

2.5: Heat Transactions, Heat Capacity, and Adiabatic Systems

As stated previously, heat (∂q) is narrowly defined as an energy transaction between the exterior and a system. For example, a gas naturally heats up when compressed in a metal piston, which becomes hot to the touch. That is, until it cools through a negative heat transaction (a negative Δq). For a positive Δq the piston will feel cold because the heat is coming out of your hand (the — exterior) into the system. There is a problem with this definition because it makes it appear that a thermally insulated system magically has no heat at all. This is very incorrect as we shall see in Chapter 4.

Concerning pure heat transactions, any thermodynamic problem must stipulate, “X Joules of energy is added to (or removed from) the system”. Great- what comes next? Taking the viewpoint that heat is added, we know that the temperature increases. Let’s calculate that, and first we must define the relationship between the addition of heat to the increase in temperature ala: $\partial q = ? \cdot \partial T$. Note that there must be some factor “?” in this equation for the simple reason that ∂q and ∂T do not have the same units. This factor is the heat capacity “C”, which can be defined by modifying the equation above as: $\frac{\partial q}{\partial T} = C$. Note that we have already established that thermodynamic processes can occur at constant volume or constant pressure, which leaves us with two possible definitions for heat capacities, one for constant volume: $\left(\frac{\partial q}{\partial T}\right)_V = C_V$ and the other for constant pressure: $\left(\frac{\partial q}{\partial T}\right)_P = C_P$. If we know the heat capacities and whether the piston of gas can expand (constant P) or is jammed shut (constant V), we can then calculate a change in temperature by integration: $\frac{\Delta q}{C_{P \text{ or } V}} = \Delta T$.

Molecule	$C_{V,m}$ (J/K/mol)	$C_{P,m}$ (J/K/mol)	$C_{P,m} - C_{V,m}$ (J/K/mol)
Ar	12.5	20.79	8.29
O ₂	21.1	29.4	8.32
CO ₂	28.8	37.1	8.32
CH ₄	27.2	35.5	8.32

Shown in Table 2.2 is a list of molecules and their per molar heat capacities. It is important to note that both $C_{V,m}$ and $C_{P,m}$ have units of $J \cdot K^{-1} mol^{-1}$, whereas the true heat capacities C_V and C_P have units of $J \cdot K^{-1}$. Thus, heat capacities are not per molar quantities and are extensive, whereas per molar heat capacities are intensive. We usually present heat capacity in the per molar form in problems and in tables because that information can be generalized. However, you must always remember to multiply the intensive representation of the heat capacity ($C_{V,m}$ or $C_{P,m}$) by the number of moles of your substance to make sure you’re working with the actual heat capacity when addressing thermodynamic problems.

There are a few noticeable trends in Table 2.2, for example, Ar has the lowest heat capacity, and everything has $C_{P,m} > C_{V,m}$. In fact, it appears that the difference $C_{P,m} - C_{V,m}$ is nearly identical to the gas constant R. There must be a physical basis for these observations and for the magnitudes of the heat capacities in general. We will explore heat capacities further by considering what happens when a gas is heated under conditions of constant volume. This is the simplest case because no heat is lost as work, and thus $\Delta U = \Delta w + \Delta q = \Delta q$ since $\Delta w = 0$ J. The Equipartition theorem states that per molar internal energy: $U_m = \frac{1}{2}RT \cdot (\text{degrees of freedom})$ can only change with temperature:

$$\partial U_m = \frac{1}{2}R \cdot (\text{degrees of freedom}) \cdot \partial T$$

which leads to:

$$\begin{aligned} C_{V,m} = \left(\frac{\partial q}{\partial T}\right)_V &= \left(\frac{\partial U_m}{\partial T}\right)_V = \frac{1}{2}R \cdot (\text{degrees of freedom}) \cdot \left(\frac{\partial T}{\partial T}\right)_V \\ &= \frac{1}{2}R \cdot (\text{degrees of freedom}) \end{aligned} \quad (2.5.1)$$

since $\left(\frac{\partial T}{\partial T}\right)_V = 1$. If you doubt this derivation, check how the numerical values of $C_{V,m}$ in Table 2.2 correlate to the terrestrial U_m in Table 2.1. Overall, it’s a good match. Later we can explain why it is that $C_P = C_V + nR$, or equivalently

$C_{P,m} - C_{V,m} = R$. Example problem 2.6 can be used to make sure you understand heat capacities.

2.6.1 Adiabatic Systems. In our exploration of work it was found that compression adds energy into a system. This should cause the gas inside to heat up; however under isothermal conditions a heat transaction with the exterior kept the temperature constant. This heat transaction is expected if the piston is made of metal and is in contact with the exterior. In contrast, example problem 2.6 was used to calculate the increase in temperature after heat energy was added to a gas- why didn't this system cool back down? It's because the piston was wrapped in thermally insulating glass wool. What if we performed compression work on the same insulated piston? For one, Δq must be 0 J because no heat transaction can occur through the thermal insulation. Furthermore, the system can't cool, and the temperature will rise, which results in an increase in ΔU . This is consistent with a positive Δw , which is equal to ΔU since $\Delta U = \Delta w + \Delta q (0 J) = \Delta w$. Of course, we have to give this thermally insulated system a peculiar-sounding name, and that is "adiabatic". Unfortunately, it has several other definitions sort of like how "bomb" is both a noun and a verb, but for this class an "adiabatic" system is a thermally insulated one.

A system could never be simultaneously both adiabatic and isothermal, as they are opposites. Furthermore, adiabatic processes can be reversible and irreversible just like isothermal transitions. As a result, we now have a total of four paths for thermodynamic processes as summarized here:

Constant temperature, reversible	Adiabatic, reversible
Constant temperature, irreversible	Adiabatic, irreversible

And for each type of transition we can calculate five variables: ΔU , Δq , Δw , C_V , and C_P . Let me correct that- we have five variables *for now*. We are going to end up with 12 by Chapter 5, times the four types of transitions, gives us $4 \times 12 = 48$ potential thermodynamic relationships!

2.6.1.1 Adiabatic, Reversible. We must consider how work changes the temperature of an adiabatic system. In fact, for all adiabatic processes the first thing we must calculate is the final temperature, since the initial temperature must be known. Normally, it would appear that we should be able to determine the final temperature using an equation of state such as the perfect gas law. However, the perfect gas law won't help us with adiabatic transitions because $PV=nRT$ is just one equation with three variables changing simultaneously (P, V, and T). Another approach is required, such as calculating all the energy imparted via work and then use the heat capacity to translate that energy into ΔT . Let's use ∂U as a conduit to realize this approach. First, $\partial U = \partial w + \partial q = \partial w$ as ∂q is **always 0 J** under adiabatic conditions. Next, as ∂U is exact it can be calculated either reversibly or irreversibly and we will get the same answer. Generally, it is easier to use the reversible path, which makes $\partial U = \partial w = -P\partial V$.

To connect $\partial U = -P\partial V$ to the change in temperature we will use the example of an adiabatic expansion shown in Figure 2.8. In this process, the volume increases with a simultaneous decrease in temperature. So how do we account for both volume and temperature change when calculating the effect on internal energy? Due to the "exactness" of ∂U we can decouple these processes into different routes with the same start and end points. For example, the system can follow path 1 where there is a change in volume at a fixed temperature; as a result there is no change in internal energy ($\Delta U_1 = 0 J$). Path 2 represents a temperature change at constant volume, which makes $\Delta U_2 = C_V \Delta T$ and thus $\Delta U_{tot} = \Delta U_1 + \Delta U_2 = C_V \Delta T$. We can also determine the same following the alternative route Path 3 + Path 4, which simply follow the reverse order yet have the same change in total U. Ultimately, $\Delta U_{tot} = C_V \Delta T$ regardless of the route followed, and this is equal to the work as discussed previously. We will switch to partial notation so that we can apply integral calculus on relationship:

$$C_V \partial T = -P \partial V \quad (2.5.2)$$

The remainder of the proof will rely on perfect gas conditions, i.e. $PV = nRT$ and thus $P = \frac{nRT}{V}$ which we plug into Equation 2.12:

$$C_V \partial T = -\frac{nRT}{V} \partial V$$

This is important because we must integrate with respect to T and V (the partials in Equation 2.12), and thus we must make sure the T and V that were "hiding" in P are now on the left and right sides. The integral limits (final minus initial) are T_f to T_i on the left and V_f to V_i on the right:

$$\int_{T_i}^{T_f} \frac{C_V}{T} \partial T = - \int_{V_i}^{V_f} \frac{nR}{V} \partial V$$

After integration we find:

$$C_V \cdot \ln\left(\frac{T_f}{T_i}\right) = -nR \cdot \ln\left(\frac{V_f}{V_i}\right)$$

Now we can apply several identities for natural logs, such as: $-\ln\left(\frac{a}{b}\right) = \ln\left(\frac{b}{a}\right)$, as well as:

$a \cdot \ln(b) = \ln(b^a)$ to make the following rearrangements:

$$\frac{C_V}{nR} \cdot \ln\left(\frac{T_f}{T_i}\right) = \ln\left(\frac{V_i}{V_f}\right)$$

and thus: $\ln\left[\left(\frac{T_f}{T_i}\right)^{\frac{C_V}{nR}}\right] = \ln\left(\frac{V_i}{V_f}\right)$

""Taking the exponential of both sides results in:

$$\left(\frac{T_f}{T_i}\right)^{\frac{C_V}{nR}} = \frac{V_i}{V_f} \quad (2.5.3)$$

which gives a method for calculating the final temperature of a reversible adiabatic process. Basically, any question on adiabatic transitions will provide all the necessary information for calculating T_f via $\left(\frac{T_f}{T_i}\right)^{\frac{C_V}{nR}} = \frac{V_i}{V_f}$ or a derivative thereof, albeit the data may be obscured using the perfect gas law. Another interesting aspect of $\left(\frac{T_f}{T_i}\right)^{\frac{C_V}{nR}} = \frac{V_i}{V_f}$, which we sometimes refer to as an ""adiabatic equation of state", is that it appears to be an alternative for the perfect gas law. However, this is incorrect as we used $PV=nRT$ in the derivation of this equation, and we can use $PV=nRT$ to make further derivations of $\left(\frac{T_f}{T_i}\right)^{\frac{C_V}{nR}} = \frac{V_i}{V_f}$ which is on several problems at the end of the chapter.

To summarize and provide some problem-solving strategies, a reversible adiabatic

transition has $\Delta U = 0$ J, and the next step is to determine ΔT via T_f . Next, the change in U is $C_V \Delta T$, which is also the work. Hopefully example problems 2.7 and 2.8 will solidify the lessons learned.

2.6.1.2 Adiabatic, Irreversible. Irreversible adiabatic work appears to be much simpler compared to the reversible, as the work is against a constant exterior pressure. As a result, $\partial w = -P_{ext} \partial V$, and as it is still true that $\partial U = \partial w = C_V \partial T$, integration yields:

$$C_V \Delta T = -P_{ext} \Delta V \quad (2.5.4)$$

Doesn't it look much easier to calculate the irreversible ΔT compared to the reversible example above? Of course, and as you can imagine that is very wrong. Example problem 2.8 will help you navigate irreversible, adiabatic equations for work.

Note that the example problem demonstrates less negative work (-621 J) than observed in the reversible problem (-828 J); this preserves the notion that we get the most (negative) work out of reversible transitions. And how did that extra work come about? It's because the reversible expansion ends up with a much colder gas, which means more internal heat was converted to expansion work. Think of it like this: if the change in temperature was calculated from $\Delta w = n \cdot C_{V,m} \cdot \Delta T$, then $\Delta T = \frac{\Delta w}{n \cdot C_{V,m}}$. Now since the reversible work is the most negative, then the reversible transition will cool the gas more compared to the irreversible transition.

Conclusion. Thus far we have shown the basics of energy, heat and work, via the 1st Law of Thermodynamics. However, we still have much to learn before analyzing chemical processes; in fact, the content of this chapter uses gas expansion and contraction in place of chemical transformations because understanding a car engine piston is much easier than burning gasoline. This will be the case until you reach Chapter 6, but for now we move on to understanding other types of energy and how they apply to the four thermodynamic transformational conditions.

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