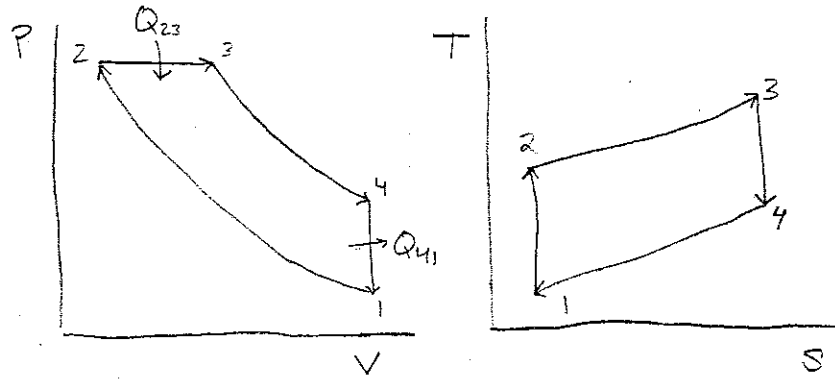
Combining, $\frac{P_2}{P_1} = \frac{P_3}{P_4} \Rightarrow \frac{P_4}{P_1} = \frac{P_3}{P_2} \quad \eta = 1 - r \left(\frac{P_1}{P_2}\right) \left(\frac{\frac{P_4}{P_1}}{\frac{P_3}{P_2} - 1}\right)$

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

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

Diesel Cycle

- > 1-2 adiabatic comp
- > 2-3 compress add heat
- > 3-4 adiabatic expansion
- > 4-1 convol eject heat



Egns

$$1-2 \quad \frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}; P_1 V_1^{\gamma} = P_2 V_2^{\gamma}$$

$$2-3 \quad Q_{23} = C_p (T_3 - T_2) \quad W_{23} = P(V_3 - V_2)$$

$$3-4 \quad \frac{T_4}{T_3} = \left(\frac{V_3}{V_4}\right)^{\gamma-1}; P_3 V_3^{\gamma} = P_4 V_4^{\gamma}$$

$$4-1 \quad Q_{41} = C_v (T_1 - T_4)$$

Thermal Efficiency. $\eta = \frac{W}{Q_{23}} = 1 + \frac{Q_{41}}{Q_{23}} = 1 - \frac{C_v (T_4 - T_1)}{C_p (T_3 - T_2)}$

Comp ratio $r = V_1/V_2$
Exp ratio $r_e = V_4/V_3$ Cutoff ratio $r_c = \frac{V_3}{V_2}$

Fund: $T_4 = T_3 \left(\frac{V_3}{V_4}\right)^{\gamma-1} = T_3 \left(\frac{1}{r_e}\right)^{\gamma-1}$ $T_1 = T_2 \left(\frac{V_2}{V_1}\right)^{\gamma-1} = T_2 \left(\frac{1}{r}\right)^{\gamma-1}$

$$\eta = 1 - \frac{1}{\gamma} \left(\frac{T_3 \left(\frac{1}{r_e}\right)^{\gamma-1} - T_2 \left(\frac{1}{r}\right)^{\gamma-1}}{T_3 - T_2} \right) = 1 - \frac{1}{\gamma} \left(\frac{\left(\frac{1}{r_e}\right)^{\gamma-1} - \frac{T_2}{T_3} \left(\frac{1}{r}\right)^{\gamma-1}}{1 - T_2/T_3} \right)$$

$P_2 V_2 = R T_2 \Rightarrow \frac{P_2}{R} = \frac{T_2}{V_2}$ $\frac{P_3}{R} = \frac{T_3}{V_3}$; $P_2 = P_3$ $\frac{P_2}{R} = \frac{T_3}{V_3}$

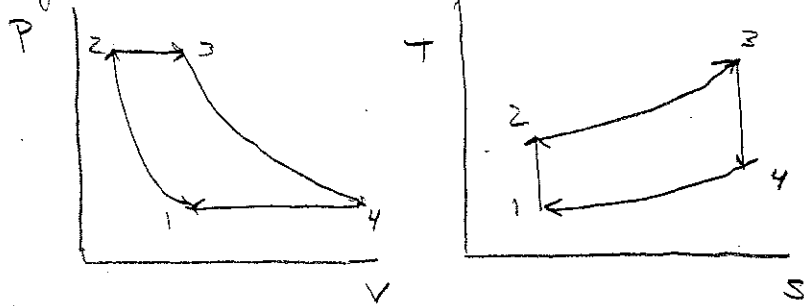
$$\frac{T_2}{V_2} = \frac{T_3}{V_3} \quad \frac{T_2}{T_3} = \frac{V_3}{V_2} = \frac{V_2/V_1}{V_3/V_4} = \frac{r_e}{r}; V_1 = V_4$$

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

Can also find $\eta = 1 - \frac{1}{r^{\gamma-1}} \left[\frac{r_e^{\gamma} - 1}{\gamma(r_e - 1)} \right]$

Brayton Cycle - model for gas turbine power plant

- > 1-2 adiabatic comp
- > 2-3 Com press add heat
- > 3-4 adiabatic exp
- > 4-1 Com press q ect heat



Equations

$$1-2 \quad \frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}}$$

$$-W_{12} = H_2 - H_1 = C_p (T_2 - T_1)$$

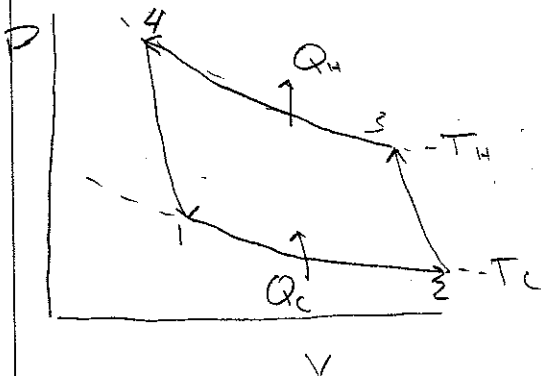
$$2-3 \quad Q_{23} = C_p (T_3 - T_2)$$

$$3-4 \quad \frac{T_4}{T_3} = \left(\frac{P_4}{P_3}\right)^{\frac{\gamma-1}{\gamma}} = \left(\frac{P_1}{P_2}\right)^{\frac{\gamma-1}{\gamma}} ; P_4 = P_1, P_2 = P_3$$

$$-W_{34} = C_p (T_4 - T_3)$$

$$\Rightarrow \eta = \frac{W_{12} + W_{34}}{Q_{23}} = 1 + \frac{(T_1 - T_4)}{(T_2 - T_3)} = 1 - \frac{T_1}{T_2} \left(\frac{T_4/T_1}{T_3/T_2} \right) = 1 - \frac{1}{(P_2/P_1)^{\frac{\gamma-1}{\gamma}}}$$

Carnot Refrigeration Cycle



2→3 } adiabatic steps.
4→1 }

$\Delta U = 0$ for cycle.

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

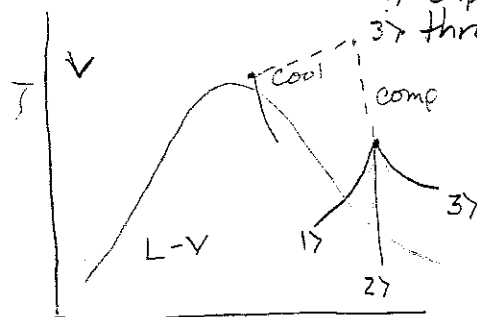
$$\text{Coeff of Performance } W = \frac{\text{heat absorbed at low temp}}{\text{net work}} = |Q_c| / |W|$$

$$\frac{1}{W} = \frac{|Q_h| - |Q_c|}{|Q_c|} = \frac{T_h}{T_c} - 1$$

Choice of Refrigerant

- toxicity
- flammability
- cost
- corrosion
- chem stability

- Liquefaction of Gases
- 1> heat exchange at constant P
 - 2> expansion in turbine where work is obtained
 - 3> throttling process (JT liquefaction)



see below for applicability.

- Polytropic Process - a process for which mechanical irreversibility is the only imposed condition. (nothing special like adiabatic / isothermal / etc)

For this:

$$\begin{aligned} dU &= dQ - dW \\ dW &= PdV \\ dQ &= C_v dT + PdV \\ dU &= C_v dT \\ dH &= C_p dT \end{aligned}$$

- Adiabatic Flame Temperature - Max Attainable temp for a process.
(usually combustion processes).
All heat used to heat products + unused reactants.

For SS process

$$\Delta h = \dot{q} - \dot{w}_s = 0$$

$$\therefore \Delta h = 0 = \Delta h_{rxn} + \Delta h_{heating}$$

$$\Delta h_{rxn} = \sum_{prod} \dot{n}_i h_{T_{rxn}}^f - \sum_{react} \dot{n}_i h_{T_{rxn}}^f$$

$$\Delta h_{heat} = \sum y_i C_{p,i} (T_{A_f} - T_{rxn})$$

So we need

- Δh_{rxn} or $h_{T_{rxn}}^f$
- product stream composition
- C_p of all species in above

Reactor Design

$$F_{j0} - F_j + G_j = \frac{dN_j}{dt}$$

$$F_{j0} - F_j + \int_V r_j dV = \frac{dN_j}{dt}$$

Batch: $F_{j0} = F_j = 0$

well mixed $r_j = f(V) \Rightarrow \frac{dN_j}{dt} = r_j V \Rightarrow \frac{d(C_j V)}{dt} = r_j V$

CSTR: SS $\frac{dN_j}{dt} = 0$

well mixed $r_j V = F_{j0} - F_j \Rightarrow V = \frac{F_{j0} - F_j}{-r_j}$

PFR: SS: $F_{j0} - F_j|_{y+y_0} = -r_j V \Rightarrow -\frac{dF_j}{dy} = -r_j A \Rightarrow \frac{dF_j}{dV} = -r_j$

Now in terms of conversion

Batch $N_{j0} \frac{dx_j}{dt} = r_j V$

CSTR $V = \frac{F_{j0} x}{-r_j}$

PFR $F_{j0} \frac{dx}{dV} = -r_j$

Stoichiometry

$$G = \frac{C_{A0} (B - \alpha_j / \alpha_A x_A)}{(1 + \epsilon x_A)}; \epsilon = y_{A0} \delta$$

$$\delta = -\sum_j \alpha_j / \alpha_A$$

Energy Balances

PFR: $\sum m_j C_{pj} \frac{dT}{dz} - \frac{\pi d_r^2}{4} \sum_i (-\Delta H_i) (r_i) - \pi d_r U (T - T_r) = 0$

BATCH: $m + \bar{C}_p \frac{dT}{dt} = V \sum_i (-\Delta H_i) (r_i) + A_k U (T_r - T)$

CSTR: $0 = \sum F_{j0} (H_j - H) + V \sum_i (-\Delta H_i) (r_i) + A_k U (T_r - T)$

→ Thermodynamic Restrictions on Form of Rate Equation.
Consider $aA + bB \rightleftharpoons cC$

Power law Kinetics $\Rightarrow (r_c) = k_f [A]^{\alpha} [B]^{\beta} [C]^{\gamma} - k_r [A]^{\alpha'} [B]^{\beta'} [C]^{\gamma'}$

Equilibrium Requirement $\Rightarrow \frac{k_f}{k_r} = [A]^{-\alpha+\alpha'} [B]^{-\beta+\beta'} [C]^{-\gamma+\gamma'}$

Also know

$$K_{eq} = \frac{[C]^c}{[A]^a [B]^b} \text{ and } K_{eq} = \left(\frac{k_f}{k_r} \right)^s ; s = \text{stoich \# of RDS}$$

So we have requirement $\frac{\alpha'-\alpha}{-a} = \frac{\beta'-\beta}{-b} = \frac{\gamma'-\gamma}{-c} = \frac{1}{s}$

→ Internal Effectiveness Factor

$$\eta = \frac{\text{actual rate for entire catalyst pellet}}{\text{rate evaluated at catalyst pellet surface}}$$

→ Thiele Modulus. • Perform shell balance for geometry.
• ND and solve to find concentration coefficient. - ϕ^2

1st Slab: $\phi = L \sqrt{\frac{k_p}{D_{eA}}}$ 1st any: $\phi = f \sqrt{\frac{k_p}{D_{eA}}}$ $f \equiv \text{shape factor} \equiv \frac{V}{S}$

Generalized: $\phi = f \sqrt{\left(\frac{n+1}{2} \right) \frac{k_p C_s^{(n-1)}}{D_{eA}}}$

Small ϕ : fast diffusion, generally $\eta \sim 1$.

Large ϕ : rate of reaction is faster so diffusion incomplete $\eta \ll 1$.

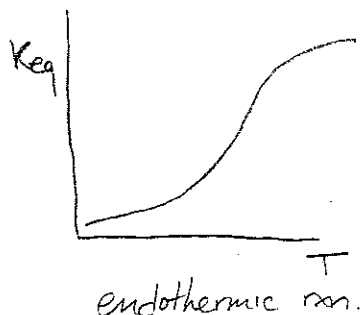
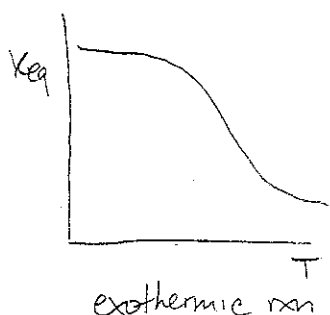
→ Falsified Kinetics.

Knudsen regime $n_{app} = \frac{n+1}{2} \quad k_{app} = \sqrt{k}$

→ Van't Hoff's Equation

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

→ $\ln \frac{K_{eq,1}}{K_{eq,2}} = \frac{\Delta H_R^\circ(T_R)}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$ → Slope of $\ln K_{eq}$ vs. $1/T$ curve is $-\Delta H_R^\circ(T_R)/R$



• Le Chatelier's Principle: for exothermic rxns, equilibrium shifts to left for increasing temperatures (converse is also true)

Mechanism Testing.

→ Integral Method: $-r_A = -\frac{dC_A}{dt} = k f(C_A) \Rightarrow kt = - \int_{C_{A0}}^{C_A} \frac{dC_A}{f(C_A)}$

• So plot of $\int \frac{dC_A}{f(C_A)}$ vs. time will be straight line for correct $f(C_A)$. So for 1st order: $-\ln \frac{C_A}{C_{A0}}$ vs. t .

• N.B. Variable volume considerations in integral.

→ Differential Method $-r_A = k C_A^m \Rightarrow \log(-r_A) = \log k + m \log C_A$.

- Plot C_A v. time and differentiate to generate $\log(-r_A)$ vs. time.
- Plot $\log C_A$ vs. $\log(-r_A)$ to obtain straight line of slope m (reaction order).

Chemical Equilibrium

- Principle of Microscopic Reversibility - at equilibrium the rate of direct conversion from a state A to another state B must exactly equal the direct conversion rate of state B to state A.
- Thermodynamic Defn of Equilibrium - the net global rate of reaction of all species is equal to zero.

Above statements are slightly different.

Equilibrium defn gives combinations for multispecies where PMR is more specific for each reaction.