Lecture 2.6
The specific heats of an ideal gas

Today we shall continue our discussion of ideal gas. Last time we talked about molecular speed and found how it is related to temperature and gas’ energy. We concluded that monatomic ideal gas, which consists of individual atoms rather than molecules, such as He, Ne, Ar, has the internal energy of

$$E = \frac{3}{2} n k T = \frac{3}{2} n N_A k T = \frac{3}{2} n R T.$$  \hfill (2.6.1)

Thus, the internal energy of monatomic ideal gas is function of temperature only. It does not depend on any other variable. This statement is true not just for monatomic but for any ideal gas, even though we shall see later that coefficient in the equation 2.6.1 may vary.

When we were talking about specific heats of different substances, we noticed that in the case of gases, specific heat depends on external conditions. It is different if the process of heating (cooling) occurs at constant volume or at constant pressure.

Let us start from the case of the constant volume. So that, $n$ moles of monatomic ideal gas are placed in the cylindrical container with insulated walls. One can control the temperature of the bottom part of the container. The initial state of this gas is at pressure $p$, volume $V$, and temperature $T$. Then we slowly (to keep it in equilibrium) heat this gas by increasing the temperature of the bottom part of the cylinder to $T + \Delta T$. At the same time we keep the piston in its original position, so the gas’ volume is not changing, but its pressure changes to $p + \Delta p$. The amount of heat transferred to the gas in such an experiment is

$$Q = n C_V \Delta T,$$

where $C_V$ is the molar specific heat at constant volume. Now let us use the first law of thermodynamics, with account of $W = 0$ at constant volume, which gives us

$$\Delta E = Q - W,$$
$$\Delta E = Q,$$
$$\Delta E = n C_V \Delta T,$$

(2.6.2)

$$C_V = \frac{\Delta E}{n \Delta T} = \frac{\frac{3}{2} n R \Delta T}{n \Delta T} = \frac{3}{2} R = 12.5 \frac{J}{mol \cdot K}.$$
So, any monatomic ideal gas has this value for its molar specific heat at constant volume, which is in agreement with experiment.

The equation for internal energy of any ideal gas (not necessarily monatomic) has the form (if the right value of the specific heat is used)

\[ E = nC_v T. \]  

(2.6.3)

It only depends on temperature but not on any other property of gas.

Let us now consider a process in which pressure is held constant. We can do it using the same cylinder, but now we have to let the piston go in such a way that pressure of the gas stays unchanged, while its volume changes from \( V \) to \( V + \Delta V \). In such a process the heat transferred to the gas has the form of

\[ Q = nC_p \Delta T, \]

where \( C_p \) is the molar specific heat at constant pressure. To calculate this specific heat we shall use the first law of thermodynamics, with account of \( W = p\Delta V \) in the case of the constant pressure, so this law takes the form

\[
\begin{align*}
\Delta E &= Q - W, \\
nC_v \Delta T &= nC_p \Delta T - p\Delta V, \\
nC_p \Delta T &= nC_v \Delta T + nR\Delta T, \\
C_p &= C_v + R.
\end{align*}
\]

(2.6.4)

This theoretical prediction also agrees with experiment and it is valid not only for monatomic but for any ideal gas.

Let us now see how one has to change the equations if the gas in not monatomic but consists of more complicated molecules. The main difference between monatomic particle-like molecule and other molecules is that the more complicated molecules can participate not only in translational but also in rotational and even oscillatory types of motion. To account for these different types of motion we shall use the theorem, known as the equipartition of energy theorem. Every kind of molecule has a certain number of degrees of freedom, which are independent ways in which the molecule can store energy. Each such degree of freedom has associated with an average energy of \( \frac{kT}{2} \) per molecule.

In the case of monatomic molecule, it only has three degrees of freedom, one for each of the three possible directions of translational motion in three-dimensional space. The
average kinetic energy of this molecule is $3kT/2$, which we have already proved. Polyatomic molecules have finite size and shape. They can not be treated as particle-like objects, since they can also rotate and have components of angular velocity in all three directions in space. This means that they have additional three degrees of freedom and the energy associated with them $3kT/2$. If we consider diatomic molecule it does not have any distribution of mass relative to the axis that connects the two of its atoms, so it can not rotate around this axis and has only two rotational degrees of freedom and the average energy of rotation is $kT$. Therefore, the internal energy of any ideal gas can be calculated as

$$E = \frac{f}{2} NkT = \frac{f}{2} nRT,$$

where $f$ is the number of degrees of freedom. The molar specific heat at constant volume has the form

$$C_v = \frac{f}{2} R = f 4.16 \frac{J}{mol \cdot K}.$$  

(2.6.5)

(2.6.6)

The quantum theory shows that at certain high temperatures, we shall also take into account the possibility for molecules to oscillate, which brings the maximum possible number of degrees of freedom to even larger number.

Let us now consider an example of one more process in which ideal gas can participate. This is an adiabatic process for which $Q = 0$. This means that we either have to have a completely thermoinsulated system (all the walls and the bottom of the container are insulators) or the process occurs so fast, that there is no time for heat exchange. The later is true for motion of sound waves in gases, which is essentially adiabatic process.

We shall consider an ideal gas in completely insulated cylinder, which now changes both its volume and its pressure. We shall use the first law of thermodynamics for this process, but we will apply it its differential form with account of $Q = 0$ and $\delta W = pdV$, so we have

$$dE = Q - pdV,$$

$$nC_v dT = -pdV.$$  

Now let us use the ideal gas law, which gives
\[ pV = nRT, \]
\[ d(pV) = nRdT, \]
\[ Vdp + pdV = nRdT, \]
\[ ndT = \frac{Vdp + pdV}{R} = \frac{Vdp + pdV}{C_p - C_v}, \]

so we have
\[ C_v \frac{Vdp + pdV}{C_p - C_v} = -pdV, \]
\[ \left( \frac{C_v}{C_p - C_v} + 1 \right)pdV + \frac{C_v}{C_p - C_v}Vdp = 0, \]
\[ \frac{C_p}{C_v} \frac{dV}{V} + \frac{dp}{p} = 0, \quad (2.6.7) \]
\[ \gamma \ln V + \ln p = const, \]
\[ pV^\gamma = const, \]

where \( \gamma = \frac{C_p}{C_v} \). The last equation shows the relation between the pressure and the volume for ideal gas during the adiabatic process. This equation can be rewritten in terms of temperature, taking into account the ideal gas law, so we have
\[ \left( \frac{nRT}{V} \right)^\gamma = const, \quad (2.6.8) \]
\[ TV^{\gamma-1} = const. \]

We have already discussed the free expansion of gas which is also an example of the adiabatic process. In that case no work is done on the gas of by the gas and no change in the gas internal energy takes place. Last two equations do not work in such a case. Since free expansion it is non-equilibrium process, we can not even represent it on \((p,V)\) coordinate plane except for the original and the final state. We can only say that for these original and final states the temperature is the same (since internal energy is the same), so
\[ T_1 = T_2, \]
\[ p_1V_1 = p_2V_2. \]