

1 Energy in Thermal Dynamics

Exchanged Quantity	Type of Equilibrium
energy	thermal
volume	mechanical
particles	diffusive

1.1 Ideal Gas

Ideal gas law

$$PV = nRT = NkT \tag{1}$$

$$N = nN_A, \quad R = 8.31 J/mol \cdot K, \quad N_A = 6.02 \cdot 10^{23} \quad k = R/N_A = 1.381 \cdot 10^{-23} J/K \tag{2}$$

1.1.1 Microscopical Model

$$\bar{P} = \frac{\bar{F}_{x, \text{ on piston}}}{A} = \frac{-\bar{F}_{x, \text{ on particle}}}{A} = -\frac{m(\frac{\Delta \bar{v}_x}{\Delta t})}{A} = \frac{mv_x^2}{V} \tag{3}$$

$$\Delta t = 2L/v_x, \quad \Delta v_x = -2v_x \tag{4}$$

$$PV = Nm\bar{v}_x^2 \Rightarrow \overline{\frac{1}{2}mv_x^2} = \frac{1}{2}kT \Rightarrow \overline{K_{trans}} = 3 \cdot \frac{1}{2}kT \tag{5}$$

$$v_{rms} = \sqrt{\bar{v}^2} = \sqrt{\frac{3kT}{m}} \tag{6}$$

1.2 Equipartition Theorem

$$U_{thermal} = N \cdot f \cdot \frac{1}{2}kT \tag{7}$$

1.3 Heat and Work

Temperature: measure of the tendency of an object to spontaneously give up energy to its surroundings. **Heat:** any spontaneous flow of energy from one object to another, caused by a difference in temperatures. **Work:** any other transfer of energy in or out of the system.

$$\Delta U = Q + W \tag{8}$$

1.4 Work on a Surface

$$W = \sigma dA \tag{9}$$

σ being the surface tension.

1.5 Compression Work

$$W = -P\Delta V \text{ (for quasistatic compression)} \tag{10}$$

With $P(V)$

$$W = -\int_{V_i}^{V_f} P(V)dV \tag{11}$$

1.5.1 Compression of Ideal Gas

$$W = NkT \ln \frac{V_i}{V_f} \Rightarrow Q = \Delta U - W = \Delta(1/2NfkT) - W = W = NkT \ln \frac{V_f}{V_i} \tag{12}$$

For adiabatic compression:

$$\Delta U = W \Rightarrow dU = \frac{1}{2}fnkdT = -PdV \Rightarrow \frac{f}{2} \frac{dT}{T} = -\frac{dV}{V} \tag{13}$$

$$V_f T_f^{f/2} = V_i T_i^{f/2} = \text{constant}, \quad VT^{f/2} = \text{constant}, \quad V^\gamma P = \text{constant} \tag{14}$$

$\gamma = (f + 2)/f$ is the adiabatic exponent. Adiabatic = constant entropy, no heat transfer! Find the tilstandsligning for the pressure. Insert this into to entropy and find values for $f(p, A) = \text{constant}$, which makes the entropy constant. This $f(p, A) = \text{constant}$ is the adiabatic equation

1.6 Heat Capacity

$$C = \frac{Q}{\Delta T} \text{ (heat capacity),} \quad c = \frac{C}{m} \text{ (specific heat capacity)} \quad (15)$$

$$C = \frac{Q}{\Delta T} = C = \frac{\Delta U - W}{\Delta T} \quad (16)$$

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V, \quad C_P = \left(\frac{\Delta U - (-P\Delta V)}{\Delta T} \right)_P = \left(\frac{\partial U}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P \quad (17)$$

1.6.1 For Ideal Gas

$$C_V = \frac{\partial}{\partial T} \frac{NfkT}{2} = \frac{Nfk}{2}, \quad \left(\frac{\partial V}{\partial T} \right)_P = \frac{\partial}{\partial T} \frac{NkT}{P} = \frac{Nk}{P} \Rightarrow C_P = C_V + Nk = C_V + nR \quad (18)$$

rule of Dulong And Petit: heat capacity of solid should go towards $3R$

1.7 Latent Heat

For phase transformation

$$L = \frac{Q}{m} \quad (19)$$

To accomplish the transformation.

1.8 Enthalpy

Total energy one has to come up with to create the system and put it into the environment

$$H = U + PV \quad (20)$$

$$\Delta H = \Delta U + P\Delta V = Q + W_{other} \text{ (constant P)} \quad (21)$$

$$C_P = \left(\frac{\partial H}{\partial T} \right)_P \quad (22)$$

1.9 Rates of Processes

1.9.1 Heat Conduction

$$Q \propto \frac{A\Delta T\Delta t}{\Delta x} \Rightarrow \frac{Q}{\Delta t} = -k_t A \frac{dT}{dx} \quad (23)$$

Fourier heat conduction law

1.9.2 Conductivity of Idea Gas

$$\ell \approx \frac{1}{4\pi r^2} \frac{V}{N}, \quad Q = -\frac{1}{2} C_V \ell \frac{dT}{dx}, \quad k_t = \frac{1}{2} \frac{C_V}{V} \ell \bar{v} \quad (24)$$

$$\bar{v} \propto \sqrt{T} \quad (25)$$

1.9.3 Viscosity

$$F_x \propto \frac{A \cdot (u_{x,top} - u_{x,bottom})}{\Delta z} \Rightarrow \frac{|F_x|}{A} = \eta \frac{du_x}{dz} \quad (26)$$

1.9.4 Diffusion

$$J_x = -D \frac{dn}{dx} \quad (27)$$

J_x , flux has units number of particles per unit area per unit time.

2 The Second Law

2.1 Two-State System

$$\text{probability of n heads} = \frac{\Omega(n)}{\Omega(all)} \quad (28)$$

$$\Omega(N, n) = \frac{N!}{n!(N-n)!} = \binom{N}{n} \quad (29)$$

For paramagnet

$$\Omega(N_\uparrow) = \binom{N}{N_\uparrow} = \frac{N!}{N_\uparrow! N_\downarrow!} \quad (30)$$

For Einstein Solid:

$$\Omega(N, q) = \binom{q+N-1}{q} = \frac{(q+N-1)!}{q!(N-1)!} \quad (31)$$

N is oscillators, q is energy units.

$$q = 0, hf, 2hf, \dots \quad (32)$$

2.2 Interacting Systems

$$N_A = N_B, \quad q_{total} = q_A + q_B \quad (33)$$

Fundamental assumption of statistical mechanics: In an isolated system in thermal equilibrium, all accessible microstates are equally probable.

2.3 Stirling's Approximation

$$N! \approx N^N e^{-N} \sqrt{2\pi N}, \quad \ln N! \approx N \ln N - N \quad (34)$$

2.4 Einstein Crystals

$$\Omega(N, q) = \binom{q + N - 1}{q} = \frac{(q + N - 1)!}{q!(N - 1)!} \approx \left(\frac{eq}{N}\right)^N \leftarrow \text{when } q \gg N \approx \frac{\left(\frac{q+N}{q}\right)^q \left(\frac{q+N}{N}\right)^N}{\sqrt{2\pi q(q+N)/N}} \leftarrow \text{when } q, N \text{ large} \quad (35)$$

$$S = k \ln(eq/N)^N = Nk[\ln(q/N) + 1] = Nk \ln U - Nk \ln(\epsilon N) + Nk \quad (36)$$

Assuming that $U = \epsilon q$. Differentiate S to find $U = NkT$. Gives $C_V = Nk$. Also get:

$$\mu = -kT \ln \left(\frac{N + q}{N} \right) \quad (37)$$

2.5 Interacting Systems

Fundamental assumption of statistical mechanics (ergodic hypothesis): "*In an isolated system in thermal equilibrium, all accessible microstates are equally probable*".

2.6 Large Systems

Sharpness of multiplicity function: For a (large) Einstein crystal:

$$\Omega = \left(\frac{eq_A}{N}\right)^N \left(\frac{eq_B}{N}\right)^N = \left(\frac{e}{N}\right)^{2N} (q_A q_B)^N \quad \Omega_{max} = \left(\frac{e}{N}\right)^{2N} \left(\frac{q}{2}\right)^{2N} \quad (38)$$

Look at *near* peak ($q_A = q/2 + x$, $q_B = q/2 - x$) to get (after series expansion of logarithm):

$$\Omega \approx \Omega_{max} \exp \left(-N \left(\frac{2x}{q} \right)^2 \right) \quad (39)$$

Gaussian with mean 0 and $\sigma = q/2\sqrt{N}$. Thermodynamic limit: *measurable fluctuations away from the most likely macrostate never occur*.

2.7 Ideal Gas

Multiplicity has to be proportional to V and V_p (volume in momentum space). Single particle: molecule's kinetic energy must be U so $U = m/2(v_x^2 + v_y^2 + v_z^2)$, $p_x^2 + p_y^2 + p_z^2 = 2mU$ (sphere with radius $L_p = \sqrt{2mU}$. Number of distinct position states is $L/\Delta x$ (with L length of the box) and distinct momentum states $L_p/\Delta p$. Total number of states $LL_p/(\Delta x \Delta p) = LL_p/h$. In 3D: $\Omega_1 = VV_p/h^3$ for a single particle. More particles: Total energy is constrained so $p_{1x}^2 + p_{2x}^2 + \dots = 2mU$. So for two particles: $\Omega_2 = V^2/h^6$. (area of momentum hypersphere). Indistinguishable:

$$\Omega_N = \frac{1}{N!} \frac{V^N}{h^{3N}} \times \text{area of momentum hypersphere} = \frac{1}{N!} \frac{V^N}{h^{3N}} \frac{2\pi^{3N/2}}{\left(\frac{3N}{2} - 1\right)!} (\sqrt{2mU})^{3N-1} \approx \frac{1}{N!} \frac{V^N}{h^{3N}} \frac{\pi^{3N/2}}{(3N/2)!} (\sqrt{2mU})^{3N} = f(N) V^N U^{3N/2} \quad (40)$$

So that entropy:

$$S = Nk \ln V + \frac{3}{2} Nk \ln U + k \ln f(N) \quad (41)$$

Interacting ideal gases: multiply functions. Width of peak: $U_{tot}/\sqrt{3N/2}$. Exchange volume: V_{tot}/\sqrt{N} .

$$S = Nk \left[\ln \left(\frac{V}{N} \left(\frac{4\pi mU}{2Nh^2} \right)^{3/2} \right) + \frac{5}{2} \right] \quad (\text{Sackur - Tetrode}) \quad \Delta S = Nk \ln \frac{V_f}{V_i} \quad (U, N \text{ fixed}) \quad (42)$$

Differentiating S and using $U = 3NkT/2$ gives:

$$\mu = -kT \ln \left[\frac{V}{N} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \right] \quad (43)$$

Alternatively: use $G = N\mu$ to get $\partial\mu/\partial P = 1/N \partial G/\partial P = V/N = kT/P$. Integrate to get:

$$\mu(T, P) = \mu^o(T) + kT \ln(P/P_0) \quad (44)$$

Ideal gas: take P to be the partial pressure.

$$\mu = -kT \ln \left[\frac{V}{N} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \right] \quad (45)$$

Differentiating the entropy gives $U = 3NKT/2$, so that $C_V = 3Nk/2$.

2.8 Multiplicity of a Large Einstein Solid

$$\Omega(N, q) \approx \frac{(q + N)!}{q!N!} \quad (46)$$

$$\ln \Omega \approx N \ln \frac{q}{N} + N + \frac{N^2}{q} \quad (47)$$

(Remember to use $\ln(x + 1) \approx x$.)

$$\Rightarrow \Omega(N, q) \approx e^{N \ln(q/N)} e^N = \left(\frac{eq}{N}\right)^N, \quad q \gg N \quad (48)$$

$$\text{width of peak} = \frac{q}{\sqrt{N}} \quad (49)$$

2.9 Ideal Gas

$$\Omega_1 \propto V \cdot V_p, \quad 2mU = p_x^2 + p_y^2 + p_z^2, \quad \Delta x \Delta p \approx h \quad (50)$$

$$\Omega_N = \frac{1}{N!} \frac{V^N}{h^{3N}} \cdot A_{\text{hypersphere}}, \quad A_{\text{hypersphere}} = \frac{2\pi^{d/2}}{(d/2 - 1)!} r^{d-1} \quad (51)$$

$$\Omega(U, V, N) = f(N) V^N U^{3N/2} \quad (52)$$

2.9.1 Interacting Ideal Gas

$$\Omega_{\text{total}} = (f(N))^2 (V_A V_B)^2 (U_A U_B)^{3N/2} \quad (53)$$

$$\text{width of peak} = \frac{U_{\text{total}}}{\sqrt{3N/2}} \quad (54)$$

If can exchange volume:

$$\text{width of peak} = \frac{V_{\text{total}}}{\sqrt{N}} \quad (55)$$

2.10 Entropy

$$S = k \ln \Omega. \quad \Omega = e^{S/k} \quad (56)$$

Entropy of mixing

Distinguishable particles, initially separated into $V/2$ then allowed to expand:

$$\Delta S = 2Nk \ln 2 \quad (\text{distinguishable}) \quad (57)$$

If a fraction of molecules, x is of species B :

$$\Delta S_{\text{mixing}} = -Nk [x \ln x + (1 - x) \ln(1 - x)] \quad (58)$$

For an ideal mixture (denser system, two types of molecules are of the same size and interact with each other the same way):

$$\Delta S_{\text{mixing}} = k \ln \binom{N}{N_A} \quad (59)$$

$\Delta S_{\text{mixing}} = S$ if there are no interaction between the two types of molecules.

2.11 Entropy of Ideal Gas

Monatomic ideal gas, Sackur-Tetrode eq:

$$S = Nk \left[\ln \left(\frac{V}{N} \left(\frac{4\pi m U}{3N h^2} \right)^{3/2} \right) + \frac{5}{2} \right] \quad (60)$$

For U , N fixed:

$$\Delta S = Nk \ln \frac{V_f}{V_i} \quad (61)$$

3 Interactions and Implications

$$\frac{\partial S_A}{\partial U_A} = \frac{\partial S_B}{\partial U_B} \quad (62)$$

at equilibrium.

$$\frac{1}{T} \equiv \left(\frac{\partial S}{\partial U} \right)_{N, V} \quad (63)$$

3.1 Entropy and Heat

3.1.1 Predicting Heat capacity

C_V = \left(\frac{\partial U}{\partial T}\right)_{N,V}

Algorithm:

- Use QM and some combinations to find an expression for Ω , in terms of U , V and N , and any other relevant variables
- Take to logarithm to find S
- Differentiate S with respect to U and the the reciprocal to find the temperature T as a function of U and other variables.

3.1.2 Measuring Entropies

For constant(or quatistatic) volume and no work

dS = \frac{dU}{T} = \frac{Q}{T}

More general

dS = \frac{C_V dT}{T}, \quad \Delta S = \int_{T_i}^{T_f} \frac{C_V}{T} dT, \quad S - S(0) = \int_{T_i}^0 \frac{C_V}{T} dT

Third law: T \to 0 \Rightarrow S \to 0

3.2 Paramagnetism

U = \mu B(N_{\downarrow} - N_{\uparrow}) = \mu B(N - 2N_{\uparrow}), \quad M = \mu(N_{\uparrow} - N_{\downarrow}) = -\frac{U}{B}

3.3 Ising

E = \sum_i \epsilon_i + \sum_{ij} \epsilon_{ij}, \quad \epsilon_{ij} = -J s_i s_j

3.3.1 Analytic Solution

S/k \approx N \ln N - N_{\uparrow} \ln N_{\uparrow} - (N - N_{\uparrow}) \ln(N - N_{\uparrow})

\frac{1}{T} = \frac{k}{2\mu B} \ln\left(\frac{N - U/\mu B}{N + U/\mu B}\right)

U = N\mu B \left(\frac{1 - e^{2\mu B/kT}}{1 + e^{2\mu B/kT}}\right) = -N\mu B \tanh \frac{\mu B}{kT}, \quad M = N\mu \tanh \frac{\mu B}{kT}

C_B = \left(\frac{\partial U}{\partial T}\right)_{N,B} = Nk \frac{(\mu B/kT)^2}{\cosh^2(\mu B/kT)}

Bohr magnetron

\mu_B = \frac{eh}{4\pi m_e} = 9.274 \cdot 10^{-24} J/T = 5.788 \cdot 10^{-5} eV/T

For \mu B/kT << 1

M \approx \frac{N\mu^2 B}{kT} \Rightarrow M \propto 1/T

Curie's law.

3.4 Summery

Thermodynamic identity

dU = TdS - PdV + \mu dN \Rightarrow \mu = -T \left(\frac{\partial S}{\partial N}\right)_{U,V} = \left(\frac{\partial U}{\partial N}\right)_{S,V}

VNP :

Type of interaction	Exchange quantity	Governing variable	Constant	Formula
thermal	energy	temperature	V,N	\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N}
mechanical	volume	pressure	U,N	\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{U,N}
diffusive	particles	chemical potential	U,V	\frac{\mu}{T} = -\left(\frac{\partial S}{\partial N}\right)_{U,V}

4 Engines and Refrigerators

4.1 Heat Engines

efficiency

$$e \equiv \frac{\text{benefit}}{\text{cost}} = \frac{W}{Q_h} \tag{76}$$

Q_h is heat from the hot reservoir with temperature T_h , and Q_c from the cold reservoir with temperature T_c .

$$Q_h = Q_c + W, \quad e = 1 - \frac{Q_c}{Q_h} \tag{77}$$

From second law

$$S_c \geq S_h \Rightarrow \frac{Q_c}{T_c} \geq \frac{Q_h}{T_h} \Rightarrow \frac{Q_c}{Q_h} \geq \frac{T_c}{T_h} \tag{78}$$

$$\Rightarrow e \leq 1 - \frac{T_c}{T_h} \tag{79}$$

4.2 Refrigerators

coefficient of preference:

$$COP \equiv \frac{\text{benefit}}{\text{cost}} = \frac{Q_c}{W} \tag{80}$$

From first law $Q_h = Q_c + W$ we get

$$COP = \frac{Q_c}{Q_h - Q_c} = \frac{1}{Q_h/Q_c - 1} \tag{81}$$

From second law (78) we get

$$COP \leq \frac{1}{T_h/T_c - 1} = \frac{T_c}{T_h - T_c} \tag{82}$$

5 Engines and Refrigerators

5.1 Heat Engines

Heat absorbed from a hot reservoir, T_h , waste heat dumped into a cold reservoir T_c . Heat absorbed from the hot reservoir is Q_h , heat expelled to the cold reservoir is Q_c . Efficiency: benefit/cost ratio: $e = W/Q_h$. For cyclic engines: must have that the heat absorbed precisely equals the heat expelled, so $Q_h = Q_c + W$. Get:

$$e = 1 - \frac{Q_c}{Q_h} \tag{83}$$

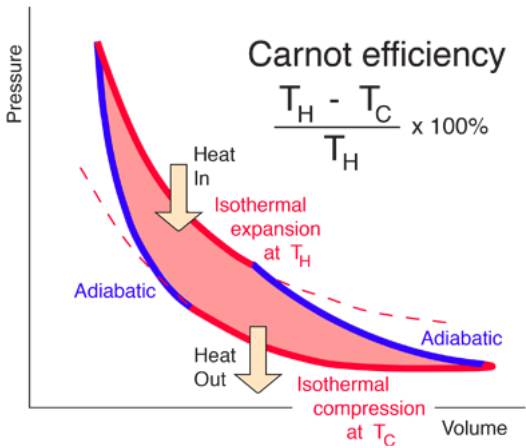
Invoke second law: entropy cannot decrease: must expel at least as much entropy as it absorbs to be cyclical. This gives:

$$\frac{Q_c}{T_c} \geq \frac{Q_h}{T_h} \implies e \leq 1 - \frac{T_c}{T_h} \tag{84}$$

Less effective: must get rid of more entropy, so the heat dumped into the cold reservoir has to increase. Note that if the temperature of the heat engine when taking in heat from the hot reservoir is less than T_h , then efficiency will be lower.

Carnot

For Carnot cycle: begin at temperature only infinitesimally smaller than T_h , absorb Q_h (slowly) - expand gas isothermally. Same when the gas is dumping the waste heat - compress isothermally. To change temperature: do an adiabatic compression/expansion (no



heat flow, so $\Delta S = 0$).

5.2 Refrigerators

Heat engine in reverse - simply reverse the arrows (put in work to suck out heat from the cold reservoir Q_c and dump it into the hot reservoir Q_h . Coefficient of performance, COP is benefit/cost = Q_c/W . By the first law, $Q_h = Q_c + W$ (we put *in* work) so that the Coefficient of Performance becomes:

$$COP = \frac{Q_c}{Q_h - Q_c} \tag{85}$$

By the second law, the inequalities are now reversed from previously (entropy flows in the opposite direction) so that:

$$\frac{Q_h}{T_h} \geq \frac{Q_c}{T_c} \tag{86}$$

Which gives:

$$COP \leq \frac{T_c}{T_h - T_c} \tag{87}$$

6 Free Energy and Chemical Thermodynamics

6.1 Free Energy as Available Work

Helmholtz Free Energy: Total energy needed to create the system, minus the heat you can get from the environment for free at temperature T . For constant T :

$$F = U - TS, \quad \Delta F = \Delta U - T\Delta S = Q + W - T\Delta S \tag{88}$$

For constant P and T , the work of a system is Gibbs Free Energy

$$G = H - TS = U - TS + PV, \quad \Delta G = \Delta U - T\Delta S + P\Delta V = Q + W - T\Delta S + P\Delta V \tag{89}$$

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6.2 Thermodynamic Identities

$$dU = TdS - PdV + \mu dN \tag{90}$$

$$dH = dU + PdV + VdP = TdS + VdP + \mu dN \tag{91}$$

$$dF = dU - TdS - SdT = -SdT - PdV + \mu dN \tag{92}$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}, \quad P = -\left(\frac{\partial F}{\partial V}\right)_{T,N}, \quad \mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} \tag{93}$$

$$dG = -SdT + VdP + \mu dN \tag{94}$$

$$S = -\left(\frac{\partial G}{\partial T}\right)_{P,N}, \quad V = \left(\frac{\partial G}{\partial P}\right)_{T,N}, \quad \mu = \left(\frac{\partial G}{\partial N}\right)_{T,P} \tag{95}$$

These identities is correct if the process is reversible. Then the first law $dE = dU = Q + W$ holds.

6.3 Free Energy as a Force towards Equilibrium

$$dS_{total} = dS + dS_R, \quad dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}dN \tag{96}$$

$$dS_R = dU_T/T_R$$

$$dS_{total} = dS + \frac{1}{T_R}dU_R \tag{97}$$

$$dU_R = -dU$$

$$dS_{total} = dS - \frac{1}{T}dU = -\frac{1}{T}(dU - TdS) = -\frac{1}{T}dF \tag{98}$$

This is for constant T , V and N . For constant P

$$dS_{total} = -\frac{1}{T}dG \tag{99}$$

6.4 Extensive and Intensive Quantities

Double the amount of stuff: Quantities that doubles are extrinsic; those who do not are intensive. **Extensive:** V, N, S, U, H, F, G, mass. **Intensive:** T, P, μ , density. Extensive \times intensive = extensive. Extensive \times extensive = neither. Type \times same type = same type. Extensive + intensive is not allowed.

Extensive: $E(\alpha N) = \alpha E(N)$. Intensive: $I(\alpha N) = I(N)$

6.5 Gibbs Free Energy and Chemical Potential

Given constant T and P we have that

$$\mu = \left(\frac{\partial G}{\partial N} \right)_{T,P} \Rightarrow G = N\mu \text{ or } G = \sum_i N_i \mu_i \quad (100)$$

$$\Rightarrow \frac{\partial \mu}{\partial P} = \frac{\partial}{\partial P} \frac{G}{N} = \frac{V}{N} = \frac{kT}{P} \quad (101)$$

Integrating

$$\mu(T, P) = \mu^\circ(T, P) + kT \ln \frac{P}{P^\circ} \quad (102)$$

P° is the atmospheric pressure, and μ° is μ at this pressure and can be found in tables for atmospheric pressures ($\mu = G/N$). For a mixture P is the partial pressure of that gas.

6.6 Phase Transformations of Pure Substances

Vapor pressure: Pressure at which a gas can coexist with its solid or liquid phase. **Triple point:** Point where all three phases can coexist. **Critical Point:** No longer a discontinuous change from liquid to gas. **Curie Temperature:** Temperature where magnetization disappears, so the phase boundary ends at a critical temperature.

6.7 Chemical Equilibrium

Equilibrium condition: Gibb's free energy minimized (if at room temperature and atmospheric pressure), i.e. $dG = \sum_i \mu_i dN_i = 0$. Generally: replace species by chemical potential, keep stoichiometric ratio. Example:

$$N_2 + 3H_2 \leftrightarrow 2NH_3 \implies \mu_{N_2} + 3\mu_{H_2} = 2\mu_{NH_3} \quad (103)$$

6.7.1 Gaseous:

Nitrogen fixation, $N_2 + 3H_2 \leftrightarrow 2NH_3$. Assume ideal gas, use $\mu_{N_2} = \mu_{N_2}^\circ + kT \ln(P_{N_2}/P_0)$, where μ_0 is the chemical potential when its partial pressure is P_0 . Gather all μ_0 on one side, and multiply through by N_A to get ΔG° . Get:

$$\frac{P_{NH_3}^2 (P^\circ)^2}{P_{N_2} P_{H_2}^3} = K = e^{-\Delta G^\circ / RT} \quad (104)$$

Where each pressure is raised to the power of its stoichiometric coefficient and there are enough powers of P° to make the expression unitless.

6.8 Disassociation:

$H_2O \leftrightarrow H^+ + OH^-$. Use $\mu_{H_2O}^\circ = \mu_{H^+}^\circ + kT \ln m_{H^+} + \mu_{OH^-}^\circ + kT \ln m_{OH^-}$ assuming the disassociation is small and m is the molality (mole solute per kilogram solvent). Get:

$$m_{H^+} m_{OH^-} = e^{-\Delta G^\circ / RT} \quad (105)$$

Where the standard states are 1 molal.

6.9 Oxygen dissolving:

$O_2(g) \leftrightarrow O_2(aq)$. Use $\mu_{gas}^\circ + kT \ln(P/P^\circ) = \mu_{solute}^\circ + kT \ln m$ to get:

$$\frac{m}{P/P^\circ} = e^{-\Delta G_0 / RT} \quad (106)$$

6.10 Ionization of hydrogen

$H \leftrightarrow p + e$. Treat all as ideal gases, use equation 45. Put in ionization energy I explicitly, so that $\mu_H = \mu - I$ where μ is from equation 45 and I is 13.6 eV. Use ideal gas law to express with pressure, use that mass of proton and hydrogen are approximately equal, and get:

$$\frac{P_p}{P_H} = \frac{kT}{P_e} \left(\frac{2\pi m_e kT}{h^2} \right)^{3/2} e^{-I/kT} \quad (\text{Saha equation}) \quad (107)$$

Note that $P_e/kT = N_e/V$.

6.11 Diamonds and Graphite

At a given temperature and pressure, the stable phase is always the one with the lower Gibbs free energy

To find the most stable state, use:

$$\left(\frac{\partial G}{\partial V} \right)_{T,N} = P, \quad \left(\frac{\partial G}{\partial T} \right)_{P,N} = -S \quad (108)$$

Since graphite has more volume and entropy its Gibbs free energy increases more with pressure and decreases more with temperature. Thus raising the pressure makes diamonds more stable, and with higher temperature higher pressure is needed.

6.12 Clausius-Clapeyron Relation

$$G_l = G_g \quad (109)$$

at phase boundary. $dG_l = dG_g$ to remain at phase boundary. Thus

$$-S_l dT + V_l dP = -S_g dT + V_g dP \quad (110)$$

$$\Rightarrow \frac{dP}{dT} = \frac{S_g - S_l}{V_g - V_l} = \frac{L}{T \Delta V} \quad (111)$$

using the (total) latent heat $S_g - S_l = L/T$ and $V_g - V_l = \Delta V$. This is the Clausius-Clapeyron Relation.

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} \Rightarrow \Delta V T \frac{dp}{dT} = l \quad (112)$$

$l = L/N$ vapor heat per particle

6.13 The van der Waals Model

$$\left(P + \frac{aN^2}{V^2}\right)(V - Nb) = NkT \quad (113)$$

$$\text{total potential pressure} = -\frac{aN^2}{V} \Rightarrow P_{\text{due to p.e.}} = -\frac{d}{dV} \left(-\frac{aN^2}{V}\right) = -\frac{aN^2}{V^2} \quad (114)$$

attractive force: $NkT/(V - Nb)$:

$$P = \frac{NkT}{V - Nb} - \frac{aN^2}{V^2} \quad (115)$$

$$G = -NkT \ln(V - Nb) + \frac{(NkT)(Nb)}{V - Nb} - \frac{2aN^2}{V} + c(T) \quad (116)$$

$$0 = \int_{loop} dG = \int_{loop} \left(\frac{\partial G}{\partial P}\right)_T dP = \int_{loop} V dP \quad (117)$$

$$V_c = 3Nb, \quad P_c = \frac{1}{27} \frac{a}{b^2}, \quad kT_c = \frac{8}{27} \frac{a}{b} \quad (118)$$

6.14 Chemical Equilibrium

$$0 = dG = \sum_i \mu_i dN_i \quad (119)$$

Le Chatelier's Principle: When you disturb a system in equilibrium, it will respond in a way that partially offsets the disturbance.

6.15 Ionization of Hydrogen

$$H \leftrightarrow p + e \quad (120)$$

Saha equation:

$$\frac{P_p}{P_H} = \frac{kT}{P_e} \left(\frac{2\pi m_e kT}{h^2}\right)^{3/2} e^{-I/kT} \quad (121)$$

7 Boltzmann Statistics

$$\text{Boltzmann factor} = e^{-E(s)/kT} \quad (122)$$

$$\mathcal{P}(s) = \frac{1}{Z} e^{-E(s)/kT}, \quad Z = \sum_s e^{-E(s)/kT} \quad (123)$$

$$\bar{E} = \frac{1}{N} \sum_s E(s) N(s) = \sum_s E(s) \mathcal{P}(s) = \frac{1}{Z} \sum_s E(s) e^{-\beta E(s)} \quad (124)$$

with $\beta = 1/kT$

$$\bar{E} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{\partial}{\partial \beta} \ln Z, \quad U = N\bar{E} \quad (125)$$

7.1 Rotation of Diatomic Molecules

$$E(j) = j(j+1)\epsilon, \quad Z_{rot} = \sum_{j=0}^{\infty} (2j+1) e^{-E(j)/kT} = \sum_{j=0}^{\infty} (2j+1) e^{-j(j+1)\epsilon/kT} \quad (126)$$

$(2j+1)$ being the degeneration.

$$Z_{rot} \approx \int_0^{\infty} (2j+1) e^{-j(j+1)\epsilon/kT} dj = \frac{kT}{\epsilon} \quad (127)$$

and $kT/2\epsilon$ for identical atoms (N_2 , O_2 etc).

7.2 Equipartition Theorem

Holds for systems where the energy is in the form of quadratic degrees of freedom $E(q) = cq^2$, where c is a constant and q is some variable (coordinate, momentum, etc).

$$Z = \sum_q e^{-\beta E(q)} = \sum_q e^{-\beta cq^2} = \frac{1}{\Delta q} \sum_q e^{-\beta cq^2} \Delta q \quad (128)$$

$$\Rightarrow \frac{1}{\Delta q} \int_{-\infty}^{\infty} e^{-\beta cq^2} dq = \frac{1}{\Delta q} \frac{1}{\sqrt{\beta c}} \int_{-\infty}^{\infty} e^{-x^2} dx = C\beta^{-1/2} \quad (129)$$

$$\Rightarrow \bar{E} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = \frac{1}{2} kT \quad (130)$$

Lennard-Jones:

$$u(x) = u_0 \left[\left(\frac{x_0}{x} \right)^{12} - 2 \left(\frac{x_0}{x} \right)^6 \right] \quad (131)$$

7.3 Maxwell Speed Distribution

$$v_{rms} = \sqrt{\frac{2kT}{m}} \quad (132)$$

$$\mathcal{D}(v) = \left(\frac{m}{2\pi kT} \right)^{3/2} 4\pi v^2 e^{-mv^2/2kT}, \quad v_{max} = \sqrt{\frac{2kT}{m}} \quad (133)$$

$$\bar{v} = \sum_{\text{all } v} v \mathcal{D}(v) dv = \sqrt{\frac{8kT}{\pi m}} \quad (134)$$

By turning this to an integral. This is a distribution to to get probability($v > x$) just integrate this from x to ∞ .

7.4 Partition Functions and Free Energy

$$F = -kT \ln Z, \quad Z = e^{-F/kT} \quad (135)$$

$$S = -k \sum_s \mathcal{P}(s) \ln \mathcal{P}(s) \quad (136)$$

7.5 Partition Functions for Composite Systems

For noninteracting, distinguishable particles

$$Z_{total} = Z_1 Z_2 \dots Z_N \quad (137)$$

For noninteracting, indistinguishable particles

$$Z_{total} = \frac{1}{N!} Z_1^N \quad (138)$$

Given a system with N_A A-particles and N_B B-particles, with $N = N_A + N_B$. The partition function becomes

$$Z = \binom{N}{N_A} Z_A^{N_A} Z_B^{N_B} \quad (139)$$

7.6 Ideal Gas Revisited

$$Z = \frac{1}{N!} Z_1^N, \quad Z_1 = Z_{tr} Z_{int} \quad (140)$$

Where E_{tr} is the transitional kinetic energy and E_{int} is the internal energy (rotational, vibrational. etc). Particle in box:

$$\lambda_n = \frac{2L}{n}, \quad p_n = \frac{h}{\lambda_n}, \quad E_n = \frac{p_n^2}{2m} = \frac{h^2 n^2}{8mL^2} \quad (141)$$

$$Z_{1D} = \sum_n e^{-E_n/kT} = \sum_n e^{-h^2 n^2 / 8mL^2 kT} \quad (142)$$

Doing this as an integration from 0 to ∞ we get

$$Z_{1D} = \sqrt{\frac{2\pi mkT}{h^2}} L = \frac{L}{\ell_Q} \Rightarrow \ell_Q = \frac{h}{\sqrt{\pi mkT}} \quad (143)$$

Quantum length.

$$Z_{tr} = \frac{L_x}{\ell_Q} \frac{L_y}{\ell_Q} \frac{L_z}{\ell_Q} = \frac{V}{v_Q} \quad (144)$$

$$\Rightarrow Z_1 = \frac{V}{v_Q} Z_{int} \Rightarrow Z = \frac{1}{N!} \left(\frac{V Z_{int}}{v_Q} \right)^N, \quad \ln Z = N(\ln V + \ln Z_{int} - \ln N - \ln v_Q + 1) \quad (145)$$

$$U = \frac{\partial}{\partial \beta} Z = U_{int} + \frac{3}{2} NkT \quad (146)$$

$$C_V = \frac{\partial U}{\partial T} = \frac{\partial U_{int}}{\partial T} + \frac{3}{2} Nk \quad (147)$$

$$F = -kT \ln Z = -NkT(\ln V - \ln N - \ln v_Q + 1) + F_{int} \quad (148)$$

$$S = Nk \left[\ln \left(\frac{V}{Nv_Q} \right) + \frac{5}{2} \right] - \frac{\partial F_{int}}{\partial T}, \quad P = \frac{NkT}{V}, \quad \mu = -kT \ln \frac{VZ_{int}}{Nv_Q} \quad (149)$$

8 Quantum Statistics

8.1 Gibbs Factor

For a system i thermal and diffusive contact with a much larger reservoir, whose temperature and chemical potential are effectively constant.

$$\text{Gibbs Factor} = e^{-(E(s) - \mu N(s))/kT} \quad (150)$$

$$\mathcal{P}(s) = \frac{1}{\mathcal{Z}} e^{-(E(s) - \mu N(s))/kT}, \quad \mathcal{Z} = \sum_s e^{-(E(s) - \mu N(s))/kT} \quad (151)$$

\mathcal{Z} is the grand partition function.

8.2 Bosons and Fermions

8.2.1 Fermions: Fermi-Dirac distribution

On states allowed are 0 and 1

$$\mathcal{Z} = 1 + e^{-(\epsilon - \mu)/kT} \Rightarrow \bar{n} = \sum_n n \mathcal{P}(n) = 0 \cdot \mathcal{P}(0) + 1 \cdot \mathcal{P}(1) = \frac{1}{1 + e^{(\epsilon - \mu)/kT}} \quad (152)$$

8.2.2 Bosons: Einstein-Bose distribution

All states allowed

$$\mathcal{Z} = 1 + e^{-(\epsilon - \mu)/kT} + e^{-2(\epsilon - \mu)/kT} \dots = 1 + e^{-(\epsilon - \mu)/kT} + \left(e^{-(\epsilon - \mu)/kT} \right)^2 \dots = \frac{1}{1 - e^{-(\epsilon - \mu)/kT}} \quad (153)$$

$$\bar{n} = \sum_n n \mathcal{P}(n) = -\frac{1}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial x} = \frac{1}{1 - e^{-(\epsilon - \mu)/kT}} \quad (154)$$

Where $x = (\epsilon - \mu)/kT$. For reference: for the Boltzmann distribution

$$\bar{n}_{\text{boltzmann}} = N \mathcal{P}(s) = \frac{N}{Z_1} e^{-\epsilon/kT} = e^{-(\epsilon - \mu)/kT} \quad (155)$$

Using $\mu = -kT \ln(Z_1/N)$

8.3 Degenerated Gas

For Boltzmann statistics to apply $V/N \gg v_Q$. Classical limit ($\epsilon - \mu = /kT \gg 1$. Then we can ignore the 1 in the FD distribution.

8.3.1 Zero Temperature

$$\epsilon_F = \mu(T = 0) \quad (156)$$

Particle in box:

$$\epsilon = \frac{|\vec{p}|^2}{2m} = \frac{h^2}{8mL^2} (n_x^2 + n_y^2 + n_z^2) \quad (157)$$

$$\epsilon_F = \frac{h^2 n_{max}^2}{8mL^2} \quad (158)$$

$$N = 2 \times (\text{volume of eighth-sphere}) = 2 \frac{1}{8} \cdot \frac{4}{3} \pi n_{max}^3 = \frac{\pi n_{max}^3}{3} \quad (159)$$

With $V = L^3$

$$\epsilon_F = \frac{h^2}{8m} \left(\frac{3N}{\pi V} \right)^{2/3} \quad (160)$$

$$U = 2 \int \int \int \epsilon(\vec{n}) dn_x dn_y dn_z = 2 \int_0^{n_{max}} dn \int_0^{\pi/2} d\theta \int_0^{\pi/2} d\phi n^2 \sin \theta \epsilon(n) = \frac{3}{5} N \epsilon_F \quad (161)$$

$$T_F = \frac{\epsilon_F}{k}, \quad P = \frac{2N\epsilon_F}{5V} = \frac{2U}{3V} \quad (162)$$

Degeneracy pressure. Bulk modulus

$$B = -V \left(\frac{\partial P}{\partial V} \right)_T = \frac{10U}{9V} \quad (163)$$

8.3.2 Low Temperature

$$U = \frac{3}{5}N\epsilon_F + \frac{\pi^2}{4}N\frac{(kT)^2}{\epsilon_F}, \quad C_V = \frac{\pi^2 N k^2 T}{2\epsilon_F} \quad (164)$$

8.3.3 Density of States

$$\epsilon = \frac{h^2}{8mL^2}n^2 \Rightarrow n = \sqrt{\frac{8mL^2}{h^2}}\sqrt{\epsilon} \Rightarrow dn = \sqrt{\frac{8mL^2}{h^2}}\frac{1}{2\sqrt{\epsilon}}d\epsilon \quad (165)$$

From

$$U = \pi \int_0^{n_{max}} \epsilon(n)n^2 dn \quad (166)$$

We get

$$U = \int_0^{\epsilon_F} \epsilon \left[\frac{\pi}{2} \left(\frac{8mL^2}{h^2} \right)^{3/2} \sqrt{\epsilon} \right] d\epsilon \quad (167)$$

at $T = 0$

$$g(\epsilon) = \frac{\pi}{2} \frac{(8m)^{3/2}}{h^3} V \sqrt{\epsilon} = \frac{3N}{2\epsilon_F^{3/2}} \sqrt{\epsilon} \quad (168)$$

For $T = 0$ we then get

$$N = \int_0^{\epsilon_F} g(\epsilon) d\epsilon \quad (169)$$

and for any T we get

$$N = \int_0^{\epsilon_F} g(\epsilon) \bar{n}_{FD}(\epsilon) d\epsilon \int_0^{\epsilon_F} g(\epsilon) \frac{1}{1 + e^{(\epsilon - \mu)/kT}} d\epsilon \quad (170)$$

$$U = \int_0^{\epsilon_F} \epsilon g(\epsilon) \bar{n}_{FD}(\epsilon) d\epsilon \int_0^{\epsilon_F} \epsilon g(\epsilon) \frac{1}{1 + e^{(\epsilon - \mu)/kT}} d\epsilon \quad (171)$$

and for $T \neq 0 \Rightarrow \mu(T) \neq \epsilon_F$

8.3.4 Sommerfeld Expansion

$$\frac{\mu}{\epsilon_F} = 1 - \frac{\pi^2}{12} \left(\frac{kT}{\epsilon_F} \right)^2 + \dots \quad (172)$$

$$U = \frac{3}{5}N\epsilon_F + \frac{\pi^2}{4}N\frac{(kT)^2}{\epsilon_F} + \dots \quad (173)$$

8.4 Blackbody radiation

Ultraviolet catastrophe: theoretically one expected infinite wavelengths with $E = 2 \cdot 1/2kT$, but this was not the case experimentally.

8.4.1 Planck Distribution

$$E_n = 0, hf, 2hf, \dots \Rightarrow Z = 1 + e^{-\beta hf} + e^{-2\beta hf} + \dots = \frac{1}{1 - e^{-\beta hf}} \quad (174)$$

$$\bar{E} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = \frac{hf}{e^{\beta hf/kT} - 1}, \quad \bar{n}_{Pl} = \frac{1}{e^{\beta hf/kT} - 1} \quad (175)$$

8.4.2 Photons

Use the Einstein-Bose distribution. And:

$$\mu = 0 \quad (176)$$

since

$$\left(\frac{\partial F}{\partial N} \right)_{T,V} = 0 \quad (177)$$

at equilibrium. This is because the number of photons N is not constrained but takes whatever value minimizes F . So a small dN should leave F untouched.

8.4.3 Summing over Modes

$$\lambda = \frac{2L}{n}, \quad p = \frac{hn}{2L}, \Rightarrow e\epsilon = pc = \frac{hcn}{2L} \quad (178)$$

$$U = 2 \int_0^\infty dn \int_0^{\pi/2} d\theta \int_0^{\pi/2} d\phi n^2 \sin \theta \frac{hcn}{2L} \frac{1}{e^{hcn/2LkT} - 1} \quad (179)$$

8.4.4 Planck Spectrum

changing variables to $\epsilon = hcn/2L$

$$\frac{U}{V} = \int_0^\infty \frac{8\pi\epsilon^3/(hc)^3}{e^{\epsilon/kT} - 1} d\epsilon \tag{180}$$

The energy density per unit photon energy or the spectrum is

$$u(\epsilon) = \frac{8\pi}{(hc)^3} \frac{\epsilon^3}{e^{\epsilon/kT} - 1} \tag{181}$$

with $x = \epsilon/kT$, with $\epsilon = hc/\lambda$

$$\frac{U}{V} = \frac{8\pi(kT)^4}{(hc)^3} \int_0^\infty \frac{x^3}{e^x - 1} dx \tag{182}$$

8.4.5 Total Energy

$$\frac{U}{V} = \frac{8\pi^5(kT)^4}{15(hc)^3} \tag{183}$$

8.4.6 Entropy of Photon Gas

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = 4aT^3 \tag{184}$$

$$a = 8\pi^5 k^4 V / 15(hc)^3$$

$$S(T) = \int_0^T \frac{C_V(T')}{T'} dT' = \frac{4}{3} aT^3 \tag{185}$$

8.5 Blackbody Radiation

Ultraviolet catastrophe: Each mode in the field has energy kT , infinite number of modes, infinite energy. Solution: $E_n = nhf$, $n \in \mathbb{N}^+$. For a single oscillator then:

$$Z = 1 + e^{-\beta hf} + e^{-2\beta hf} + \dots = \frac{1}{1 - e^{-\beta hf}} \quad \overline{E} = \frac{hf}{e^{hf/kT} - 1} \tag{186}$$

Average number of "units of energy"(photons) in a single oscillator is $\bar{n} = 1/(\exp(hf/kT) - 1)$ (Planck Distribution). But photons are bosons, must follow Bose-Einstein $\rightarrow \mu = 0$ for photons (follows also because N arbitrary for photons so $(\partial F/\partial N)_{T,V} = 0 = \mu$ or from $e \leftrightarrow e + \gamma \implies \mu_e = \mu_e + \mu_\gamma$). Energy for photons is $\epsilon = pc = hcn/2L$. Each wave shape can hold two photons. Gives the total energy per unit volume as:

$$\frac{U}{V} = \int_0^\infty \underbrace{\frac{8\pi\epsilon^3/(hc)^3}{\exp(\epsilon/kT) - 1}}_{\text{Spectrum of photon}} d\epsilon = \frac{8\pi^5(kT)^4}{15(hc)^3} \tag{187}$$

Spectrum peaks at $\epsilon = 2.82kT$ (Wien's law). Heat capacity/entropy:

$$C_V = 4aT^3 \quad S(T) = \int_0^T \frac{C_V(T')}{T'} dT' = 4aT^3 \quad N = 8\pi V \left(\frac{kT}{hc}\right)^3 \int_0^\infty \frac{x^2}{e^x - 1} dx \tag{188}$$

Where $a = 8\pi^5 k^4 V / 15(hc)^3$.

From **TDI**:

$$dU = TdS - PdV \Rightarrow \left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial S}{\partial V}\right)_T - P \left(\frac{\partial V}{\partial V}\right)_T = T \left(\frac{\partial S}{\partial V}\right)_T - P \tag{189}$$

Use Maxwell relation

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \tag{190}$$

And $U = uV$

$$u = u \left(\frac{\partial V}{\partial V}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P \tag{191}$$

Use that the radiation pressure is $P = u/3$

$$u = \frac{T}{3} \left(\frac{\partial U}{\partial T}\right)_V - \frac{u}{3} \Rightarrow \frac{4u}{3} = \frac{T}{3} \frac{du}{dT} \Rightarrow \frac{dT}{T} = \frac{1}{4} \frac{du}{u} \Rightarrow u = aT^4 \tag{192}$$

8.6 Photons Escaping through a Hole

Spectrum outside of box with hole is same as inside, as all photons travel at the same speed. Energy comes from spherical shell, distance R from hole, with angle θ to the normal of the hole. Look at chunk of spherical shell: volume $R^2 \sin \theta c dt d\theta d\phi$. Energy is this times U/V . Probability of escape is $A \cos \theta / 4\pi R^2$ with A aperture size. Total energy escaping:

$$\int_0^{2\pi} d\phi \int_0^{\pi/2} d\theta \frac{A \cos \theta}{4\pi} \frac{U}{V} c dt \sin \theta = \frac{A}{4} \frac{U}{V} c dt \tag{193}$$

Which gives power per unit area as:

$$P = \frac{2\pi^5}{15} \frac{(kT)^4}{h^3 c^2} = \sigma T^4 \text{ (Stefan - Boltzmann law)} \tag{194}$$

If reflecting: remember to include emissivity, e .

8.6.1 Radiation from Other Object

Emissivity ϵ :

$$\text{power} = \sigma \epsilon A T^4 \tag{195}$$

8.6.2 Sun and Earth

Luminosity: Sun $3.9 \cdot 10^6$ watts.

$$T = \left(\frac{\text{luminosity}}{\sigma A} \right)^{1/4} = 5800 K \Rightarrow \epsilon = 2.82 kT = 1.41 eV \tag{196}$$

$$\epsilon = 2.82 kT \tag{197}$$

$$Absorbed power : solar constant \times \pi R^2 = 4 \pi R^2 \sigma T^4 : emitted power. \Rightarrow T_{earth} = 279 K \tag{198}$$

Real: 288 K

9 Div:

9.1 Div:

tilstandsliking = pressure

$$n = \frac{N}{V} = \frac{P}{kT}, \quad (\text{From } PV = NkT) \tag{199}$$

viralutviklingen

$$\frac{PV}{NkT} = 1 + A\rho + B\rho^2, \quad \rho = N/V \tag{200}$$

9.2 Maxwell's relations

$$\left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial P}{\partial S} \right)_V, \quad \left(\frac{\partial T}{\partial P} \right)_S = \left(\frac{\partial V}{\partial S} \right)_P \tag{201}$$

$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V, \quad - \left(\frac{\partial S}{\partial P} \right)_T = \left(\frac{\partial V}{\partial T} \right)_P \tag{202}$$

These comes from the fact that

$$\left(\frac{\partial^2 F}{\partial x \partial y} \right) = \left(\frac{\partial^2 F}{\partial y \partial x} \right) \tag{203}$$

9.3 Ensembles

9.3.1 Micro canonical

(NVU) isolated. Multiplicity Ω and entropy $S = k \ln \Omega$

9.3.2 Canonical

(NVT). N and V constant, U varies (exchanges heat with a reservoir).

- Boltzmann Factor $e^{-\beta E(i)}$
- State: $Z = \sum_i e^{-\beta E(i)}$
- T in equilibrium
- Probability $P(i) = \frac{1}{Z} e^{-\beta E_i}$
- $\bar{E} = \frac{1}{Z} \frac{\partial Z}{\partial \beta}$
- Helmholtz $F = -kT \ln Z$

9.3.3 Grand Canonical

(μ VT) (exchanges heat and particles with a reservoir)

- V constant
- T and μ in equilibrium
- Gibbs factor $e^{-\beta E(i) - \mu N(i)}$
- $\bar{n} = \frac{kT}{Z} \frac{\partial Z}{\partial \beta}$
- Grand Potential $\Phi = U - TS - \mu N = -kT \ln Z$

9.4 Laws

9.4.1 First

$$dU = Q + W$$

(204)

9.4.2 Second

For isolated systems (NVE) $\Delta S \geq 0$. For NVT $\Delta F \leq 0$. For NPT $\Delta G \leq 0$

9.4.3 Third

$S \rightarrow \text{constant}$ when $T \rightarrow 0$

9.5 Random walk(virrevandring)

Step i is $s_i = \pm 1$. Distance from origin $x = \sum_i x_i$. Midlere kvadratisk distanse: $\langle x^2 \rangle = 2Dt$. t er tid, og D er diffusjonskoeffisienten.

9.6 Law of Corresponding State

All gases at corresponding states should behave similarly. The law of corresponding states is an empirical law which encapsulates the finding that the equations of state for many real gases are remarkably similar when they are expressed in terms of reduced temperatures $T_r = T/T_c$, pressures, $p_r = p/p_c$ and volumes $V_r = V/V_c$. According to van der Waals, the theorem of corresponding states (or principle of corresponding states) indicates that all fluids, when compared at the same reduced temperature and reduced pressure, have approximately the same compressibility factor and all deviate from ideal gas behavior to about the same degree

9.7 Div Functions

$$e^x + e^{-x} = 2 \cosh x$$

(205)

$$P(\text{noyaktig saa mange riktige paa saa mange forsoek}) = \binom{N}{n} p^n (1 - p)^{N-n}$$

(206)

Potential	Natural independent variables	Conjugated dependent variables	Maxwell relations and others
INTERNAL ENERGY U	S, V, N	$T = \left(\frac{\partial U}{\partial S}\right)_{V,N}$ $P = -\left(\frac{\partial U}{\partial V}\right)_{S,N}$ $\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}$	$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$
ENTROPY S	U, V, N	$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N}$ $\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{U,N}$ $-\frac{\mu}{T} = \left(\frac{\partial S}{\partial N}\right)_{U,N}$	
FREE ENERGY $F = U - TS$	T, V, N	$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}$ $P = -\left(\frac{\partial F}{\partial V}\right)_{T,N}$ $\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}$	$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ $U = -T^2 \frac{\partial}{\partial T} \left(\frac{F}{T}\right)$
ENTHALPY $H = U + PV$	S, P, N	$T = \left(\frac{\partial H}{\partial S}\right)_{P,N}$ $V = \left(\frac{\partial H}{\partial P}\right)_{S,N}$ $\mu = \left(\frac{\partial H}{\partial N}\right)_{S,P}$	$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$
GIBBS ENTHALPY $G = H - TS = N\mu$	T, P, N	$S = -\left(\frac{\partial G}{\partial T}\right)_{P,N}$ $V = \left(\frac{\partial G}{\partial P}\right)_{T,N}$ $\mu = \left(\frac{\partial G}{\partial N}\right)_{T,P}$	$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$ $H = -T^2 \frac{\partial}{\partial T} \left(\frac{G}{T}\right)$

Potential	Natural independent variables	Conjugated dependent variables	Maxwell relations and others
<p>GRAND CANONICAL POTENTIAL</p> $\Omega = F - \mu N = -PV$	T, V, μ	$S = - \left(\frac{\partial \Omega}{\partial T} \right)_{V, \mu}$ $P = - \left(\frac{\partial \Omega}{\partial V} \right)_{T, \mu}$ $N = - \left(\frac{\partial \Omega}{\partial \mu} \right)_{T, V}$	
<p>CHEMICAL POTENTIAL</p> $\mu = \frac{G}{N}$	T P	$s = \frac{S}{N} = - \left(\frac{\partial \mu}{\partial T} \right)_P$ $v = \frac{V}{N} = \left(\frac{\partial \mu}{\partial P} \right)_T$	