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 $\rightarrow$ *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 $\rightarrow$ 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 momentum hypersphere). "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: $\frac{\partial S_A}{\partial U_A} = \frac{\partial S_B}{\partial U_B} = 0$ at equilibrium with N_A, N_B fixed.