

Remember J NOT kJ, and account for MOLES

Heat Engines

efficiency $e = \frac{\text{benefit}}{\text{cost}} = \frac{W}{Q_h} = 1 - \frac{Q_c}{Q_h}$

$Q_h = Q_c + W \quad e \leq 1 - \frac{T_c}{T_h}$

Carnot Cycle: Max possible efficiency

But too slow for real use

1. isothermal expansion at T_h (heat abs.)
2. adiabatic expansion to T_c
3. isothermal compression at T_c (heat exp.)
4. adiabatic compression to T_h

Real Heat Engines

Otto Cycle (gasoline):

$e = 1 - \left(\frac{V_2}{V_1}\right)^{\gamma-1} \quad \gamma = (f+2)/f$

V_2/V_1 is the compression ratio

Fuel intake, two adiabatic processes,

two constant V processes

Exhaust Process

Diesel:

$e = 1 - \frac{1}{\gamma} \frac{r^{-\gamma} E - r^{-\gamma} C}{r^{-1} E - r^{-1} C}$

Binomial: $(1+x)^n \simeq 1 + nx + ((n(n-1))x^2)/2$

Refrigerators/AC

$\text{COP} = \frac{\text{benefit}}{\text{cost}} = \frac{Q_c}{W} = \frac{Q_c}{Q_h - Q_c} = \frac{T_c}{T_h - T_c}$

W is the energy drawn in from outside source

$\frac{Q_h}{Q_c} \geq \frac{T_h}{T_c}$

Real Refrigerators: Joule-Thompson Process

(Constriction/Throttling)



$P_1, V_1 \rightarrow P_2, V_2 \quad \Delta U = U_2 - U_1 = W_{1-2}$
 $\Delta U = -P_2 V_2 + P_1 V_1 \quad U_2 + P_2 V_2 = U_1 + P_1 V_1$

Phase Changes

On phase change line, (s/l for example,) $G_s = G_l$ (states in equil.)

Vapor pressure: where S & L coexist

$V = \left(\frac{\partial G}{\partial P}\right)_{N,T} \quad S = -\left(\frac{\partial G}{\partial T}\right)_{P,N} \quad \frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{L}{T\Delta V}$ (Cl-Clap)

The stable phase in the one with lower G; the more stable phase can change with change in P with different slopes (V) for each state (shown in G vs. P graph)

$G_l = G_s \rightarrow \Delta G_l = \Delta G_s \rightarrow \mu_s = \mu_l$

IG: $\frac{P(T)}{P_\infty} = \exp(-L/NkT)$ (P_∞ can be found by plugging in known vals)

Phase Transformations of Mixtures

Unmixed A & B: $G = (1-x)G_A^\circ + xG_B^\circ$ (x is frac. of B molecules)

$\Delta S_{\text{mixing}} = -R[x \ln x + (1-x) \ln(1-x)]$

Ideal Mixture: $G = (1-x)G_A^\circ + xG_B^\circ + RT[x \ln x + (1-x) \ln(1-x)]$

↑ This is literally just $G = G_{\text{unmixed}} - T\Delta S_{\text{mixing}}$

Solubility gap means immiscible (bump in G vs. x graph)

Miscible Mixtures

Eutectic System (x axis is x)

Lever rule: prop of L to G = $\frac{x-x_a}{x_b-x}$ (for mixtures at some T)

x_a is comp. of gas phase at T, x_b is comp of liquid phase.

Non-ideal Mixtures

Fuel Cell

$\Delta G = W_{\text{other}} \quad V = \frac{\Delta G_{\text{rxn}}}{n_e \times -9.649 \times 10^4}$

$V = \frac{\text{electrical work}}{\text{total charge}}$

n_e is the number of electrons

pushed through the circuit.

Methane has $n_e = 8$, hydrogen cell has $n_e = 2$

efficiency = $\frac{W_{\text{other}}}{\Delta H}$

Waste heat is $\Delta H - \Delta G$

Output work is ΔG (Maybe V as well)

Isentropic Process: Quasistatic Adiabatic, $\Delta S = 0$

Chemical Potential

$\mu = \left(\frac{\partial G}{\partial N}\right)_{T,P} \quad G = \sum_i N_i \mu_i$

IDEAL GAS:

IG: $\mu(T, P) = \mu^\circ(T) + kT \ln(P/P^\circ)$

P° is 1 bar

Law of Mass Action Derivation Example

Given $N_2 + 3H_2 \leftrightarrow 2NH_3$:

$\mu_{N_2} + 3\mu_{H_2} = 2\mu_{NH_3}$

$\mu_{N_2}^\circ + kT \ln \frac{P_{N_2}}{P^\circ} + 3\mu_{H_2}^\circ + 3kT \ln \frac{P_{H_2}}{P^\circ} =$

$2\mu_{NH_3}^\circ + 2kT \ln \frac{P_{NH_3}}{P^\circ}$

$kT \ln \frac{P_{N_2}}{P^\circ} + 3kT \ln \frac{P_{H_2}}{P^\circ} - 2kT \ln \frac{P_{NH_3}}{P^\circ} =$

$2\mu_{NH_3}^\circ - \mu_{N_2}^\circ - 3\mu_{H_2}^\circ$

Multiple both sides by Avogadro's Number:

Right side is now ΔG° of the rxn.

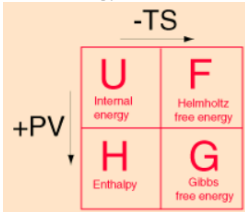
Then, bring the number coefs on right side

into logs as exponents, let $N_A kt = RT$

Which simply rearranges to

$\frac{P_{NH_3}^2 (P^\circ)^2}{P_{N_2} P_{H_2}^3} = e^{-\Delta G^\circ / RT}$

Free Energy



Neg. G: spontaneous in forward ;G = 0: equil

PV: work done to put thing in environment

TS: energy obtained from environment

H: energy needed to created something

G: work done needed to create something minus the heat from env.

$F = U - TS \quad \Delta F = \Delta U - \Delta TS - T\Delta S \quad (\Delta F \leq W)_{\text{const. T}}$

$G = F + PV \quad \Delta G = \Delta H - \Delta TS - T\Delta S \quad (\Delta G \leq W_{\text{other}})_{\text{const. T,P}}$

Use F for const P, G for changing P and/or T

$\Delta G = \Delta U + P\Delta V - T\Delta S \quad \Delta G = \Delta H - Q$

$\Delta H = Q + W_{\text{other}} \quad G = H - TS$

Thermodynamic Identities (IMPORTANT, derive partials from these be setting things constant)

$dU = T dS - P dV + \mu dN \quad dH = T dS + V dP + \mu dN$

$dF = -S dT - P dV + \mu dN \quad dG = -S dT + V dP + \mu dN$

if multiple particle types, use $\sum \mu_i dN_i$ instead of μdN .

At const. T, V, N; F tends to decrease (thermal res.)

At const. T, P, N; G tends to decrease (P, T res.)

Some Maxwell Relations

$\left(\frac{\partial S}{\partial P}\right)_{T,N} = -\left(\frac{\partial V}{\partial T}\right)_{P,N} \quad \left(\frac{\partial S}{\partial V}\right)_{T,N} = \left(\frac{\partial P}{\partial T}\right)_{V,N}$

(more can be derived from the thermodynamic identities)

Nonideal Gas

Lennard-Jones Potential: $U(r) \propto \frac{r_0^{12}}{r^{12}} - \frac{r_0^6}{r^6}$

r_0 is min on graph (steadystate):

Other model: Van der Waals:

$\left(P + \frac{aN^2}{V^2}\right)(V - Nb) = NkT \quad U_{\text{tot}} = -\frac{aN^2}{V}$

reduced variables: $\left(p + \frac{3}{v^2}\right)\left(v - \frac{1}{3}\right) = \frac{8}{3}t$

$p = \frac{P}{P_c} \quad v = \frac{V}{V_c} \quad t = \frac{T}{T_c}$

$P_c = \frac{1}{27}ab^2 \quad V_c = 3Nb \quad kT_c = \frac{8}{27}\frac{a}{b} \quad \frac{NkT_c}{P_c V_c} = \frac{8}{3}$

VdW isotherm: $p(v, t) = \frac{8t}{3v-1} - \frac{3}{v^2}$

on VdW iso, draw line enclosing equal areas

(maxwell construction)

where p_c is, also found with $g(p, t) = \frac{G}{NkT_c}$

van't Hoff Derivation

$K = e^{-\Delta G^\circ / RT} \rightarrow \ln K = \frac{-\Delta G^\circ}{RT}$

Take $\frac{\partial}{\partial T}$ of both sides (product rule as G is a fn of T)

$\frac{d \ln K}{dT} = \frac{\Delta G^\circ}{RT^2} - \frac{1}{RT} \frac{\partial \Delta G^\circ}{\partial T}$

$\frac{\partial G}{\partial T} = -S \rightarrow \frac{\partial \Delta G^\circ}{\partial T} = -\Delta S^\circ$

$\frac{d \ln K}{dT} = \frac{\Delta G^\circ}{RT^2} + \frac{\Delta S^\circ}{RT}$

$\Delta T = 0 \rightarrow \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$:

$\frac{d \ln K}{dT} = \frac{\Delta H^\circ - T\Delta S^\circ}{RT^2} + \frac{\Delta S^\circ}{RT}$

$\frac{d \ln K}{dT} = \frac{\Delta H^\circ}{RT^2} - \frac{\Delta S^\circ}{RT} + \frac{\Delta S^\circ}{RT}$

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

Partial Pressure EQ example

From mass action law (minibox to left):

$P_{NH_3}^2 = K P_{N_2} P_{H_2}^3$ (total P =200 atm)

Due to stoich, and b/c they're all in same container:

$3P_{N_2} = P_{H_2} \rightarrow P_{NH_3}^2 = 27K P_{N_2}^4$

$200 = P_{N_2} + P_{H_2} + P_{NH_3} = P_{N_2} + 3P_{N_2} + P_{NH_3}$

$200 = 4P_{N_2} + P_{NH_3} = 4P_{N_2} + \sqrt{27K} P_{H_2}^2$

Solve quadratically to find P_{N_2} ,

Then plug into $P_{NH_3}^2 = 27K P_{N_2}^4$ to get P_{NH_3}

Quasistatic: slow enough ΔV s.t. gas stays in equil.

Isothermal Comp.: so slow that $\Delta T = 0$, PV is constant. || **Quasistatic Isothermal Compression:** $Q = -W$ || **Adiabatic Comp:** so fast that $Q = 0$.

0th Law: After 2 systems in thermal contact for long enough, thermal equil (same T). 1st, 2nd laws on other side. **3rd law:** the entropy at absolute zero of a perfect crystal is zero.

Equilibria types (eqns on other side:)diffu: molcs free to move around with no tendency to go one way over another. mechanical: large scale motions can take place, but no long do.

Enthalpy: E required to create system out of nothing (U) AND put i t into the environment (PV \equiv W). W_{other} is work that doesn't involve ΔV .

Pressure is NOT really directional; more like a scalar quantity (like in the atmosphere).

Degrees of freedom: monatomic has 3 (trans.), diatomic+ has 5 (trans, rot.), and these both gain 2 (vibr) at high temps (although usually not the case unless mentioned)

Heat is the spontaneous flow of energy from a hot object to a cold one. **Magnetization:** total magnetic moment of whole paramagnet. **Temperature:** Willingness to give up energy.

Derivatives: $\sinh(x) \rightarrow \cosh(x)$, $\cosh(x) \rightarrow \sinh(x)$, $\tanh(x) \rightarrow \text{sech}^2(x) = 1/\cosh^2(x)$ **Approximating lns:** $\ln(1+x) \approx x$ if $|x| \ll 1$ **Peak Width of Mon. IG:** $1/\sqrt{N}$

More approximations: $\Omega \simeq \left(\frac{q\epsilon}{N}\right)^N$ if $q \gg N$ (High T). $\Omega \simeq \left(\frac{N\epsilon}{q}\right)^q$ if $N \gg q$, $U = N\epsilon e^{-\epsilon/kT}$ (low T). **Isentropic Process:** Quasistatic Adiabatic, $\Delta S = 0$

Latent Heat: a type of ΔH || Einstein Solid: $U_{\text{tot}} = q\hbar\omega = q\epsilon$ **ENTROPY IS ADDITIVE** || Free expansion of mon IG: $\Delta S N k \ln(V_f/V_i)$

Entropy of Mixing Mon IG: disti: $\Delta S = 2Nk \ln 2$, indist: $\Delta S = 0$

Reversible processes must be quasistatic. **Diffusive Eq** same as Chem Eq

Dilute Solutions Basics

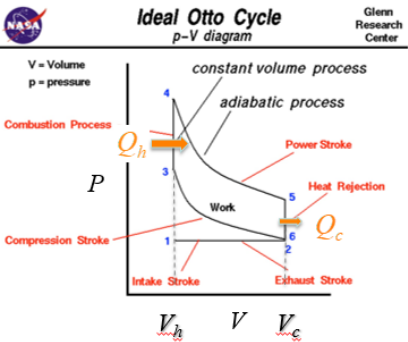
For pure solvent A: $G = N_A \mu_0(T, P)$
 $G_{\text{solution}} = N_A \mu_0(T, P) + N_B f(T, P) - N_B kT \ln N_A + N_B kT \ln N_B - N_B kT$
for more than 1 solute, repeat all terms in this except first, now with N_C, N_D , etc.
 $\mu_A = \left(\frac{\partial G}{\partial N_A}\right)_{T,P,N_B} = \mu_0(T, P) - \frac{N_B kT}{N_A}$
 $\mu_B = \left(\frac{\partial G}{\partial N_B}\right)_{T,P,N_A} = f(T, P) + kT \ln(N_B/N_A) = \mu^\circ(T, P) + kT \ln m_B$
where μ° is at standard condition of $m = 1$.
molality $m = \frac{\text{mol solute B (small one)}}{\text{kg solvent A}}$

Osmotic Pressure

$\mu_0(T, P_1) = \mu_0(T, P_2) - \frac{N_B kT}{N_A}$
 P_1 is pressue on side of pure solvent
 P_2 is pressure on side of soln
 $(P_2 - P_1) = \frac{N_B kT}{V} = \frac{n_B R T}{V}$
Poiseuille's Law: $\frac{P(x+L)-P(x)}{L} = \frac{8\eta}{\pi r^4} \times \text{flow rate}$
Boiling & Freezing Points
BP: $\mu_{A,l} = \mu_{A,g}$ FP: $\mu_{A,l} = \mu_{A,s}$
 $\mu_{0,l}(T, P) - \frac{N_B kT}{N_A} = \mu_{A,g}(T, P)$
Boiling pt Elevation: $T - T_0 = \frac{N_B kT_0^2}{L_{\text{vap}}}$
Freezing pt Depression: $T - T_0 = -\frac{N_B kT_0^2}{L_{\text{melting}}}$
($T \approx T_0$)
Vapor P: Raoult's Law: $\frac{P}{P_0} = 1 - \frac{N_B}{N_A}$

Chemical Equilibrium

In Equil: $\sum \mu_{\text{products}} = \sum \mu_{\text{reactants}}$
 $K = \exp\left(-\Delta G^\circ / RT\right)$
for $2A + 3B \leftrightarrow 4C$:
 $K = \frac{P_C^4}{P_A^2 P_B^3}$
van't Hoff: $\frac{d \ln K}{dT} = \frac{\Delta H_{\text{rxn}}^\circ}{RT^2}$
 $\rightarrow \ln K(T_2) - \ln K(T_1) = \frac{\Delta H_{\text{rxn}}^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$
 $\text{pH} = -\log_{10} m_{H^+}$ $m \equiv \frac{\text{mol solute}}{\text{kg solvent}}$
Gas dissolved in water: $\mu_g = \mu_{\text{solute}}$
Liquid and Gas reactions:
 $\mu_{\text{gas}}^\circ + kT \ln(P/P^\circ) = \mu_{\text{solute}}^\circ + kT \ln m$
Henry's Law: $\frac{m}{P/P^\circ} = \exp\left(-\frac{\Delta G^\circ}{RT}\right)$



Blackbody Radiation:

EM rad (harm oscil) in a "box"
1 oscil: $Z = 1/(1 - e^{-\beta \hbar f})$
 $\bar{E} = \hbar f / (e^{\hbar f / kT} - 1)$
 $\bar{n}_{PI} = 1/(e^{\hbar f / kT} - 1)$ (for γ)
This is \bar{n}_{BE} as $\mu = 0$ for γ
 $u(x) \propto x^3 / (e^x - 1)$, $x = \epsilon / kT$
in box, $\frac{U}{V} = \frac{8\pi^5 (kT)^4}{15 (hc)^3}$
 $C_V = 4aT^3$, $a = 8\pi^5 k^4 V / 15 (hc)^3$
 $S = \frac{32\pi^5}{45} V \left(\frac{kT}{hc}\right)^3 k$
Total E escaping from hole in dt:
 $= \frac{4}{3} \frac{V}{c} c dt$, hole area A
Power = $\sigma e A T^4$, $\sigma = 5.67 \times 10^{-8}$
 $Pressure = (1/3) \sigma T^4$,
 $dU = 4\sigma V T^3 dT + \sigma T^4 dV$
 $U = \sigma V T^4$
Debye Solids:

Einstein: $C_V = 3Nk \frac{(\epsilon/kT)^2 e^{\epsilon/kT}}{(e^{\epsilon/kT} - 1)^2}$
Sound: $c_s = \sqrt{\tau/\rho}$, $\epsilon = \hbar f = \hbar \frac{c_s}{\lambda}$
 $n \frac{\lambda}{2} = L \Rightarrow \lambda_n = \frac{2L}{n} \Rightarrow f_n = \frac{c_s}{2L} n$
 $\epsilon_n = \hbar \frac{c_s}{2L} \sqrt{n_x^2 + n_y^2 + n_z^2}$
3D sys, N partic: $n_{max} = \left(\frac{6N}{\pi}\right)^{1/3}$
 n_{max} is highest number of antinodes
 $U = \frac{9NkT^4}{T_D^3} \int_0^{T_D/T} \frac{x^3 dx}{e^x - 1}$
 $U = \frac{3\pi^4}{5} \frac{NkT^4}{T_D^3}$ when $T \ll T_D$
 $x = \hbar c_s n / 2LkT$; $T_D = \hbar c_s n_{\text{max}} / 2Lk$
 $T_D = \frac{\hbar c_s}{2k} \left(\frac{6N}{\pi V}\right)^{1/3}$
 $T \gg T_D$: $C_V = 3Nk$
 $T \ll T_D$: $C_V = \frac{12\pi^4}{5} \left(\frac{T}{T_D}\right)^3 Nk$
Metals at low temp: $T \ll T_D$:
 $\frac{C_V}{T} = \gamma + \frac{12\pi^4 Nk}{5T^3} T^2$
 $C_V = (\partial U / \partial T)_{(V)}$

(1) $I.G. : PV = nRT = NkT$, $\bar{K}_{\text{trans}} = \frac{3}{2} kT$, $v_{rms} = \sqrt{\frac{3kT}{m}}$, $U_{\text{therm}} = \frac{f}{2} NkT = \frac{f}{2} PV$ | $\Delta U = Q + W$ | $W_{\text{quasistatic}} = -P\Delta V = -\int_{V_i}^{V_f} P(V) dV$ | $W_{\text{isothermal}} = NkT \ln \frac{V_f}{V_i} = -Q$
 $\Delta T = 0$, $PV = \text{const}$ | $Q_{\text{isothermal (out)}} = NkT \ln \frac{V_f}{V_i}$ | (adiabatic) $V_i^\gamma P_i = V_f^\gamma P_f$, $V_i T_i^{f/2} = V_f T_f^{f/2}$, $Q = 0$, $\gamma = \frac{f+2}{2}$ | $C_V = \left(\frac{\partial U}{\partial T}\right)_V$ | $C_P = \left(\frac{\partial U}{\partial T}\right)_P = P \left(\frac{\partial V}{\partial T}\right)_P$ |
 $C_V = \frac{Nf}{2} k$, $C_P = C_V + Nk$ (I.G. only) | $H = U + PV$, $\Delta H = Q + W_{\text{other}}$ | $C_P = \left(\frac{\partial H}{\partial T}\right)_P$ | $Q = m\Delta TC$ | No. micro for 1 system of N 2 - states : 2^N
(2) $\Omega(N \text{ coins}, n \text{ heads}) = \frac{N!}{n!(N-n)!} = \binom{N}{n}$ | $P(n \text{ heads}) = \frac{\Omega(n)}{\Omega(\text{all})}$ | $\Omega_{1 \text{ system}}(N \text{ oscillators}, q \text{ energy units}) = \binom{q+N-1}{q} = \frac{(q+N-1)!}{q!(N-1)!}$ | Two systems : total micro = $\Omega(N_{\text{tot}}, q_{\text{tot}})$ |
specific microstate : $\Omega = \Omega(N_A, q_A) \Omega_B(N_B, q_B)$ | Stirling : $N! \approx N^N e^{-N} \sqrt{2\pi N}$ | $\Delta x \Delta p_x \approx \hbar$ | $S = k \ln \Omega$ | mon. I.G. : $\Omega(U, V, N) \approx \frac{1}{N!} \frac{V^N}{h^3 N} \frac{\pi^{3N/2}}{(3N/2)!} (\sqrt{2mU})^{3N} = f(N) V^N U^{3N/2}$,
 $S = Nk \left[\ln \left(\frac{V}{N} \left(\frac{4\pi m U}{3N h^2} \right)^{3/2} \right) + \frac{5}{2} \right]$ | Mon. I.G. : $(\Delta S)_{U,N} = Nk \ln \frac{V_f}{V_i}$, $Q = -W$ (quasist. isother. comp.) | free exp : $\Delta U = Q + W = 0 + 0 = 0$ | $\Delta S = \frac{Q}{T}$ (if $\Delta T = 0$, works for quasistat)
SECOND LAW: $dS \geq 0$ | Eins. solid w/q $\gg N$: $(U)_{N,V} = NkT$ | $\Omega(N, q) \approx \left(\frac{q+N}{q}\right)^q \left(\frac{q+N}{N}\right)^N$ | No. of macstats for 2 eins. sols w shared q: $q+1$.
(3) | 2 eins. solids at equil : $\frac{\partial S_A}{\partial U_A} = \frac{\partial S_B}{\partial U_B}$ (fixed N, V) $\rightarrow T_A = T_B$ | $\frac{1}{T} \equiv \left(\frac{\partial S}{\partial U}\right)_{N,V} = \frac{\partial N_\uparrow}{\partial U} \frac{\partial S}{\partial N_\uparrow}$ | $C_V \equiv \left(\frac{\partial U}{\partial T}\right)_{N,V}$ | E.S. : $C_V = Nk$ | Mon. I.G. : $C_V = \frac{3}{2} Nk$ |
 $(dS)_{\Delta V, W=0} = \frac{dU}{T} = \frac{Q}{T}$ | $\Delta S = \int_{T_i}^{T_f} \frac{C_V}{T} dT$ | PARAMAGNETISM : (μ = magnetic moment constant) : $U = \mu B(N - 2N_\uparrow) = -N\mu B \tanh\left(\frac{\mu B}{kT}\right)$ | $U_{\text{dipole for } \uparrow / \downarrow} = -/+ \mu B$ |
 $M = \mu(N_\uparrow - N_\downarrow) = -\frac{U}{B} = N\mu \tanh\left(\frac{\mu B}{kT}\right)$ | $\Omega(N_\uparrow) = \binom{N}{N_\uparrow} = \frac{N!}{N_\uparrow! N_\downarrow!}$ | $\frac{S}{k} = N \ln N - N_\uparrow \ln N_\uparrow - (N - N_\uparrow) \ln(N - N_\uparrow)$ | $\sinh(x) = \frac{1}{2}(e^x - e^{-x})$ | $\cosh(x) = \frac{1}{2}(e^x + e^{-x})$ |
 $\tanh(x) = \frac{\sinh(x)}{\cosh(x)}$ | $C_B = \left(\frac{\partial U}{\partial T}\right)_{N,B} = Nk \frac{(\mu B/kT)^2}{\cosh^2(\mu B/kT)}$ | Curie's Law : $M \approx \frac{N\mu^2 B}{kT}$ when $\mu B \ll kT$ | $\mu_B = 9.274 \times 10^{-24} \text{ J/T}$ mech. equil : $\frac{\partial S_A}{\partial V_A} = \frac{\partial S_B}{\partial V_B}$ (fixed U, N) $\rightarrow V_A = V_B$ |
 $P = T \left(\frac{\partial S}{\partial V}\right)_{U,N}$ | $(\Delta S)_P = \int_{T_i}^{T_f} \frac{C_P}{T} dT$ | diffusive equil : $\frac{\partial S_A}{\partial N_A} = \frac{\partial S_B}{\partial N_B}$ (fixed U, V) $\rightarrow \mu_A = \mu_B$ | $\mu \equiv -T \left(\frac{\partial S}{\partial N}\right)_{U,V}$ |
heat lost/gained for objects A and B; A is has higher T_i than B: $m_A C_A (T_A - T_f) = m_B C_B (T_f - T_B)$ | diatomic gas: $C_P = \frac{7}{2} nR$ || mech. equil: $P_A = P_B$

Boltzmann Statistics

can exchange heat with reservoir
 $\frac{\mathcal{P}(s_2)}{\mathcal{P}(s_1)} = \frac{e^{-E(s_2)/kT}}{e^{-E(s_1)/kT}}$ (Boltzmann factors)
 $\mathcal{P}(s) = \frac{1}{Z} e^{-E(s)/kT}$ $Z = \sum_s e^{-E(s)/kT}$
For any $X(s)$ (like E), $\langle \beta \rangle = 1/kT$
 $\bar{X} = \sum_s X(s) \mathcal{P}(s) = \frac{1}{Z} \sum_s X(s) e^{-E(s)/kT}$
 $U = N\bar{E}$, $\bar{E} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta}$, $\bar{E}^2 = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2}$
Harmonic Oscill: $\bar{E} = \frac{\hbar \omega}{e^{\hbar \omega / kT} - 1}$
Rotat Diat Molec: $E(j) = j(j+1)\epsilon$, $j=0,1,2,\dots$
 $Z_{\text{rot}} = \sum_{j=0}^{\infty} (2j+1) e^{-j(j+1)\epsilon/kT}$
High T: $Z_{\text{rot}} \approx \int_0^{\infty} (2j+1) e^{-E(j)\beta} dj = \frac{kT}{\epsilon}$
2-state Paramag, 1 dipole: $E = \pm \mu B$
 $Z = 2/\cosh(\beta \mu B)$ $\bar{E} = -\mu B \tanh(\beta \mu B)$
Equipartition: $\bar{E} = \frac{1}{2} kT$
Use partials of F to find S, μ .

More Boltzmann Statistics

Maxwell Speed Dist: $v_{rms} = \sqrt{\frac{3kT}{m}}$
 $\mathcal{D}(v) = \left(\frac{m}{2\pi kT}\right)^{3/2} 4\pi v^2 e^{-mv^2/2kT}$
 $\bar{v} = \sqrt{\frac{8kT}{\pi m}}$
IG revisit: $Z = \frac{1}{N!} Z_1^N$ (N indist molec)
 $Z_1 = Z_{\text{tr}} Z_{\text{int}}$, 1D: $Z_1 = \frac{\ell_Q}{L}$ (box L)
 $\ell_Q = \frac{h}{\sqrt{2\pi m kT}}$, 3D: $Z_{\text{tr}} = \frac{V}{v_Q}$, $v_Q = \ell_Q^3 Q$
3D: $Z_1 = \frac{V}{v_Q} Z_{\text{int}}$,
N molec: $Z = \frac{1}{N!} \left(\frac{V Z_{\text{int}}}{v_Q}\right)^N$
 $\ln Z = N \left[\ln \left(\frac{V}{N v_Q} \right) + 1 + \ln Z_{\text{int}} \right]$
Free Energy: $F = -kT \ln Z$, $Z = e^{-F/kT}$
 $S = -k \ln \mathcal{P}(s)$
N Non-int high T, low ρ particles: $Z \approx \frac{(Z_1)^N}{N!}$

Quantum Statistics (Gibbs factors)

Can exchange E & N w/ reservoir
 $\frac{\mathcal{P}(s_2)}{\mathcal{P}(s_1)} = \frac{e^{-[E(s_2) - \mu N(s_2)]/kT}}{e^{-[E(s_1) - \mu N(s_1)]/kT}}$
 $\mathcal{P}(s) = \frac{1}{Z} e^{-[E(s) - \mu N(s)]/kT}$
 $Z = \sum_s e^{-[E(s) - \mu N(s)]/kT}$
If > 1 types of partic in sys, sum μN
Langmuir Adsorption: frac of sites occ (IG):
 $\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = -kT \ln \left(\frac{kT Z_{\text{int}}}{P v_Q} \right)$
frac occ: $f = \frac{P}{P_0 + P}$, $P_0 = kT Z_{\text{int}} e^{\epsilon/kT} / v_Q$
fermions: $Z = 1 + e^{-(\epsilon - \mu)/kT}$
avg no. of fermions in certain state:
 $\bar{n}_{FD} = \frac{1}{e^{(\epsilon - \mu)/kT} + 1}$
Bosons: $\bar{n}_{BE} = \frac{1}{e^{(\epsilon - \mu)/kT} - 1}$
 $\bar{n}_{\text{Boltzmann}} = e^{-(\epsilon - \mu)/kT}$
 $U = \sum_s \epsilon \bar{n}(s)$

Degen Fermi Gas

Low T, so $V/N \ll v_Q$ and $kT \ll \epsilon_F$
At $T \approx 0$: Fermi E $\epsilon_F \equiv \mu(T=0)$
nearly all states above ϵ_F unoccupied
 $\epsilon_F = \frac{\hbar^2}{8m} \left(\frac{3N}{\pi V}\right)^{2/3}$ (highest E of particles)
 $U_{\text{tot}} = (3/5) N \epsilon_F$, $P = \frac{2}{3} \frac{U}{V}$
Bulk Mod. $B = -V \left(\frac{\partial P}{\partial V}\right)_T = \frac{10}{9} \frac{U}{V}$ ($T > 0$)
(change in pressure when compressed)
 $C_V = (\pi^2 N k^2 T) / (2\epsilon_F)$, $P = \frac{2U}{3V}$ ($T > 0$)
DFG Density of States
No. of single-partic states per unit E
 $g(\epsilon) = \frac{\pi (8m)^{3/2}}{2\hbar^3} V \sqrt{\epsilon} = \sqrt{\epsilon} (3N) / (2\epsilon_F^{3/2})$
integr. b/w ϵ_1 and ϵ_2 for no. of states b/w
For system: $N = \int_0^\infty g(\epsilon) \bar{n}_{FD}(\epsilon) d\epsilon$
 $U = \int_0^\infty \epsilon g(\epsilon) \bar{n}_{FD}(\epsilon) d\epsilon$
for spin-1/2 particles:
3D: $g(\epsilon) = g_0 \sqrt{\epsilon}$, $g_0 = \frac{\pi}{2} V \left(\frac{2m}{\hbar^2}\right)^{3/2}$
2D: $g(\epsilon) \propto \text{constant}$; 1D: $g(\epsilon) \propto \epsilon^{-1/2}$
3D at $T > 0$:
 $N = \frac{2}{3} g_0 \mu^{3/2} + \frac{1}{4} g_0 \frac{(kT)^2}{\mu^{1/2}} \frac{\pi^2}{3} + \dots$
 $U = \frac{3}{5} N \epsilon_F + \frac{\pi^2}{4} N \frac{(kT)^2}{\epsilon_F} + \dots$