

Making Sense of the Equation Sheet

Physics 213

Fundamental Laws/Principles:

First Law: $dU = dQ + dW$

Energy is conserved—the change in the internal energy of a system is equal to the heat that flows into or out of the system plus the work done on or by the system.

Second Law: $d\sigma/dt \geq 0$

As a system comes to equilibrium, the entropy of the system plus the environment always increases. In equilibrium, the total equilibrium is maximized and does not change in time.

Dimensionless entropy: $\sigma(A) = \ln \Omega(A)$, $\Omega(A) = e^{\sigma(A)}$, $P(A) \propto \Omega(A)$

$\Omega(A)$ = number of microstates corresponding to the macrostate A , P = probability of observing the macrostate A .

Classical equipartition: Every quadratic degree of freedom has an on average $\frac{1}{2} kT$ of thermal energy.

This is true provided the characteristic thermal energy scale $kT \gg$ energy level spacing (e.g., $kT \gg \epsilon$, where ϵ is the harmonic oscillator level spacing.) Translational motion persists to zero temperature, therefore equipartition applies at all temperatures. For example, if we consider the motion of the nuclei in a solid, each acts like a mass on springs to each of its nearest neighbors, i.e., 3 harmonic oscillators $\rightarrow U = 3NkT$ [=N atoms x (3 directions) x (kT/2 for KE + kT/2 for potential energy)]

Entropy and Temperature:

Entropy with dimensions of J/K: $S = k\sigma = k \ln \Omega$

General definition of temperature: $\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N}$

Anytime two systems exchange energy (keeping the volume and the number of each system constant) their temperatures become equal; this maximizes the total entropy.

Heat capacity: $C = dQ/dT$ (thermal energy needed to increase the temperature of a system by dT).

Two common cases:

volume is kept constant, in which case no work is done (since $dW = pdV$), and $dQ=dU$.

pressure is kept constant, so more energy is needed to raise T (since some goes into work).

For a typical solid/liquid these are essentially the same, since volume changes little with T .

The heat capacity depends on how much material there is, and also a property of the type of material = “specific heat” c : $C = mc$ (here c is given as the specific heat per mass; another option is ‘per mole’)

α -Ideal Gases: $\alpha = \frac{1}{2}$ the number of degrees of freedom (d.o.f.)

Examples: Monatomic gas: 3 translational d.o.f. ($\alpha=3/2$)

Diatomic gas: 3 translational d.o.f. + 2 rotational d.o.f. ($\alpha=5/2$)

Work done by a gas in an isothermal expansion ($T = \text{constant}$): $W_{by} = NkT \ln(V_f/V_i)$

Relations for an adiabatic process ($Q = 0$):

$$VT^\alpha = \text{const.} \quad PV^\gamma = \text{const.} \quad \gamma = (\alpha + 1)/\alpha$$

Work done in an adiabatic process: $W_{by} = \Delta U = \alpha Nk (T_1 - T_2) = \alpha(P_1V_1 - P_2V_2)$

General expression for the change in entropy when both volume and temperature vary (but assuming the heat capacity is constant over the range of temperatures considered):

$$\Delta S = C_V \ln(T_f/T_i) + Nk \ln(V_f/V_i)$$

Processes, Heat engines

If we put heat into a system, that can either increase the thermal energy ΔU , and/or allow the system to do work: $Q = \Delta U + W_{by}$

For a quasi-static (i.e., essentially in equilibrium throughout) process, $dS = dQ/T$. We can get the total change in entropy by integrating this. IF the heat capacity doesn't depend on T , then $\Delta S = C \ln(T_f/T_i)$

We can allow temperature flow from a hot reservoir into a cold one to power a heat engine. The work out is then given by $W_{out} = Q_{hot} - Q_{cold}$, where Q_{hot} (Q_{cold}) is the energy removed from (deposited into) the hot (cold) reservoir on each cycle of the engine.

The efficiency is defined as the work out divided by heat in: $\epsilon = \frac{W_{out}}{Q_{hot}} = 1 - \frac{Q_{cold}}{Q_{hot}}$

This is true for ANY heat engine.

If we have a "Carnot" engine, using only reversible processes (isothermal and adiabatic), then

$$\Delta S_{tot} = \Delta S_{hot} + \Delta S_{cold} = -Q_{hot}/T_{hot} + Q_{cold}/T_{cold} = 0 \rightarrow Q_{cold}/Q_{hot} = T_{cold}/T_{hot} \text{ so } \epsilon = 1 - T_{cold}/T_{hot}.$$

Diffusion:

This process can be modeled as a random walk. The rms displacement from the starting location is then proportional to the square root of the number of steps taken (which in turn is proportional to the total time for diffusion to occur). For particles diffusing in 3 dimensions, we have $\langle x^2 \rangle = 2Dt$ (this tells about diffusion along a *particular* direction, e.g. from one surface to another, or from one point to another) and $\langle r^2 \rangle = 6Dt$ (if we ask about diffusion in *all* directions, e.g., from the center of a sphere to *any* point on its surface). Here the diffusion constant $D = v l / 3 = l^2 / 3\tau$ depends on the average velocity v , mean free path between scattering events l , and mean free time between scattering events τ .

Heat Conduction:

The rate of heat flow (e.g., in Watts) H is proportional to the cross sectional area A and the heat current density J . The latter varies as the temperature gradient ($\sim \Delta T / \Delta x$) and the thermal conductivity κ . We can then write $H = \Delta T / R_{th}$, where the thermal resistance is $R_{th} = d / \kappa A$, is for a slab of thickness d and area A ; thermal resistances combine just like electrical resistances (e.g., in series or parallel).

If an object with heat capacity C at initial temperature T_{A0} is put into contact with a thermal reservoir at temperature T_f , the heat flow from the object will just be $(T_{A0} - T_f) / R_{th}$. However, as the object temperature becomes closer to T_f , less heat will flow, and the temperature of the object will approach T_f with an exponential decay, with decay time constant $\tau = R_{th} C$.

Spins:

Binomial distribution: Applies to probabilistic events with two possible outcomes. Examples include coin toss (heads or tails), spins (spin up or spin down), 1-D random walk (step left or step right). If each outcome is equally probable, then the number of microstates corresponding to a particular macrostate is given by

$$\Omega(N, N_{up}) = \frac{N!}{N_{up}! (N - N_{up})!}$$

where N is the number of coin tosses and the macrostate is specified by N_{up} . When N is large, the binomial distribution is approximately given by the Gaussian distribution

$$\Omega(m) = 2^N \sqrt{\frac{2}{\pi N}} e^{-m^2/2N}$$

Here, $m = N_{up} - N_{down}$. For a 1-D random walk m is the displacement away from zero. The probability of obtaining a particular macrostate m is $P(m) = \Omega(m) / \Omega_{tot}$, where $\Omega_{tot} = 2^N$ is the total number of microstates.

Spins in a magnetic field: In a magnetic field the magnetic energy of a spin with magnetic moment $\vec{\mu}$ is $E = -\vec{\mu} \cdot \vec{B}$. The net magnetic moment for N spins is

$$\langle M \rangle = N\mu(P_{\uparrow} - P_{\downarrow})$$

To calculate probabilities from the Boltzmann distribution, use

$$P(E) = \frac{d_n e^{-E/kT}}{Z}$$

where Z is the partition function.

Z : Sum over all states of the Boltzmann factor $e^{-E_n/kT}$

$$Z = \sum_n d_n e^{-E_n/kT}$$

d_n = degeneracy

For a spin a magnetic field B : $Z = e^{-\mu B/kT} + e^{\mu B/kT}$

Probability for the spin to be aligned parallel to the magnetic field: $P_{\uparrow} = \frac{e^{\mu B/kT}}{Z}$

Probability that the spin and field are aligned antiparallel: $P_{\downarrow} = \frac{e^{-\mu B/kT}}{Z}$

$$\langle M \rangle = N\mu \tanh\left(\frac{\mu B}{kT}\right)$$

High temperature limit: $\langle M \rangle = N\mu^2 B/kT$. This relationship is known as the Curie Law.

Simple Harmonic Oscillator (SHO):

The quantum harmonic oscillator has equally spaced energy levels $U = n\epsilon$, where $n = 0, 1, 2, \dots$ and the energy level spacing is $\epsilon = hf$; h = Planck's constant, and $f = \sqrt{K/m}$ is the classical oscillation frequency.

The probability of the oscillator being in the n^{th} vibrational level is: $P_n = \frac{e^{-n\epsilon/kT}}{Z}$

where $Z = \sum_{n=0}^{\infty} e^{-n\epsilon/kT}$. This sum converges to $Z = 1/(1 - e^{-\epsilon/kT})$. This gives the following result

$$P_n = (1 - e^{-\epsilon/kT})e^{-n\epsilon/kT}$$

The average energy is $\langle E \rangle = \sum_{n=0}^{\infty} n \epsilon P_n = \frac{\epsilon}{(e^{\epsilon/kT} - 1)}$

When calculating the entropy associated with having q quanta of energy shared among N oscillators, we need to find the number of microstates. The corresponding number of microstates is given by

$$\Omega = \frac{(q + N - 1)!}{q! (N - 1)!}$$

Counting:

If we want to calculate the entropy associated with having N particles in M bins, the answer depends on whether the bins can hold multiple particles, or only one ("single occupancy"), and whether the particles are in principle distinguishable ("distinct") or not ("identical", in which case we usually overcount, e.g., by $N!$, so we divide by that). When there are many more bins than particles ("dilute" case), we can just use the simpler 'unlimited occupancy' formulas.

For $N \gg 1$ use Sterling's approximation, $\ln N! \approx N \ln N - N$.

Equilibrium:

When we considered two systems that could exchange volume or energy, we found the equilibrium properties (pressure, density, temperature) by maximizing the combined entropy of both systems. When we consider a small system connected to a large reservoir whose temperature is fixed, then it is more convenient to consider the free energy. This is because the free energy deals only with the entropy and internal energy of the small system. In equilibrium, the free energy of the system must be a minimum. In contrast, the total entropy of the system plus the environment is a maximum.

$$\text{Helmholtz free energy} = F = U_{sys} - T_{env} S_{sys}$$

The free energy per particle is the chemical potential: $\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T}$

$$\text{Ideal gas chemical potential: } \mu = \left(\frac{\partial F}{\partial N}\right)_{V,T} = -|\Delta| + kT \ln\left(\frac{n}{n_Q}\right)$$

where Δ is the internal energy per particle (here negative, as we're thinking of some sort of binding energy), $n = N/V$ is the density and n_Q is the quantum density, i.e., the maximum number of states per volume, as allowed by quantum mechanics. For a monatomic non-interacting gas we have: $n_Q = \left(\frac{2\pi mkT}{h^2}\right)^{3/2}$

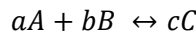
If, for example, there are also 2 spin states, then we would multiply by 2. If there also, e.g., rotations or vibrations, these would also increase n_Q , though we didn't discuss how to calculate that in detail. In all the cases we consider, $n \ll n_Q$, therefore the natural log term in μ is negative.

Chemical potential and equilibrium:

In a reaction involving the creation of different types of particles (examples: interstitial-vacancy pairs and electron-hole pairs in semiconductors), the equilibrium condition is given by

$$\sum_i (\Delta N)_i \mu_i = 0$$

where ΔN_i refers to the number of particles of type i involved in the reaction. As an example, consider the chemical reaction



where A, B and C refer to the particle type, and a, b, and c are the number of each type. From the general form of the equilibrium condition

$$a\mu_A + b\mu_B = c\mu_C$$

If we treat each species as an ideal gas, liquid, or solid, then

$$\frac{n_C^c}{n_A^a n_B^b} = \frac{n_{QC}^c}{n_{QA}^a n_{QB}^b} e^{\Delta/kT}, \text{ where } \Delta = c\Delta_C - a\Delta_A - b\Delta_B.$$

Phase transitions:

In phase transitions, the volume between the two different phases is often different, for example consider a molecule of water going between the liquid and gas phase. If work is done while reaching equilibrium (e.g., to create the extra space needed for the gas, assuming a transition at constant pressure), then it is the Gibbs free energy which is minimized.

$$\text{Gibbs free energy} = G = U - TS + PV = F + PV$$

We can express the Gibbs free energy involving different phases as

$$G = N_s \mu_s + N_l \mu_l + N_g \mu_g$$

where the subscripts (*s, l, g*) refer to solid, liquid, and gas, respectively. In equilibrium, the phase with the lowest chemical potential is the stable phase. By maximizing the number of particles corresponding to the phase with the lowest μ , G is minimized.

Thermal Radiation

Power per unit area radiated by a black body (units W/m^2): $J = \epsilon \sigma_{SB} T^4$

σ_{SB} = Stefan-Boltzmann constant

ϵ = emissivity. $\epsilon = 1$ for a perfect black body and is between 0 and 1 for all other materials.

By thermodynamics arguments, the emissivity of an object must equal its absorbance at each wavelength.

Wien's displacement law: $\lambda_{max} T = 0.0029 \text{ m} \cdot \text{K}$ – Describes the location of the peak in the black body spectrum as a function of temperature.