School of Physics and Astronomy

Junior Honours **Thermodynamics**   GJA 2019-2020

Lecture TOPIC 7 (Finn: 5.6, 5.8, 5.9, 5.10)

Synopsis: The Second Law of Thermodynamics (review) and the Central Equation of Thermodynamics. Entropy of an ideal gas. Entropy, probability and disorder.

The Principle of Increasing Entropy: corollary

Imagine the system of interest plus its surroundings to be enclosed by an adiabatic wall (e.g. a small system and a large but finite volume of surrounding whose T,P will remain essentially unchanged). Then for the ensemble $đq = 0 \Rightarrow \Delta S \geq 0$.

> The entropy of a thermally isolated ensemble comprising the system plus surroundings can never decrease.

This will be used later to examine conditions for equilibrium in system with various boundary conditions (surroundings).

The Central Equation of Thermodynamics

This combines the first and second laws for **infinitesimal reversible** processes in differential form:

$$dU = đQ + đW \quad \rightarrow \quad \boxed{dU = TdS - PdV}$$

Although valid only if both T and P are well defined (reversible processes) it involves **only state variables**. It always be integrated along any path to calculate changes of state variables, even when those changes occur via irreversible processes. This trick uses the path-independence to replace the actual irreversible path with an equivalent reversible path along which the integrals can be done. Choosing a path to make the integrals easy is an important skill. Owing to its usefulness and generality it is called the central equation of thermodynamics and is also usefully written:

$$TdS = dU + PdV \qquad \text{or} \qquad Tds = du + Pdv.$$

Using either extensive or intensive quantities.

If applied to a system which is not a simple fluid, the equation has to be augmented to allow for other variables. For electric charge (denoted by Z, avoiding confusion with heat) driven through a system by an emf ($\mathscr{E}$, to avoid confusion with V), the equation becomes $dU = TdS - PdV + \mathscr{E}dZ$. For a one dimensional system like a rubber band under tension $\mathscr{F}$, changes in length L dominate, so the the equation becomes $dU = TdS + \mathscr{F}dL$.

Entropy of an ideal gas ; a problem

For an Ideal gas $u = u(T)$, so that $du = c_v dT$. The central equation for the molar entropy ds then gives:

$$ds = c_v \frac{dT}{T} + R \frac{dv}{v}$$

where the Ideal gas equation has been used to re-express the second term. Integrating the above gives:

$$\boxed{\begin{aligned} s &= c_v \ln T/T_0 + R \ln v/v_0 + s_0 \\ &= c_P \ln T/T_0 - R \ln P/P_0 + s_0 \end{aligned}}$$

The "problem" is that as T or P go to zero, the entropy becomes infinite.

The constant of integration is written as $s_0 - c_v \ln T_0 + R \ln v_0$ to emphasize that this is entropy relative to a particular reference state, and that choosing $T_0 = 0$ and $P_0 = 0$ is problematic. This is the fundamental reason why chemists relate things to "Standard Temperature and Pressure" (STP= 273.15 K, 101.3kPa)

In a Joule, or "free" expansion of an ideal gas, U does not change, nor therefore does T. However, because v changes, there must be a change in entropy s. For 1 mole of ideal gas, the change in entropy during a free expansion is:

$$s_f - s_i = c_v \ln T_f + R \ln v_f + s_0 - (c_v \ln T_i + R \ln v_i + s_0) = R \ln \frac{v_f}{v_i}$$

An example, "heating water on a stove"

Question: Calculate the change in entropy of water heated from 20^oC to 100^oC on a stove.

method 1: as per topic 06. A reversible path is constructed involving a series of heat baths between initial and final temperatures T_i and T_f with the water brought into contact with each bath in turn. The thermodynamic definition of entropy relates changes of entropy to reversible heat transfers, which can be applied along this alternative path between T_i and T_f:

$$\Delta S = \int_{T_i}^{T_f} \frac{d q_R}{T} = \int_{T_i}^{T_f} \frac{C_p dT}{T}$$

The change of entropy of the water is the same as in the irreversible process that actually occurs since entropy is a state function and the initial and final equilibrium states match.

method 2: Brute force solution applying the central equation:

$$\Delta S = \int_i^f \frac{dU}{T} + \int_i^f \frac{p}{T} dV$$

We know only T_i and T_f and $p_i = p_f$, but not U_i and U_f or V_i and V_f. Therefore we need to expand dU and dV in terms of $\{p,T\}$.

$$\Delta S = \int_i^f \frac{\left(\frac{\partial U}{\partial T}\right)_p dT + \left(\frac{\partial U}{\partial p}\right)_T dp}{T} + \int_i^f \frac{p}{T}\left[\left(\frac{\partial V}{\partial T}\right)_p dT + \left(\frac{\partial V}{\partial p}\right)_T dp\right]$$

The pot is open to atmosphere, so the natural choice of path is isobaric $p = p_i = p_f$ for which $dp = 0$.

$$\Delta S = \int_{T_i}^{T_f} \frac{\left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p}{T} dT = \int_{T_i}^{T_f} \frac{\left(\frac{\partial (U+pV)}{\partial T}\right)_p}{T} dT = \int_{T_i}^{T_f} \frac{\left(\frac{\partial H}{\partial T}\right)_p}{T} dT = \int_{T_i}^{T_f} \frac{C_p}{T} dT$$

method 3: The water is heated at constant pressure so it is likely to be more convenient to work with H=U+PV rather than U, which combined with the central equation gives

$$dH = dU + pdV + Vdp = (TdS - pdV) + pdV + Vdp = TdS + Vdp$$

$$\Rightarrow \boxed{dH = TdS + Vdp}$$

The above is an equivalent form of the central equation. We can integrate this choosing the path $p =$const to get

$$\int_{p=\text{const}} dS = \int_{p=\text{const}} \frac{dH}{T}$$

Writing $H = H(T,P) \Rightarrow dH = \left(\frac{\partial H}{\partial T}\right)_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp = C_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp$. Thus along the path $p =$const $dH|_p = C_p dT$

$$\Rightarrow \Delta S = \int_{T_i}^{T_f} \frac{C_p}{T} dT \qquad \text{as found previously.}$$

In methods (2) & (3) we have not to had to think explicitly about an equivalent reversible path for the irreversible process as done in method (1). The central equation deals with this implicitly.

Another example, "electrical work"

Consider a current I flowing through a resistor R. The power delivered is $\mathscr{E}I = I^2R$. Suppose the resistor, regarded as the system, completely fills a box with adiabatic walls. The power is dissipated irreversibly in the resistor, which therefore heats up.

From the 1st law the change in internal energy of the system in time interval Δt is $\Delta U = (q = 0) + w = I^2R\Delta t$ (assuming the volume is fixed so that no mechanical work is done). We can relate changes of U to changes of temperature for a constant volume process with $dU = C_V dT|_{\text{V const}}$. The change in temperature is then:

$$I^2R\Delta t = \int_{T_i}^{T_f} C_V dT = C_V \Delta T$$

where the last equality follows if C_V can be approximated as constant (independent of temperature) $\Rightarrow \Delta T = I^2R\Delta t/C_V$.

What is the change of entropy?
<u>method 2</u> The change of entropy can be calculated with the central equation $dS = dU/T|_{\text{V const}} \Rightarrow dS = C_V dT/T|_{\text{V const}} \Rightarrow \Delta S = \int_{T_i}^{T_f} \frac{C_V}{T} dT$ with T_f calculated above.

<u>method 1</u> The same answer can be found by thinking of a reversible process leading to the same change of state variables between the initial and final equilibrium states, in this case a change of temperature ΔT. This could be achieved by putting the resistor successively in thermal contact with a sequence of heat reservoirs, starting with one at T_i and ending with one at T_f giving:

$$\Delta S = \int_{T_i}^{T_f} dq_R/T = \int_{T_i}^{T_f} C_v dT/T$$

ie we have considered an alternative process where **heat** enters the system reversibly but **no work** of any kind is done.

The connection between Entropy, Counting, and Probability

a preview of subject matter to be developed in next term's statistical mechanics course

The Second Law means that the total entropy of an isolated system must increase and is maximised at equilibrium. In statistical physics we expect a system to change from a less probable initial state to a more probable final state. This implies a relationship between probability and entropy.

As an example, reconsider the Joule expansion of a large number of atoms, N, of an ideal gas. Initially, all the gas is on the left hand side of the container, whereas in the final state the gas has an equal density everywhere.

Using the Central Equation, remembering that $\Delta U = 0$ in the free expansion of an ideal gas, this gives:

$$\Delta S = \int dS = \int \frac{PdV}{T} = \int \frac{nRdV}{V} = nR\ln\frac{V_f}{V_i} = nR\ln 2$$

To relate this to probabilities, denote the left hand side of the container by A and the right hand side by B with $V_A = V_B = V$. A long time after the partition has been removed and assuming the system is free to explore all possible states available to it (respecting energy conservation), the probability that any one molecule is in A is $1/2$. The probability of finding the system in its initial state a long time after the wall has been removed (i.e. the molecules in A) is $(1/2)^N$.

Now, define a *microstate* as a fully specified set of momenta and positions for all molecules. Denote the total number of possible microstates available with energy E and all the particles in A, to be $\Omega_A \equiv \Omega(N, V_A, E)$. Notice that for Ω to be countable number, momenta and position states must be quantised.

Similarly, denote the total number of states with energy E, N particles, and volume $V_A + V_B$ with the particles located anywhere within volume $V_A + V_B$ as $\Omega_{A+B} \equiv \Omega(N, V_{A+B}, E)$. Assuming that all the
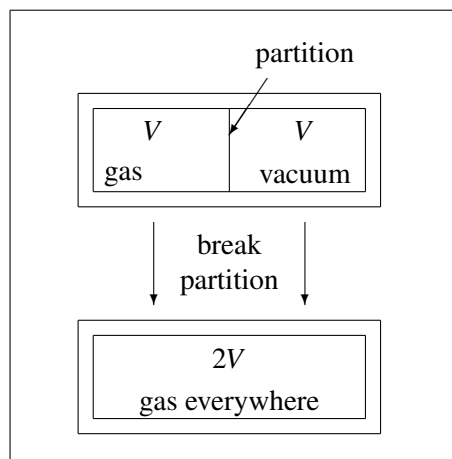
accessible microstates are equally likely,

$$\frac{\Omega_A}{\Omega_{A+B}} = \frac{\Omega(N,V,E)}{\Omega(N,2V,E)} = \left(\frac{1}{2}\right)^N \tag{1}$$

Suppose that there is a relationship between the entropy and the number, Ω, of microstates available; $S = f(\Omega)$ where f is a function to be determined. Entropy is extensive, so if we consider twice as much gas, we should have twice as much entropy, whereas the total number of microstates available grows much faster, as the product $\Omega_1\Omega_2$. Therefore we require that,

$$f(\Omega_1\Omega_2) = f(\Omega_1) + f(\Omega_2) \tag{2}$$

It may be obvious that only a logarithm can achieve this. If not, then a formal proof:

$$f'(\Omega_1\Omega_2)\Omega_2 = f'(\Omega_1) \qquad \text{(differentiating EQN 2 w.r.t. } \Omega_1) \tag{3}$$

$$f''(\Omega_1\Omega_2)\Omega_1\Omega_2 + f'(\Omega_1\Omega_2) = 0 \qquad \text{(differentiating EQN 3 w.r.t. } \Omega_2) \tag{4}$$

$$\implies f''(x)x + f'(x) = \frac{d(xf'(x))}{dx} = 0 \qquad \text{(substituting } \Omega_1\Omega_2 = x \text{ in EQN 4)} \tag{5}$$

$$\implies f'(x) = k_B/x \qquad (k_B \text{ is an arbitrary constant at this stage)} \tag{6}$$

$$\implies f(x) = k_B \ln(x) + const \tag{7}$$

So *if* S and Ω are related *then* the relationship must be of the form $S = k_B \ln(\Omega) + S_0$. Setting the constant S_0 to zero defines a natural zero for the entropy, when the is only one possible state ($\Omega = 1$, eg the system is in a quantum ground state).

$$\boxed{S = k_B \ln(\Omega)} \qquad \text{Definition of statistical entropy for fixed energy} \tag{8}$$

Entropy of a system always increases with increasing temperature, because more states are accessible.

Taking the logarithm of our expression for an Ideal gas, EQN 1, we have:

$$S_{A+B} - S_A = k_B N \ln(2) \tag{9}$$

S_{A+B} is the statistical entropy of the gas freely occupying the whole volume, which is the final equilibrium state of the system. S_A is the statistical entropy when the gas is restricted to be in volume V_A, which is the initial state of the system. The expression is identical to the expression for the change in the thermodynamic entropy if we identify $k_B N_A = R$, where $N_A = N/n$ is Avogadro's number and k_B is Boltzmann's constant.

Phase Space and the Existence of Quantum Mechanics

The exact state of a classical system on N particles (*microstate* requires us to specify the positions and momenta of all the particles. We imagine a mathematical space with an axis for each (component of) position and velocity. This is a 6N-dimensional space. Any microstate of the system is a *point* in this space. As the system evolves in time, this point moves around. The *ergodic hypothesis* is that each of these microstate is equally likely, provided it satisfies the boundary conditions.

The Boltzmann entropy is then defined by counting the number of possible arrangements of particles in this phase space. But in order to *count*, the space must be *countable*, i.e. divisible into discrete chunks. Considering one particle in one direction (say x), there should be a minimum *area* in the phase space $\Delta p_x \Delta x$, it being impossible to measure the position in phase space more accurately. This idea is now called "Heisenberg's uncertainty principle"