Course Title

PHS 101 / PHYSICS

Presenter

THERMODYNAMICS

The area of physics concerned with the relationship between heat and work is THERMODYNAMICS. The main focus of it is the study of the motion of heat. We will begin the discussion of thermodynamics with concept of what is called an isolated system or simply a system. By definition the internal energy U of a system is the sum of all the potential and kinetic energy contained within that system. When heat (Q) is added to a system, ΔU is positive, and when heat (Q) is removed from a system, ΔU is negative. If no work is done on the system, change in internal energy (ΔU) equals the heat absorbed or released by the system i.e

$$U_2 - U_1 = \Delta U = Q_2 - Q_1 = \Delta Q$$

$$\Delta U = \Delta Q \ldots\ldots\ldots\ldots\ldots\ldots\ldots (xiii)$$

When an amount of heat Q is added to system, some of this added energy remains in the system increasing its internal energy by an amount ΔU while the rest of the added energy leaves the system as the system does work W. Thus first law can also be stated as

$$\Delta U = Q + W \ldots\ldots\ldots\ldots\ldots\ldots\ldots (xv)$$

Note: In thermodynamics, two specific regions are the main focus. There are (a) The System – which is the region of interest where we wish to know the state parameters such as pressure, temperature and volume.

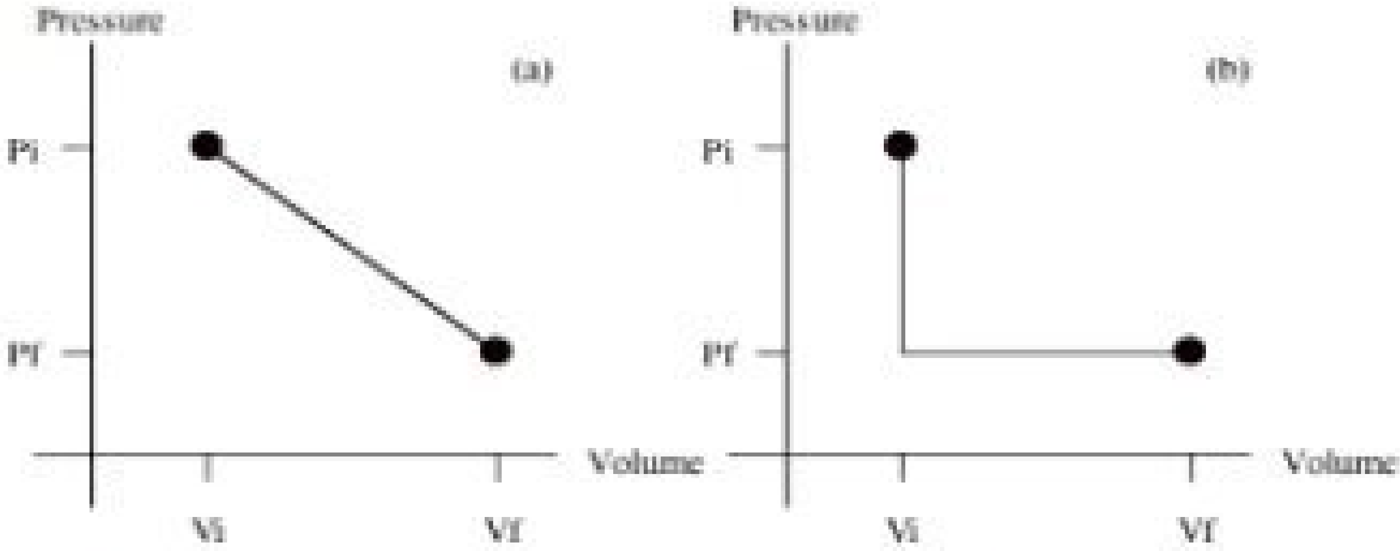
(b) The environment – which is the region that contains the system.

(c) The work done on the system (W) is the exact opposite of the work done on the environment i.e $W = - W_{env}$

(d) System that is completely isolated from the environment is called a closed system.

Work

Suppose a system starts from an initial state described by pressure, volume and temperature P_i, V_i and T_i respectively. The final state of the system is described by P_f, V_f and T_f. The transformation from the initial state to the final state can be achieved in a variety of ways (see Fig 3a)



A gas filled cylinder with a piston is the simplest form of a heat engine. If the pressure of a gas increases, it can move a piston (this happens in an engine). In this case, work is done by the system as the expanding gas lifts the piston. On the other hand, if we increase the weight of the piston, work will be done on the system as the piston falls. The force exerted by the gas on the piston is equal to PA where A is the area of the piston and P is the pressure. If the piston is displaced by a distance ds, the amount of work done is

$$dw = F.ds = (pA)ds = pdv[dw = -pdv]$$

The total work done during a finite displacement of the piston is calculated by

$$W = \int dW = \int_{v_i}^{v_f} p dV$$

If W is positive, work was done by the system (for example, the expanding gas lifts the piston). A negative value of W tells us that work was done on the system (the piston is pressed down to compress the gas). For a monoatomic ideal gas i.e the gas particles consists of a single atomic species, the internal energy of such gas is given by

$$U = \frac{3}{2} nRT \dots\dots\dots\dots\dots\dots (xvi)$$

The change in internal energy for such a gas (assuming no gas escapes or is brought into the system) is then given by

$$\Delta U = \frac{3}{2} n R\Delta T \dots\dots\dots\dots\dots\dots (xvii)$$

The molar specific heat at constant volume for monoatomic ideal gas is given by

$$C_v = \frac{3}{2} R$$

$\therefore$ equation (xvii) can be rewritten as

$$\Delta U = nC_v\Delta T \dots\dots\dots\dots (xviii)$$

There are four specific types of processes involving energy in thermodynamics.

A. <u>Isobaric Processes:</u> Here the pressure remains constant during the process. Under these conditions, the thermal energy $Q = \Delta U - W = \Delta U + P\Delta V$

$$Q = \Delta U + P\Delta V \ldots\ldots\ldots\ldots\ldots\ldots (xix)$$

For an ideal gas, $P\Delta V = nR\Delta T$

$$Q = \Delta U + P\Delta V = \frac{3}{2}nR\Delta T + nR\Delta T = \frac{5}{2}nR\Delta T \ldots\ldots\ldots\ldots\ldots\ldots (xx)$$

Note:

i. If the system does work on the environment, $W < O$ and $\Delta U < O$. This is because the system uses its internal energy to supply work to the outside environment.

ii. It the system requires work from the environment, $W > O$ and $\Delta U > O$. Here the environment supply work to the system and increases the system internal energy as a result

Click to add title

Adiabatic Processes: Heat does not enter or leave the system. A good example of an adiabatic process is anything that happens so rapidly that heat does not have time to flow in or out of the system during the process.

∴ for adiabatic process, $Q = 0$ and

$\Delta U = Q - W$ become $\Delta U = -W$ ……………………….(xxi)

Note:

i. If the system does work on the environment, $W > O$ and $\Delta U < O$. This is because the system uses its internal energy to supply work to the outside environment.

ii. It the system requires work from the environment, $W < O$ and $\Delta U > O$. Here the environment supply work to the system and increases the system internal energy as a result

Click to add title

<u>Isothermal Processes:</u> Here the temperature does not change during the process. In Isothermal processes, $\Delta U = O$ and $\Delta U = Q - W$ become $\boxed{W = Q}$ ……………..(xxii)

Work done on the environment by the system during an isothermal process is given by

$$W_{env} = nRT \ln\left(\frac{V_f}{V_i}\right) \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (xxiii)$$

While the work done on the system is just the negative of work done on the environment i.e $W_{env} = -nRT \ln\left(\frac{V_f}{V_i}\right) \dots\dots (xxiv)$

Click to add title

Isochoric Processes: Volume does not change during the process. Since volume does not change, no work can be done on the system.

I: $\Delta U = Q - W$ becomes $\Delta U = Q$ (isochoric process)……………………..(XXV)

i.e In an isochoric process, the change in internal energy of a system equals the energy transferred to the system by heat.

For an ideal gas, $\Delta U = \frac{3}{2} n\, RT$

For an isochoric process, $\Delta U = Q = n\, C_v \Delta T$

$$Q = n\, C_v \Delta T\ (isochoric\ process)$$

Enthalpy

This refers to heat energy associated with phase changes. Through the use of 1st law of thermodynamics, we can introduce a new state variable associated with phase changes.

Note that heat of transformation Q = ± mL. Usually, there is also a volume change when matter changes from one state to another. A volume change results in work either being performed on or by the system.

Therefore from $\Delta U = Q + W$

$$U_2 - U_1 = mL - P\Delta V$$

$$U_2 - U_1 = mL - P(V_2 - V_1)$$

Solving this equation for the latent heat term gives

$$mL = (U_2 + PV_2) - (U_1 + PV_1) = H_2 - H_1$$

$\therefore$ $mL = H_2 - H_1$ where H = u + PV is called the enthalphy of the system.

Note that enthalpy is another state variable which is a function of the 3 other state variables

(T, P and V)

Example 5

A movable piston having a mass of 8kg and a cross sectional area of $5cm^2$ traps 0.2mol of an ideal gas in a vertical cylinder. If the piston slides without friction in the cylinder. Calculate work done on the gas when its temperature is increased from 20^0C to 300^0C?

Solution

For an ideal gas, as temperature increases, the volume increases

$$\Delta V = V_f - V_i = \frac{nRT_f}{P_f} - \frac{nRT_i}{P_i}$$

If the pressure is held constant, then $P_i = P_f = P$

$$\Delta V = \frac{nR}{P}(T_f - T_i) = \frac{nR\Delta T}{P}$$

$$\Delta T = (300 + 273)k - (20 + 273)k = 280k$$

The work done on the gas is ∴ $W = -P\Delta V$

$$W = -nR(\Delta T) = -0.2mol \times 8.31J/mol.k \times 280k$$

$$W = -465J$$

Example 6

A thermodynamic system undergoes a process in which the internal energy decreases by 500J. If at the same time, 220J of work is done on the system, find the energy transferred to or from it by heat.

Solution

$$\Delta U = Q + W, \quad \text{here } \Delta U = -500J \quad W = -220$$

$$-500 = Q - 220 \qquad Q = (-500 + 220)J = -280J$$

$$Q = -280J$$

$\therefore$ Heat energy is transferred from the system

HEAT ENGINE

A heat engine is a kind of device that converts internal energy into some other forms of energy e.g electricity, mechanical energy e.t.c. Assuming a typical heat engine is represented by a cylinder with piston in it. The total work done by a heat engine is the heat flow into the cylinder.

Thus $W = |Q_H| - |Q_C|$

where $|Q_H|$ and $|Q_C|$ are the magnitude of heat that flowed into the system i.e engine and magnitude of heat that flowed out of the system respectively. The thermal efficiency e of any system is the ratio of the work done to the heat input.

Example 7

The energy absorbed by an engine is three times greater than the work it performs. Calculate (a) its thermal efficiency? (b) What fraction of energy absorbed is expelled by the cold reservoir?

Solution

(a) Using $e = \frac{W}{|Q_H|} = \frac{w}{3w} = \frac{1}{3} = 0.33\ or\ 33.3\%$

(b) $e = 1 - \frac{|Q_C|}{|Q_H|} \therefore \frac{|Q_C|}{|Q_H|} = 1 - e = 1 - \frac{1}{3} = \frac{2}{3} \therefore e = \frac{2}{3}$

Second Law of Thermodynamics

The first law of thermodynamics is concerned only with the conservation of energy. It says nothing about the direction towards which the processes proceed.

The second law of thermodynamics states that once energy is converted to heat, it is partially unavailable. Entropy describes the amount of energy that is unavailable when it is transformed. In a closed system, entropy is either constant or increases. Second law of thermodynamics also predict the movement of heat from hot objects (ordered) to cold objects (disordered). This means that entropy is a measure of disorder.

As defined above, Entropy is a measure of how much energy or heat is unavailable for conversion into work.

When a system at temperature T (in kelvin) undergoes a reversible processes by absorbing an amount of heat Q, its increases in entropy ΔS is given by

$$\Delta S = \frac{\Delta Q}{T} = \frac{Q}{T}$$

If Q > O, heat is absorbed by the system and entropy increases while if Q < O, heat is expelled by the system and entropy decreases.

For reversible process, Q = O and the entropy change is zero.

Note that $Q = T\Delta S$. This Q is the amount of energy that is no longer capable of conversion in useful work.

We can use the concept of "unavailable energy" versus "available energy" to develop a different form for the 1st law of Thermodynamics. If we define the total energy E of the system as the sum of its internal energy, the K.E and the P.E, E = U + K.E + P.E

We can also express the total energy E as

$$E = F + TS$$

Where TS represent the energy that is unavailable to be converted to work and F called the Helmholtz free energy is the energy available to be converted to work.

The first law can then be rewritten as

$$\Delta E = \Delta F + T\Delta S + S\Delta T$$

Example 8

A 70kg log falls from a height of 25m into a lake. If the log, the lake and the air are all at 300K.find the change of entropy of the universe for this process?

Solution

$$\Delta Q = \Delta(PE) = mg\Delta y = mgh = 70 \times 9.8 \times 25 = 1.715 \times 10^4 J$$

$$\therefore \Delta S = \frac{\Delta Q}{T} = \frac{1.715 \times 10^4}{300} = 57.2 J/K$$