Thermodynamics
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Lecture 20
First law of thermodynamics

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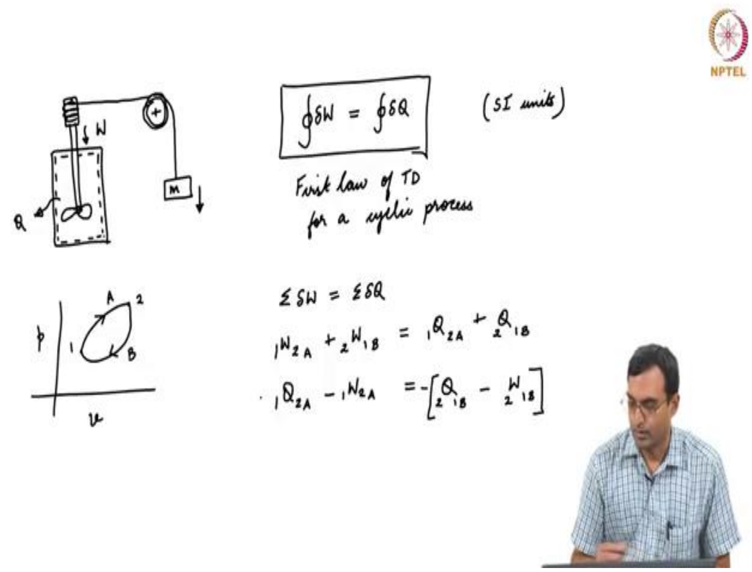

Figure 1.

Let's look at the first law of thermodynamics which is also known as the law of conservation of energy. Before formally stating the first law, we should look at the experiments Joule did because these experiments lead to terms involved in the first law of thermodynamics.

Joule had a mechanism as shown in top left corner of Fig. 1. It consisted of a rigid chamber filled with say water with paddle wheel inside it. The paddle wheel was connected to a mass by a string which went over a pulley as shown. As the mass falls down through height h, the paddle wheel rotates and churns water. Here, the rigid chamber is the system. As the mass lowers and the paddle wheel rotates, work is done on the system. We can calculate this work. We call small amount of work as δW.

Let's do an experiment. Let the mass fall down through some height h. This movement of the mass rotates the paddle wheel, and the water is churned. Because of this churning, the temperature of the water increases. Now, let the water dissipate this extra gained heat through the walls of the system and return to its initial state (which is the state which it had before the mass was lowered). So, after the process, the system returns to the same original state. Hence, it is a cyclic process. The work done in lowering the mass (which is also the work done on the system) and heat dissipated by the water through the walls of the rigid chamber to return to its initial state can be measured. Joule did a similar experiment and found that the work done and heat dissipated/transferred by the water were proportionate. Joule used different units for work and heat. However, when you use SI units for heat and work and take the cyclic integral of heat and work, they come out to be equal. Mathematically, $\oint \delta W = \oint \delta Q$. So in a cyclic process, the work transfer and heat transfer are equal. This is the first law of thermodynamics for a cyclic process. There is no proof of this law. However, there has not been a case where this law was proven wrong. What about a non-cyclic process?

Consider a system undergoing a process from some state 1 to 2 through path A and coming back to state 1 through path B. The system undergoes a cyclic process. According to first law for a cyclic process,

$$\oint \delta W = \oint \delta Q$$

We can split the work and heat transfers for a process 1 to 2 through path A and for a process 2 to 1 through path B as,

$${}_1W_{2A} + {}_2W_{1B} = {}_1Q_{2A} + {}_2Q_{1B} \quad .....(1)$$

$${}_1Q_{2A} - {}_1W_{2A} = -({}_2Q_{1B} - {}_2W_{1B})$$

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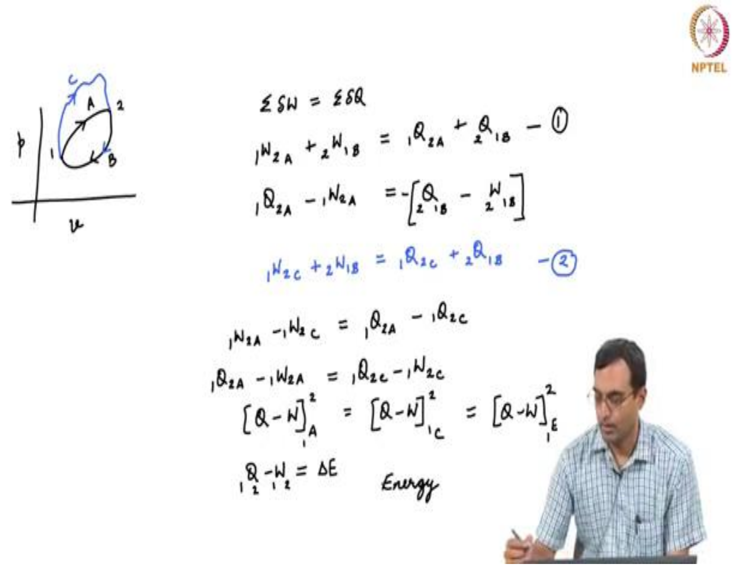

Figure 2.

Now, let the system go from 1 to 2 through other path C as shown Fig. 2 and come back through path B. Hence, according to the first law,

$$ {}_1W_{2C} + {}_2W_{1B} = {}_1Q_{2C} + {}_2Q_{1B} \;\ldots..(2) $$

Eq. (1) – Eq. (2) implies,

$$ {}_1W_{2A} - {}_1W_{2C} = {}_1Q_{2A} - {}_1Q_{2C} $$

$$ {}_1Q_{2A} - {}_1W_{2A} = {}_1Q_{2C} - {}_1W_{2C} $$

$$ [Q-W]^2_{1_A} = [Q-W]^2_{1_C} = [Q-W]^2_{1_B} $$

It shows that the difference between the heat transfer and the work done for a process is the same irrespective of the path taken to carry out the process though work and heat themselves are path functions. We know that the properties are state functions. Their values depend only on the end states. Here, the difference between the heat transfer and the work done during the process depends only on the end states and not on the path taken by the process. Hence, this difference must be representing some property. We call it energy. For a system undergoing a process, difference between heat transferred and work done is the difference in energy between the end states of that process.

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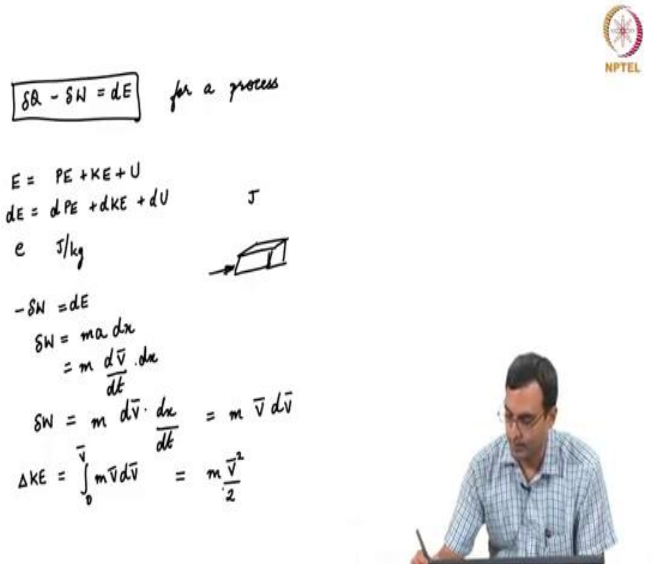

Figure 3.

In the differential form, we can write as,

$$\delta Q - \delta W = dE, \ldots ..(3)$$

where δQ and δW are small amounts of heat transferred and work done and dE represents small change in energy. Equation 3 is an expression for the first law of thermodynamics for a process (non-cyclic). From eq. 3, we can obtain the expression for the first law of thermodynamics for a cyclic process by taking cyclic integral and setting dE = 0 as E is a property and for a cyclic process change is property is 0, i.e. dE = 0.

Eq. 3 gives us the change in energy between two states when integrated over a process. It does not give the absolute value of energy. E in dE can be split into kinetic energy (KE), potential energy (PE) and internal energy (U) as,

$$dE = dKE + dPE + dU \ldots ..(4)$$

The object has kinetic energy by virtue of its motion (the object has velocity). The object has potential energy when it is lifted with respect to some reference/datum. There are other forms of energy which are lumped together in the form of U. We will discuss these forms later on. Hence, change in energy (dE) of a system undergoing a process equals change in kinetic energy (dKE), change in potential energy (dPE) and change in internal energy (dU).

Energy (E) is extensive property. It has the same units as work or heat. Specific energy (e) has units J/kg.

Consider an object (a system) at rest. Suppose it starts moving horizontally and attains velocity V. There is change in its kinetic energy. There is no change in its potential and internal energy. To move the object, work was done on it. Assume that there is no heat transfer involved. Then Eqs. 3 and 4 give, $-\delta W = dKE$. Work is force into displacement, i.e. mass into acceleration into displacement. $\delta W = max = m\frac{dV}{dt}x = mdV\frac{dx}{dt} = mVdV$. Hence, $-\delta W = -mVdV = dKE$. Integrating it from V=0 to V=V, $\Delta KE = -\int_0^V mVdV = -\frac{mV^2}{2}$. Here, work done on the object (system) is equal to the change in its kinetic energy.

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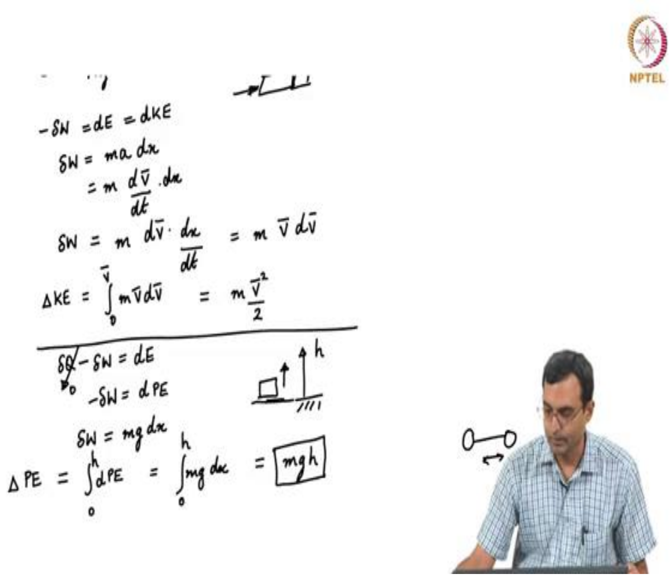

Figure 4.

Consider an object (a system) which is lifted through height h from some datum as shown in Fig. 4. In this process of lifting, there is only a change in potential energy. There is no heat transfer. There is no change in the temperature of the object. Eqs. 3 and 4 give $-\delta W = dPE$. So change in the potential energy of the object is negative of the work done on the object (the system). We are raising the object against gravity. Hence, the small amount of work done to raise the object through small height dh is $\delta W = mgdh$, where m is the mass of the object and g is the acceleration due to gravity. To get the total change in potential energy in the entire process of lifting the object through height h, we need to integrate as, $\Delta PE = \int_0^h dPE = -W = -\int_0^h mgdh = -mgh$. The work done is negative as it is being done on the system.

Let's discuss about internal energy. It is something which exists because of interaction between molecules. The molecules of a substance may have vibrational energy, translational energy or rotational energy. All these constitute internal energy for a substance. We will look at it in a more detail when we discuss the concept of ideal gas.

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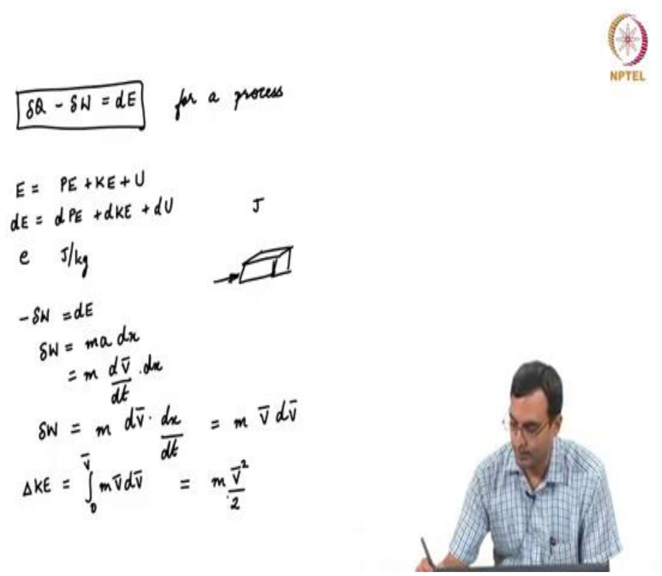

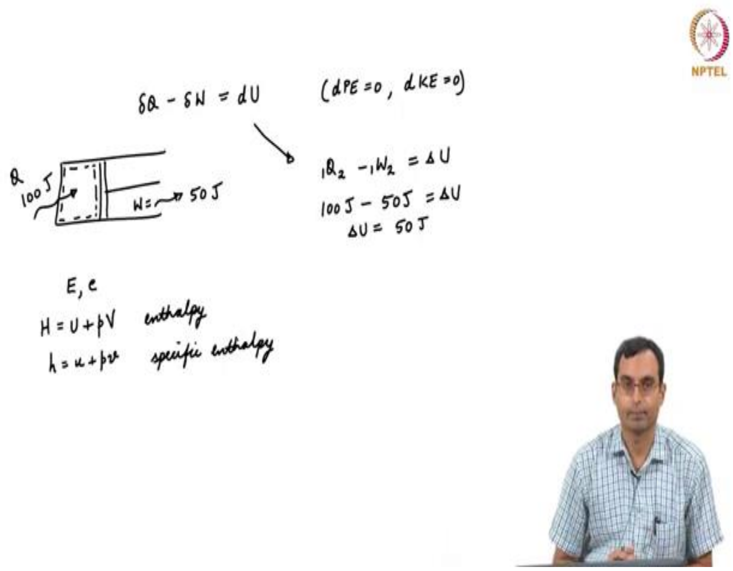

Figure 5.

When changes in kinetic and potential energy of a system undergoing a process are negligible and there are heat and work transfers, eqns. 3 and 4 give $\delta Q - \delta W = dU$. Consider a piston-cylinder arrangement as shown in Fig. 5. The system is the gas inside the cylinder as marked by the dashed line. Assume that there is heat transfer of 100 J to the system and the gas expands inside moving the piston and doing work of 50 J. According to first law for a process, $\delta Q - \delta W = dU$. After integration, ${}_1Q_2 - {}_1W_2 = \Delta U \rightarrow 100 - 50 = 50$. Hence, the internal energy of the system has increased over the process by 50 J. Here, the piton-cylinder system itself is at rest. Also, it is not being raised during the process. Hence, the changes in kinetic and potential energy are ignored. Thus, difference of heat transferred and work done is the difference between internal energy of the system between the end states. In the above example, signs of heat transferred and work done are taken according to the convention mentioned in previous lectures: heat entering the system is positive and work done by the system on the surroundings is positive.

In upcoming lectures, we will come across a combination of internal energy, pressure and volume a lot of times. This combination is also a property called as enthalpy (H) and H = U+pV. Specific enthalpy is the enthalpy per unit mass denoted as h=u+pv, where h is specific enthalpy, u is specific internal energy and v is specific volume.