

Physics 161: Thermodynamics

Lecture #4

Energy, Enthalpy and Heat Capacity & Introduction to Adiabatic Processes

To specify the state of a pure fluid (in a single phase), we must give two thermodynamic variables. For example, for an ideal gas, we specify the state by giving T and V ; we can then use the equation of state to find the third variable, the pressure,

$$P = \frac{nRT}{V}.$$

Alternatively, could specify the state by giving T and P , or we could specify V and P . To represent this dependence in a formal manner, we write, for example,

$$P = P(T, V)$$

This equation reads " P is determined by the two variables T and V ". Similarly, we could write

$$V = V(T, P),$$

to indicate that V is a function of T and P , or we could instead write

$$T = T(P, V).$$

to indicate that T is a function of P and V .

1 The energy U is a state variable

Recall now the first law of thermodynamics. There are really *two parts* to the first law. The first is a statement of energy conservation,

$$\Delta U = Q - W.$$

The second is the postulate that the internal energy U is a state variable, or state function (In this context we use the terms variable and function interchangeably). Let us discuss this second part of the first law for a moment. If U is a state variable, then since the state of the system is entirely determined by any two state variables, we can consider U to be a function of, say, T and V , which we would indicate by writing

$$U = U(T, V). \tag{1}$$

How do we describe the manner in which U depends on T and V ? One way is to consider a small change dU , and ask how this depends on a small change

in temperature dT , or a small change in volume dV . Formally we can write the expansion of the differential dU as

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV. \quad (2)$$

We have already discussed this formal expansion in Lecture 2. If we know the two expansion coefficients, $\left(\frac{\partial U}{\partial T}\right)_V$, and $\left(\frac{\partial U}{\partial V}\right)_T$, over a range of temperature and volume, we can in principle integrate to find an expression for $U(T, V)$ which is valid in that range.

1.1 U for an ideal gas

The expansion coefficients are very simple for an ideal gas. It turns out that,

$$\left(\frac{\partial U}{\partial T}\right)_V = K, \text{ (a constant)} \quad (3)$$

$$\left(\frac{\partial U}{\partial V}\right)_T = 0. \quad (4)$$

The first, expression (3), is found to be true from experiments on gases at low densities, and is obeyed over a wide range of temperatures. The second coefficient is zero. ~~It can be proved that if $\left(\frac{\partial U}{\partial T}\right)_V = K$, then $\left(\frac{\partial U}{\partial V}\right)_T = 0$ is the only possibility. We will not go through the proof at this time.~~ Inserting (3) and (4) into (2), we have

$$dU = KdT$$

and upon integration of both sides (and leaving out the integration constant), it follows that

$$U = KT. \quad (5)$$

The energy increases linearly with temperature.

1.2 U for a monatomic gas and U for a diatomic gas

The value of the constant K depends on the gas. Here are some common examples. For a dilute monatomic gas, such as helium, it is found that

$$U = \frac{3}{2}nRT \quad (6)$$

For a dilute diatomic gas, such as nitrogen, it is found that

$$U = \frac{5}{2}nRT \quad (7)$$

This was discussed in class last Friday.

(It can be proved that $dU/dV=0$ if $PV=nRT$.)

1.3 U is a function of T only for ideal gas

Look at equations (6) and (7), and notice that U is a function of T only for an ideal gas. It does not depend on V , as we had suggested in ought to in the most general case in writing equation (1). It does not depend on P either. We often express this fact about ideal gases by writing

$$U = U(T)$$

and leaving the other variables V and P out of the parentheses. This means that when we are dealing with an ideal gas, for an isothermal process, $\Delta U = 0$.

2 The enthalpy H is a state variable

Another state function of interest that is related to the energy U is the enthalpy H . The enthalpy is defined as follows:

$$H = U + PV. \tag{8}$$

It is obviously a state function; U , P , and V are each state functions, so any combination thereof will also be a state function. The usefulness of the enthalpy will become evident shortly. For now, let us just accept that H is another state variable that has units of energy, and let us assume that we will actually have need to calculate ΔH for some processes.

For an ideal gas, H has a particularly simple form. Substituting nRT for PV on the right hand side of equation (8), we have

$$H = H(T) = KT + nRT \tag{9}$$

We see that the enthalpy is also a function of only T for an ideal gas. For a monatomic gas such as helium, it follows that

$$H = \frac{5}{2}nRT. \tag{10}$$

For a diatomic gas such as nitrogen, it follows that

$$H = \frac{7}{2}nRT. \tag{11}$$

3 The heat capacity

You are probably familiar with the term "specific heat" from your high school chemistry class. You probably learned that the specific heat of water is 1, that is

$$\begin{aligned}c_{(\text{H}_2\text{O})} &= 1 \frac{\text{calorie}}{\text{gram} \times ^\circ\text{C}} \\ &= 4.186 \frac{\text{Joules}}{\text{gram} \times ^\circ\text{C}}\end{aligned}$$

This means that 1 calorie of heat is required to raise one gram of water by 1 degree Celsius.

What is the relation between the specific heat and the heat capacity? The heat capacity is the product of the specific heat and the total number of grams. For example, if you have 3 grams of water, the heat capacity is

$$C_{(\text{H}_2\text{O})} = 3 \frac{\text{calories}}{^\circ\text{C}}.$$

Your textbook distinguishes between specific heat and heat capacity by using a small c for the former and a large C for the latter. Another notation that is common is to denote the specific heat as \bar{C} with a bar on top. The bar can indicate the heat capacity per gram, or it can also indicate heat capacity per mole. It is easier to use the bar notation at the blackboard, where it is difficult to control font sizes to allow students to distinguish between lower case and upper case.

3.1 Heat capacity at constant volume

Start with the expression for the first law,

$$\Delta U = Q - W$$

and write this for small changes,

$$dU = \delta Q - \delta W \tag{12}$$

(Here I will use the kronecker-delta symbol δ in front of Q and W to indicate that these are small quantities because my typewriter does not have a d with a slash through it.) The ratio of the amount of heat divided by the change in temperature is the heat capacity. Hence, rearranging (12) and dividing both sides by dT , we find that

$$C = \frac{\delta Q}{dT} = \frac{dU}{dT} + \frac{\delta W}{dT}. \tag{13}$$

Suppose now that the gas is in a rigid container as it is heated, so that its volume is held constant. This prevents the gas from doing work on the surroundings as

it is heated, so $\delta W = 0$. It follows from (13) that the heat capacity is given by the change in U with respect to temperature,

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V \quad (14)$$

This is called the "heat capacity at constant volume", and we have put on the subscript V to indicate that the volume is held constant so that the system can't do any work. (I have already mentioned that the change in the differential notation on the right hand side, from d to ∂ , is superfluous, since the presence of the subscript V already indicates that the derivative is to be taken holding the volume constant. But it is standard to use the ∂ notation for the derivative when something must be held constant, so we will use it.)

What is the heat capacity at constant volume for an ideal gas? If the gas is monatomic, we substitute (6) into the rhs of (14), and take the derivative with respect to T . This gives

$$C_V = \frac{\partial}{\partial T} \left(\frac{3}{2} nRT \right)_V = \frac{3}{2} nR. \quad (15)$$

Similarly, if the gas is diatomic, we have

$$C_V = \frac{5}{2} nR. \quad (16)$$

The molar heat capacity for a diatomic gas is found by dividing the heat capacity by the number of moles n :

$$\begin{aligned} \overline{C_V} &= \frac{5}{2} R = 20.8 \frac{\text{J}}{\text{mole} \cdot ^\circ\text{C}} \\ &= 20.8 \frac{\text{J}}{\text{mole} \cdot \text{K}} \end{aligned} \quad (17)$$

It doesn't matter if we use the temperature in Celsius or the temperature in Kelvin in defining the units of heat capacity, for a 1 degree change in Celsius is the same as a 1 degree change in Kelvin.

It is useful to note that an ideal gas has a constant heat capacity.

3.2 Heat capacity at constant pressure

If the substance to be heated is not confined to a vessel of constant volume, then the situation is different. For example, if a gas is heated in a soft container such as a partially inflated plastic bag, it is free to expand against the surrounding atmosphere as the temperature increases. Consequently the volume will not be constant, and $\delta W \neq 0$. What will be constant instead is the pressure, which for example will be 1 atm if the heating is conducted at sea level. For the case of

constant pressure, it is convenient to work with the enthalpy when discussing heat. To see this, proceed as follows. Starting with the first law,

$$\Delta U = Q - W$$

add the product PV to both sides of the equation. This gives us an expression for ΔH :

$$\Delta H = \Delta(U + PV) = Q - W + \Delta(PV) \quad (18)$$

For small changes, equation (18) becomes

$$dH = \delta Q - \delta W + VdP + PdV \quad (19)$$

We have used the fact that for small changes, $\Delta(PV) \rightarrow d(PV)$, and then used the chain rule $d(PV) = PdV + VdP$. Let us now insert the fact that $\delta W = PdV$ into the rhs. This gives

$$dH = \delta Q - PdV + VdP + PdV \quad (20)$$

Here now is the crux; the two PdV terms on the rhs of (20) cancel out, leaving us with

$$dH = \delta Q + VdP. \quad (21)$$

If the pressure is held constant, dP is zero, and we simply have

$$dH = \delta Q \quad (22)$$

Thus we have shown that the heat added to a system at constant pressure is equal to the change in the enthalpy. Dividing by dT , we obtain a relation between the heat capacity and the enthalpy:

$$C_P = \left(\frac{\delta Q}{dT} \right)_P = \left(\frac{\partial H}{\partial T} \right)_P. \quad (23)$$

The subscript P indicates that this is the heat capacity at constant pressure.

For a monatomic ideal gas, it follows from equation (10) and (23) that

$$C_P = \frac{\partial}{\partial T} \left(\frac{5}{2}nRT \right)_P = \frac{5}{2}nR \quad (24)$$

For a diatomic ideal gas, it follows from equation (11) and (23) that

$$C_P = \frac{\partial}{\partial T} \left(\frac{7}{2}nRT \right)_P = \frac{7}{2}nR \quad (25)$$

For an ideal gas in general, the general relation between H and U is expressed as follows:

$$\begin{aligned} H &= U + PV \\ &= KT + nRT \end{aligned}$$

It follows that for an ideal gas,

$$C_P = C_V + nR \quad (26)$$

You should not that $C_P > C_V$ for an ideal gas. It can be proved that the heat capacity at constant pressure will always be larger than the heat capacity at constant volume, for any substance.

4 Heating Examples

Example 1: Heating at constant volume.

Calculate ΔU , Q , and W when 10 moles of N_2 gas are heated at constant V from 25 °C to 75 °C. Take $\overline{C_V} = 5/2 R$, independent of temperature in the range of interest.

Solution:

Since U is a state function, let us write

$$U = U(T, V)$$

and formally write the expansion for dU :

$$dU = \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV.$$

Since the volume is held constant during the heating, $dV = 0$, which means that

$$\begin{aligned} dU &= \left(\frac{\partial U}{\partial T} \right)_V dT \\ &= C_V dT. \end{aligned}$$

Integrating both sides of the equation from 25 °C to 75 °C, we have

$$\begin{aligned} \Delta U &= \frac{5}{2} nR \int_{298}^{348} dT \\ &= \frac{5}{2} \times 10 \text{ moles} \times 8.314 \frac{\text{Joules}}{\text{mole} \cdot \text{K}} \times (T_2 - T_1) \\ &= \frac{5}{2} \times 10 \text{ moles} \times 8.314 \frac{\text{Joules}}{\text{mole} \cdot \text{K}} \times (348 \text{ K} - 298 \text{ K}) \\ &= \frac{5}{2} \times 10 \text{ moles} \times 8.314 \frac{\text{Joules}}{\text{mole} \cdot \text{K}} \times 50 \text{ K} \\ &= 10393 \text{ Joules} \end{aligned}$$

Because the gas was heated at constant volume, $W = 0$, which means that

$$Q = \Delta U = 10393 \text{ J.}$$

Some of you may be concerned about whether or not to convert the temperature from Celsius to Kelvin. There are expressions that are only true if T is the absolute temperature. The ideal gas law, $PV = nRT$ is such an expression. You will never be wrong if you work with temperature in Kelvin, but you may make serious mistakes if you attempt to keep the temperature in Celsius. It was with this in mind that I converted 25 °C to 298 K, and 75 °C to 348 K, by adding 273 to each temperature. Notice, however, that in the end, only the difference in temperature was important for this problem; $348 - 298 = 50$, but so too $75 - 25 = 50$. This is obviously an example where it is not important to make the conversion from Celsius to Kelvin.

Example 2: Heating at constant pressure.

Suppose that 10 moles of N_2 gas are heated at constant pressure $P = 1$ atm, from 25 °C to 75 °C. Calculate ΔU , Q , and W . Take $\bar{C}_V = 5/2 R$ to be independent of temperature in the range of interest. Also assume that we have ideal gas behavior.

Solution:

As we have discussed above, for a constant pressure process, the heat added to the system is given by the change in the state function enthalpy:

$$Q = \Delta H$$

To calculate ΔH in a formal way, let us write H as an expansion over the variables T and P :

$$dH = \left(\frac{\partial H}{\partial T} \right)_P dT + \left(\frac{\partial H}{\partial P} \right)_T dP.$$

(We could have expanded over T and V , or over V and P , but it is wisest to use T and P because one term cancels out, and we recognize the other one, as we will see below.)

Since the process is carried out at constant pressure, $dP = 0$, and our formal expansion above simplifies to having only one term,

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

The coefficient is one that we happen to recognize; recall that $\left(\frac{\partial H}{\partial T} \right)_P$ is the heat capacity at constant pressure, C_P . What is C_P ? Recall also that for an ideal gas, $C_P = C_V + nR$. Since \bar{C}_V is given as $\frac{5}{2}R$, this means that

$$C_P = \frac{7}{2}nR.$$

It follows that

$$dH = C_P dT = \frac{7}{2}nR dT.$$

Integrating both sides of this equation, we obtain a relation between the enthalpy change and the temperature change,

$$\Delta H = \frac{7}{2}nR\Delta T.$$

Finally, since $Q = \Delta H$ for a constant pressure process, the heat added at constant pressure is

$$\begin{aligned} Q &= \frac{7}{2}nR(75 - 25) \\ &= \frac{7}{2} \times 10 \text{ moles} \times 8.314 \frac{\text{Joules}}{\text{mole} \cdot \text{K}} \times 50 \text{ K} \\ &= 14548 \text{ Joules.} \end{aligned}$$

To finish the problem, note that

$$\begin{aligned} \Delta U &= \Delta H - \Delta(PV) \\ &= \Delta H - nR\Delta T \\ &= 14548 \text{ Joules} - 10 \text{ moles} \times 8.314 \frac{\text{Joules}}{\text{mole} \cdot \text{K}} \times 50 \text{ K} \\ &= 10393 \text{ Joules.} \end{aligned}$$

Also, using the first law,

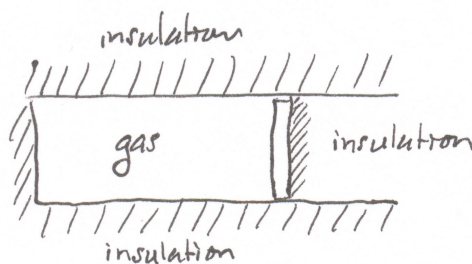
$$\Delta U = Q - W$$

we can solve for the work,

$$\begin{aligned} W &= Q - \Delta U \\ &= 14548 \text{ Joules} - 10393 \text{ Joules} \\ &= 4160 \text{ Joules.} \end{aligned}$$

5 Introduction to Adiabatic Processes

An adiabatic process is a process in which no heat is exchanged with the environment; $Q = 0$. For our examples of expanding gas, the implication is that the cylinder and piston are well insulated. We will be interested in both reversible and irreversible adiabatic expansions (and compressions) of a gas.



$$Q = 0 \text{ (Adiabatic Expansion)}$$

Example 3:

Consider 10 moles of ideal gas, expanded adiabatically from 400 K to 300 K. Find ΔU , ΔH , Q , and W . Take $C_P = \frac{7}{2}nR$.

Solution: Adiabatic expansion, path unspecified.

First of all, by adiabatic, we mean that $Q = 0$. This means that

$$\Delta U = -W$$

We may not know how the expansion is carried out, and we may not know the change in volume, but we can calculate ΔU because we know that for an ideal gas that U is a function of T only;

$$\Delta U = C_V \Delta T$$

Although we are given $C_P = \frac{7}{2}nR$, for an ideal gas that $C_P - C_V = nR$. This means that $C_V = \frac{5}{2}nR$. It follows that

$$\begin{aligned}\Delta U &= \frac{5}{2}nR\Delta T = \frac{5}{2}nR(T_2 - T_1) \\ &= \frac{5}{2} \times 10 \times 8.314 \times (300 - 400) \\ &= -20.8 \text{ kJ}\end{aligned}$$

It follows that the work is given by

$$W = 20.8 \text{ kJ}.$$

It is also straightforward to calculate the change in enthalpy.

$$\begin{aligned}\Delta H &= \Delta U + \Delta(PV) \\ &= -20.8 \text{ kJ} + nR\Delta T \\ &= -20.8 \text{ kJ} + 10 \times 8.314 \times (300 - 400) \\ &= -2.91 \text{ kJ}\end{aligned}$$

Did the expansion take place reversibly or irreversibly? We don't know, but we didn't have to know anything about the path to find ΔH , ΔU , Q , and W . Notice also that we didn't know the complete state of the system initially. We knew that the temperature was 400 K, but we didn't know the initial pressure, and we didn't know the initial volume. Similarly, we were told that the final temperature was 300 K, but we didn't know anything about the final pressure or volume.

Example 4: *Reversible* adiabatic compression

An ideal gas for which $C_V = \frac{5}{2}R$ is compressed adiabatically and reversibly from a pressure of 1 atm and volume of 1.0 liters to a volume of 0.25 liters. What is the final pressure? What is the final temperature if the initial temperature is 300 K?

Solution:

It is helpful to memorize the following expression for an ideal gas undergoing an adiabatic reversible process.

$$P \cdot V^\gamma = \text{constant}$$

where the exponent

$$\gamma = \frac{C_P}{C_V}$$

is the ratio of the heat capacity at constant pressure to the heat capacity at constant volume. We will derive this in the next lecture. The way to use it for the present problem is as follows. First, using the fact that $C_P - C_V = nR$ for an ideal gas, we know that $C_V = \frac{7}{2}R$, and therefore the exponent is

$$\gamma = \frac{\left(\frac{7}{2}\right)}{\left(\frac{5}{2}\right)} = \frac{7}{5}$$

Next, since $PV^\gamma = \text{constant}$, it follows that

$$P_1 V_1^\gamma = P_2 V_2^\gamma$$

We know $P_1 = 1 \text{ atm}$, $V_1 = 1 \text{ liter}$, and $V_2 = 0.25 \text{ liters}$. It follows that

$$P_2 = P_1 \frac{V_1^\gamma}{V_2^\gamma} = 1 \text{ atm} \times \left(\frac{1}{0.25}\right)^{7/5} = 7 \text{ atm}.$$

Now, using the ideal gas law, we can find the final temperature,

$$T_2 = \frac{P_2 V_2}{nR}$$

$$\begin{aligned} T_1 &= \frac{P_1 V_1}{nR} \\ \therefore T_2 &= T_1 \cdot \frac{P_2 V_2}{P_1 V_1} \\ &= 300 \text{ K} \cdot \frac{7 \text{ atm} \cdot 0.25 \ell}{1 \text{ atm} \cdot 1.0 \ell} \\ &= 525 \text{ K}. \end{aligned}$$