

Physics 3700

Heat Capacity. Enthalpy. Magnetic Systems.

Relevant sections in text: §1.4, 1.5, 1.6

Heat Capacity

When the state of a system changes by heat transfer of energy, it is natural and important to ask how the temperature of the system changes for any given amount of heat. The answer is, of course: “it depends”. Naturally you expect a positive (negative) Q will contribute to an increase (decrease) in temperature. But we can be considerably more precise about it.

The idea of *heat capacity* is that it characterizes the change in temperature ΔT for a given amount of heat Q . For many purposes the ratio $Q/\Delta T$ is a constant over some range of values for the relevant observables. But even if this is the case, the ratio will depend upon what is going on during the heat transfer. So we will have to consider the process which led to the heat Q in the first place. To see this, simply consider the ratio in light of the first law:

$$\frac{Q}{\Delta T} = \frac{\Delta U - W}{\Delta T}.$$

Suppose for example that U is proportional to T , as it is for an ideal gas. In this case the ratio depends upon the work being done. As we have seen, this varies depending upon the process (isobaric, isothermal, adiabatic, *etc.*). We thus have different heat capacities for different situations. With this in mind ...

Let δQ represent a small (mathematically, infinitesimal) heat transfer of energy for some process denoted $\star$, which can be isobaric, isochoric, *etc.* See below. Let dT represent the corresponding small (infinitesimal) change in temperature. We define the heat capacity with respect to the process $\star$ to be

$$C_{\star} = \left(\frac{\delta Q}{dT} \right)_{\star}.$$

Let us try to explain this formula.

First of all, we always have an infinitesimal relation of the form

$$\delta Q = C_{\star} dT.$$

As long as we are in a range of observables/states in which the relevant heat capacity is constant (which is very often the case in applications), we have by integration the familiar result

$$Q = C_{\star} \Delta T.$$

It is tempting to think of the ratio $\frac{\delta Q}{dT}$ as some kind of derivative of heat with respect to temperature. Unlike in real life, you should resist temptation. Heat is not an observable in the sense we are using the word; it represents a transfer of energy during relaxation. It is not a function of anything! This is why we use δQ instead of dQ to denote an infinitesimal amount of heat. (The book just uses Q , which is understood to be infinitesimal when appropriate.) On the other hand, observables can be functions of things like pressure, volume, energy, temperature, *etc.* For example, an ideal gas has

$$T = \frac{PV}{Nk}.$$

So it makes sense to take differentials of observables, *e.g.*, (exercise)

$$dT = \frac{1}{Nk} (PdV + VdP - kTdN).$$

Next, note that, *a priori*, heat capacity – like heat – is not really an observable in the sense we have defined the word. *A priori* heat capacity represents the response of a system’s observable (Temperature) to a given external stimulus (heat) which changes the state. Like heat, the heat capacity *can* be expressed in terms of observables — we can measure it — but the expression of heat capacity in terms of observables depends upon the assumptions made about the process. The symbol $\star$ in the definition of heat capacity is a placeholder for specification of the process. Once the process is specified you can express Q in terms of observables and take a derivative.

As an important example, consider the following (very common) situation: among the system’s observables we have pressure P and volume V and we suppose that the only work which could be done is by compression/expansion, as we had with the ideal gas in a piston. Let us restrict attention to a quasi-static process. Then, infinitesimally, the work being done (on the system!) is $-PdV$. If the heat transfer occurs with the volume held fixed, then no compressional work is done. Using the first law we can then identify $dU = \delta Q$ for this isochoric process. The *heat capacity at constant volume* is then the change in energy with respect to temperature holding the volume fixed:

$$C_V := \left(\frac{\delta Q}{dT} \right)_V = \left(\frac{\partial U}{\partial T} \right)_V.$$

The first equality is the definition of C_V . The second equality comes from using the first law in conjunction with our assumptions of quasi-static, compressional work and constant volume. Since we assume that there is no other kind of work being done, we can say that C_V is the heat capacity when there is no work done.

One can get C_V by seeing how the internal energy changes with respect to temperature for a process which keeps the volume constant. The easiest way to compute C_V is to find

a formula for U as a function of V and T (and whatever other observables may be hanging around); the partial derivative of U with respect to T then automatically holds V fixed. As a simple but important example, consider an ideal gas – or, more generally – consider any system where “equipartition” holds (see your text). In this case we have

$$U = \frac{f}{2}NkT,$$

so that U doesn’t even depend upon volume and it easily follows that

$$C_V = \frac{f}{2}Nk.$$

Does this make good physical sense? Let’s see. . . . The f in the equipartition formula is the number of different ways that energy can be distributed into the particles making up the system (via translational, rotational and vibrational degrees of freedom). And remember that, roughly speaking, temperature is a measure of energy per degree of freedom. If no work is done, all the heat does is add/remove energy to/from the system. The equipartition idea is that this energy gets divided up equally among all the Nf degrees of freedom. If Nf is very large, the energy from heat gets divided into many little pieces; none of the degrees of freedom get very excited — the temperature change is relatively small. The relatively large heat capacity in this case means that it takes a lot of heat to get a small change in temperature. If Nf is small, each degree of freedom gets a bigger chunk of energy; it doesn’t take much heat to cause significant excitation of the degrees of freedom — the temperature change is relatively high for a given amount of heat.

Does nature agree with this theoretical analysis? If you measure the heat capacities of various materials (at constant volume) one finds pretty good agreement at high enough temperatures (see your text for some graphs). As the temperatures get lower, certain degrees of freedom begin to “freeze out”, which invalidates the simple-minded equipartition idea, strictly speaking. In fact $C_V \rightarrow 0$ as $T \rightarrow 0$ (T measured in Kelvin!). This is a good example of using heat capacities, which are relatively straightforward to measure, as a test of microscopic models of various systems.

For a gas it is straightforward to add energy (via heat) without changing the volume. For other kinds of systems (e.g. solids) or for other situations one more easily keeps the pressure held fixed and the volume may vary during the heating/cooling process. Note that allowing the volume to change means there will be some (“compressional”) work – think of the gas in the cylinder with the piston. Some of the energy will go into work, some into raising/lowering the temperature. So you expect that it will take more heat transfer to get a given change in temperature in the constant pressure case, *i.e.*, we expect $C_P > C_V$. How do we check this, *i.e.*, how to compute the heat capacity at constant

pressure? From the first law. Assuming the infinitesimal work δW done in the process is purely due to compression/expansion (in the quasi-static approximation):

$$\delta W = -PdV,$$

we then have the *heat capacity at constant pressure* given by

$$C_P := \left(\frac{\delta Q}{dT} \right)_P = \left(\frac{dU - (-PdV)}{dT} \right)_P = \left(\frac{\partial U}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P.$$

We take this as the definition of C_P . Note that the work term is positive provided volume increases monotonically with temperature. The easiest way to use this formula for C_P is to express U and V as a function of P and T , then partial differentiation with respect to T automatically holds P fixed. For example, for an ideal gas at constant pressure P we have

$$U = \frac{1}{2}NfkT, \quad V = \frac{NkT}{P},$$

so that

$$C_P = \frac{1}{2}Nfk + Nk = C_V + Nk.$$

So, at least in the ideal gas case, our intuition that $C_P > C_V$ is confirmed.

In general, the difference between C_P and C_V is small if the volume of the system does not change appreciably with temperature, as is the case with solids except at higher temperatures. Thus for many materials which obey equipartition we expect

$$C_P \approx \frac{1}{2}Nfk,$$

except at higher temperatures. Since equipartition doesn't really work at very low temperatures – degrees of freedom “freeze out” – we get a corresponding drop in C_P at sufficiently low temperatures. As with C_V , $C_P \rightarrow 0$ as $T \rightarrow 0$. See your text for some data on C_P which back up all these assertions.

Heat Capacity: Example

Here's a problem from the book (Problem 1.42). Suppose you toss $m_p = 340g$ of pasta (sitting at room temperature: $T_p = 25C$) into $V_w = 1.5$ liters of boiling water ($T_w = 100C$). Ignoring energy transfer to/from the air, and ignoring any work — which should be relatively negligible, what happens to the temperature of the water?

The strategy is that, after equilibrium is attained at some temperature – call it T , the energy lost by the water is the energy gained by the pasta. Our assumptions have all the energy transfer between pasta and water as occurring via heat. The heat capacities are viewed as constants, so we have for both pasta and water relations of this form:

$$Q = C\Delta T.$$

Here the we model the processes as isobaric, so we will use the heat capacity at constant pressure. Equating the energy transfer to the pasta to the energy lost from the water we have:

$$C_p(T - T_p) = -C_w(T - T_w).$$

Let us introduce the *specific heat capacity*, which is the heat capacity per unit mass and is denoted with lowercase c . We can then write the previous equation as

$$m_p c_p (T - T_p) = -m_w c_w (T - T_w),$$

where the m 's are the respective masses which we know (see below). The only unknown in this equation is T , so we are in good shape, mathematically speaking. Solving for T :

$$T = \frac{m_w c_w T_w + m_p c_p T_p}{m_w c_w + m_p c_p}.$$

Let's put in some numbers. Assume the *specific heat capacity* (at constant pressure) of the pasta is $c_p = 1.8 \text{ J/g} \cdot \text{C}$. For water the specific heat capacity at constant pressure is $c_w = 4.2 \text{ J/g} \cdot \text{C}$. We need to compute the mass of the water. The density of water is 10^3 g/L , so $m_w = 1500 \text{ g}$. Putting this and the rest of the numbers in we get $T \approx 93 \text{ C}$. So the water temperature drops by 7 degrees C. Note that the bigger m_w is the closer the final result is to T_w . So a bigger pot is better for cooking pasta.

Enthalpy

In any given process we can use the first law to deduce the heat transfer *provided no work is done*. In this case we have $Q = \Delta U$ so that one can measure the change in the observable U to get at the heat. What observable can we use to measure heat when there *is* work done? Well, it depends upon precisely how the work is done. An observable that can be used for measuring heat for isobaric processes is called the *enthalpy*. Enthalpy comes from a Greek word meaning, roughly, "heating".

The enthalpy is an observable defined by

$$H := U + PV.$$

Note that the enthalpy has units of energy. The enthalpy is an observable and is defined for any thermodynamic state. You can measure its change for any process. But it is particularly useful for constant pressure processes: *the change in enthalpy after a quasi-static isobaric process with only compressional work is precisely the energy transferred by heat*. I will demonstrate this below. But let me must emphasize that the enthalpy is defined (as above) whether or not you are keeping the pressure constant in some process. It is just that the enthalpy tells you about heat in the isobaric situation.

Let us now prove the above assertion about the enthalpy. Suppose there is a quasi-static constant pressure process leading to a change of state of the system.* There will be a corresponding transfer of energy via heat Q and work $W = -P\Delta V + W^*$ for this isobaric process, where W^* is any other non-compressional work being done on the system. In general the enthalpy changes by

$$\Delta H = \Delta U + \Delta(PV).$$

But since the process under consideration is isobaric we have

$$\Delta H = \Delta U + P\Delta V = \Delta Q + W^*,$$

where we used the first law to get the last equality. You can see that the enthalpy measures the energy transfer to the system from all sources *except* compressional work. We see, in particular, that if only compressional work is done ($W^* = 0$), then the change in enthalpy is precisely the heat transfer (note that we call enthalpy “ H ” for “heat”).

Another way to think about the enthalpy is that it is the quantity whose change with respect to temperature due to an isobaric process gives the heat capacity. Indeed, recall that our previous analysis of C_P had

$$C_P := \left(\frac{\delta Q}{dT} \right)_P = \left(\frac{dU - (-PdV)}{dT} \right)_P = \left(\frac{\partial U}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P.$$

Since $H = U + PV$ we have

$$\left(\frac{\partial U}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P = \left(\frac{\partial H}{\partial T} \right)_P,$$

so that

$$C_P = \left(\frac{\partial H}{\partial T} \right)_P.$$

So, just as you can monitor the internal energy to measure the heat and heat capacity in an isochoric process, if you have a (quasi-static) constant pressure process, you can just monitor the change in enthalpy to measure the heat and heat capacity.

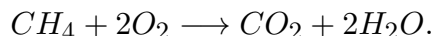
Your text has yet another, somewhat metaphysical way to think about the meaning of the enthalpy observable: The enthalpy of a system in a given state corresponds to the amount of energy it takes to create *from nothing* the system in the given state with energy U and volume V in equilibrium with an environment sitting at pressure P . How to see this? Well, think of the creation of the system as occurring in two steps. First you create the object and then you have to place it into three-dimensional space. You will need

* I remind you, “state” refers to the state of all the observables, not the phase (solid, liquid, ...) of some material.

to use an amount of energy U to create the object, and then do work $P\Delta V = PV$ on the environment to make room for it. The enthalpy H is then the total cost in energy. Conversely, the enthalpy of an object is how much energy you could extract from it if you annihilated it: you get the energy in the object *and* the work done by the environment as it collapses to fill the empty space.

Enthalpy: Example

(The following is taken from problem 1.50 in the text.) Methane burns; the result is carbon dioxide, water and energy. The chemical reaction is



Suppose the system is at $T = 298K$ and $P = 10^5 Pa$ (STP) before and after the reaction. How much energy is released when you burn a mole of methane?

We can model this reaction as occurring at constant pressure and with negligible compressional work being done. Thus we can get the energy released by computing the change in enthalpy for the system. To compute this change in enthalpy, we will need to use the table of thermodynamic properties in the back of the book. There you can find the *enthalpy of formation* of 1 mole of various compounds at constant standard pressure ($10^5 Pa = 1$ bar). This is the change in enthalpy associated with building the given compound from its stable constituents. View the reaction as breaking down CH_4 into its stable constituents ($C, 2 \times H_2$) and then combining with the $2O_2$ to make the resulting products. The change in enthalpy to break down CH_4 is 74.81 kJ (this is energy added to the system). The change in enthalpy to form CO_2 (from C and O_2) is -393.51 kJ (the minus sign means energy leaves the system in this particular step). The change in enthalpy for forming $2H_2O$ from $2H_2$ and O_2 depends upon whether it is in liquid or gas form; we get -571.66 kJ or -483.64 kJ, respectively. All these minus signs signify energy released from the system. All together, the change in enthalpy is

$$\Delta H = 74.81kJ - 393.51kJ - 483.64kJ = -802.34kJ,$$

if the H_2O released is a gas, and

$$\Delta H = 74.81kJ - 393.51kJ - 571.66kJ = -890.36kJ,$$

if the H_2O appears as a liquid. At STP the actual product is water vapor (gas). Under the given conditions, the change in volume is therefore negligible if we model the system as an ideal gas (we have 3 moles of gas before and after the reaction, the temperature and pressure are fixed). Thus no compressional work is done. The change in enthalpy is the energy released, 802.34 kJ. Note that since no compressional work is done, the energy released is just the change in energy of the system.

It is instructive to consider the alternative (purely hypothetical) scenario where the water appears as liquid. We have already seen that the energy released is bigger in this case. Let us see what happens to the total energy of the system during the process. We can get at the energy as follows. First of all, we know ΔH — we just computed it. Since $\Delta P = 0$, we have

$$\Delta U = \Delta H - P\Delta V.$$

So, we need ΔV and then we have ΔU . To get at ΔV we will treat the gases as ideal and use the ideal gas law in the form

$$PV = nRT,$$

where n is the number of moles of gas and R is the gas constant. We start off with $n = 3$ moles of methane and oxygen. We only have $n = 1$ moles of carbon dioxide after the reaction, and the water's volume is negligible, so we have

$$\Delta V = \frac{RT}{P}\Delta n = -2\frac{RT}{P}.$$

The change in energy of the system is therefore

$$\Delta U = \Delta H - P\Delta V = \Delta H + 2RT = -885.40 \text{ kJ}.$$

You can see that the energy released by the chemical reaction is *bigger* than the change in internal energy of the system. The difference is coming from the work done by the atmosphere to compress the system to a smaller volume.

Magnetic Systems

Thermodynamics isn't just about ideal gases, pressure, volume *etc.* It is *very* general. Let me demonstrate this via the important example of a paramagnetic solid. We shall see that magnetic materials have thermodynamic properties analogous to what we found for an ideal gas.

First a little review. There are three types of possible magnetic responses of a material to an applied magnetic field. These responses occur according to whether there are atoms with permanent magnetic dipole moments or not in the material. Diamagnetic materials do not have (many) such atoms; when a magnetic field is applied an induced dipole moment occurs which opposes the applied field. This phenomenon is universal and temperature independent; it is not so interesting thermodynamically. Paramagnetic materials have atoms with permanent dipole moments. An applied field tends to line them up to some extent (swamping other diamagnetic effects and overcoming thermal agitation) leading to a magnetic moment which reinforces the field. This effect is proportional to the applied field (until the system saturates). The effect decreases with increasing temperature; thermal

agitation tends to disalign the dipoles. It increases with decreasing temperature until the thermal agitation is small enough such that the various atomic dipole moments can interact enough to establish and maintain a long range order - the material has become a ferromagnet. The temperature of the paramagnetic/ferromagnetic transition is called the Curie temperature. (We will make precise sense of “thermal agitation” a little later in the class.)

For temperatures well above the Curie temperature we can ignore the interactions among the dipole moments in a paramagnetic material. This is analogous to ignoring molecular interactions in an ideal gas. In this setting a relatively simple thermodynamic description of the paramagnet and its response to an applied magnetic field can be given.

We focus on the first law: the energy of the paramagnetic system and the how work and heat can change that energy. When a magnetic field is applied to the system, energy from the field is used to align the magnetic moments of the atoms - this is work done on the system. Let me sketch how you can compute the work. Let the region occupied by the paramagnetic system be denoted by the volume V . Let $\vec{B}$ represent the magnetic field that a given current configuration *would* produce in the volume V if the paramagnetic material were not present. The energy in this magnetic field is

$$E_B = \frac{1}{2\mu_0} \int_V dV B^2.$$

So, in the absence of the paramagnetic material, we would have to do work $W_B = E_B$ to create $\vec{B}$. Now consider the response of the paramagnetic material to the applied field. Let the vector field $\vec{M}$ be the total induced magnetic moment at each point of the system. $\vec{M}$ is the *magnetization* of the paramagnetic material. It is a standard result of electromagnetic theory that the *additional work* needed to establish $\vec{M}$ is

$$W_M = \int_{M_i}^{M_f} \vec{B} \cdot d\vec{M}.$$

The quantity E_B does not pertain to the “system” – the paramagnetic material – and it is convenient to define the internal energy of the system relative to E_B :

$$U = \text{Energy} - E_B.$$

The infinitesimal form of the first law can now be written:

$$dU = \delta Q - PdV + \vec{B} \cdot d\vec{M}.$$

(For many applications, the volume of the material is constant and compressional work can be ignored completely.) We see that as far as magnetic work is concerned, $\vec{B}$ is analogous to P and $\vec{M}$ is analogous to V . Note that both P and $\vec{B}$ are intensive variables,

while V and $\vec{M}$ are extensive variables. Let me also mention that a microscopic model of a paramagnet (due to Langevin), under the assumption of weak B and small intrinsic magnetic moments μ of the atoms/molecules, gives an equation of state analogous to the ideal gas law:

$$\vec{M} = \frac{N\mu^2}{3kT}\vec{B}.$$