The First Law of Thermodynamics

This is simply energy conservation. Joule was the first to demonstrate the conversion of mechanical work into heat. His apparatus is shown in figure 19-2 of Tipler.

It is customary to write W for the work done by the system on its surroundings, for example if a gas expands against a piston. The heat Q is taken positive when it is put into the system. Using these conventions and denoting the internal energy of the system by U, the first law of thermodynamics reads

$$Q = \triangle U + W \ .$$

The Internal Energy of an Ideal Gas

We have already seen that the kinetic energy K of the molecules of an ideal gas is related to the absolute temperature T by $K = 3\,n\,R\,T/2$, where n is the number of moles of a gas and R is the universal gas constant. If the internal energy of a gas is just the translational kinetic energy, then

$$U = K = \frac{3}{2}\,n\,R\,T\ .$$

If the molecules have other types of energy in addition to the translational energy, such as rotation, the internal energy will be larger, adding $n\,R\,T/2$ for every additional degree of freedom according to the equipartition theorem. Again, the internal energy depends only on the temperature, and not on the volume or the pressure:

$$U = U(T) \quad \text{for the ideal gas.}$$

Joule verified this by finding no temperature decrease in the free expansion experiment of figure 19-5 of Tipler. Precision measurements show a small temperature decrease due to slightly non-ideal behavior of real gases.

Work and the PV Diagram for a Gas

In many types of engines work is done by a gas expanding against a movable piston. Examples are steam and gasoline engines.

Quasi-static Processes:

Figure 19-6 of Tipler shows an ideal gas confined in a container with a tightly fitting piston, assumed to be frictionless. We move the piston slowly in small steps, so that equilibrium holds after each step. Such a process is called quasi-static. Let A be the area of the piston. If the piston moves a small distance x, the work done by the gas on the piston is

$$dW = F\,dx = P\,A\,dx = P\,dV$$

where $dV = A\,dx$ is the increase in the volume of the gas.

PV Diagrams:

We can represent the states of a gas on a diagram P versus V. Figure 19-7 of Tipler shows shows a PV diagram with a horizontal line representing states which all have the same value of P. Such a process is called an isobaric expansion. The work done by the gas is equal to the area under the P versus V curve:

$$W = \int P \, dV \ .$$

Figure 19-8 of Tipler shows three different paths on a PV diagram for a gas that is initially in the state (P_1, V_1, T) and finally in the state (P_2, V_2, T). As the initial and final temperatures agree $P_1 \, V_1 = P_2 \, V_2 = n \, R \, T$ holds.

Figure 19-a: The gas is heated at constant pressure and then cooled at constant volume. The work done is $P_1 \, (V_2 - V_1)$.

Figure 19-b: The gas is cooled at constant volume and then heated at constant pressure. The work done is $P_2 \, (V_2 - V_1)$. Clearly,

$$P_2 \, (V_2 - V_1) \ < \ P_1 \, (V_2 - V_1) \ .$$

Figure 19-c: Path C represents an isothermal expansion, meaning that the temperature remains constant. We calculate the work done using $P = n\,R\,T/V$:

$$dW_{\mathrm{isothermal}} = P\,dV = \frac{n\,R\,T}{V}\,dV \ ,$$

$$W_{\mathrm{isothermal}} = n\,R\,T \int_{V_1}^{V_2} \frac{dV}{V} = n\,R\,T\,\ln\left(\frac{V_1}{V_2}\right) \ .$$

We see that the amount of work done by the gas is different for each process illustrated.

Since $U_2 = U_1$ for these states, the net amount of heat added must also be different for each of the processes.

This illustrates that the work done and the heat added depend on how the system moves from one state to another, whereas the change in the internal energy does not.

Heat Capacities of Gases

The heat capacity at constant pressure C_P is greater than the heat capacity at constant volume C_V, because when heat is added at constant pressure, the substance expands and work.

When heat is added to a gas at constant volume, we have

$$Q_V = C_V \, \Delta T = \Delta U + W = \Delta U$$

because no work is done. Therefore,

$$dU = C_V \, dT \quad \text{and} \quad C_V = \frac{dU}{dT} \; .$$

When heat is added at constant pressure, we have

$$Q_P = C_P \, \Delta T = \Delta U + W = \Delta U + P \, \Delta V \; .$$

For infinitesimal changes this becomes

$$C_P \, dT = dU + P \, dV = C_V \, dT + P \, dV \; .$$

From the ideal gas law, $P\,V = n\,R\,T$, we get for constant pressure

$$d(P\,V) = P \, dV + V \, dP = P \, dV = n \, R \, dT \; .$$

Substituting this in the previous equation gives

$$C_p\,dT = C_V\,dT + n\,R\,dT\ .$$

Dividing dT out, we get

$$C_P = C_V + n\,R\ .$$

For an ideal gas, the heat capacity at constant pressure is greater than that at constant volume by the amount $n\,R$.

For an ideal monatomic gas the internal energy consists of translational energy only,

$$U = \frac{3}{2}\,n\,R\,T\ .$$

The heat capacities are then

$$C_V = \frac{dU}{dT} = \frac{3}{2}\,n\,R$$

and

$$C_P = C_V + n\,R = \frac{5}{2}\,n\,R\ .$$

Heat Capacities and the Equipartition Theorem:

Table 19-3 of Tipler collects the heat capacities of various gases. Some agree well with the predictions for monatomic gases, but for others the heat capacities are greater than predicted. The reason is that such molecules can have other types of energy.

From the table we see that nitrogen, oxygen, hydrogen, and carbon monoxide all have molar heat capacities at constant volume close to

$$c' = \frac{5}{2} R \; .$$

Thus, these molecules appear to have five degrees of freedom. About 1880, Clausius proposed that these gases consist of diatomic molecules, which can rotate about two axes, see figure 19-11 of Tipler. The kinetic energy of the molecule is then

$$K = \frac{1}{2} m \, v_x^2 + \frac{1}{2} m \, v_y^2 + \frac{1}{2} m \, v_z^2 + \frac{1}{2} I_{x'} \, \omega_{x'}^2 + \frac{1}{2} I_{y'} \, \omega_{y'}^2 \; .$$

According to the equipartition theorem

$$U = 5 \times \left(\frac{1}{2} n \, R \, T \right) = \frac{5}{2} n \, R \, T \;\Rightarrow\; C_V = \frac{5}{2} n \, R \; .$$

Quantum Effects:

Apparently, a diatomic gas does not rotate about the axis joining the two atoms and monatomic gases do not rotate at all. These effects are explained by modern physics. Quantum mechanics confines the rotational levels to discrete energy values (Figure 7-16 of Tipler shows the discrete energy levels for a quantized oscillator, which is a similar case). If

$$\triangle E \gg kT$$

holds, where $\triangle E$ is the typical difference between quantum energy levels, thermal fluctuations cannot excite them and the equipartition theorem fails. The equipartition theorem holds only for

$$kT \gg \triangle E \ .$$

There are huge differences of $\triangle E$ for the rotations of molecules. They are related to similar difference between the diameter of a single atom and the distance between two atoms in a molecule.

Heat Capacities of Solids

The metals listed in Table 19-1 of Tipler have approximately equal molar specific heats of about

$$c' = 3\,R = 24.9\,\mathrm{J/mol\cdot K}\ .$$

This results is known as the Dulong-Petit law, which can be understood by applying the equipartition theorem to a simple model for a solid. According to this model, a solid consists of a regular array of atoms which are connected by harmonic forces to their neighbors, see figure 19-12 of Tipler.

Each atom can vibrate in the x, y, and z direction. Thus, the total energy of an atom in the solid is

$$E = \frac{1}{2}\,m\,(v_x^2 + v_y^2 + v_z^2) + \frac{1}{2}\,k_{\mathrm{eff}}\,(x^2 + y^2 + z^2)$$

where k_{eff} is the effective force constant of the oscillators. Each atom thus has six degrees of freedom and the equipartition theorem states

$$U = 6 \times \frac{1}{2}\,n\,R\,T \ \Rightarrow\ c' = 3R\ .$$