

Lecture 28 : Energy in thermal processes II

We have introduced the idea of internal energy which is the sum of the kinetic energies of the particles in the system plus the potential energy of the particles in the system. Heat is also energy, but it is the energy transferred from one body to another due to a temperature difference. From mechanics we know that we can also change the energy of a system by doing work on it. Now we are going to put together these concepts, ie internal energy U , heat Q and work W . But first we need to understand work more precisely.

Work in thermal systems

In mechanics, we know that if the force is a constant, then the work done by the force is $\vec{F} \cdot \Delta\vec{x}$. Now consider compressing a gas using a piston which applies a constant pressure. If the area of the piston is A , and the piston moves a distance Δx , then the work done by the piston is,

$$\text{Work}(\text{constant pressure}) = \vec{F} \cdot \Delta\vec{x} = -PA\Delta x = -P\Delta V \quad (1)$$

Notice that by Newton's third law, the pressure of the gas P is in the opposite direction to the applied force, so we introduce a minus sign when we introduce the gas pressure, P , which acts against the applied force of the piston. Notice that we are assuming that none of the work goes into accelerating the piston, so that the compression of the gas must be done slowly. In this example positive work is done on the gas by the piston. If we instead allow the gas to expand by reducing the pressure of the piston, then work is done on the piston by the gas.

In general, the work done is the area under the graph of pressure versus volume. During expansion (increasing volume) the gas does positive work, while during compression, the gas does negative work. Refrigerators, air conditioners ... use thermodynamics cycles to carry out their functions and understanding the work done by the gas and on the gas in these cycles is essential to their engineering.

The first law of thermodynamics (energy conservation)

First law of thermodynamics: Consider a gas which goes from an initial state i to a final state f . During this transition, an amount of heat Q is added to the system(gas), and an amount of work W is done on the gas,

then the change in internal energy of the gas is given by,

$$\Delta U = U_f - U_i = Q + W \quad (2)$$

In calorimetry we already noted that the specific heat is the heat required to raise the temperature of a piece of material in units of Joules/Kelvin kg. However with gases, work may also be done on the gas or by the gas, so we need to define more than one specific heat. Actually this is also true of liquids and solids, but there the effect is really small because the work done is small, so we ignored it. In gases the specific heat depends on the boundary conditions and traditionally we consider two specific heats, constant volume and constant pressure. Also in gases we usually give the specific heat per Joules/Kelvin mole, and it is therefore called the molar specific heat.

Thermodynamic processes and specific heat

Many of the cycles which are used in engineering, e.g. engines and refrigerators, use paths where one thermodynamic variable is fixed. Four that are important are those at constant volume, constant pressure, constant heat and at constant temperature. The first three are the most important for engineering. In each of these cases, we need to understand the amount of heat required for the process and the amount of work done during the process.

Another thing which we want to understand is the specific heat. We have already looked at the specific heat and we wrote $Q = mC\Delta T$. However in gases, the value of C depends on the thermodynamic variable which is kept constant. If nothing is explicitly specified, we can assume that the volume is kept constant as this is the most common one. For example the value quoted for steam in table 11.1 can be assumed to apply to the case of constant volume. For solids and liquids that are incompressible, the volume is fixed. Real solids and liquids deform a little bit, but not enough to change C significantly, at least for the purposes of this course. We shall calculate the specific heat of ideal gases and constant volume and at constant pressure and demonstrate their differences. Note that in gases it is conventional to use the molar specific heat, $Q/n\Delta T$ instead of the specific heat per unit mass $Q/m\Delta T$ which we used for solids and liquids.

Processes at constant volume (isovolumetric processes)

At constant volume there is no change in volume during the process, so

no work is done so we have,

$$W = P\Delta V = 0 \quad \textit{isovolumetric process} \quad (3)$$

Therefore from the first Law of thermodynamics, Eq. (2), we have $\Delta U = Q$. The rate at which the internal energy changes with temperature is then,

$$\frac{\Delta U}{\Delta T} = \frac{Q}{\Delta T} \quad \textit{(isovolumetric process)} \quad (4)$$

For an ideal gas we have,

$$U = \frac{1}{2}m\overline{v^2} = \frac{3}{2}Nk_B T = \frac{3}{2}nRT \quad (5)$$

which implies that

$$\Delta U = \frac{3}{2}nR\Delta T \quad (6)$$

so that,

$$\frac{\Delta U}{\Delta T} = \frac{3}{2}nR \quad \textit{(ideal gas)} \quad (7)$$

The molar specific heat, C_v , is the specific heat per mole and is hence found by setting $Q/n\Delta T$ so that $C_v = 3R/2$ for an ideal gas. We may then write,

$$\Delta U = nC_v\Delta T \quad (8)$$

This equation is strictly only true for an ideal gas.

Processes at constant pressure (isobaric processes)

At constant pressure

$$W = -P\Delta V \quad (9)$$

so the relation between the change in internal energy, work and heat is,

$$\Delta U = Q - P\Delta V. \quad (10)$$

For an ideal gas, we know that,

$$\Delta U = nC_v\Delta T = Q - P\Delta V. \quad (11)$$

The molar specific heat is then

$$\frac{Q}{n\Delta T} = \frac{1}{n}[\Delta U + P\Delta V] \quad (12)$$

For an ideal gas, we use $\Delta U = nC_v\Delta T$ and $P\Delta V = nR\Delta T$, and find,

$$C_p = C_v + R = 5R/2 \quad (13)$$

which shows that the specific heat at constant pressure is larger than the specific heat at constant volume (Why??).

Processes at constant temperature (isothermal processes)

In an isothermal process, the internal energy of an ideal gas does not change, so we have,

$$Q = -W \quad (\text{isothermal process}) \quad (14)$$

The pressure and volume are related by,

$$P = \frac{nRT}{V} \quad (15)$$

from which we can find the work

$$W = nRT \ln(V_f/V_i) \quad (16)$$

We will learn more about this process in later lectures.

Processes where no heat is transferred (Adiabatic processes)

In an adiabatic process, $Q = 0$, so we have

$$\Delta U = W \quad (17)$$

Furthermore, it can be shown that,

$$PV^\gamma = \text{constant} \quad (18)$$

where $\gamma = C_p/C_v$ is called the adiabatic index of the gas. We will learn more about this process in later lectures.