Problem 1 (Warmup)

Suppose gaseous H_2 (hydrogen) is heated so that the temperature is increased by ΔT. What is the change in the internal energy? What if instead of gaseous hydrogen it were gaseous helium (He)? Assume vibrational degrees of freedom are frozen out.

Solution

The key idea is that the equipartition theorem tells us that the internal energy of a gas U is proportional to its temperature T. The proportionality constant depneds on the number of degrees of freedom. Let's first understand what degrees of freedom are. A gas molecule can translate, rotate, or vibrate. Translation means "how many components does the velocity have"? If the gas is in 3D (which it generally is), then it can have 3 components (v_x, v_y, v_z). If it were confined to a 2D plane, it would only have 2. This translation can be thought of as the translation of the center of mass. But we can additional have rotation about the center. For H_2, a linear molecule, we have 2 independent axes of angular rotation. Finally, although vibrational degrees of freedom are frozen out, meaning we should not count them, let's go ahead and discuss it anyway. Vibrational degrees of freedom correspond to displacements along the bonds of a molecule. If we view each bond as a spring, then it is the stretching and compressing of that spring. Now, let's write out the total energy of this molecule:

$$E = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2 + \frac{1}{2}I_x\omega_x^2 + \frac{1}{2}I_y\omega_y^2 + \frac{1}{2}k(\Delta x)^2 \tag{1}$$

where the last term denotes the spring constant and displacement of the bond. Note that each term is quadratic. The equipartition theorem tells us that for every such term, we should add $(1/2)k_BT$ per molecule to the internal energy U. Of course, now we account for the fact that vibrational degrees of freedom are frozen out, so we do not count this one. This leaves us with 5 terms. So

$$\frac{U}{N} = \frac{5}{2}k_BT \tag{2}$$

So the change in internal energy per molecule $(\Delta U/N)$ is

$$\frac{\Delta U}{N} = \frac{5}{2}k_B\Delta T \tag{3}$$

Now, if this gas had been helium, there would be no rotational degrees of freedom, nor vibrational ones. So there would only be three degrees of freedom and we would have

$$\frac{\Delta U}{N} = \frac{3}{2}k_B\Delta T \tag{4}$$

Problem 2 (Isochoric Heating)

Suppose heat Q is added isochorically to N molecules of gaseous H_2. Again, assume vibrational degrees of freedom are frozen out.

1. How much work is done during this process?
2. What is the change in internal energy?
3. What is the change in temperature?
4. What is C_V, the heat capacity at constant volume, for this gas?

Solution

1. "Isochoric" means constant volume. Since work is equal to force × displacement or equivalently

$$W = \int P dV \tag{5}$$

we can see that there can be no work done during this process since there is no change in volume. $\boxed{W = 0}$
2. Since $W = 0$ and $\Delta U = Q - W$, we must have $\boxed{\Delta U = Q}$. That is, the change in internal energy comes solely from the heat added. 3. The key idea is that now that we know ΔU, we can use the fact that internal energy is proportional to temperature. If we know one, we know the other. The proportionality constant was found in the previous problem:

$$U = \frac{5}{2} N k_B T \tag{6}$$

So

$$\Delta U = \frac{5}{2} N k_B \Delta T \tag{7}$$

So

$$\boxed{\Delta T = \frac{2}{5} \frac{Q}{N k_B}} \tag{8}$$

4. The key idea here is that in an isochoric process, the heat added and the resulting change in temperature are related by the constant C_V through

$$Q = N C_V \Delta T \tag{9}$$

In this problem, we were given Q and we know ΔT now. So we are left only with solving for C_V:

$$C_V = \frac{Q}{N \Delta T} = \frac{Q}{N \frac{2}{5} \frac{Q}{N k_B}} = \boxed{\frac{5}{2} k_B} \tag{10}$$

Note

This essentially derives a formula you may have seen in lecture:

$$C_V = \frac{\text{\# of degrees of freedom}}{2} k_B \tag{11}$$

Problem 3 (Isobaric expansion)

Suppose heat Q is added isobarically to N molecules of gaseous H_2. Again, assume vibrational degrees of freedom are frozen out.

1. What are C_V and C_P? Why is C_P higher than C_V?
2. What is the change in temperature?
3. What is the change in internal energy?
4. How much work is done by the gas during this process?

Solution

1. "Isobaric" means constant pressure. The change in temperature during such a process is related to the heat added through the proportionality constant C_P. From lecture you know that

$$C_P = C_V + k_B \tag{12}$$

For us, $C_V = 5/2k_B$, so $\boxed{C_P = 7/2k_B}$. Clearly C_P is always larger than C_V. In this process, the pressure is constant but the volume may change. This means that generally, some amount of work is done by the gas. But since the change in temperature is proportional to the change in internal energy, and the change in internal energy is $Q - W$, that means that to raise the temperature of the gas by a certain amount, it will take more heat to do it isobarically than to do it isochorically because when it is done isobarically, some nonzero amount of work will take energy out of the system at the same time as the heat is added. Therefore more heat is needed and $C_P > C_V$. 2. For an isobaric process,

$$Q = NC_P\Delta T \tag{13}$$

So

$$\Delta T = \frac{Q}{NC_P} = \frac{Q}{N\frac{7}{2}k_B} = \boxed{\frac{2}{7}\frac{Q}{Nk_B}} \tag{14}$$

3. Remember again, internal energy is proportional to temperature, so their changes are proportional too. Whenever we know one, we typically know the other.

$$\Delta U = \frac{5}{2}Nk_B\Delta T = \frac{5}{2}Nk_B\frac{2}{7}\frac{Q}{Nk_B} = \boxed{\frac{5}{7}Q} \tag{15}$$

This shows exactly what we explained above: not all of the Q gets stored in the gas, only 5/7ths of it does. Where does the other 2/7ths go? It must be lost as work. Let's check that now. 4. Since

$$\Delta U = Q - W \tag{16}$$

we have

$$W = Q - \Delta U = Q - \frac{5}{7}Q = \boxed{\frac{2}{7}Q} \tag{17}$$

Problem 4 (Thermodynamic Cycle 1)

A cyclic thermodynamic process is one in which the system ends up in the same state as it started. We often draw these as a PV diagram composed of individual subprocesses. Here we have a rectangular cycle composed of 4 processes. Suppose N molecules of an ideal gas begin at pressure P_0 and temperature T_0.

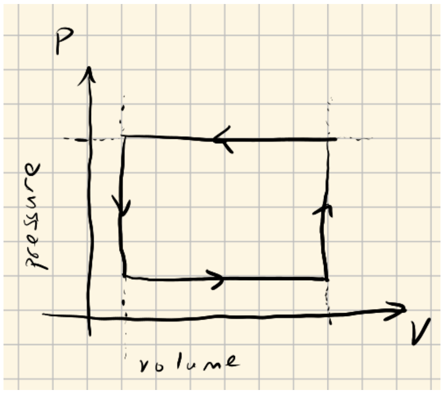

Figure 2: Process (a) is bottom leg. Process (b) is right-most leg. Process (c) is top leg. Process (d) is left-most leg.

The gas undergoes the following cycle depicted above.

1. Process a: isobaric expansion to volume V_1
2. Process b: isochoric heating to temperature T_1
3. Process c: isobaric compression to the initial volume
4. Process d: isochoric cooling to the initial temperature

What is the work done during each of the four processes?

Solution

First, it is a good idea to label all of the vertices of the process in the PV diagram with the known quantities at each point. This gives us a sense of what variables we do know an which ones we would need to solve for:

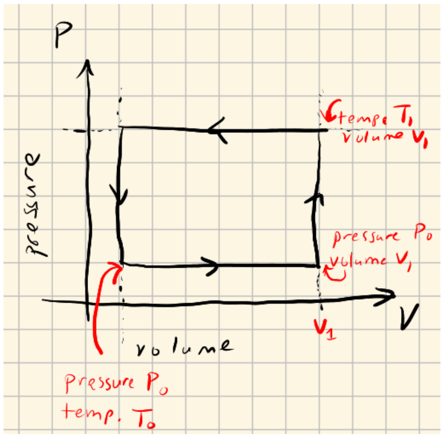

Figure 3: Process (a) is bottom leg. Process (b) is right-most leg. Process (c) is top leg. Process (d) is left-most leg.

Next, we can deal with all of the isochoric processes. Since the change in volume is zero in any isochoric processes, $\boxed{W = 0}$ for processes b and d.
Now, let us compute the work done in process a. In process a, the pressure is constant, P_0. However, the inital volume is not given. But the initial pressure and temperature are given, so we can use the ideal gas law to solve for it:

$$V_f = V_1 \tag{18}$$

$$V_i = \frac{Nk_BT_0}{P_0} \tag{19}$$

Now

$$W = \int PdV = P_0 \int dV = P_0 \left(V_1 - \frac{Nk_BT_0}{P_0} \right) = \boxed{P_0V_1 - Nk_BT_0} \tag{20}$$

Next, let us compute the work done in process c. In process c, the pressure is constant but it is unknown. However, we know the volume (V_1) and temperature (T_1) at the initial point, so we can use the ideal gas law to determine the pressure. I will denote this pressure P_1. Note that the final volume of this process is the volume of the gas at the beginning which we found above.

$$P_1 = \frac{Nk_BT_1}{V_1} \tag{21}$$

$$W = \int PdV = P_1 \left(\frac{Nk_BT_0}{P_0} - V_1 \right) = \boxed{\frac{Nk_BT_1}{V_1} \left(\frac{Nk_BT_0}{P_0} - V_1 \right)} \tag{22}$$

Tips

1. For most thermodynamic quantities, there are usually at least two ways of computing them. Whenever you need to find such a quantity, you should ask yourself what ways you could go about it. Usually

one of them is simpler and allows you to use the information you already have at hand. For example, you might have $\Delta U = (5/2)k_B\Delta T$ but also $\Delta U = Q - W$. Which one should you use? Depends on what variables you already know. You might have $W = \int PdV$ but also $\Delta U = Q - W$. Which one should you use? Depends on what variables you already know.

2. When you come across a thermodynamic cycle, first draw it in the PV plane. Then note down what quantities are given for each vertex of the cycle. Use that to determine what quantities need to be filled in (e.g. by using ideal gas law) to calculate everything else (e.g. work, heat, change in temperature, change in internal energy).