

First Law of Thermodynamics



**Discipline Course-I
Semester-II**

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Lesson: First Law of Thermodynamics

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First Law of Thermodynamics

Learning Objectives

After reading the lesson, you should be able to

- 1) understand the basis of first law of thermodynamics.
- 2) develop the concept of specific heat of a gas, internal energy.
- 3) understand the phenomena of isothermal and adiabatic process.
- 4) develop the concept of compressibility and expansion coefficient
- 5) apply your knowledge to the practical life.



Chapter: Title First Law of Thermodynamics

1.1 Introduction

The first law of thermodynamics is an extension of the principle of conservation of mechanical energy. It gives us information that the net flow of energy across the boundary of a system is equal to the change in energy of the system. For the purpose of thermodynamics it is sufficient to consider only two types of energy flow across a boundary. First one is work done on or by the system. And the other is a flow of heat, either by conduction or radiation.

1.2 Formulation of the first law

Let us imagine that a closed system undergoes a process by which it passes from initial state X to state Y .

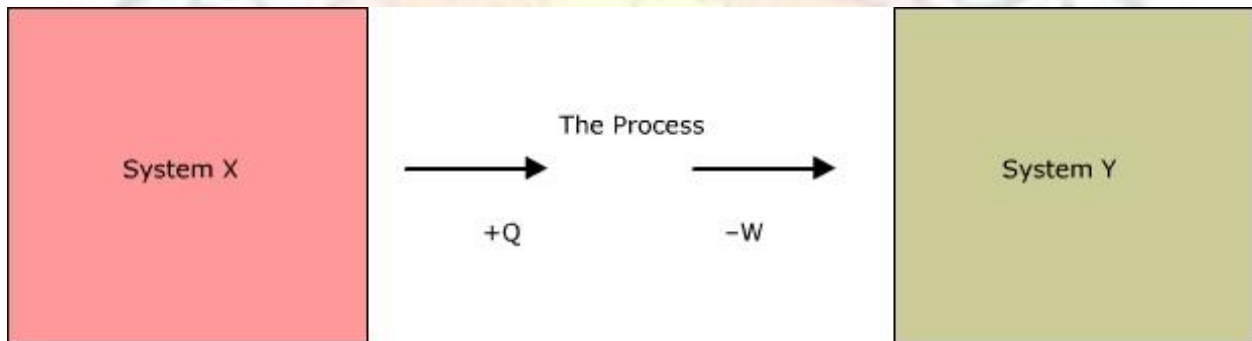


Fig 1.1

If the only interaction with its surroundings is in the form of transfer of heat Q to the system or performance of work W by the system, the change in U will be

$$\Delta U = U_Y - U_X = Q - W \quad (1)$$

Therefore, the change in internal energy must be equal to the energy absorbed in the process from the surroundings in the form of heat minus the energy lost to the surroundings in the form of external work (W) done by the system. This equation is a mathematical expression of the first law. For a differential change, equation (1) becomes

$$dU = dQ - dW \quad (2)$$

The first law has often been defined in terms of the universal human experience i.e. it is impossible to construct a "perpetual-motion machine". This machine produces useful work by a cyclic process with no change in its surroundings.

Consider a cyclic process from initial state X to state Y and back to X again. If perpetual motion were ever possible, it would sometimes be possible to obtain net energy increase by such a cycle.

First Law of Thermodynamics

$$\Delta U = (U_Y - U_X) + (U_X - U_Y) = 0$$

$$\Delta U = 0$$

or for any cyclic process,

$$\oint dU = 0$$

Note: It is to be remembered that heat, Q , is taken positive if the heat is supplied to the system and negative if heat is taken or removed from the system. Similarly work done, W , is taken positive if external work is done by the system like in the case of expansion and negative if the work is done on the system like in the case of compression.

1.3 Differential Form of First Law

Consider a quantity dQ of heat supplied to a system. This energy is in general distributed in three parts:

- (i) Partially it is used in increasing the temperature of the body which is equivalent of increasing its internal kinetic energy.
- (ii) A part of it is used in doing internal work against molecular attractions which is equivalent of increasing the internal potential energy of the system.
- (iii) Rest of the heat energy is spent in expanding the system against the external pressure i.e. in doing external work.

If dU_{Kin} and dU_{Pot} are respectively the change in internal kinetic energy and internal potential energy and dW is the external work done. Law of conservation of energy states "energy can neither be created nor destroyed but only converted from one form to another". So, we can write

$$dQ = dU_{Kin} + dU_{Pot} + dW$$

But $dU_{Kin} + dU_{Pot} = dU$ = increase in total internal energy of the system.

$$\text{Hence } dQ = dU + dW \quad (3)$$

This is differential form of first law of thermodynamics. This may be stated as "In all transformations the heat energy supplied must be balanced by the external work done plus the increase in internal energy".

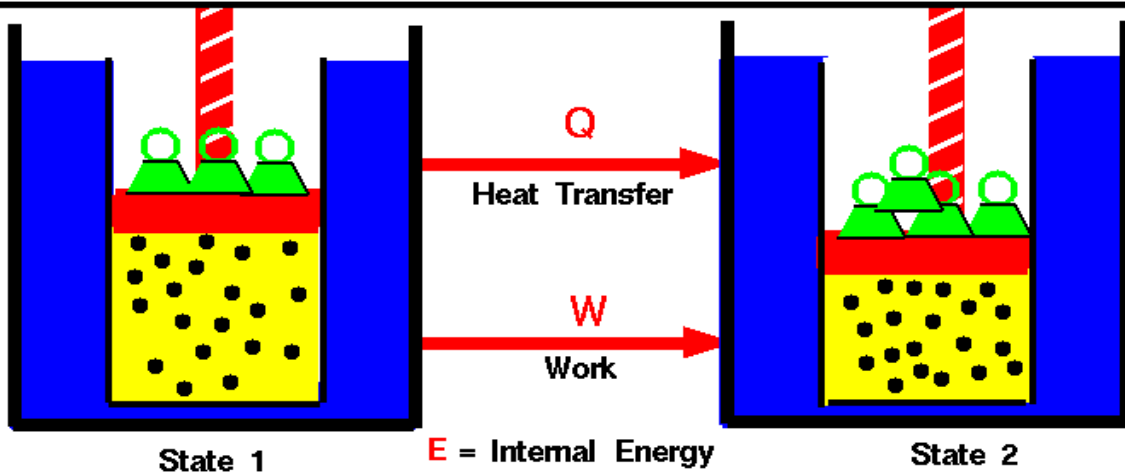
The first law of thermodynamics gives an exact relationship between heat and work.

Value Addition: First Law of Thermodynamics



First Law of Thermodynamics

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Any thermodynamic system in an equilibrium state possesses a state variable called the internal energy (E). Between any two equilibrium states, the change in internal energy is equal to the difference of the heat transfer into the system and work done by the system.

For more content click the links given below

<http://www.grc.nasa.gov/WWW/k-12/airplane/thermo1.html>

<https://www.google.co.in/search?tbm=isch&source=univ&sa=X&ei=rqDuUqH1C8f-rAeGy4GwBA&ved=0CFEQsAQ&biw=1366&bih=677&q=Animations%20on%20first%20law%20of%20thermodynamics>

1.4 Heat content (Enthalpy) and Heat capacity

Enthalpy is defined as the sum of internal energy and product of pressure and volume.

$$H = U + PV \quad (4)$$

where U denotes the total internal energy of the system and PV is the work energy.

This property of the system has a particular significance. Differentiation of above equation yields

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$$dH = dU + d(PV)$$

$$dH = dU + PdV + VdP \quad (5)$$

If the process occurs at constant pressure i.e. $dP = 0$, we have

$$dH = dU + PdV$$

$$dH = dU + dW \quad (6)$$

Also from differential form of the first law of thermodynamics

$$dQ = dU + dW \quad (7)$$

Comparing equation (6) and equation (7):

$$dH = dQ \quad (8)$$

i.e. the quantity of heat given to the system from an external source at constant pressure. This explains the name of heat content or enthalpy given to it.

Heat capacities

In case of solid or liquid the change of volume with temperature is practically negligible. But in case of a gas the change in volume is not negligible. Therefore the amount of heat required to raise the temperature through 1deg Celsius at constant volume and at constant pressure are not same. So a gas possesses two specific heats. The heat capacity of the system is defined as the ratio of the heat energy absorbed by the system from the surroundings to the increase in temperature of the system.

$$C = \frac{dQ}{dT} \quad (9)$$

We can determine heat capacity of a system by adding a measured quantity of heat energy to the system and measuring the resulting change in temperature. Heat capacities can be measured at constant volume and at constant pressure. The heat capacity at constant volume C_v of a system is defined as the ratio of heat energy absorbed by the system from the surrounding to the increase in temperature of the system, while the system remains at constant volume.

$$C_v = \left(\frac{dQ}{dT} \right)_v \quad (10)$$

Here since volume is constant, there is no work energy. Only heat energy plays its role. When we apply first law of thermodynamics to this process, it gives

$$dQ = dU + dW = dU + PdV = dU + 0 = dU$$

$$\text{whence } C_v = \left(\frac{\partial U}{\partial T} \right)_v \quad (11)$$

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Heat capacity at constant pressure C_p

Heat capacity of a system is defined as the ratio of heat energy absorbed by the system from the surroundings to the increase in temperature of the system. Pressure is kept constant.

$$C_p = \left(\frac{dQ}{dT} \right)_p \quad (12)$$

Since pressure is constant, we can write work energy as

$$dW = PdV$$

From first law of thermodynamics, we have

$$dQ = dU + PdV$$

Pressure being constant $PdV = d(PV)$

Therefore $dQ = dU + d(PV)$

$$dQ = d(U + PV) = dH$$

$$\text{whence } C_p = \left(\frac{\partial H}{\partial T} \right)_p \quad (13)$$

1.5 Relation between C_p and C_v

Comparing (11) and (13)

$$C_p - C_v = \left(\frac{\partial H}{\partial T} \right)_p - \left(\frac{\partial U}{\partial T} \right)_v$$

As $H = U + PV$

$$\text{So, } C_p - C_v = \left(\frac{\partial U}{\partial T} \right)_p + P \left(\frac{\partial V}{\partial T} \right)_p - \left(\frac{\partial U}{\partial T} \right)_v \quad (14)$$

Also as U is a function of volume V and temperature T ,

$$dU = \left(\frac{\partial U}{\partial V} \right)_T dV + \left(\frac{\partial U}{\partial T} \right)_V dT$$

$$\text{which yields } \left(\frac{\partial U}{\partial T} \right)_p = \left(\frac{\partial U}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_p + \left(\frac{\partial U}{\partial T} \right)_V$$

Substituting this value in equation (14), we get

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$$C_p - C_v = \left(\frac{\partial U}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_p + \left(\frac{\partial U}{\partial T} \right)_v + P \left(\frac{\partial V}{\partial T} \right)_p - \left(\frac{\partial U}{\partial T} \right)_v \quad (15)$$

$$C_p - C_v = \left(\frac{\partial V}{\partial T} \right)_p \left[P + \left(\frac{\partial U}{\partial V} \right)_T \right] \quad (16)$$

If we consider energy as a function of pressure P and temperature T , then similar equation will be obtained.

$$dU = \left(\frac{\partial U}{\partial P} \right)_T dP + \left(\frac{\partial U}{\partial T} \right)_p dT$$

which yields $\left(\frac{\partial U}{\partial T} \right)_v = \left(\frac{\partial U}{\partial P} \right)_T \left(\frac{\partial P}{\partial T} \right)_v + \left(\frac{\partial U}{\partial T} \right)_p$

Substituting this value in equation (14), we get

$$C_p - C_v = \left(\frac{\partial U}{\partial T} \right)_p + P \left(\frac{\partial V}{\partial T} \right)_p - \left(\frac{\partial U}{\partial P} \right)_T \left(\frac{\partial P}{\partial T} \right)_v - \left(\frac{\partial U}{\partial T} \right)_p \quad (17)$$

$$C_p - C_v = P \left(\frac{\partial V}{\partial T} \right)_p - \left(\frac{\partial U}{\partial P} \right)_T \left(\frac{\partial P}{\partial T} \right)_v \quad (18)$$

For an ideal gas:

An ideal gas is defined by the following properties:

- i) It follows the equation of state $PV = nRT$ (19)
- ii) The internal energy of an ideal gas is independent of its volume and pressure; it is a function of its temperature only i.e. $U = U(T)$

$$\left(\frac{\partial U}{\partial V} \right)_T = \left(\frac{\partial U}{\partial P} \right)_T = 0$$

$$\left(\frac{\partial U}{\partial T} \right)_p = \left(\frac{\partial U}{\partial T} \right)_v$$

So from equation (14), for an ideal gas we can write

$$C_p - C_v = P \left(\frac{\partial V}{\partial T} \right)_p \quad (20)$$

Equation (19) reduces to

$$\left(\frac{\partial V}{\partial T} \right)_p = \frac{nR}{P} \quad (21)$$

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Substituting this value of $\left(\frac{\partial V}{\partial T}\right)_p$ in equation (20), finally we get

$$C_p - C_v = nR$$

This is the relation between C_p and C_v for an ideal gas.

1.6 Isothermal Process

Process in which temperature remains constant is called isothermal process. If the system is an ideal gas, then the internal energy must therefore also remain constant, and the first law leads to

$$Q - W = 0 \text{ (isothermal process)}$$

If an amount of work W is done on the gas, an equivalent amount of heat $Q = W$ is released by the gas to the environment. None of the work done on the gas remains with the gas as stored internal energy.

Work done during isothermal

If the gas expands or contracts at constant temperature, the relationship between P and V , given by the ideal gas law $PV = nRT$

is $PV = \text{constant}$

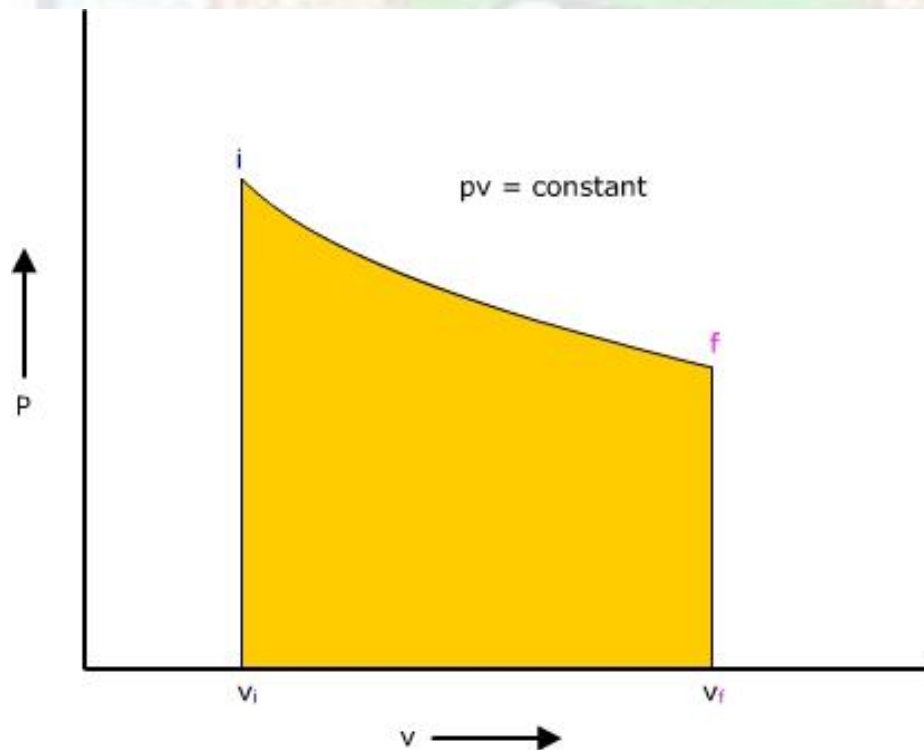


Fig 1.2

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A process done at constant temperature is known as isothermal process and the corresponding hyperbolic curve on the PV diagram is called an isotherm.

Here we have to find the work done on a gas during an isothermal process. Starting with

$$W = - \int_{V_i}^{V_f} PdV$$

From Ideal gas equation $P = \frac{nRT}{V}$

$$W = - \int_{V_i}^{V_f} PdV = - \int_{V_i}^{V_f} \frac{nRT}{V} dV = -nRT \int_{V_i}^{V_f} \frac{dV}{V}$$

So, we get

$$W = -nRT \ln \left(\frac{V_f}{V_i} \right) \quad (22)$$

1.7 Adiabatic Process

In an adiabatic process, the system is well insulated so that no heat exchange takes place i.e. $Q = 0$. From first law we can write

$$\Delta U \text{ or } \Delta E_{\text{int}} = W$$

Now to derive the relationship between P and V for an adiabatic process. For an ideal gas, we can write

$$dE_{\text{int}} = nC_V dT \quad (23)$$

where n is the number of moles and C_V is the molar heat capacity at constant volume.

$$\text{Thus } PdV = -dW = -dE_{\text{int}} = -nC_V dT \quad (24)$$

The equation of state of the gas can be written in differential form as

$$d(PV) = d(nRT)$$

$$PdV + VdP = nRdT$$

$$VdP = nC_V dT + nRdT$$

$$VdP = nC_p dT \quad (25)$$

From equation (24) and (25)

$$\frac{VdP}{PdV} = \frac{nC_p dT}{-nC_V dT} = \frac{C_p}{-C_V} = -\gamma$$

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$$\text{Rewriting } \frac{dP}{P} = -\gamma \frac{dV}{V}$$

Integrating between initial state i and final state f , we get

$$\int_{P_i}^{P_f} \frac{dP}{P} = -\gamma \int_{V_i}^{V_f} \frac{dV}{V}$$

$$\text{Or } \ln\left(\frac{P_f}{P_i}\right) = -\gamma \ln\left(\frac{V_f}{V_i}\right) \text{ which can be written as}$$

$$P_i V_i^\gamma = P_f V_f^\gamma$$

$$\text{or } PV^\gamma = \text{constant} \quad (26)$$

Work done during adiabatic process

System is insulated in this process. Consider a gas cylinder which was initially in contact with a thermal reservoir is now placed on a slab of insulating material (after removing the thermal reservoir). The gas will then be in complete thermal isolation from its surroundings; if we do work on it, its temperature will change, in contrast to its behaviour when it was in contact with the thermal reservoir. A process carried out in thermal isolation is called an adiabatic curve, shown below (Fig 1.3).

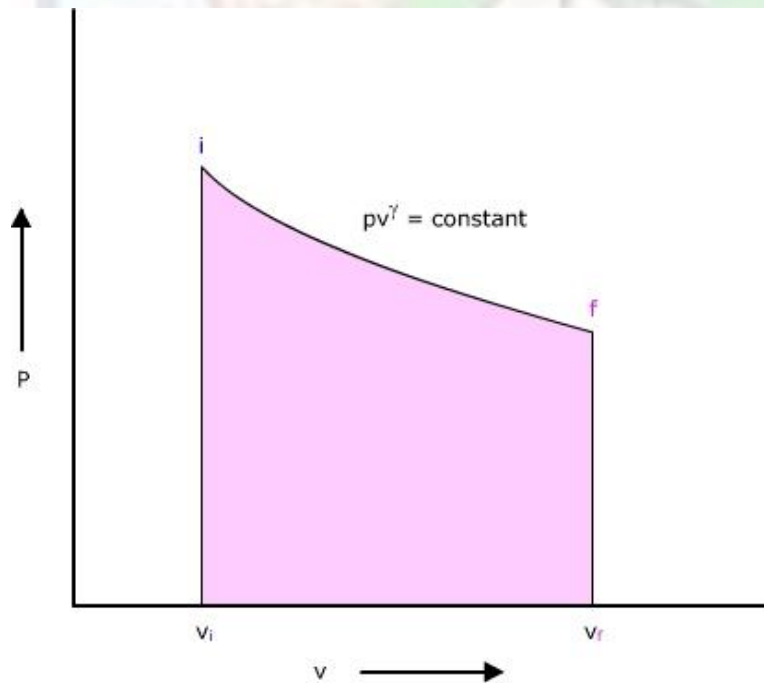


Fig 1.3

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If we allow the gas to change its volume with no other constraints, then the path it will follow is represented on a PV diagram by the parabola like curve.

$$PV^\gamma = \text{constant}$$

$$PV^\gamma = P_i V_i^\gamma$$

$$P = \frac{P_i V_i^\gamma}{V^\gamma}$$

$$W = -\int_{V_i}^{V_f} P dV = -\int_{V_i}^{V_f} \frac{P_i V_i^\gamma}{V^\gamma} dV = -P_i V_i^\gamma \int_{V_i}^{V_f} \frac{dV}{V^\gamma}$$

$$= -\frac{P_i V_i^\gamma}{\gamma - 1} (V_i^{1-\gamma} - V_f^{1-\gamma})$$

$$W = -\frac{P_i V_i^\gamma}{\gamma - 1} \left(\frac{1}{V_i^{\gamma-1}} - \frac{1}{V_f^{\gamma-1}} \right)$$

If the gas expands then $\frac{V_i}{V_f} < 1$

Now since $P_i V_i^\gamma = P_f V_f^\gamma$

$$\text{We can write } W = \frac{1}{\gamma - 1} (P_f V_f - P_i V_i) \quad (27)$$

where $\gamma = \frac{C_p}{C_v}$

1.8 Internal energy

A thermodynamic system performs work without any supply of external energy. Every system has within itself a quantity of energy called internal or intrinsic energy of the system.

Internal energy of 1 mol of an ideal monoatomic gas is $E_{\text{int}} = \frac{3}{2} RT$

and for n moles $E_{\text{int}} = \frac{3}{2} nRT$

Consider a molecule consisting of two point particles apart from each other (Fig 1.4). The rotational kinetic energy is

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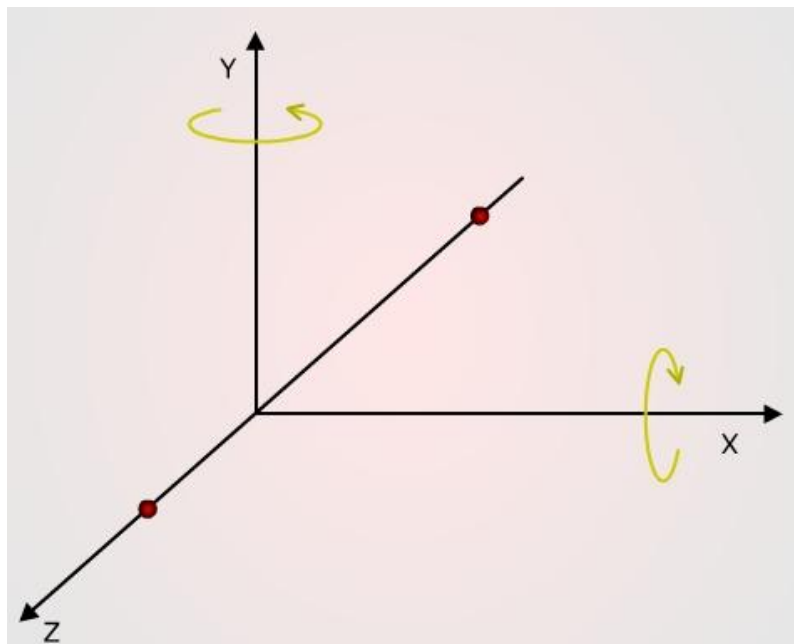


Fig 1.4

$$K_{rot} = \frac{1}{2}I_x\omega_x^2 + \frac{1}{2}I_y\omega_y^2$$

where I is the rotational inertia of the molecule for rotation about a particular axis.

For point masses, no kinetic energy is associated with rotation about the z-axis because $I_z = 0$. The total kinetic energy of the diatomic molecule is

$$K = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2 + \frac{1}{2}I_x\omega_x^2 + \frac{1}{2}I_y\omega_y^2$$

To find the total internal energy of the gas we must find the average energy of a single molecule and then multiply by the number of molecules. The five terms in this equation represent independent ways in which a molecule can absorb energy and are called degrees of freedom. A monoatomic molecule has three degrees of freedom. A diatomic molecule has five degrees of freedom in which three are translational and two are rotational.

For a monoatomic gas

$$E_{int} = N\left(\frac{3}{2}k_B T\right) = \frac{3}{2}nRT$$

For a diatomic gas

$$E_{int} = N\left(\frac{5}{2}k_B T\right) = \frac{5}{2}nRT$$

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Polyatomic gas

$$E_{\text{int}} = N \left(\frac{6}{2} k_B T \right) = 3nRT$$

Ex. Derive the P - V relation for a monoatomic gas (ideal gas), undergoing an adiabatic process.

Sol. The first law of thermodynamics is $dE = -dW$ is for the adiabatic process. The energy of a monoatomic process is

$$E = \frac{3}{2} Nk_B T$$

$$dE = \frac{3}{2} Nk_B dT$$

Using ideal gas law

$$dW = PdV = \frac{Nk_B T}{V} dV$$

$$\text{Thus } \frac{3}{2} Nk_B dT = -\frac{Nk_B T}{V} dV$$

$$\frac{dT}{T} + \frac{2}{3} \frac{dV}{V} = 0$$

On integrating it, we get

$$\ln T + \frac{2}{3} \ln V = \text{constant}$$

$$TV^{2/3} = \text{constant}$$

Now substituting for T from the ideal gas law,

$$PV^{5/3} = \text{constant}$$

1.9 Compressibility and Expansion Coefficient

Thermal expansion is the property of a matter due to which it has the tendency to change in volume in response to a change in temperature. When heat energy is given to a material, its particles start moving apart and thus usually maintain a greater average separation. The degree of expansion divided by the change in temperature is called the material's coefficient of thermal expansion and it generally varies with temperature.

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$$

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This coefficient explains how the size of an object changes with respect to temperature. It measures the fractional change in size per degree change in temperature at a constant pressure. Various types of coefficients are known: linear, area and volumetric. In case of solids, we consider the change along a length, or over some area.

The volumetric thermal expansion coefficient is the most basic thermal expansion coefficient. In general, substances expand or contract when their temperature changes. Here expansion or contraction occurs in all directions. Substances that expand at the same rate in every direction are called isotropic. For isotropic materials, the area and linear coefficients may be calculated from the volumetric coefficient. Compressibility is the degree of expansion divided by the change in pressure. It is denoted by K .

$$K = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$$

Summary

1. The first law of thermodynamics follows the principal of conservation of mechanical energy.
2. For an adiabatic process
 $PV^\gamma = \text{constant}$
3. For an isothermal process $PV = \text{constant}$
4. Every system has within itself a quantity of energy called internal or intrinsic energy of the system.
5. Compressibility is the degree of expansion divided by the change in pressure.
6. $C_p - C_v = nR$
7. Work done during isothermal process (when a system goes from initial state i to final state f) is given by $W = -nRT \ln \left(\frac{V_f}{V_i} \right)$.
8. Work done during adiabatic process is $W = \frac{1}{\gamma - 1} (P_f V_f - P_i V_i)$.

Fill in the blank.

1. In an isothermal process, _____ remains constant.
2. In an adiabatic process _____ energy is not exchanged.
3. Adiabatic curve is _____ than isothermal curve.
4. Process in which volume remains constant is _____ process.
5. In an isobaric process, _____ does not change.
6. The degree of expansion divided by the change in temperature is called the material's coefficient of _____.
7. _____ is the degree of expansion divided by the change in pressure.
8. A monoatomic gas has _____ degrees of freedom.
9. Temperature of the gas _____ as it is compressed.
10. Amount of heat required to raise the temperature of 1 gram-molecule of a gas through 1deg Celsius is known as _____ of a gas.

Answers

First Law of Thermodynamics

1. Temperature 2. Heat 3. Steeper 4. Isochoric 5. Pressure 6. Thermal expansion 7. Compressibility 8. Three 9. Rises 10. Molar specific heat

MCQ

1. First law of thermodynamics can be expressed as

- a) $dQ = dU + dW$
- b) $dU = dW$
- c) $dU = dQ + dW$
- d) $dQ = dU - dW$

2. γ is given as

- a) $\gamma = \frac{C_P}{mC_V}$
- b) $\gamma = \frac{2C_P}{C_V}$
- c) $\gamma = \frac{mC_P}{C_V}$
- d) $\gamma = \frac{C_P}{C_V}$

3. Slope of adiabatic curve is given by

- a) $\frac{dP}{dV} = -\gamma \frac{P}{V}$
- b) $\frac{dP}{dV} = \frac{P}{V}$
- c) $\frac{dP}{dV} = -\frac{P}{V}$
- d) $\frac{dP}{dV} = \gamma \frac{P}{V}$

4. Internal energy of a diatomic gas is

- a) $E_{\text{int}} = \frac{3}{2}nRT$
- b) $E_{\text{int}} = \frac{5}{2}nRT$
- c) $E_{\text{int}} = \frac{7}{2}nRT$
- d) $E_{\text{int}} = \frac{1}{2}nRT$

5. For an adiabatic process,

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- a) $PV = \text{constant}$
- b) $TPV^\gamma = \text{constant}$
- c) $PV^\gamma = \text{constant}$
- d) $2PV^\gamma = \text{constant}$

Answers

1. a 2. d 3. a 4. b 5. c

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