

## 0. PHYSICAL CONSTANTS

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

## 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.**  $PV = nRT = Nk_B T$ .  $n$  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  $\Delta V$  gives  $W = F\Delta x = P\Delta x = -P\Delta V$ .

**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.  $VT^{f/2} = \text{constant}$ ,  $V^\gamma P = \text{constant}$ .  $\gamma = \frac{f+2}{f}$  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  $V = \text{constant}$  is called 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  $P$ ,  $Q$  is 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 phase 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.  $\Omega(N, n) = \frac{N!}{n!(N-n)!} = \binom{N}{n}$ . How many ways to pick  $n$  objects out of  $N$ . Permutations:  $nP_k = n(n-1)(n-2)\dots(n-k) = \frac{n!}{(n-k)!}$ . Unordered permutations:  $nC_k = nP_k/k! = \binom{n}{k}$ .

**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  $|x| \ll 1$ , a Taylor expansion gives  $\ln(x+1) \approx x$ . If  $N \gg 1$  one can apply *Stirling's approximation*:  $N! \approx N^N e^{-N} \sqrt{2\pi N}$ . 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  $q \gg N$  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" =  $\frac{2\pi^{d/2}}{(d-1)} r^{d-1}$ , 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:  $S = Nk \left[ \ln \left( \frac{V}{N} \left( \frac{4\pi m U}{3N h^2} \right)^{3/2} \right) + \frac{5}{2} \right]$  (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  $\Omega$  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  $C_V \rightarrow 0$  as  $T \rightarrow 0$ . 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  $\mathbf{B}$ . 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:  $\Omega = f(N)V^N U^{3N/2}$ ,  $S = Nk \ln V + \frac{3}{2}Nk \ln U + k \ln f(N)$ ,  $P = T \frac{\partial}{\partial V}(Nk \ln V) = \frac{NkT}{V} \rightarrow PV = NkT$ .

3.4.1. *Thermodynamic identity.* Two steps:  $\Delta U$  and  $\Delta V$ . 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  $\rightarrow$  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  $\epsilon$  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