AEP 4230: Thermodynamics

Contents

In this section, we introduce and derive some general results in thermodynamics. To get a feeling for just how powerful thermodynamics is, let us think about the types of objects and phenomena it deals with. A canonical phenomenon described by thermodynamics is heat exchange: if we place two bodies in thermal contact, A and B, where the temperature of A, T_A is higher than than of B T_B, heat will flow from object A to object B, until the two temperatures are equal, and the bodies are in thermal equilibrium.

Suppose we wanted to use the laws of classical physics to describe this phenomenon, and let us suppose that heat is transported primarily through conduction at the interface between the two objects. We can imagine then that there is an interaction between the constituents ("atoms") of A and the atoms of B where the materials make contact, and that this transfers energy and momentum from A to B. Therefore, the Newtonian approach to describing this heat transfer would be to write equations of motion for each of the N_A number of atoms in A and each of the N_B number of atoms in B. We would need to specify the internal forces between atoms in body A and in body B, as well as the forces of interaction between atoms in material A versus material B. This problem is essentially impossible to solve as stated, because it requires keeping track of a very large number of atoms *with interactions*, similar to Avogadro's number ($\sim 10^{23}$) [1]. The scale of these problems also evades any computational treatment, since, even if we wished to store the $6(N_A + N_B)$ positions and momenta of these particles, we would require on the order of 10^{25} bytes to even store the state as double-precision floating point values. For context, the total shared date in the world is estimated to be a few hundred times smaller than this, and we are still only talking about storing the system state. To understand heating, we would then need to simulate the dynamics in time, updating and storing the state.

Evidently, we need a simpler set of principles to describe the transfer of energy, momentum, particle number and so on in these *macroscopic systems*, where macroscopic means $N \gg 1$. This is accomplished with the framework of *thermodynamics*, which reduces the description of a macroscopic body to a description in terms of a *macrostate* described by a small number of *thermodynamic variables*. For example, we might describe an ideal gas by a macrostate M whose specification is in terms of temperature, volume, and particle number: $M = (T, V, N)$. Remarkably, these three thermodynamic variables are all we need to know in order to specify the thermodynamic state of an ideal gas, and gives us everything that we need to know what are its energy, entropy, heat capacity, compressibility, and so on. That is

[1] The interactions between atoms is the key point of complexity. If all of the atoms were independent, then we could probably cleverly use the solution to the dynamics of a single atom to say something about the many-atom case. But interactions, even two-body interactions, make such a program untenable.

the power of thermodynamics: we eschew the description of a system in terms of microscopic states, *microstates*, specified by Avogadro's number of positions and momenta, as Newton might have preferred. Instead, we can understand important details of the transfer of heat from our object A to our object B in terms of a small number of thermodynamic variables.

Thermodynamics is very much an experimental science: the laws and phenomena were discovered by examining how heat, volume, and particle number are exchanged between systems as a result of external influences that we control, such as temperature, pressure, chemical potential and so on. Scientists then developed a mathematical formalism that summarizes these experimental observations and predicts new relationships that can be tested in experiment.

We now develop the program of thermodynamics. We start from the basic laws of thermodynamics, and then develop a mathematical framework that allows us to understand the way that systems undergo various transformations due to the application of heat or work.

I. THE ZEROTH LAW OF THERMODYNAMICS

Consider three systems: A, B, C. They are in mutual mechanical equilibrium with each other. They have the ability to exchange heat with each other, and change their temperature as a result. If heat is not exchanged between two objects, say A and B, their state will not change and they are said to be in thermal equilibrium.

The statement of the *zeroth law* of thermodynamics is that if bodies A and B are in thermal equilibrium, and bodies B and C are in thermal equilibrium, then bodies A and C are also in thermal equilibrium.

While this statement sounds trivial, it implies the existence of a function of state (state meaning thermodynamic variables) called temperature, which can be defined for *any* object in equilibrium. Further, this "temperature" is equal for all objects in equilibrium with each other. It is interesting to see how this follows from the ostensibly simple statement of the zeroth law. Let us now show that the zeroth law is equivalent to the claim that there is a property of an object called temperature, defined uniquely in terms of the thermodynamic variables of that object, which is the same between all objects in mutual thermal equilibrium [2].

Suppose we denote the thermodynamic state of our bodies (the macrostate, M) as $M_A = (A_1, A_2, \ldots)$, $M_B = (B_1, B_2, \ldots)$, $M_C = (C_1, C_2, \ldots)$. Then if bodies A and B are in thermal equilibrium when placed in thermal contact, there is some constraint, depending on the states of A and B, that enforces that these properties do not change. Another way to say it is that generically, if we put two systems next to each other, something will happen, violating the condition of equilibrium. So, there must be some relationship between the states of the two systems. We may write that constraint as

$$f_{AB}(A_1, A_2, \ldots, B_1, B_2 \ldots) = 0. \tag{1}$$

Physically, we expect that this entails that we could write some particular thermodynamic variable, such as B_1 in terms of all the other quantities [3]:

$$B_1 = f(M_A, B_2, B_3, \ldots). \tag{2}$$

Here, I will introduce another thermodynamic fact which is supported experimentally. It is possible to vary the thermodynamic variables of A without disturbing the equilibrium with B. There is in general a continuous manifold of states, specified by $\Theta = \Theta_A(M_A)$, which leads to the same observed B_1. Therefore, we may write:

$$B_1 = f(\Theta, B_2, B_3, \ldots) \implies \Theta = \Theta_B(M_B) = \Theta_A(M_A). \tag{3}$$

Thus, there is some property whose value Θ is the same between the two bodies when they are in thermal equilibrium. We can say that thermal equilibrium between two

[2] Most texts skip this discussion. Our course textbook does not. I am presenting the equivalence differently, but do not get bent out of shape working through it. It is mostly fine for you to come away with the following form of the zeroth law: "if bodies A and B are in thermal equilibrium, and bodies B and C are in thermal equilibrium, then bodies A and C are also in thermal equilibrium, and their temperatures are all equal: $T_A = T_B = T_C$." Or simply: "thermal equilibrium is transitive and implies equality of temperature between objects".

[3] In general, there is not a constraint that B_1 be uniquely specified by the other variables in this generically nonlinear constraint equation. We're imposing it as a physical requirement that if I have two bodies in equilibrium, with macrostates M_A and M_B, that there is a definite, single value of B, denoted B_1.

objects is a condition such that defines two manifolds M_A, M_B such that movement along them does not lead to heat flow.

Now, suppose that bodies B and C are in equilibrium: then we may repeat the manipulations above to arrive at:

$$\Theta' = \Theta'_B(M_B) = \Theta_C(M_C). \tag{4}$$

At this stage, we should be clear that we do not know that $\Theta' = \Theta$. In other words, if I take B, and place it in thermal contact with C, I do not a priori know that moving along the manifold of macrostates defined by $\Theta = \Theta_B(M_B)$ will preserve the thermal equilibrium with C (it does, of course, but we cannot say this from the information given). However, suppose that we now say that A and C are in equilibrium, as given by the zeroth law. Then, I could place all three bodies in thermal contact: I could place A in thermal contact with B, connecting them via a thermally conducting barrier, and I could place B and C in contact via a thermally conducting barrier. If moving along the manifold of microstates of B, $\Theta = \Theta_B(M_B)$, that causes no heat flow with A, causes heat flow between B and C, then B and C are not in equilibrium, violating our assumption. Therefore, the only possibility is that $\Theta' = \Theta = \Theta_C(M_C)$ and that all three bodies have the same value of the property Θ. We will refer to this property Θ as the *empirical temperature*.

A. Example

Let us consider as an example three physical systems: (A) a wire of length L with tension F, (B) a gas of volume V at pressure P, and (C) a paramagnet of magnetization M in a magnetic field B.

You are doing experiments on these systems, and you find that when these systems are in equilibrium, the following constraints hold in equilibrium. Between (A) and (B), you find:

$$\left(a + \frac{P}{V^2}\right)(V - b)(L - L_0) - c(F - K(L - L_0)) = 0. \tag{5}$$

As promised there are two manifolds of states (P, V) and (F, L) for which the equilibrium relation would not change:

$$\Theta_A(F, L) = c\left(\frac{F}{L - L_0} - K\right). \tag{6}$$

and

$$\Theta_B(P, V) = \left(a + \frac{P}{V^2}\right)(V - b) \tag{7}$$

Between (B) and (C), you find:

$$\left(a + \frac{P}{V^2}\right)(V - b)M - dB = 0 \implies \Theta_B(P, V) = dB/M = \Theta_C(B, M). \tag{8}$$

As further promised, the manifold of (P, V) states that keeps Θ_B fixed also maintains the thermal equilibrium with C.

We may rearrange these into three quantities, depending only on thermodynamic variables of *one system*, as follows:

$$\Theta = \left(a + \frac{P}{V^2}\right)(V - b) = c\left(\frac{F}{L - L_0} - K\right) = d\frac{B}{M}. \tag{9}$$

We may then say, in the language of the previous discussion of the zeroth law $\Theta_A(F, L) = c\left(\frac{F}{L-L_0} - K\right)$, $\Theta_C(P, V) \sim \left(a + \frac{P}{V^2}\right)(V - b)$, and $\Theta_B(B, M) = d\frac{B}{M}$. What you should notice is that I can't write just any set of equations relating the three systems: a generic equation can't be re-arranged into temperature functions dependent only on the state of one system at a time.

For example, suppose I instead claimed that I found a relationship: $\left(a + \frac{P}{V^2}\right)(V - b)M - dB(V - b) = 0$ (all I've done is add another factor of $V - b$ on the right-hand side). I also claim that I think these three objects are in mutual thermal equilibrium. We know that the manifold of (P, V) states defined by $\Theta = \Theta_B(P, V)$ maintains equilibrium between the gas and the wire. Generic points on that manifold however no longer preserve equilibrium between the gas and the paramagnet. Now, if I place all three objects in mutual thermal contact, and move along the manifold of (P, V): $\Theta = \Theta_B(P, V)$, the factor $(a + P/V^2)$ changes, requiring that dB/M also changes. Therefore B and C are not in equilibrium as I had stated, *or* the relationship that I found is not a valid equilibrium relationship. This should indicate that the condition of thermal equilibrium puts a huge constraint on the space of possible relationships between macrostates of distinct physical objects.

B. Measuring empirical temperature

The zeroth law tells us that there are isotherms: $\Theta = \Theta(M)$ with M the macrostate of an object. How do we know which isotherm we are on? Historically, the ideal gas played a major role. Empirical observations show that the product of pressure and volume is constant along the isotherms of a sufficiently dilute gas: $\Theta(P, V) = \alpha PV$ with α a constant (one could determine this by setting up a series of dilute gases of different pressures and volumes and placing them in thermal contact).

The constant of proportionality is determined by reference to the triple-point of water. This is the temperature at which ice, liquid water, and water vapor, are in equilibrium with each other. It turns out that there is only one pressure and temperature at which this occurs, and it is *defined* to be 273.16 Kelvin. Now, let us take an ideal gas and place it in thermal contact with the ice-water-gas system. If the two systems are in equilibrium, then we have

$$\alpha = 273.16/(PV)_{\text{ice-water-gas}} \implies \Theta[K] = 273.16 \times \frac{(PV)}{(PV)_{\text{ice-water-gas}}}, \tag{10}$$

where $(PV)_{\text{ice-water-gas}}$ refers to the pressure-volume product of the ideal gas when it is in equilibrium with the ice-water-gas system.

II. FIRST LAW OF THERMODYNAMICS: WORK AND HEAT

Consider a thermally isolated system, so heat cannot flow into or out of it. We will refer to such a system as *adiabatically isolated*. The first law of thermodynamics would then state that the amount of work needed to change the state of the system depends only on the initial and final states and not on the way that the work was performed, or on the intermediate states through which the system passes. Therefore, we can say

$$W = W(M_i, M_f), \tag{11}$$

where $M_{i,f}$ are the initial and final macrostate of the system we are doing work on. Assuming that the work corresponds to the change in energy of the system (there is no reason that conservation of energy, which is microscopically true, would no longer hold macroscopically), we must have that

$$\Delta E = E_f - E_i = W(M_i, M_f). \tag{12}$$

Up to a constant that is irrelevant, we may thus define an *internal energy* which depends only on the state: $E = E(M)$.

How does this work depend on the change in the thermodynamic variables describing a system? To start, let us think about the example of a spring of equilibrium length L_0 and at current length L_i under the presence of a force F. Let us stretch or compress the spring to a new length L_f, sufficiently slowly such that no kinetic energy is given to the spring: the force I apply is always equal to the spring force at any given extension. When this happens, no heat will be generated from friction (since the dissipated power depends on the velocity of the spring), and the work done will only be equal to the change in potential energy. That work will be $W = \int_{L_i}^{L_f} dLF$, which is positive if the spring extends. In other words, we define the work to be positive if the energy of the system (the spring) increases and negative if that energy decreases. The infinitesimal work is given by $dW = FdL$, where I have omitted the bar since we have stated that no heat is allowed to move in or out.

Different thermodynamic systems have different ways of doing work. We write in general $dW = \mathbf{J} \cdot d\mathbf{x}$, where $\mathbf{J}$ is a collection of *generalized forces* and $\mathbf{x}$ is a collection of *generalized coordinate* (with dx being a generalized displacement).

1. For a **wire**: the generalized force J is a tension force F and the generalized coordinate is the length of the wire, L.

2. For a **fluid**: the generalized force $-p$ is a pressure (up to a minus sign) and the generalized coordinate is the volume of the fluid V. For the fluid, we define the force with a minus sign the pressure is the (outward) force on the walls of the container by the fluid, but an inward (compressive) force would be needed to put energy into the system.

3. For a **magnet**: the generalized force $\mathbf{H}$ is a magnetic field and the generalized coordinate is the magnetization $\mathbf{M}$.

4. For a **chemical compound**: a generalized force is the chemical potential μ while the generalized coordinate is the number of molecules N.

It is important to note that for work, they typically occur in this form Jdx where J is an *intensive* quantity, independent of the system size. In equilibrium J tends to be uniform in all parts of the sample. Meanwhile, x is an *extensive quantity* which are proportional to system size (the exact meaning of extensivity will be dealt with shortly).

Further observations indicate that once the adiabatic constraint is removed, and heat can flow into or out of the system, then the amount of work is no longer equal to the change in internal energy. We may define the difference as the *heat intake*, via

$$\Delta E = Q + W, \tag{13}$$

where ΔQ is the heat intake. Imagine now an infinitesimal transformation of the system state, we write:

$$dE = \bar{d}Q + \bar{d}W, \tag{14}$$

where the bar is indicating that the work and heat themselves depend on the means by which the work was done, and not only the initial and final states. The energy however still only depends on the initial and final states, in analogue to the potential energy of a mechanical system in the action of conservative forces [4].

We need to define a few other useful quantities that appear constantly in thermodynamics, all of which are called *response functions*: they measure how thermodynamic coordinates of a system change as we change or apply some kind of probe or generalized force.

1. *Heat capacities* tell us about how the temperature of a system changes when we supply heat to it. Because heat is not a function of state, we need to specify how we apply the heat. For example, if we supply heat to an ideal gas, keeping

[4] This analogy goes further: recall that for nonconservative forces such as friction, the force cannot be written as the gradient of a potential, and the energy change is not solely set by the work done. Due to friction, there is energy lost irreversibly to an environment (which heats up).

the volume of the system fixed, that will lead to a different temperature change than if we supply heat to a gas, keeping the pressure fixed. That is because if we keep the volume fixed, no work can be done. While in the constant pressure case, heating the gas will cause it to expand and lose energy. The energy of an gas, if it is ideal, depends only on temperature, meaning that expansion will tend to try to lower the gas temperature. Therefore, more heat is needed to sustain a given temperature increase dT in the gas, compared to the constant volume case. We may make this quantitative as follows:

The specific heat at constant volume is defined by

$$C_V = \frac{\bar{d}Q}{dT}\bigg|_V = \frac{dE}{dT}\bigg|_V, \tag{15}$$

where the $\big|_V$ denotes that we keep the volume fixed. At constant pressure, we instead have:

$$C_P = \frac{\bar{d}Q}{dT}\bigg|_P = \frac{dE}{dT}\bigg|_P + P\frac{dV}{dT}\bigg|_P. \tag{16}$$

For an ideal gas, since the internal energy depends only on temperature (and in fact, $E = \frac{3}{2}Nk_BT$, where N is the number of gas molecules, k_B is a constant called Boltzmann's constant, and T is thermodynamic temperature, which is equivalent to empirical temperature Θ as we will show soon). Therefore, we may find that $C_V = \frac{3}{2}Nk_B$ and $C_P = \frac{5}{2}Nk_B$. As you can see, heat capacity is an extensive quantity: the larger the system is (the larger N is), the more heat is needed to change the temperature, as you probably know all too well from trying to boil a large pot of water. For a more general system with $E = E(T)$, we can also see from the above that $C_P - C_V = Nk_B$.

2. *Force constants* measure the ratio of infinitesimal displacement to infinitesimal force, similar to a spring constant. These are most useful when the relationship between force and displacement is linear. Examples of this include the isothermal compressibility of a gas $\kappa_T \equiv -V^{-1}\frac{\partial V}{\partial P}\big|_T$ (the minus sign is to make the response function positive) and the magnetic susceptibility $\chi_T \equiv \frac{\partial M}{\partial H}\big|_T$. In both of these response functions, it should be understood that these expressions apply in the zero force limit.

3. *Thermal responses* measure the change in thermodynamic coordinates with temperature. An example is the thermal expansion coefficient of a gas $\alpha_P = \frac{1}{V}\frac{\partial V}{\partial T}\Big|_P$, which is $1/T$ for the ideal gas.

III. THE SECOND LAW OF THERMODYNAMICS

The first law is essentially a statement of energy conservation. We can change the energy of a system by heating it or by applying generalized forces to it, doing work. What the first law does not preclude is that I could put heat Q into a system and convert it all into work $W = Q$. To be more concrete, consider a steam engine: a steam engine which converts water into steam (via heating). The expansion of the steam pushes a piston, doing work on the outside world which can be harnessed as mechanical (motional) energy. A steam engine is an example of what is called a *heat engine*: a system that converts heat into work (generically, the work generated will be less than the heat supplied).

If I could convert heat into work perfectly, I have what is called an *perpetual motion machine (of the second kind)* [5]. In particular, imagine I had a block moving on a surface with friction. In the block is a heat engine that takes in heat and converts that heat into work which pushes the block. Because the block moves, it experiences kinetic friction which tends to slow down the block and generate heat. Suppose now that I could take the frictionally-generated heat and feed it back into the block. If I could convert all of that heat into work, then I can replenish the frictionally-lost (kinetic) energy of the block and the block moves at its original velocity. Notice that I only had to supply heat *once* to keep the block moving indefinitely: any lost energy was harnessed and converted back into mechanical energy. This is the essence of a perpetual motion machine of the second kind: only a small one-time energy input is needed to sustain an indefinite motion. This would of course be an incredible thing, and energy scarcity is something our planet would hardly have to worry about.

[5] A perpetual motion machine of the first kind is an object that moves indefinitely in the absence of any force, violating conservation of energy, or the first law of thermodynamics.

It is this that is forbidden by the second law of thermodynamics. In what follows, we state two equivalent forms of the second law of thermodynamics, prove their equivalence, and use the second law to infer the existence of a function of state called entropy, which we show is maximized by spontaneous thermodynamic processes. Among key consequences of the second law of thermodynamics are: (a) no perpetual motion machines of the second kind (b) heat does not spontaneously move from a cold body to a hot body (c) there is a maximum efficiency of any possible heat engine operating in equilibrium (d) the thermodynamic temperature is equivalent to the empirical ideal gas temperature and (e) the entropy of the universe increases without bound. It is typically remarked that thermodynamics is a somewhat unusual story in the development of physics, because a huge number of very general and abstract laws emerge from very practical considerations about the efficiency of a heat engine.

A. Kelvin and Clausius statements of the second law

1. The *Kelvin statement* (K) of the second law of thermodynamics is that it is impossible to perform a transformation whose sole result is the complete conversion of heat into work.

2. The *Clausius statement* (C) of the second law of thermodynamics is that it is impossible to perform a transformation whose sole result is movement of heat from a colder body to a hotter body.

These two statements K and C are equivalent. Let's prove this. We start by showing that $\neg K \implies \neg C$ (so $C \implies K$) and then we show $\neg C \implies \neg K$ (so $K \implies C$, and $K \leftrightarrow C$).

1. $\neg K \implies \neg C$ [6]. Suppose we have a heat engine such that heat is converted into work. The heat engine consists of two reservoirs: a hot reservoir at temperature T_H and a cold reservoir at temperature T_C. A reservoir has the

[6] Derivation references diagram drawn in class.

property that adding or losing heat to it does not significantly change its temperature (its specific heat is infinite). The engine pulls heat from the hot reservoir, Q We can always construct a second engine, running in reverse, that takes in work, and moves it from a colder body to a hotter body (this is called a *refrigerator*) - the cold and hot bodies are the same reservoirs as for the heat engine. Suppose that we have a perfect heat engine which takes heat Q and converts it into work $W = Q$. Let use that work to power an imperfect refrigerator. For that refrigerator, the heat drawn from the cold reservoir, plus the work, equals the heat delivered to the hot reservoir: $Q'_c + W = Q'_h$. Clearly, $Q'_h > Q$.

The "net result" of this (drawing heat from a hot body, doing work, and feeding it into a refrigerator) is that we have moved heat from a colder body to a hotter body without any work done. Why? The work done in this process is zero because the work generated by the heat engine is used up somewhere else. At the same time, the heat intake by the hot body is $Q'_h - Q_h > 0$. So, the net result is that we have moved heat from a hot body to a cold body with no other transformation.

2. $\neg C \implies \neg K$ [7]. Suppose we have a device that draws heat from a cold body at temperature T_C and moves it to a hot body at temperature T_H, with no work required. Then the heat drawn from the cold body Q_C is equal to the heat deposited into the hot body T_H. Now suppose we have an imperfect heat engine which is powered with the heat delivered to the hot body (that heat is equal to Q_H), while the heat dumped into the cold reservoir is Q'_C and the work output is W'. The net result is that heat $Q_C - Q'_C$ is drawn from some body (as configured here: the cold body) and work is done, with no heat deposited elsewhere. That is equivalent to a perfect heat engine (since the net result has no idea if the body at T_C is the cold body or the hot body).

We have thus proven that the Kelvin and Clausius statements of the second law are equivalent.

[7] Derivation references diagram drawn in class.

B. Carnot engine

Somewhat incredibly, from these statements alone, it is also possible to show that there is an upper limit to the efficiency of a heat engine. First, let us introduce the idea of a Carnot engine. A Carnot engine is defined as an engine which is *reversible*, *cyclic*, and has all of its heat exchanges occur at two temperatures, T_H (the source) and T_C (the sink). We take $T_H > T_C$ without loss of generality.

A *reversible* engine is one that can be run backwards, reversing the inputs and outputs (as an example: a heat engine run in reverse would take in work, and push heat from a cold reservoir to a hot reservoir. The net heat and work in the cycle would flip sign relative to the heat engine. A reversible process is typically required to pass through equilibrium states. Suppose in our thermodynamic process that we pass through non-equilibrium states: they will generically relax to equilibrium (think of a spring relaxing to a motionless state due to friction). This relaxation is irreversible. This also suggests that a reversible process ought to be quasi-static: we pass through a path of states in the thermodynamic state space slowly to ensure that the system does not pass through any non-equilibrium steps.

A *cyclic* process is one where the initial and final states of the transformation are the same. For reversible cyclic processes, functions of state do not change as a result of the cycle. Of course, since neither heat nor work are functions of state, there can be a net heat transfer into or out of the working substance of a heat engine, and there can be net work done on or by the substance. The change in internal energy however is zero.

IV. CARNOT'S THEOREM

Next, we show that the second law of thermodynamics implies that no heat engine *which runs between two temperatures T_H and T_C* can have an efficiency greater than a Carnot engine. The basic idea (of any theorem like this) is that we can use a hypothetical engine with an efficiency greater than the Carnot efficiency (we do not even need to know what that efficiency is), and show that if we powered a

Carnot refrigerator with the work generated, we would violate the second law of thermodynamics.

Suppose $\eta_{\text{Non-Carnot}} = W_{\text{Non-Carnot}}/Q_{\text{Non-Carnot}} > \eta_{\text{Carnot}} = W_{\text{Carnot}}/Q_{\text{Carnot}}$. Now use the work output from the Non-Carnot-engine (NCE) to power the Carnot engine (CE). An analysis of the diagram [8] shows that $Q_H < Q'_H$ and $Q'_c > Q_c$ which implies that the net result of this process is to move heat from the cold body to the hot body without any work, violating the second law (Clausius statement). You might be left feeling that this argument is a little mysterious: it looks like we used almost no information to get to this result. What's special about the Carnot engine? It is that all heat exchanges occur between two temperatures T_C and T_H. That allowed us to define two heat engines with the same sink and source and combine them to form a composite engine.

Carnot's theorem has a corollary that all Carnot engines have the same efficiency, that depends only on the source and sink temperatures, This is because if it did not, that Carnot engine with a different efficiency could power a Carnot engine in reverse and this would allow us to construct another violation of the second law.

Apparently then, there is a single *universal* efficiency that a Carnot engine can have: $\eta_{\text{Carnot}} \equiv \eta_c(T_C, T_H)$. The only variables that specify a Carnot engine are the temperatures of the source and sink. If we can compute the efficiency of *any* Carnot cycle, then we know it for a Carnot engine made out of any working substance. We shall undertake this calculation for the ideal gas. But before that, let us take a quick detour.

V. THERMODYNAMIC TEMPERATURE SCALES

The fact that the efficiency of a Carnot engine depends only on the sink and source temperatures, and has no dependence on the materials used to construct the engine, allows us to define a temperature scale based on the Carnot cycle. As of now, we know nothing of the functional dependence of η on the source and sink temperatures.

[8] Presented during lecture

In what follows we will work out a relationship between the efficiency of two Carnot engines where the sink temperature of one is the source temperature of the other.

Suppose we have two Carnot engines running in series: the first between temperatures T_1 and T_2, the second between temperatures T_2 and T_3 with $T_1 > T_2 > T_3$). Denote the heat exchanges and work outputs by Q_H, Q_C, W and Q'_H, Q'_C, W'. Series means that the heat dumped by the first engine is the intake for the second. This system is equivalent to a Carnot engine running between temperatures T_1 and T_3. We can use that fact to relate the efficiency of the composite Carnot engine to the individual ones.

The engine running between T_1 and T_2 has a work output $W = \eta(T_1, T_2)Q_H$ and a heat exhaust $Q_C = Q_H(1 - \eta(T_1, T_2))$ into the sink. The second reservoir has similarly $W' = \eta(T_2, T_3)Q'_H$ and a heat exhaust $Q'_C = Q'_H(1 - \eta(T_2, T_3))$, where $Q'_H = Q_H(1 - \eta(T_1, T_2))$. The composite engine has a heat intake Q_H and outputs work $W + W' = (\eta(T_1, T_2) + \eta(T_2, T_3)(1 - \eta(T_1, T_2)))\, Q_H = \eta(T_1, T_3)Q_H$. Therefore, we may write

$$\eta(T_1, T_3) = \eta(T_1, T_2) + \eta(T_2, T_3)(1 - \eta(T_1, T_2)). \tag{17}$$

It will be more convenient to write:

$$1-\eta(T_1, T_3) = 1-\eta(T_1, T_2)-\eta(T_2, T_3)+\eta(T_1, T_2)\eta(T_2, T_3) = (1-\eta(T_1, T_2))(1-\eta(T_2, T_3)). \tag{18}$$

We want to use the fact that the efficiency η (or equivalently, $1 - \eta$) depends only on temperatures to define a temperature scale. In other words, we want to *define* temperature based on this relationship. Let us express $f(T_1, T_2) = 1 - \eta(T_1, T_2)$, which casts the previous equation as

$$f(T_1, T_3) = f(T_1, T_2)f(T_2, T_3). \tag{19}$$

A general solution to this equation is $f(T_1, T_2) = g(T_1)/g(T_2)$ for any g. Therefore, we can write

$$g(T_1) = (1 - \eta(T_1, T_2))g(T_2). \tag{20}$$

If we fix the source temperature T_2 (e.g., let T_2 be the triple point of water and define it as 273.16 K), then measure the efficiency as we vary T_1, then we can solve this equation to get T_1 as a function of the efficiency η.

We make the simplest reasonable choice, which is to say $g(T_1) = T_1$ and therefore we define the *thermodynamic temperature* such that

$$\eta(T_C, T_H) = 1 - \frac{T_C}{T_H}. \tag{21}$$

This scale needs a reference point: it can be taken such that if we run a heat engine where water at its triple point is the sink, then $T_C \equiv 273.16K$.

We should emphasize that this thermodynamic temperature is in principle different from the empirical temperature discussed and developed in the previous sections. I could have chosen *any* function g to define temperature. For example, I could have chosen $g' = T_1^2/T_2^2$ such that $\eta' = 1 - T_1^2/T_2^2$. But this linear choice makes the thermodynamic and empirical temperature scales equivalent.

VI. UNIVERSAL EFFICIENCY OF A CARNOT ENGINE

Let us construct and analyze a Carnot engine using an ideal gas as the working substance. For the ideal gas, we know that the internal energy depends only on the temperature of the gas. We can perform a Carnot cycle as follows: (1) an isothermal process at temperature Θ_H, followed by an adiabatic process which lowers the temperature to Θ_C, followed by another isothermal process at temperature Θ_C, and finally an adiabatic process connecting back to the initial state. I am using the empirical temperatures here to make a point. We will show based on the following argument that the empirical and thermodynamic temperature scales are equivalent.

Let us label the coordinates of this gas by (P, V) and represent them on a PV-diagram. Let us analyze the efficiency of this cyclic process.

For an isothermal process, the change in internal energy is zero for an ideal gas, where the internal energy depends only on temperature. Therefore, the work done is

$$W = -\int_{V_i}^{V_f} dV\, P = -Nk_B\Theta \ln(V_f/V_i). \tag{22}$$

While the heat intake is $Q = -W = Nk_B\Theta \ln(V_f/V_i)$.

For an adiabatic process, the constraint that there is no heat intake implies that the entire change in internal energy comes from work. The internal energy of an ideal gas is $E = \frac{3}{2}Nk_B\Theta$ and so $dE = \frac{3}{2}Nk_B d\Theta = -PdV = -Nk_B\Theta/V$. Therefore $V\Theta^{3/2} = \text{const.}$ or $PV^{5/3} = \text{const.}'$. This can be used to evaluate the work done in terms of the initial and final volumes. However, for our purposes, all we will need is that the work done is the change in internal energy, which is $W = \frac{3}{2}Nk_B(\Theta_f - \Theta_i)$..

The net work done in the cycle is simply the difference in work in the two isothermal processes (the work done along the two adiabats cancel). The net work in the Carnot cycle on the environment is therefore (note the sign)

$$W_{\text{Carnot}} = Nk_B\Theta_H \ln(V_2/V_1) - Nk_B\Theta_C \ln(V_3/V_4), \tag{23}$$

while the heat intake is given by the isothermal expansion $Q_H = Nk_B\Theta_H \ln(V_2/V_1)$. Therefore, the efficiency is given by

$$\eta = \frac{W}{Q_H} = 1 - \frac{\Theta_C}{\Theta_H}\frac{\ln(V_3/V_4)}{\ln(V_2/V_1)} = 1 - \frac{T_C}{T_H}. \tag{24}$$

This last equality is found by exploiting that for an adiabatic process $V\Theta^{3/2}$ is constant. Using this, one can show that $\frac{V_1V_3}{V_2V_4} = 1$.

As promised, the efficiency depends only on the sink and source temperatures, and takes a remarkably simple form. Also, we can see that if we identify $\Theta = T$, we arrive at the same form of the efficiency dictated by the thermodynamic temperature scale, making the two scales equivalent. Therefore, from now on, we no longer distinguish these two temperature scales and use the letter T in what follows to refer to temperature.

VII. ENTROPY

A. Clausius' theorem

We now develop a function of state which is conjugate to temperature. To do this requires that we establish Clausius' theorem: for any cyclic process, the following inequality holds:

$$\oint \frac{dQ}{T} \leq 0. \tag{25}$$

To prove this, subdivide the cycle into a series of infinitesimal steps in which heat is either liberated or taken up by the system. In all cases, direct the heat exchanges into one port of a Carnot engine with the reservoir operating at $T_0 > T$. For example, to deliver heat into the system at some stage, the engine has to extract heat dQ_R from the reservoir. If the heat is delivered to a part of the system at temperature T, then we know that

$$dQ_R = T_0 \frac{dQ}{T}. \tag{26}$$

This equality also holds if the system releases heat, which is the result if the engine is run in reverse. The net result of this process is to extract heat from the reservoir $Q_R = \oint dQ_R$ and convert it into work W. By the second law, we must have that $W = \oint dQ_R < 0$ (one needs to do work to maintain the cycle since energy is dissipated). Therefore:

$$\oint \frac{dQ}{T} \leq 0. \tag{27}$$

B. Consequence of Clausius' theorem

1. For any reversible cyclic process, $\int \frac{dQ_{\text{rev}}}{T} = 0$. Suppose we have a generic cyclic process, then $\oint \frac{dQ}{T} \leq 0$. If the process is reversible, we can perform the thermodynamic cycle in reverse. That will flip the sign of dQ everywhere along the path, flipping the sign of the integral. The only way that can be consistent with the Clausius theorem is if $\oint \frac{dQ_{\text{rev}}}{T} = 0$.

2. Clausius' theorem defines a function of state S, which we call *entropy*, such that

$$S(B) - S(A) = \int_A^B \frac{dQ_{\text{rev}}}{T} \tag{28}$$

is independent of the path taken to get from A to B. Note that S is defined only up to a constant, not unlike other functions of state such as internal energy (or potential energy in mechanics).

3. For any non-cyclic transformation of a system from state A to state B, it must be that the entropy change in *reversibly* going from A to B, $S(B) - S(A) = \int_A^B \frac{dQ_{\rm rev}}{T} \geq \int_A^B \frac{dQ}{T}$, where the second dQ is assuming that we get from A to B potentially irreversibly. To see this, consider what happens when we go from A to B potentially irreversibly, and go from B to A reversibly. Then Clausius' theorem tells us $\oint \frac{dQ}{T} = \int_A^B \frac{dQ}{T} + \int_B^A \frac{dQ_{\rm rev}}{T} = \int_A^B \frac{dQ}{T} + (S(A) - S(B)) \leq 0 \implies S(B) - S(A) \geq \int_A^B \frac{dQ}{T}$.

   A key consequence of this result is that for an adiabatically isolated system (no heat exchange), we can say that $\delta S \geq 0$, where the δ refers to an out-of-equilibrium variation. A consequence is that the entropy of the Universe (ostensibly a closed system) cannot decrease.

4. For a reversible infinitesimal transformation, we may write the first law as

$$dE = TdS + \mathbf{J} \cdot d\mathbf{x} + \mu dN, \tag{29}$$

   where I have explicitly separated out the term associated with chemical work. Such an infinitesimal form can be integrated to find a function of state. For example $E = E(S, \mathbf{x}, N)$ or $E = E(T, \mathbf{x}, N)$. In fact, in this functional dependence, we can always trade out extensive quantities for intensive quantities. Therefore we see that if $\mathbf{J}$ encompasses n ways of doing work on the system, then there are $n + 2$ independent variables we can control. For something like a gas (not necessarily ideal), we may express a function of state such as the internal energy like $E = E(S, V, N)$.

   The infinitesimal relation here is typically considered to be the most useful and most fundamental relation in thermodynamics. Get comfortable with it.

VIII. APPROACH TO EQUILIBRIUM AND THERMODYNAMIC POTENTIALS

A key concept in thermodynamics is that a system not originally in equilibrium, over time, can reach a state of equilibrium. We have already seen that for an adiabatically isolated system, the entropy cannot decrease ($\Delta S \geq 0$). What if the system is not adiabatically isolated or it is subject to certain external forces? Then something else should be minimized. This something else is called a thermodynamic potential, in analog with potential energy, which is what is minimized in mechanical equilibrium.

1. *Enthalpy* is the function that gets minimized when the system is adiabatically isolated, but it is subject to an external force $\mathbf{J}$. To see this, note that for a reversible transformation $dE = \mathbf{J} \cdot d\mathbf{x}$. For an irreversible transformation $\delta E < \mathbf{J} \cdot \delta\mathbf{x}$, because some of that work done by the external agent gets dissipated (note that in the absence of an external force, it is internal energy which is spontaneously minimized). We may then write $\delta(E - \mathbf{J} \cdot \mathbf{x}) \equiv \delta H < 0$, where I have used that the mechanical force is constant, and defined the *enthalpy* H.

   A separate but related concept is how the enthalpy changes between *equilibrium* states due to an infinitesimal reversible transformation where the force may change. The differential change in enthalpy is simply

$$dH = dE + d(\mathbf{J} \cdot \mathbf{x}) = T dS - \mathbf{x} \cdot d\mathbf{J} + \mu dN. \tag{30}$$

2. *Helmholtz free energy* is what is relevant when the system is not under an external force, but is not adiabatically isolated. Consider a system in contact with a reservoir at temperature T. The system and reservoir are adiabatically isolated from the rest of the Universe. The energy of the system and reservoir is conserved such that a general non-equilibrium variation of the energy satisfies $\delta E_s + \delta E_r = 0$. Since the system is adiabatically isolated, we have: $\delta Q_s + \delta Q_r = 0$. The reservoir only changes its energy by heat such that $\delta E_r = \delta Q_r = -\delta Q_s$. Therefore: $\delta E_s - \delta Q_s = 0$. For a non-equilibrium variation of the system, Clausius' theorem applies, such that $\delta Q_s \leq T \delta S_s$ which results in $\delta E_s - T \delta S_s \equiv \delta F_s \leq 0$ where $F = E - TS$ is the *Helmholtz free energy*.

   Infinitesimal reversible changes lead to the relation

$$dF = -S dT - \mathbf{J} \cdot d\mathbf{x} + \mu dN. \tag{31}$$

3. *Gibbs free energy* is what is minimized when the system is not adiabatically isolated and also under a constant external force. It is straightforward to show that the arguments above related to the Helmholtz free energy and enthalpy can be combined to show that $\delta G = E - \mathbf{J} \cdot \mathbf{x} - TS \leq 0$.

   The corresponding equilibrium variations are given by

$$dG = -S\,dT - \mathbf{x} \cdot d\mathbf{J} + \mu dN. \tag{32}$$

A. Example: Equilibration of supersaturated steam

Let us apply the ideas in this section to analyze how an out-of-equilibrium system approaches equilibrium. We will consider the example on pages 18 and 19 of Kardar: N particles of supersaturated steam in a container of volume V at temperature T.

The approach to thinking about these systems is very much akin to classical mechanics: identify the relevant "coordinates" (thermodynamic coordinates) of the system, and apply the appropriate equilibrium condition to the system. The fixed coordinates of the system are N (the number of H_2O molecules does not change when vapor converts into water), the temperature (imagine that the system is in equilibrium with ambient air which acts as a thermal reservoir over long enough times), and the volume V. The volume should be interpreted as the volume of the container, which is the volume filled by the vapor. While water also takes up volume, it takes up considerably less since the densities are different by nearly a factor of 1,000, so that if we converted the entire mass of vapor into liquid water, the volume would be much smaller. In principle, one could parameterize the system in terms of two volume, the volume of liquid water, V_w and the volume of vapor $V - V_w$. We will approximate $V_w \approx 0$.

To fully describe the system, even in this approximation where the volume of water is negligible, we need to also specify the number of water and vapor molecules. They are not independent. If we take the number of water molecules as N_w, then the number of vapor molecules is $N - N_w$. Notice that this is the only "coordinate" which is not fixed: the condensation of supersaturated steam will change this number.

To put a constraint on it, we must apply an equilibrium condition. That condition is that the Helmholtz free energy is minimized: this is the choice to make when there is no external force on the system but when the system is not adiabatically isolated. How do we know the system is not adiabatically isolated? The conversion of steam into water releases a latent heat of vaporization: in order to keep the temperature of the vessel fixed, that vessel needs to be able to release that heat into the external reservoir it is coupled to. Now, let us analyze a general non-equilibrium variation of the free energy $F = F(T, V, N_w, N_s)$. It is given by

$$\delta F = \frac{\partial F}{\partial T}\Big|_{V,N_s,N_w} \delta T + \frac{\partial F}{\partial V}\Big|_{T,N,N_w} \delta V + \frac{\partial F}{\partial N_w}\Big|_{T,V,N_s} \delta N_w + \frac{\partial F}{\partial N_s}\Big|_{T,V,N_w} \delta N_s, \tag{33}$$

which based on the specified conditions of the problem, reduces to

$$\delta F = \frac{\partial F}{\partial N_w}\Big|_{T,V,N_s} \delta N_w - \frac{\partial F}{\partial N_s}\Big|_{T,V,N_w} \delta N_w, \tag{34}$$

since the conservation of $N = N_w + N_s$ implies that we're considering specific variations $\delta N_w + \delta N_s = \delta N = 0$.

At equilibrium, the free energy should not change upon changing N_w (it should be at a minimum), which leads to:

$$\frac{\partial F}{\partial N_w}\Big|_{T,V,N_s} = \frac{\partial F}{\partial N_s}\Big|_{T,V,N_w}. \tag{35}$$

In equilibrium, we could write an inifinitesimal change in the free energy as $dF = -S\,dT - pdV + \mu_w dN_w + \mu_s dN_s$, which enforces that

$$\mu_w(T, V, N_w, N - N_w) = \mu_s(T, V, N_w, N - N_w). \tag{36}$$

In other words, that the chemical potentials of the two phases are the same at equilibrium.

IX. USEFUL MATHEMATICAL RESULTS

In this section, we explore various constraints that emerge between different thermodynamic functions of state. These mathematical relations are of critical importance for solving practical problems in thermodynamics, and more importantly, the *methods* used to derive these relations are of critical importance, as they let you derive many other important relations we do not state here.

1. *Extensivity* The first law, including chemical work, reads

$$dE = TdS + \mathbf{J} \cdot d\mathbf{x} + \mu dN. \tag{37}$$

Here, the differentials are of extensive quantities while the quantities multiplying the differentials are intensive quantities. We may mathematically define extensivity as follows: if we scale all of the intensive quantities by λ, then the value of some extensive function of these quantities also scales by λ. More compactly:

$$\lambda E(S, \mathbf{x}, N) = E(\lambda S, \lambda \mathbf{x}, \lambda N). \tag{38}$$

If we differentiate with respect to λ, we find:

$$E = E(S, \mathbf{x}, N) = \frac{\partial E}{\partial S}\Big|_{\mathbf{x},N}(\lambda S, \lambda \mathbf{x}, \lambda N)S + \frac{\partial E}{\partial \mathbf{x}}\Big|_{S,N}(\lambda S, \lambda \mathbf{x}, \lambda N)\cdot\mathbf{x} + \frac{\partial E}{\partial N}\Big|_{\mathbf{x},N}(\lambda S, \lambda \mathbf{x}, \lambda N)N. \tag{39}$$

If we evaluate this quantity at $\lambda = 1$, we find:

$$E = E(S, \mathbf{x}, N) = T(S, \mathbf{x}, N) \times S + \mathbf{J}(S, \mathbf{x}, N) \cdot \mathbf{x} + \mu(S, \mathbf{x}, N) \times N. \tag{40}$$

This is called an *extensivity relation*.

We can get another relation, called the *Gibbs-Duhem relation* by taking the differential of the above equation and comparing it to the first law:

$$dE = TdS + SdT + \mathbf{J}\cdot d\mathbf{x} + d\mathbf{J}\cdot\mathbf{x} + \mu dN + Nd\mu \implies SdT + \mathbf{x}\cdot d\mathbf{J} + Nd\mu = 0. \tag{41}$$

It is worth noting that extensivity is not necessarily obvious. For systems with long-range interaction, the energy can depend on the number of particles in a non-extensive way. As an example of the Gibbs-Duhem relation, we consider an ideal gas undergoing an isothermal transformation. The Gibbs-Duhem relation tells us that

$$-Vdp + Nd\mu = 0 \implies \frac{\partial \mu}{\partial p}\Big|_T = V/N = k_B T/p \implies \mu(p) - \mu(p_0) = k_B T \ln p/p_0. \tag{42}$$

2. *Maxwell relations*. The commutativity of partial derivative ($\partial_x \partial_y f(x, y) = \partial_y \partial_x f(x, y)$) imposes additional constraints on thermodynamic quantities. For example, consider the first law. Identifying

$$T = \frac{\partial E}{\partial S}\Big|_{\mathbf{x},N}, \; J_i = \frac{\partial E}{\partial x_i}\Big|_{\mathbf{S},N}, \tag{43}$$

it follows from the commutativity of partial derivatives that

$$\frac{\partial T}{\partial x_i}\Big|_{S,N} = \frac{\partial J_i}{\partial S}\Big|_{\mathbf{x},N}. \tag{44}$$

For exact differentials, it is the case that $\partial x/\partial y = (\partial y/\partial x)^{-1}$, and so we can also write

$$\frac{\partial S}{\partial J_i}\Big|_{\mathbf{x}} = \frac{\partial x_i}{\partial T}\Big|_{S}. \tag{45}$$

As another example, consider the Helmholtz free energy. You should be able to show by writing the differential form for the free energy that

$$-\frac{\partial S}{\partial x_i}\Big|_{T,N} = \frac{\partial J_i}{\partial T}\Big|_{\mathbf{x},N}. \tag{46}$$

As a third example, you should be able to show, by considering some thermodynamic potential that for a gas:

$$\frac{\partial \mu}{\partial p}\Big|_{N,T} = \frac{\partial V}{\partial N}\Big|_{p,T}. \tag{47}$$

3. *Gibbs phase rule*. The Gibbs phase rule tells us that if there are p phases in coexistence, then the dimensionality of the loci of coexistence points in phase space is

$$f = n + c + 1 - p. \tag{48}$$

4. *Stability criterion*

The requirement that a system is in a stable *thermodynamic* equilibrium requires that non-equilibrium changes about the equilibrium point satisfy

$$\delta S\, \delta T + \delta J \cdot \delta \mathbf{x} + \delta\mu \delta n > 0, \tag{49}$$

for *any* variations. This requires for example that the heat capacity and the isothermal compressibility are positive.

X. THIRD LAW OF THERMODYNAMICS

We introduce the third law of thermodynamics, as formulated by Nernst. It says that the entropy of any system, as temperature goes to zero, approaches a constant that can be taken to zero. This is a strong statement which constrains the zero-temperature behavior of a variety of thermodynamic properties. A few consequences of this rule are as follows:

1. The entropy being zero at zero temperature must hold for any other values of the thermodynamic coordinates. Therefore, $\partial S/\partial x(T = 0, x) = 0$ for any x.

2. Heat capacities must vanish at zero temperature.This follows from

$$S(T, \mathbf{x}) - S(0, \mathbf{x}) = S(T, \mathbf{x}) = \int_0^T dT' \, \frac{C_v(T', \mathbf{x})}{T'}, \tag{50}$$

   If the heat capacity approaches a finite constant (or diverges as $T \to 0$), then the entropy would diverge, which is non-physical.

3. Thermal expansivities vanish at low temperature also. This can be seen from the Maxwell relation

$$\frac{\partial x_i}{\partial T} = \frac{\partial S}{\partial J_i}. \tag{51}$$

   The right-hand side vanishes by virtue of the first property that we worked out.

4. The temperature of a system cannot be brought to exactly zero in a finite number of steps. The basic intuition here is that the heat capacity goes to zero as we attempt to approach zero temperature, requiring that we ultimately have to supply an infinite amount of heat.