0. Physical constants

$k = 1.381 \times 10^{-23} J/K = 8.617 \times 10^{-5} eV/K$, $N_A = 6.022 \times 10^{23}$, $R = 8.315 J/mol \cdot K$, $h = 6.626 \times 10^{-34} J \cdot s = 4.136 \times 10^{-15} eV \cdot S$

1. Energy in Thermal Physics

1.1. Thermal equilibrium.
Temperature is a measure of the tendency of an object to spontaneously give up energy to its surroundings. When two objects are in thermal contact, the one that tends to spontaneously *lose* energy is at the *higher* energy. Room temperature $300K$

1.2. The ideal gas.
$PV = nRT = Nk_BT$. n is no of moles, $N = nN_A$ is number of molecules. $k_B = R/N_A$. Latter equation is valid when avg. space b/w molecules is larger than size of molecules. $\bar{E}_{K,trans} = \frac{3}{2}kT$.

1.3. Equipartition of energy.
Theorem: at temperature T, the average energy of any quadratic degree of freedom is $\frac{1}{2}kT$. $U_{thermal} = Nf\frac{1}{2}kT$. Monoatomic gas: $f = 3$. Diatomic gas: $f = 5, 6$ (3 trans., 2-3, rot.) or $f = 8$ (3 trans., 3 rot., 2 vibr. K, P). Solid: $f = 6$ (6 vibr. 3K, 3P). Some vibrational energies may be "frozen out" at room temperature.

1.4. Heat and work.
First law of thermodynamics $\Delta U = Q + W$. The change in energy is equal to the heat added and the work done. Heat transfer happens by *conduction*, *convection* and *radiation*.

1.5. Compression work.
Consider a piston. The force is $F = PA$. Assumes that the pressure is uniform. Compression must be slow enough so the gas has time to continually equilibrate to the changing conditions → *quasistatic*. A compressed gas, i.e. negative ΔV gives $W = F\Delta x = PA\Delta x = -P\Delta V$.

1.5.1. *Compression of ideal gas.*
Two idealised ways: *Isothermal* compression is so slow that the temperature of the gas does not rise (quasistatic). *Adiabatic* compression is so fast that no heat escapes during the compression. $VT^{f/2} =$ constant, $V^\gamma P =$ constant. $\gamma = \frac{f+2}{f}$ is the adiabatic exponent.

1.6. Heat capacities.
Amount of heat needed to raise an object's temperature, per degree temperature increase: $C = \frac{Q}{\Delta T} = \frac{\Delta U - W}{\Delta T}$. $W = 0$ and $V =$ constant is called heat capacity heat capacity at *constant volume*, else there would be compression work, $-P\Delta V$. $C_V = \left(\frac{\partial U}{\partial T}\right)_V$. If an object expand when heated and do work on surroundings, there is negative W. At constant P, Q i unambiguous → heat capacity at *constant pressure*: $C_P = \left(\frac{\Delta U - (-P\Delta V)}{\Delta T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + P\frac{\partial V}{\partial T}_P$.

1.6.1. *Latent heat.*
During a face transformation $C = \frac{Q}{\Delta T} = \frac{Q}{0} = \infty$. While $L = \frac{Q}{m}$ is the heat required to accomplish the transformation, the *latent heat*.

1.6.2. *Enthalpy.*
To create a rabbit out of nothing, the sorcerer must summon up not only the energy U of the rabbit, but also some additional energy, equal to PV, to push the atmosphere out of the way to make room. The *enthalpy*: $H = U + PV$. At constant P, $\Delta H = Q + W_{other}$.

2. The Second Law

Entropy, and multiplicity, tends to increase.

2.1. Two-state systems.
Multiplicity is given by the binomial coefficient. $\Omega(N, n) = \frac{N!}{n! \cdot (N-n)!} = \binom{N}{n}$. How many ways to pick n objects out of N. Permutations: $_nP_k = n(n-1)(n-2)\ldots(n-k) = \frac{n!}{(n-k)!}$. Unordered permutations: $_nC_k =_n P_k/k! = \binom{n}{k}$.

2.2. Einstein model of a solid.
One energy unit is $h\nu = \hbar\omega$. Multiplicity of Einstein solid with N oscillators (N/3 atoms) and q energy units: $\Omega(N, q) = \binom{q+N-1}{q}$.

2.3. Interacting systems.
Two solids are *weakly coupled* when flow of energy between them is much slower than flow of energy between atoms within each solid. Macrostate is the combined system, specified by temporarily constrained values U_A, U_B. Over time they will change, with the sum $U_{tot} = U_A + U_B$ remaining fixed. All parameters in such a system is N_A, N_B, $q_{tot} = q_A + q_B$, $\Omega_{tot} = \Omega_A\Omega_B$. Fundamental assumption of statistical mechanics: In an isolated system, all accessible microstates are equally probable.

2.4. Large systems.
If $|x| << 1$, a Taylor expansion gives $\ln(x + 1) \approx x$. If $N >> 1$ one can apply *Stirling's approximation*: $N! \approx N^N e^{-1}\sqrt{2\pi N}$. If N is a large number, and $N!$ is very large, the square root factor can be omitted. This is usually good enough: $\ln N! = N \ln N - N$. In a large Einstein solid $q >> N$ is the high temperature limit: $\Omega \approx \frac{(q+N)!}{q!N!}$, $\ln\Omega \approx (q+N)\ln(q+N) - q\ln q - N\ln N$, where $\ln(q+N) \approx \ln q + \frac{N}{q}$. S.T.: $\ln\Omega \approx N\ln\frac{q}{N} + N + \frac{N^2}{q}$.

2.5. The ideal gas.
$\Omega(U, V, N) = f(N)V^N U^{3N/2}$, where $f(N)$ is a complicated function of N. $\Omega_N = \frac{1}{N!}\frac{V^N}{h^{3N}} \times$(area of mon "area" $= \frac{2\pi^{d/2}}{(\frac{d}{2}-1)}r^{d-1}$, where in general $d = 3N$ and $r = \sqrt{2mU}$.

2.6. Entropy.
$S = k\ln\Omega$. Now you see why the logarithm of the multiplicity is nice to have. Entropy of an ideal gas: $S = Nk\left[\ln\left(\frac{V}{N}\left(\frac{4\pi mU}{3Nh^2}\right)^{3/2}\right) + \frac{5}{2}\right]$ (The Sackur-Tetrode equation). Depends on V, E, N. Increasing any of them increases S.

2.6.1. *Mixing.*
One gas into another chamber: $\Delta S_A = Nk\ln\frac{V_f}{V_i} = Nk\ln 2$. Two gases mixing, by removing a partition: $\Delta S_{tot} = \Delta S_A + \Delta S_B = 2Nk\ln 2$. Must be distinguishable gases. Gibbs Paradox.

2.6.2. *Irreversible.*
Processes that create new entropy are said to be irreversible. A sudden expansion is irreversible. A reversible volume change must in fact be quasistatic S.T. $W = -P\Delta V$.

3. Interactions and Implications

3.1. Temperature.
Two Einstein solids: $\frac{\partial S_A}{\partial U_A} = \frac{\partial S_B}{\partial U_B}$ at equilibrium with N_A, N_B fixed. Temperature is defined as $\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{N,V}$. If the slope is large the temperature must be small and vice versa.

3.2. Entropy and heat.
Algorithm to predict the heat capacity of a system: 1. Express the multiplicity Ω as a function of N, V and N. 2. Take the logarithm to find the entropy: $S = k \ln \Omega$. 3. Differentiate with respect to U and take the reciprocal to find the temperature, T as a function of U and other var's. 4. Solve for U as a function of T (and others). 5. Differentiate $U(T)$ to obtain a prediction of heat capacity (others held fixed). $C_V = \left(\frac{\partial U}{\partial T}\right)_{N,V}$. At very low temperatures all degrees of freedom must "freeze out", meaning $C_V \to 0$ as $T \to 0$. This is the *third law*.

3.3. Paramagnetism.
A system consists of N spin-$\frac{1}{2}$ particles, often referred to as dipoles, immersed in a constant magnetic field **B**. Total energy is $U = \mu B(N_\downarrow + N_\uparrow) = \mu B(N - 2N_\uparrow)$. Magnetisation is $M = \mu(N_\downarrow - N_\uparrow) = -\frac{U}{B}$. Multiplicity is $\Omega(N_\uparrow) = \binom{N}{N_\uparrow} = \frac{N!}{N_\uparrow! N_\downarrow!}$.

3.4. Mechanical equilibrium and pressure.
Pressure is $P = \left(\frac{\partial S}{\partial V}\right)_{U,N}$. Another proof of ideal gas law: $\Omega = f(N)V^N U^{3N/2}$, $S = Nk \ln V + \frac{3}{2}Nk \ln U + k \ln f(N)$, $P = T\frac{\partial}{\partial V}(Nk \ln V) = \frac{NkT}{V} \to PV = NkT$.

3.4.1. Thermodynamic identity.
Two steps: ΔU and ΔV. Sum of entropy change: $\Delta S = (\Delta S)_1 + (\Delta S)_2$. S.T. $dS = \left(\frac{\Delta S}{\Delta U}\right)_V \Delta U + \left(\frac{\Delta S}{\Delta V}\right)_U \Delta V$, then for a small change $dS = \left(\frac{\partial S}{\partial U}\right)_V dU + \left(\frac{\partial S}{\partial V}\right)_U dV$. Inserting definitions of temperature and pressure yields $dS = \frac{1}{T}dU + \frac{P}{T}dV$ which can be rearranged to $dU = TdS - PdV$.

3.4.2. Entropy and heat again.
$dU = Tds - PdV = Q + W$ if any volume change is quasistatic. If $Q = 0$ the process is also adiabatic $\to$ isentropic. We have $(\Delta S)_V = \int_{T_i}^{T_f} \frac{C_V}{T}dT$ and $(\Delta S)_P = \int_{T_i}^{T_f} \frac{C_P}{T}dT$

3.5. Diffusive equilibrium and chemical potential.
The chemical potential is $\mu = -T\left(\frac{\partial S}{\partial N}\right)_{U,V} = \left(\frac{\Delta U}{\Delta N}\right)_S = -\epsilon$, where ϵ is the size of a unit of energy. The generalised thermodynamic identity becomes $dU = TdS - PdV + \sum \mu_i dN_i$

4. Engines and Refrigerators

4.1. Heat engine.
A device that absorbs heat and converts part of that energy into work. The work produced is the difference between the heat absorbed and the waste expelled: $W = Q_h - Q_c$, where Q_h is heat absorbed from the hot reservoir and Q_c is heat expelled to cold reservoir. Efficiency: $e \equiv \frac{W}{Q_h} = \frac{Q_h - Q_c}{Q_h} = 1 - \frac{Q_c}{Q_h}$. First law: energy is conserved. Second law: entropy is a fluid that can be created but never destroyed, ergo $\frac{Q_c}{t_c} \geq \frac{Q_h}{T_h}$ and $\frac{Q_c}{Q_h} \geq \frac{T_c}{T_h}$. One concludes $e \leq 1 - \frac{T_c}{T_h}$.

4.1.1. The Carnot cycle (max efficiency).
Four steps: 1. Isothermal expansion at T_h while absorbing heat. 2. adiabatic expansion to T_c. 3. Isothermal compression at T_c while expelling heat. 4. Adiabatic compression back to T_h. The system must be but in contact with the hot reservoir during step 1 and with the cold reservoir during step 3.

4.2. Refrigerators.
A heat engine in reverse. Efficiency now called coefficient of performance COP $= \frac{Q_c}{W} = \frac{Q_c}{Q_h - Q_c} = \frac{1}{Q_h/Q_c - 1}$. Some inequalities: $\frac{Q_h}{T_h} \geq \frac{Q_c}{T_c}$ which gives $\frac{Q_h}{Q_c} \geq \frac{T_h}{T_c}$. One can conclude COP $\leq \frac{1}{T_h/T_c - 1} = \frac{T_c}{T_h - T_c}$.

5. Free energy and Chemical thermodynamics

Processes that are not cyclic. Interaction with environment s.t. T and P are constant, not E and V.

5.1. Free Energy as Available work.
Environment with constant P, related to *enthalpy* is **Helmholtz free energy**: $F \equiv U - TS = U - T\Delta S$. Energy needed to create system, minus energy for from environment at temp T.

Environment with constant P and T, work needed to create/destroy is Gibbs free energy $G = U - TS + PV = H - TS$. The magician needs not the entire enthalpy, some comes for free as heat.

The four functions U, H, F and G are called **thermodynamic potentials**. Identities: H: $dH = dU + PdV + VdP = TdS + VdP + \mu dN$, F: $dF = dU - TdS - SdT = -SdT - PdV + \mu dN$, $S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}$, $P = \left(\frac{\partial F}{\partial V}\right)_{T,N}$, $\mu = \left(\frac{\partial F}{\partial N}\right)_{T_P}$. G: $dG = -SdT + VdP + \mu dN$, $S = -\left(\frac{\partial G}{\partial T}\right)_{P,N}$, $V = \left(\frac{\partial G}{\partial P}\right)_{T,N}$, $\mu = \left(\frac{\partial G}{\partial N}\right)_{T,P}$.

Example of **Maxwell relation**: $\left(\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right)_{V,N}\right)_{S,N} = \left(\frac{\partial}{\partial S}\left(\frac{\partial U}{\partial V}\right)\right)$ $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$.

5.2. Free Energy as a Force toward Equilibrium.
An increase in total entropy. Constant N, U, V: S increase. Constant N, T, V: F decrease. Constant N, T, P: G decrease. Extensive properties: V, N, S, U, H, F, G, m. Intensive properties: T, P, μ, ρ.

5.3. Phase Transformations of Pure Substances.
The **Clausius-Clapyron relation**: $G_l = G_g$ at phase boundary, to remain $G_l = dG_g$. Thermodynamic identity for G: $-S_l dT + V_l dP = -S_g dT + V_g dP$ gives $\frac{dP}{dT} = \frac{S_g - S_l}{V_g - V_l}$. Write $S_g - S_l = \frac{L}{T}$, where L is latent heat, to get $\frac{dP}{dT} = \frac{L}{T\Delta V}$. Applies to the slope of any phase boundary line on a PT diagram.

The **van der Waals equation** is $\left(P + \frac{aN^2}{V^2}\right)(V - Nb) = NkT$. Mod of ideal gas with molecular interaction.

6. Boltzmann Statistics

6.1. The Boltzmann factor.
System in contact with reservoir and assume equal probability for all microstates. Boltzmann factor $= e^{-E(s)/kT}$. Partition function: $Z = \sum_s e^{-E(s)/kT}$. Botlzmann/canonical distribution: $\mathcal{P}(s) = \frac{1}{Z}e^{-E(s)/kT}$.

6.2. Average Values.

$\bar{X} = \sum_s X(s)P(s)$. $\bar{E} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{\partial \ln Z}{\partial \beta}$. Example: Rotation of diatomic molecules (2 rot d.o.f.). Assuming low density. Allowed energies $E(j) = j(j+1)\epsilon$, $j = 0, 1, \ldots$ with degeneracy $\Omega(j))2j + 1$. Then $X_{rot} = \sum_{j=0}^{\infty}(2j+1)e^{-E(j)/kT}$. One can approximate with an integral if $kt >> \epsilon$: $Z_{rot} \approx \int_0^{\infty}(2j+1)e^{-E(k)/kT}dj = \frac{kT}{\epsilon} \to \bar{E} = kT$ in agreement with the equipartition theorem (identical atoms, divide by 2). $C_V = \frac{\partial \bar{E}}{\partial T} = k$. At low T, $C_V \to 0$ according to third law. Agrees with exact Z.

6.3. The Equipartition Theorem.

Applies to systems with energy in the form of quadratic degrees of freedom: $E(q) = cq^2$ where c is a constant and q is a coordinate or momentum variable (x, p_x, L_x). Each q corresponds to a separate, independent state. Pretend they're discretely spaced, separated by intervals Δq. $Z = \sum_q e^{-\beta cq^2} \approx \frac{1}{\Delta q}\int_{-\infty}^{\infty}e^{-\beta cq^2}dq$. Approximate to integral if Δq is small. Bell curve. Calculate $\bar{E} = \frac{1}{2}kT$ from this to confirm equipartition theorem. Only true in high T limit, or when spacing b/w energy levels i much less than kT.

6.4. The Maxwell Speed Distribution.

From equipartition theorem, $v_{rms} = \sqrt{\frac{3kT}{m}}$. This is an average, we want a distributions for speed of molecules. v can vary continuously $\to$ infinitely small probabilities. Use intervals, area under graph: $\mathcal{P}(v_1 \ldots v_2) = \int_{v_1}^{v_2}\mathcal{D}(v)dv$, where $\mathcal{P}(v) \propto e^{-mv^2/2kT}$ and $\mathcal{D}(v) \propto \mathcal{P}(v) \times \Omega(v)$, where $\Omega(v)$ is no of vectors $\vec{v}$ corresponding to v ($\propto 4\pi v^2$). Must be set of vectors on surface of sphere with Area $= 4\pi v^2$. Then $\mathcal{D}(s) = C \cdot 4\pi v^2 e^{-mv^2/2kT}$. Find C by normalising, with substitute $x = \sqrt{m/2kT}$, $1 = 4\pi C \left(\frac{2kT}{m}\right)^{3/2}\int_0^{\infty}x^2 e^{-x^2}dx \to C = (m/2\pi kT)^{3/2}$. Final result: $\mathcal{D}(v) = \left(\frac{m}{2\pi kT}\right)^{3/2}4\pi v^2 e^{-mv^2/2kT}$, note that $\bar{v} = \sqrt{\frac{8kT}{\pi m}}$.

6.5. Partition Functions and Free Energy.

System at fixed U in contact with reservoir at T. $Z(T)$ analogous to $\Omega(T)$. $F = U - TS = -kT\ln Z$, tends to decrease. $S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}$, $P = -\left(\frac{\partial F}{\partial V}\right)_{T,N}$, $\mu = +\left(\frac{\partial F}{\partial N}\right)_{T,V}$.

6.6. Partition Functions for Composite Systems.

Two particles: $Z_{tot} = \sum_s e^{-\beta[E_1(s)+E_2(s)]} = \sum_s e^{-\beta E_1(s)}e^{-\beta E_2(s)}$. Distinguishable $Z_{tot} = \sum_{s_1}\sum_{s_2}e^{-\beta E_1(s_1)}e^{-\beta E_2(s_2)} = Z_1 Z_2$. Indistinguishable $Z_{tot} = \frac{1}{2}Z_1 Z_2$. N **particles**: Distinguishable $Z_{tot} = Z_1 Z_2 Z_3 \ldots Z_N$. Indistinguishable $Z_{tot}\frac{1}{Z}Z_1^N$. Assumes low density, i.e.

6.7. Ideal gas revisited.

Boltzmann factors $e^{-E(s)/kT} = e^{-E_{tr}(s)/kT}e^{-E_{int}(s)/kT}$, additionally $Z_1 = Z_{tr}Z_{int}$. Translational first: Standing wave patterns are limited to $\lambda_n = \frac{2L}{n}$, using de Broglie $(p = h/\lambda)$, $p_n = \frac{h}{\lambda_n} = \frac{hn}{2L}$. Energy-momentum relation $(E = p^2/2m)$, $E_n = \frac{p_n^2}{2m} = \frac{h^2 n^2}{8mL^2}$. $Z_{1D} = \sum_n e^{-E_n/kT} = \sum_n e^{-h^2 n^2/8mL^2 kT}$. Integral approx $Z_{1D} = \int_0^{\infty}e^{-h^2 n^2/8mL^2 kT}dn = \frac{\sqrt{\pi}}{2}\sqrt{\frac{8mL^2 kT}{h^2}} = \sqrt{\frac{2\pi mkT}{h^2}}L \equiv \frac{L}{\ell_Q}$. In 3D: $E_{tr} = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m}$ and $Z_{tr} = \frac{L_x}{\ell_Q}\frac{L_y}{\ell_Q}\frac{L_z}{\ell_Q} = \frac{V}{v_Q}$. Partition function for one particle: $Z_1 = \frac{V}{v_Q}Z_{int}$ and for N: $Z = \frac{1}{N!}\left(\frac{VZ_{int}}{v_Q}\right)^N$.

7. Quantum Statistics

7.1. The Gibbs Factor.

Gibbs factor $= e^{-[E(s)-\mu N(s)]/kT}$. $\mathcal{P}(s) = \frac{1}{\mathcal{Z}}e^{-[E(s)-\mu N(s)]/kT}$. The grand partition function $\mathcal{Z} = \sum_s e^{-[E(s)-\mu N(s)]/kT}$.

7.2. Bosons and Fermions.

Particles with integer spin are bosons, while particles with half-integer spin are fermions. Two identical fermions cannot occupy the same space (**Pauli exclusion principle**). If $Z_1 >> N$ chance of two particles in same state is negligible. For ideal gas $Z_1 = \frac{VZ_{int}}{v_q}$. The quantum volume is $v_Q = \ell_Q^3 = \left(\frac{h}{\sqrt{2\pi mkT}}\right)^3$, a cube of the average de Broglie wavelength. Then: $\frac{V}{N} >> v_q$. Distance b/w particles must be greater than de Broglie w.l. **Fermi-Dirac**: n can only be 0 or 1, so $\mathcal{Z} = 1 + e^{-(\epsilon-\mu)/kT}$. Occupancy: $\bar{n} = \sum_n = n\mathcal{P}(n) = 0 \cdot \mathcal{P}(0) + 1 \cdot \mathcal{P}(1) = \frac{e^{-(\epsilon-\mu)/kT}}{1+e^{-(\epsilon-\mu)/kT}}$. Simplification yields distribution $\bar{n}_{FD} = \frac{1}{e^{(\epsilon-\mu)/kT}+1}$. **Bose-Einstein**: n can be any non-negative integer, so the grand partition function is $\mathcal{Z} = 1 + e^{-(\epsilon-\mu)/kT} + e^{-2(\epsilon-\mu)/kT} + \cdots = 1 + e^{-(\epsilon-\mu)/kT} + (e^{-(\epsilon-\mu)/kT})^2 + \cdots = \frac{1}{1-e^{-(\epsilon-\mu)/kT}}$. μ must be less than ϵ, the series must converge. Occupancy: $\bar{n} = \sum_n n\mathcal{P}(n) = 0 \cdot \mathcal{P}(0) + 1 \cdot \mathcal{P}(1) + 2 \cdot \mathcal{P}(2) + \ldots$, abbreviate $x \equiv (\epsilon - \mu)/kT$. Then $\bar{n} = \sum_n \frac{e^{-nx}}{\mathcal{Z}} = -\frac{1}{\mathcal{Z}}\sum_n \frac{\partial}{\partial x}e^{-nx} = -\frac{1}{\mathcal{Z}}\frac{\partial \mathcal{Z}}{\partial x}$. Distribution: $\bar{n}_{BE} = -(1 - e^{-x})\frac{\partial}{\partial x}(1 - e^{-x}) = (1 - e^{-x})(1 - e^{-x})^{-2}(e^{-x}) = \frac{1}{e^{(\epsilon-\mu)/kT}-1}$