

# SPECIFIC HEAT CAPACITIES OF GASES

## 27.1 TWO KINDS OF SPECIFIC HEAT CAPACITIES OF GASES

The specific heat capacity of a substance is defined as the heat supplied per unit mass of the substance per unit rise in the temperature. If an amount  $\Delta Q$  of heat is given to a mass  $m$  of the substance and its temperature rises by  $\Delta T$ , the specific heat capacity  $s$  is given by the equation

$$s = \frac{\Delta Q}{m \Delta T} \quad \dots (27.1)$$

This definition applies to any mode of the substance, solid, liquid or gas.

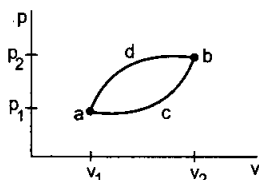


Figure 27.1

Consider a mass  $m$  of a gas at pressure  $p_1$ , volume  $V_1$  and temperature  $T_1$ . We show this state by the point  $a$  in the  $p$ - $V$  diagram of figure (27.1). The point  $b$  represents another state in which the pressure is  $p_2$ , the volume is  $V_2$  and the temperature is  $T_2$ . The change in temperature as the system is taken from  $a$  to  $b$  is  $\Delta T = T_2 - T_1$ . The internal energy of the gas at  $a$  is  $U_1$  and at  $b$  it is  $U_2$ . The change in internal energy as the system is taken from  $a$  to  $b$  is  $\Delta U = U_2 - U_1$ . If the work done by the gas in taking it from  $a$  to  $b$  is  $\Delta W$  and the heat supplied is  $\Delta Q$ , from the first law of thermodynamics,

$$\Delta Q = \Delta U + \Delta W.$$

Now, the work done  $\Delta W$  depends on the process by which the gas is taken from  $a$  to  $b$ . For example, the work done is smaller if the gas is taken through the process  $acb$  and is larger if the process is  $adb$ . Accordingly,  $\Delta Q$  is smaller in the process  $acb$  and is larger in the process  $adb$ . In both these processes, the

change in temperature  $\Delta T$  is the same. So the heat  $\Delta Q$  given to raise the temperature of a gas by  $\Delta T$ , depends on the process involved. From equation (27.1), the specific heat capacity  $s$  also depends on the process. Thus, to define the specific heat capacity of a gas the process should also be specified.

Suppose, the volume of a gas of mass  $m$  is kept constant and heat  $\Delta Q$  is given to it. If its temperature rises by  $\Delta T$ , the specific heat capacity given by equation (27.1) is called the *specific heat capacity at constant volume* and is denoted by the symbol  $s_v$ . Thus,

$$s_v = \left( \frac{\Delta Q}{m \Delta T} \right)_{\text{constant volume}} \quad \dots (27.2)$$

Next suppose, the pressure of a gas of mass  $m$  is kept constant and heat  $\Delta Q$  is given to it. If the temperature rises by  $\Delta T$ , the specific heat capacity given by equation (27.1) is called the *specific heat capacity at constant pressure* and is denoted by the symbol  $s_p$ . Thus,

$$s_p = \left( \frac{\Delta Q}{m \Delta T} \right)_{\text{constant pressure}} \quad \dots (27.3)$$

There can be many more processes, but these two are more important and correspondingly two specific heat capacities are defined for gases.

The above discussion is also valid for solids and liquids. However, in these systems the expansion is quite small and hence the work done in a process is small. Thus, the specific heat capacity depends only slightly on the process and the process is generally not mentioned.

The molar heat capacities of a gas are defined as the heat given per mole of the gas per unit rise in the temperature. The *molar heat capacity at constant volume*, denoted by  $C_v$ , is

$$C_v = \left( \frac{\Delta Q}{n \Delta T} \right)_{\text{constant volume}} \quad \dots (27.4)$$

and the *molar heat capacity at constant pressure*, denoted by  $C_p$ , is

$$C_p = \left( \frac{\Delta Q}{n \Delta T} \right)_{\text{constant pressure}} \quad \dots (27.5)$$

where  $n$  is the amount of the gas in number of moles. Quite often, the term *specific heat capacity* or *specific heat* is used for molar heat capacity. It is advised that the unit be carefully noted to determine the actual meaning. The unit of specific heat capacity is  $\text{J kg}^{-1} \text{K}^{-1}$  whereas that of molar heat capacity is  $\text{J K}^{-1} \text{mol}^{-1}$ .

#### Example 27.1

0.32 g of oxygen is kept in a rigid container and is heated. Find the amount of heat needed to raise the temperature from  $25^\circ\text{C}$  to  $35^\circ\text{C}$ . The molar heat capacity of oxygen at constant volume is  $20 \text{ J K}^{-1} \text{mol}^{-1}$ .

**Solution :** The molecular weight of oxygen =  $32 \text{ g mol}^{-1}$ .

The amount of the gas in moles is

$$n = \frac{0.32 \text{ g}}{32 \text{ g mol}^{-1}} = 0.01 \text{ mol.}$$

The amount of heat needed is  $Q = nC_v \Delta T$

$$= (0.01 \text{ mol}) (20 \text{ J K}^{-1} \text{mol}^{-1}) (10 \text{ K}) = 2.0 \text{ J.}$$

#### Example 27.2

A tank of volume  $0.2 \text{ m}^3$  contains helium gas at a temperature of  $300 \text{ K}$  and pressure  $1.0 \times 10^5 \text{ N m}^{-2}$ . Find the amount of heat required to raise the temperature to  $400 \text{ K}$ . The molar heat capacity of helium at constant volume is  $3.0 \text{ cal K}^{-1} \text{mol}^{-1}$ . Neglect any expansion in the volume of the tank.

**Solution :** The amount of the gas in moles is

$$n = \frac{pV}{RT} = \frac{(1.0 \times 10^5 \text{ N m}^{-2}) (0.2 \text{ m}^3)}{(8.31 \text{ J K}^{-1} \text{mol}^{-1}) (300 \text{ K})} = 8.0 \text{ mol.}$$

The amount of heat required is

$$\Delta Q = nC_v \Delta T = (8.0 \text{ mol}) (3.0 \text{ cal mol}^{-1} \text{K}^{-1}) (100 \text{ K}) = 2400 \text{ cal.}$$

### 27.2 RELATION BETWEEN $C_p$ AND $C_v$ FOR AN IDEAL GAS

Suppose, the volume of a gas is kept constant and heat is supplied to it. The work done by the gas is zero. The entire heat supplied goes as internal energy of the gas and is used to increase the temperature. Now consider a process in which the pressure is kept constant. If heat is supplied to the gas, its volume increases. A part of the heat supplied is used by the gas to do work in the expansion. Only the remaining part goes as increase in the internal energy which increases the temperature. Thus, for a given amount  $\Delta Q$  of heat, the rise in temperature of a gas at constant

pressure is smaller than the rise in temperature at constant volume. Thus,  $C_p > C_v$ .

Consider an amount  $n$  (in moles) of an ideal gas kept in a rigid container at an initial pressure  $p$ , volume  $V$  and temperature  $T$ . An amount  $(dQ)_v$  of heat is supplied to the gas. Its temperature rises from  $T$  to  $T + dT$  whereas the volume remains constant. The work done by the gas is  $dW = 0$ . From the first law of thermodynamics, the internal energy changes by  $dU$  such that

$$(dQ)_v = dU. \quad \dots (i)$$

Now suppose, the same sample of the gas is taken in a vessel with a movable light piston of cross-sectional area  $A$  (figure 27.2). The initial pressure, volume and temperature are  $p$ ,  $V$  and  $T$ . The piston is pushed by a constant external force  $F = pA$ . The pressure inside the gas thus remains constant at the value  $p$ .



Figure 27.2

The gas is given heat  $(dQ)_p$  which raises the temperature by the same amount  $dT$ . The piston moves out so that the volume increases by  $dV$ . The work done by the gas is  $p dV$  and from the first law of thermodynamics,

$$(dQ)_p = dU' + p dV. \quad \dots (ii)$$

For an ideal gas,  $pV = nRT$ .

As the pressure remains constant,

$$p(V + dV) = nR(T + dT)$$

and hence,

$$p dV = nR dT.$$

From (ii),

$$(dQ)_p = dU' + nR dT. \quad \dots (iii)$$

As the temperature rises by the same amount in the two cases and the internal energy of an ideal gas depends only on its temperature,

$$dU = dU'.$$

Thus, from (i) and (iii),

$$(dQ)_p = (dQ)_v + nR dT$$

$$\text{or, } \frac{1}{n} \frac{(dQ)_p}{dT} = \frac{1}{n} \frac{(dQ)_v}{dT} + R. \quad \dots (iv)$$

But  $(dQ)_p$  is the heat given to increase the temperature of the gas by  $dT$  at constant pressure. Thus, by definition,

$$C_p = \frac{1}{n} \frac{(dQ)_p}{dT}.$$

Similarly,  $C_V = \frac{1}{n} \frac{(dQ)_V}{dT}$

and (iv) becomes

$$C_p = C_V + R$$

or,  $C_p - C_V = R. \quad \dots (27.6)$

### Relations of $C_V$ with energy

From (i),  $(dQ)_V = dU$

or,  $\frac{1}{n} \frac{(dQ)_V}{dT} = \frac{1}{n} \frac{dU}{dT}$

or,  $C_V = \frac{1}{n} \frac{dU}{dT} \quad \dots (27.7)$

or,  $dU = nC_V dT.$

Taking the energy to be zero at  $T = 0$ ,

$$U = nC_V T. \quad \dots (27.8)$$

### Example 27.3

The molar heat capacity of a gas at constant volume is found to be  $5 \text{ cal mol}^{-1} \text{ K}^{-1}$ . Find the ratio  $\gamma = C_p / C_V$  for the gas. The gas constant  $R = 2 \text{ cal mol}^{-1} \text{ K}^{-1}$ .

**Solution :** We have  $C_V = 5 \text{ cal mol}^{-1} \text{ K}^{-1}$ .

$$\begin{aligned} \text{Thus, } C_p &= C_V + R = 5 \text{ cal mol}^{-1} \text{ K}^{-1} + 2 \text{ cal mol}^{-1} \text{ K}^{-1} \\ &= 7 \text{ cal mol}^{-1} \text{ K}^{-1} \end{aligned}$$

or,  $\frac{C_p}{C_V} = \frac{7}{5} = 1.4.$

### 27.3 DETERMINATION OF $C_p$ OF A GAS

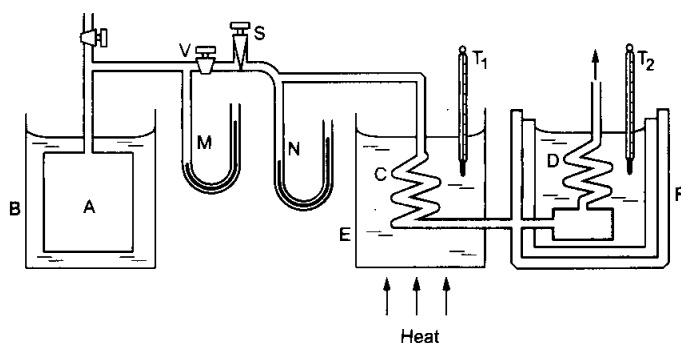


Figure 27.3

Figure (27.3) shows a schematic diagram of the Regnault's apparatus to measure  $C_p$  of a gas. The experimental gas is taken at a high pressure in a large tank A immersed in water at a constant temperature. The tank is connected through a tube to two copper coils C and D. A valve V in the tube opens or closes the path for the gas to flow. The rate of flow can be increased or decreased by adjusting a screw valve S. The first copper coil C is immersed in a hot oil bath E and the second copper coil D is immersed in a

calorimeter F containing water. Thermometers  $T_1$  and  $T_2$  are provided in the bath E and the calorimeter F. A manometer M connected close to the tank measures the pressure of the gas in the tank. Another manometer N connected after the screw valve S measures the pressure of the gas flowing in the calorimeter.

To do the experiment, the oil bath is heated with a burner to keep it at a high temperature which is measured by the thermometer  $T_1$ . A measured mass  $m$  of water is taken in the calorimeter. The calorimeter should be almost full with water so that the gas flowing through the coil D gets maximum time to exchange heat with the water. The initial temperature of the water is measured by  $T_2$ . The difference in the heights of mercury in the two arms of the manometer M is noted. The valve V is opened to allow the gas to flow through the system. As the amount of the gas in the tank reduces, the pressure in it decreases and the rate of flow tends to decrease. The screw valve S is continuously adjusted to keep the rate of flow constant. This is decided by keeping the difference in the levels of mercury in manometer N constant. The pressure of the gas going in the coil then remains constant. The gas is allowed to flow for some time and the final temperature of water and the final difference in the mercury levels in the manometer M are noted.

Let the water equivalent of the calorimeter together with the coil D

$$= W$$

$$\text{mass of the water} = m$$

$$\text{temperature of the oil bath} = \theta_1$$

$$\text{initial temperature of water} = \theta_2$$

$$\text{final temperature of water} = \theta_3$$

and the amount of the gas (in moles) passed through the water =  $n$ .

The gas at temperature  $\theta_1$  enters the coil D. In the beginning of the experiment, the gas leaves the coil D at temperature  $\theta_2$ . This temperature gradually increases and at the end of the experiment it becomes  $\theta_3$ . The average temperature of the gas leaving the coil D is, therefore,  $\frac{\theta_2 + \theta_3}{2}$ . The heat lost by the gas is

$$\Delta Q = n C_p \left[ \theta_1 - \frac{\theta_2 + \theta_3}{2} \right]. \quad \dots (i)$$

This heat is used to increase the temperature of the calorimeter, the water and the coil D from  $\theta_2$  to  $\theta_3$ . The heat received by them is

$$\Delta Q = (W + m)s (\theta_3 - \theta_2) \quad \dots (ii)$$

where  $s$  is the specific heat capacity of water. From (i) and (ii),

$$n C_p \left[ \theta_1 - \frac{\theta_2 + \theta_3}{2} \right] = (W + m)s (\theta_3 - \theta_2)$$

$$\text{or, } C_p = \frac{(W + m)s(\theta_3 - \theta_2)}{n \left[ \theta_1 - \frac{\theta_2 + \theta_3}{2} \right]} \quad \dots \text{ (iii)}$$

### Determination of $n$

Suppose the difference in the mercury levels in the manometer  $M$  is  $h$  and the atmospheric pressure is equal to a height  $H$  of mercury. The pressure in the tank is  $p$ , equal to a height  $H + h$  of mercury. By noting the difference  $h$  at the beginning and at the end of the experiment, the initial pressure  $p_1$  and the final pressure  $p_2$  are determined. Assuming the gas to be ideal,

$$p_1 V = n_1 RT$$

and

$$p_2 V = n_2 RT.$$

Here  $n_1, n_2$  are the amounts of the gas (in moles) in the tank at the beginning and at the end respectively,  $V$  is the volume of the tank and  $T$  is the absolute temperature of the tank. Thus,

$$(p_1 - p_2)V = (n_1 - n_2)RT$$

$$\text{or, } n = n_1 - n_2 = \frac{(p_1 - p_2)V}{RT}.$$

Putting in (iii), one can find the value of  $C_p$ .

### 27.4 DETERMINATION OF $C_V$ OF A GAS

Figure (27.4) shows a schematic diagram of Joly's differential steam calorimeter used to measure  $C_V$  of a gas. Two hollow copper spheres  $A$  and  $B$  are suspended from the pans of a sensitive balance. The spheres are enclosed in a steam chamber. The balance is placed over the steam chamber. Two pans  $C$  and  $D$  are fitted below the spheres.

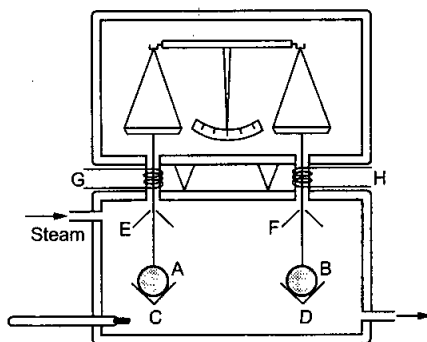


Figure 27.4

Umbrella-like shields  $E, F$  are provided over the spheres. Plaster of paris tubes are provided at the holes in the steam chamber through which the suspension wires pass. These are heated electrically by the coils  $G, H$ . This ensures that when steam is sent into the steam chamber, no drops are formed on

the wires and they move freely as the balance pans oscillate. The shields  $E, F$  do not allow the drops to fall on the spheres or on the pans. A thermometer is fitted in the steam chamber.

To do the experiment, air is pumped out of the spheres and the spheres are balanced. The experimental gas is filled in one of the spheres, say  $B$ , and additional weights are put on the balance pan so that the spheres are again balanced. This gives the mass of the gas. The temperature of the steam chamber is noted. This gives the initial temperature of the gas.

Steam is now passed through the steam chamber. The steam condenses on the spheres and the water formed is collected in the pans  $C$  and  $D$ . The temperatures of the spheres rise. More steam condenses on the pan which is below the sphere containing the gas. This is because the steam has to raise the temperature of the sphere as well as of the gas. When the temperature becomes steady, the spheres are again balanced by putting extra weights. This extra weight gives the amount of steam needed to raise the temperature of the gas only. The final temperature in steady state is noted.

Suppose,

the mass of the gas taken	$= m_1$
the mass of the extra steam condensed	$= m_2$
initial temperature of the gas	$= \theta_1$
final temperature of the gas	$= \theta_2$
specific latent heat of vaporization of water	$= L.$

If the molecular weight of the gas is  $M$ , the amount of the gas in moles is  $n = m_1 / M$ . The heat lost by the steam is  $= m_2 L$  and the heat gained by the gas is  $n C_V (\theta_2 - \theta_1)$ .

$$\text{Thus, } m_2 L = n C_V (\theta_2 - \theta_1) = \frac{m_1}{M} C_V (\theta_2 - \theta_1)$$

$$\text{or, } C_V = \frac{M m_2 L}{m_1 (\theta_2 - \theta_1)}.$$

In this we have neglected the increase in the volumes of the spheres as the temperature rises.

### 27.5 ISOTHERMAL AND ADIABATIC PROCESSES

#### Isothermal Process

A process on a system is called isothermal if the temperature of the system remains constant. In case of an ideal gas the internal energy remains constant in such a process. The amount of heat supplied is equal to the work done by the gas. The gas obeys Boyle's law and the work done by the gas is

$$W = \int_{V_i}^{V_f} p dV = \int_{V_i}^{V_f} n \frac{RT}{V} dV = nRT \ln(V_f / V_i).$$

This is also the amount of heat given as the volume of the gas is changed from  $V_i$  to  $V_f$ . As the change in temperature is zero, the molar heat capacity in such a process is

$$C_{isothermal} = \frac{\Delta Q}{n \Delta T} = \text{infinity}.$$

An isothermal process may be achieved by immersing the system in a large reservoir and performing the process very slowly. The temperature of the system then remains equal to the temperature of the reservoir. Heat may be exchanged between the reservoir and the system if necessary.

As an example, if a gas is taken in a metal cylinder (good conductor of heat) fitted with a piston and the piston is moved slowly, the temperature of the gas does not change. It remains equal to the temperature of the surrounding air. If the temperature tends to increase, heat is conducted from the gas to the air through the metallic walls. Similarly, if the temperature tends to decrease, heat is conducted from the surrounding air to the gas through the metallic walls. Here the surrounding air acts as a large reservoir.

### Adiabatic Process

A process on a system is called adiabatic if no heat is supplied to it or extracted from it. In such a case, the temperature changes without adding any heat. The molar heat capacity in such a process is

$$C_{adiabatic} = \frac{\Delta Q}{n \Delta T} = \text{zero}.$$

The work done by the gas in an adiabatic process equals the decrease in its internal energy. Thus, if a gas enclosed in a container with adiabatic walls expands, the internal energy decreases and hence the temperature falls. If the gas is compressed adiabatically, the temperature rises.

## 27.6 RELATIONS BETWEEN $p$ , $V$ , $T$ IN A REVERSIBLE ADIABATIC PROCESS

### Relation between $p$ and $V$

Consider an adiabatic process on an ideal gas. During a short part of the process, the pressure, the volume and the temperature change from  $p$ ,  $V$ ,  $T$  to  $p + dp$ ,  $V + dV$  and  $T + dT$  respectively. The internal energy changes from  $U$  to  $U + dU$ . As the amount of heat supplied is zero, the first law of thermodynamics gives

$$0 = dU + p dV. \quad \dots (i)$$

$$\text{We have,} \quad C_V = \frac{1}{n} \frac{dU}{dT}$$

$$\text{or,} \quad dU = nC_V dT.$$

Thus, from (i),

$$nC_V dT + p dV = 0. \quad \dots (ii)$$

As the gas is ideal,

$$pV = nRT$$

$$\text{or,} \quad p dV + V dp = nR dT$$

$$\text{or,} \quad dT = \frac{p dV + V dp}{nR}.$$

Substituting this expression for  $dT$  in (ii),

$$C_V \left( \frac{p dV + V dp}{R} \right) + p dV = 0$$

$$\text{or,} \quad (C_V + R) p dV + C_V V dp = 0$$

$$\text{or,} \quad C_p p dV + C_V V dp = 0$$

$$\text{or,} \quad \frac{C_p}{C_V} \frac{dV}{V} + \frac{dp}{p} = 0$$

$$\text{or,} \quad \gamma \frac{dV}{V} = - \frac{dp}{p}$$

where  $\gamma = C_p / C_V$ .

Let the initial pressure and volume be  $p_i$  and  $V_i$  respectively and the final pressure and volume be  $p_f$  and  $V_f$  respectively. Then

$$\int_{V_i}^{V_f} \gamma \frac{dV}{V} = - \int_{p_i}^{p_f} \frac{dp}{p}.$$

$$\text{or,} \quad \gamma \ln \frac{V_f}{V_i} = - \ln \frac{p_f}{p_i}$$

$$\text{or,} \quad \ln \left( \frac{V_f}{V_i} \right)^\gamma = \ln \left( \frac{p_i}{p_f} \right)$$

$$\text{or,} \quad \frac{V_f^\gamma}{V_i^\gamma} = \frac{p_i}{p_f}$$

$$\text{or,} \quad p_i V_i^\gamma = p_f V_f^\gamma$$

$$\text{or,} \quad pV^\gamma = \text{constant}. \quad \dots (27.9)$$

Thus,  $pV^\gamma$  remains constant in a reversible adiabatic process.

### Relation between $p$ and $T$

$$\text{We have} \quad pV = nRT$$

$$\text{or,} \quad V = \frac{nRT}{p}.$$

Putting in (27.9),

$$p \left( \frac{nRT}{p} \right)^\gamma = \text{constant}$$

$$\text{or,} \quad p^{1-\gamma} T^\gamma = \text{constant}$$

$$\text{or, } \frac{T^\gamma}{p^{\gamma-1}} = \text{constant.} \quad \dots (27.10)$$

### Relation between $V$ and $T$

$$\text{We have } pV = nRT$$

$$\text{or, } p = \frac{nRT}{V}$$

Putting in (27.9),

$$\left(\frac{nRT}{V}\right) V^\gamma = \text{constant}$$

$$\text{or, } TV^{\gamma-1} = \text{constant.} \quad \dots (27.11)$$

### Example 27.4

Dry air at  $15^\circ\text{C}$  and 10 atm is suddenly released at atmospheric pressure. Find the final temperature of the air [ $C_p/C_v = 1.41$ ].

**Solution :** As the air is suddenly released, it does not get time to exchange heat with the surrounding. Thus the process is adiabatic. Assuming the process to be reversible,

$$\frac{T^\gamma}{p^{\gamma-1}} = \text{constant}$$

$$\text{or, } \frac{T_1^\gamma}{p_1^{\gamma-1}} = \frac{T_2^\gamma}{p_2^{\gamma-1}}$$

$$\text{or, } \left(\frac{T_2}{T_1}\right)^\gamma = \left(\frac{p_2}{p_1}\right)^{\gamma-1}$$

$$\text{or, } T_2 = T_1 \left(\frac{p_2}{p_1}\right)^{\frac{\gamma-1}{\gamma}}$$

Taking  $p_1 = 10$  atm,  $p_2 = 1$  atm,  $\gamma = 1.41$  and  $T_1 = (273 + 15) \text{ K} = 288 \text{ K}$ , the final temperature is  $T_2 = 148 \text{ K}$ .

### 27.7 WORK DONE IN AN ADIABATIC PROCESS

Suppose a sample of gas has initial pressure  $p_1$  and initial volume  $V_1$ . In an adiabatic process, the pressure and volume change to  $p_2$  and  $V_2$ . We have

$$pV^\gamma = p_1V_1^\gamma = p_2V_2^\gamma = K. \quad \dots (i)$$

$$\text{Thus, } p = \frac{K}{V^\gamma}$$

The work done by the gas in the process is

$$W = \int_{V_1}^{V_2} p dV = \int_{V_1}^{V_2} \frac{K}{V^\gamma} dV$$

$$= \frac{1}{1-\gamma} \left[ \frac{K}{V_2^{\gamma-1}} - \frac{K}{V_1^{\gamma-1}} \right]$$

$$\text{From (i), } \frac{K}{V_2^\gamma} = p_2 \text{ and } \frac{K}{V_1^\gamma} = p_1.$$

$$\text{Thus, } W = -\frac{1}{\gamma-1} (p_2V_2 - p_1V_1)$$

$$= \frac{p_1V_1 - p_2V_2}{\gamma-1} \quad \dots (27.12)$$

### 27.8 EQUIPARTITION OF ENERGY

When we assume the molecules of a gas to be like hard spheres of negligible size, the energy of each molecule may be written as

$$E = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2.$$

There are three terms in this expression and each may be treated independently. The above picture is suitable for monatomic gases. In diatomic gases the molecules are assumed to be in the shape of dumbbells, two hard spheres of negligible size at a separation. Apart from translational motion, the molecule can rotate about its centre. The energy is the sum of translational kinetic energy and rotational kinetic energy. If the line joining the two particles is taken as the  $z$ -axis, the rotational kinetic energy may be written as

$$\frac{1}{2}I_x\omega_x^2 + \frac{1}{2}I_y\omega_y^2,$$

the first term describing the energy of rotation about the  $x$ -axis and the second term describing the energy of rotation about the  $y$ -axis. As the size of each atom is assumed negligible, the moment of inertia  $I_z$  is negligible and no term like  $\frac{1}{2}I_z\omega_z^2$  is added. The total energy is then

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

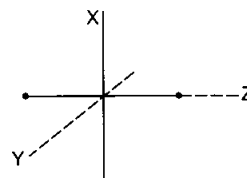


Figure 27.5

The number of independent terms in this expression is 5. If the two atoms of a diatomic molecule vibrate along its length, additional energy results. Such a vibration involves kinetic energy of vibration as well as the potential energy of the pair of atoms. The energy of vibration will be of the form

$$\frac{1}{2}\mu v^2 + \frac{1}{2}kr^2$$

where  $r$  is the separation between the atoms and  $v = (dr/dt)$ . The constant  $\mu$  is related to the mass of the molecule and  $k$  is related to the force constant of the system. The total energy of a molecule is

$$E = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2 + \frac{1}{2}I_x\omega_x^2 + \frac{1}{2}I_y\omega_y^2 + \frac{1}{2}\mu v^2 + \frac{1}{2}kr^2.$$

There are 7 independent terms.

For a polyatomic molecule, the number of terms in the rotational and vibrational energy depends on the actual arrangement of atoms in the molecule.

The number of independent terms in the expression of energy of a molecule is called its *degree of freedom*. Thus, the degree of freedom is 3 for a monatomic gas molecule, it is 5 for a diatomic molecule if the molecule does not vibrate and is 7 if it vibrates.

*Equipartition of energy* states that the average energy of a molecule in a gas associated with each degree of freedom is  $\frac{1}{2}kT$  where  $k$  is the Boltzmann constant and  $T$  is its absolute temperature.

The theorem may be proved using more advanced techniques of statistical mechanics.

According to the equipartition theorem, the average energy of a molecule in a monatomic gas is  $\frac{3}{2}kT$  as the degree of freedom is 3. This is also the result of the kinetic theory of gases.

For diatomic gases, the average energy per molecule is  $\frac{5}{2}kT$  if the molecules translate and rotate but do not vibrate, and is  $\frac{7}{2}kT$  if they vibrate also.

Now consider a sample of amount  $n$  (in moles) of an ideal gas. The total number of molecules is  $nN_A$  where  $N_A$  is the Avogadro number. If the gas is monatomic, the internal energy of the gas is

$$U = nN_A \left( \frac{3}{2}kT \right) = n \frac{3}{2}RT.$$

The molar heat capacity at constant volume is

$$C_V = \frac{1}{n} \frac{dU}{dT} = \frac{3}{2}R.$$

The molar heat capacity at constant pressure is

$$C_p = C_V + R = \frac{3}{2}R + R = \frac{5}{2}R.$$

Thus,  $\gamma = \frac{C_p}{C_V} = \frac{5}{3} = 1.67$ .

For a sample of a diatomic gas,

$$U = nN_A \left( \frac{5}{2}kT \right) = n \frac{5}{2}RT$$

if the molecules do not vibrate. In this case,

$$C_V = \frac{1}{n} \frac{dU}{dT} = \frac{5}{2}R$$

and

$$C_p = C_V + R = \frac{5}{2}R + R = \frac{7}{2}R.$$

Thus,

$$\gamma = \frac{C_p}{C_V} = \frac{7}{5} = 1.40.$$

If the molecules do vibrate,

$$U = n \frac{7}{2}RT$$

so that,

$$C_V = \frac{7}{2}R, C_p = \frac{9}{2}R$$

and

$$\gamma = \frac{C_p}{C_V} = \frac{9}{7} = 1.29.$$

Our expectations about  $C_V$ ,  $C_p$  and  $\gamma$  are summarized in table (27.1a) and the experimental values for a number of gases are given in table (27.1b).

**Table 27.1a: Expected values of  $C_V$ ,  $C_p$  and  $\gamma$**

Nature of the gas	$C_V$ (J K <sup>-1</sup> mol <sup>-1</sup> )	$C_p$ (J K <sup>-1</sup> mol <sup>-1</sup> )	$C_p - C_V$ (J K <sup>-1</sup> mol <sup>-1</sup> )	$\gamma$
Monatomic	12.5	20.8	8.31	1.67
Diatomic, assuming no vibrations	20.8	29.1	8.31	1.40
Diatomic, assuming vibrations	29.1	37.4	8.31	1.29

**Table 27.1b: Experimental values of  $C_V$ ,  $C_p$  and  $\gamma$**

gas (15°C)	$C_V$ (J K <sup>-1</sup> mol <sup>-1</sup> )	$C_p$ (J K <sup>-1</sup> mol <sup>-1</sup> )	$C_p - C_V$ (J K <sup>-1</sup> mol <sup>-1</sup> )	$\gamma$
He	12.5	20.8	8.30	1.66
Ne	12.7	20.8	8.12	1.64
Ar	12.5	20.8	8.30	1.67
Kr	12.3	20.8	8.49	1.69
Xe	12.6	21.0	8.36	1.67
H <sub>2</sub>	20.4	28.8	8.45	1.41
O <sub>2</sub>	21.0	29.3	8.32	1.40
N <sub>2</sub>	20.8	29.1	8.32	1.40
CO	20.6	29.0	8.45	1.41
HCl	21.0	29.6	8.61	1.41
CO <sub>2</sub>	28.2	36.5	8.32	1.30
H <sub>2</sub> O (200°C)	27.0	35.4	8.35	1.31
CH <sub>4</sub>	27.1	35.4	8.36	1.31

We find excellent agreement between the prediction of the equipartition theorem and the experimental values. The results also suggest that diatomic molecules do not vibrate at ordinary temperatures. The table suggests that the degree of freedom of polyatomic molecules CO<sub>2</sub>, H<sub>2</sub>O and CH<sub>4</sub> is 6.

According to the equipartition theorem, the molar heat capacities should be independent of temperature. However, variations in  $C_V$  and  $C_p$  are observed as the

temperature changes. At very high temperatures, vibrations are also important and that affects the values of  $C_V$  and  $C_p$  for diatomic and polyatomic gases.

### Example 27.5

Calculate the internal energy of 1 g of oxygen at STP.

**Solution :** Oxygen is a diatomic gas. The average energy per molecule is, therefore,  $\frac{5}{2} kT$  and the average energy per mole is  $\frac{5}{2} RT$ . As the molecular weight of oxygen is  $32 \text{ g mol}^{-1}$ , 1 g of oxygen has

$$n = \frac{1 \text{ g}}{32 \text{ g mol}^{-1}} = \frac{1}{32} \text{ mol}.$$

The temperature of oxygen is 273 K. Thus, the internal energy is

$$\begin{aligned} U &= n \left( \frac{5}{2} RT \right) \\ &= \left( \frac{1}{32} \text{ mol} \right) \left( \frac{5}{2} \right) (8.31 \text{ J K}^{-1} \text{ mol}^{-1}) (273 \text{ K}) \\ &= 177 \text{ J}. \end{aligned}$$

### Worked Out Examples

1. Calculate the value of mechanical equivalent of heat from the following data. Specific heat capacity of air at constant volume =  $170 \text{ cal kg}^{-1} \text{ K}^{-1}$ ,  $\gamma = C_p / C_V = 1.4$  and the density of air at STP is  $1.29 \text{ kg m}^{-3}$ . Gas constant  $R = 8.3 \text{ J K}^{-1} \text{ mol}^{-1}$ .

**Solution :** Using  $pV = nRT$ , the volume of 1 mole of air at STP is

$$\begin{aligned} V &= \frac{nRT}{p} = \frac{(1 \text{ mol}) \times (8.3 \text{ J K}^{-1} \text{ mol}^{-1}) \times (273 \text{ K})}{1.0 \times 10^5 \text{ N m}^{-2}} \\ &= 0.0224 \text{ m}^3. \end{aligned}$$

The mass of 1 mole is, therefore,

$$(1.29 \text{ kg m}^{-3}) \times (0.0224 \text{ m}^3) = 0.029 \text{ kg}.$$

The number of moles in 1 kg is  $\frac{1}{0.029}$ . The molar heat capacity at constant volume is

$$\begin{aligned} C_V &= \frac{170 \text{ cal}}{(1/0.029) \text{ mol K}^{-1}} \\ &= 4.93 \text{ cal K}^{-1} \text{ mol}^{-1}. \end{aligned}$$

Hence,  $C_p = \gamma C_V = 1.4 \times 4.93 \text{ cal K}^{-1} \text{ mol}^{-1}$

$$\begin{aligned} \text{or, } C_p - C_V &= 0.4 \times 4.93 \text{ cal K}^{-1} \text{ mol}^{-1} \\ &= 1.97 \text{ cal K}^{-1} \text{ mol}^{-1}. \end{aligned}$$

Also,

$$C_p - C_V = R = 8.3 \text{ J K}^{-1} \text{ mol}^{-1}.$$

Thus,  $8.3 \text{ J} = 1.97 \text{ cal}$ .

The mechanical equivalent of heat is

$$\frac{8.3 \text{ J}}{1.97 \text{ cal}} = 4.2 \text{ J cal}^{-1}.$$

2. An ideal gas has a molar heat capacity at constant pressure  $C_p = 2.5 R$ . The gas is kept in a closed vessel of volume  $0.0083 \text{ m}^3$ , at a temperature of 300 K and a pressure of  $1.6 \times 10^6 \text{ N m}^{-2}$ . An amount  $2.49 \times 10^4 \text{ J}$  of

heat energy is supplied to the gas. Calculate the final temperature and pressure of the gas.

**Solution :** We have

$$C_V = C_p - R = 2.5 R - R = 1.5 R.$$

The amount of the gas (in moles) is  $n = \frac{pV}{RT}$

$$= \frac{(1.6 \times 10^6 \text{ N m}^{-2}) \times (0.0083 \text{ m}^3)}{(8.3 \text{ J K}^{-1} \text{ mol}^{-1}) (300 \text{ K})} = 5.3 \text{ mol}.$$

As the gas is kept in a closed vessel, its volume is constant. Thus, we have

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

$$\text{or, } \Delta T = \frac{\Delta Q}{nC_V}$$

$$= \frac{2.49 \times 10^4 \text{ J}}{(5.3 \text{ mol}) (1.5 \times 8.3 \text{ J K}^{-1} \text{ mol}^{-1})} = 377 \text{ K}.$$

The final temperature is  $300 \text{ K} + 377 \text{ K} = 677 \text{ K}$ .

We have,

$$\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}.$$

Here  $V_1 = V_2$ . Thus,  $p_2 = \frac{T_2}{T_1} p_1$

$$= \frac{677}{300} \times 1.6 \times 10^6 \text{ N m}^{-2} = 3.6 \times 10^6 \text{ N m}^{-2}.$$

3. A sample of ideal gas ( $\gamma = 1.4$ ) is heated at constant pressure. If an amount 140 J of heat is supplied to the gas, find (a) the change in internal energy of the gas, (b) the work done by the gas.

**Solution :** Suppose the sample contains  $n$  moles. Also, suppose the volume changes from  $V_1$  to  $V_2$  and the temperature changes from  $T_1$  to  $T_2$ .

The heat supplied is

$$\Delta Q = n C_p (T_2 - T_1).$$

- (a) The change in internal energy is



$$\begin{aligned}\Delta U &= nC_V(T_2 - T_1) = \frac{C_V}{C_p} nC_p(T_2 - T_1) \\ &= \frac{C_V}{C_p} \Delta Q = \frac{140 \text{ J}}{1.4} = 100 \text{ J}.\end{aligned}$$

(b) The work done by the gas is

$$\begin{aligned}\Delta W &= \Delta Q - \Delta U \\ &= 140 \text{ J} - 100 \text{ J} = 40 \text{ J}.\end{aligned}$$

4. An experiment is performed to measure the molar heat capacity of a gas at constant pressure using Regnault's method. The gas is initially contained in a cubical reservoir of size 40 cm × 40 cm × 40 cm at 600 kPa at 27°C. A part of the gas is brought out, heated to 100°C and is passed through a calorimeter at constant pressure. The water equivalent of the calorimeter and its contents is 100 g. The temperature of the calorimeter and its contents increases from 20°C to 30°C during the experiment and the pressure in the reservoir decreases to 525 kPa. Specific heat capacity of water = 4200 J kg<sup>-1</sup> K<sup>-1</sup>. Calculate the molar heat capacity  $C_p$  from these data.

**Solution :** We have  $pV = nRT$  or,  $n = \frac{pV}{RT}$ . The amount of the gas in the reservoir is  $n_1 = \frac{p_1 V}{RT}$  before the gas is taken out and  $n_2 = \frac{p_2 V}{RT}$  after the gas is taken out. The amount taken out is

$$\begin{aligned}\Delta n &= n_1 - n_2 = (p_1 - p_2) \frac{V}{RT} \\ &= \frac{(600 - 525) \times 10^3 \text{ N m}^{-2} \times (40 \times 10^{-2} \text{ m})^3}{(8.3 \text{ J K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K})} \\ &= 1.925 \text{ mol}.\end{aligned}$$

The gas is heated to 100°C and cools down as it passes through the calorimeter. The average final temperature of the gas is  $\frac{20^\circ\text{C} + 30^\circ\text{C}}{2} = 25^\circ\text{C}$ . Thus, the average decrease in temperature of the gas is

$$\Delta T = (100^\circ\text{C} - 25^\circ\text{C}) = 75^\circ\text{C}$$

or,  $\Delta T = 75 \text{ K}$ .

The heat lost by the gas is

$$\Delta Q = \Delta n C_p \Delta T.$$

The heat gained by the calorimeter and its contents is (100 g) (4200 J kg<sup>-1</sup> K<sup>-1</sup>) (30 - 20)°C = 4200 J.

Thus,  $\Delta n C_p \Delta T = 4200 \text{ J}$

$$\text{or, } C_p = \frac{4200 \text{ J}}{(1.925 \text{ mol}) (75 \text{ K})} = 29 \text{ J K}^{-1} \text{ mol}^{-1}.$$

5. A quantity of air is kept in a container having walls which are slightly conducting. The initial temperature and volume are 27°C (equal to the temperature of the surrounding) and 800 cm<sup>3</sup> respectively. Find the rise in

the temperature if the gas is compressed to 200 cm<sup>3</sup> (a) in a short time (b) in a long time. Take  $\gamma = 1.4$ .

**Solution :** (a) When the gas is compressed in a short time, the process is adiabatic. Thus,

$$T_2 V_2^{\gamma-1} = T_1 V_1^{\gamma-1}$$

$$\text{or, } T_2 = T_1 \left( \frac{V_1}{V_2} \right)^{\gamma-1}$$

$$= (300 \text{ K}) \times \left[ \frac{800}{200} \right]^{0.4} = 522 \text{ K}.$$

Rise in temperature =  $T_2 - T_1 = 222 \text{ K}$ .

(b) When the gas is compressed in a long time, the process is isothermal. Thus, the temperature remains equal to the temperature of the surrounding that is 27°C. The rise in temperature = 0.

6. A sample of gas ( $\gamma = 1.5$ ) is taken through an adiabatic process in which the volume is compressed from 1600 cm<sup>3</sup> to 400 cm<sup>3</sup>. If the initial pressure is 150 kPa, (a) what is the final pressure and (b) how much work is done by the gas in the process?

**Solution :** (a) For an adiabatic process,

$$p_1 V_1^\gamma = p_2 V_2^\gamma.$$

Thus,

$$\begin{aligned}p_2 &= p_1 \left( \frac{V_1}{V_2} \right)^\gamma \\ &= (150 \text{ kPa}) \left( \frac{1600 \text{ cm}^3}{400 \text{ cm}^3} \right)^{3/2} = 1200 \text{ kPa}.\end{aligned}$$

(b) Work done by the gas in an adiabatic process is

$$\begin{aligned}W &= \frac{p_1 V_1 - p_2 V_2}{\gamma - 1} \\ &= \frac{(150 \text{ kPa}) (1600 \text{ cm}^3) - (1200 \text{ kPa}) (400 \text{ cm}^3)}{1.5 - 1} \\ &= \frac{240 \text{ J} - 480 \text{ J}}{0.5} = -480 \text{ J}.\end{aligned}$$

7. Two moles of helium gas ( $\gamma = 5/3$ ) are initially at 27°C and occupy a volume of 20 litres. The gas is first expanded at constant pressure until the volume is doubled. Then it undergoes an adiabatic change until the temperature returns to its initial value. (a) Sketch the process in a  $p$ - $V$  diagram. (b) What is the final volume and pressure of the gas? (c) What is the work done by the gas?

**Solution :** (a) The process is shown in figure (27-W1).

During the part  $ab$ , the pressure is constant.

We have,

$$\frac{p_a V_a}{T_a} = \frac{p_b V_b}{T_b}$$

or,  $T_b = \frac{V_b}{V_a} T_a = 2T_a = 600 \text{ K}.$

During the part  $bc$ , the gas is adiabatically returned to the temperature  $T_a$ . The point  $a$  and the point  $c$  are on the same isotherm. Thus, we draw an adiabatic curve from  $b$  and an isotherm from  $a$  and look for the point of intersection  $c$ . That is the final state.

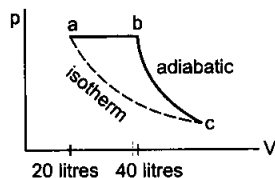


Figure 27-W1

(b) From the isotherm  $ac$ ,  
 $p_a V_a = p_c V_c \quad \dots (i)$

and from the adiabatic curve  $bc$ ,

$$p_b V_b^\gamma = p_c V_c^\gamma$$

or,  $p_a (2V_a)^\gamma = p_c V_c^\gamma \quad \dots (ii)$

Dividing (ii) by (i),

$$2^\gamma (V_a)^{\gamma-1} = (V_c)^{\gamma-1}$$

or,  $V_c = 2^{1/(\gamma-1)} V_a = 4\sqrt{2} V_a = 113 \text{ litres}.$

From (i),  $p_c = \frac{p_a V_a}{V_c} = \frac{nRT_a}{V_c}$   

$$= \frac{2 \text{ mol} \times (8.3 \text{ J K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K})}{113 \times 10^{-3} \text{ m}^3}$$

$$= 4.4 \times 10^4 \text{ Pa}.$$

(c) Work done by the gas in the part  $ab$

$$= p_a (V_b - V_a)$$

$$= p_b V_b - p_a V_a$$

$$= nRT_2 - nRT_1$$

$$= 2 \text{ mol} \times (8.3 \text{ J K}^{-1} \text{ mol}^{-1}) \times (600 \text{ K} - 300 \text{ K})$$

$$= 4980 \text{ J}.$$

The work done in the adiabatic part  $bc$

$$= \frac{p_b V_b - p_c V_c}{\gamma - 1}$$

$$= \frac{nR (T_2 - T_1)}{\gamma - 1}$$

$$= \frac{4980 \text{ J}}{5/3 - 1} = 7470 \text{ J}.$$

The net work done by the gas

$$= 4980 \text{ J} + 7470 \text{ J} = 12450 \text{ J}.$$

8. An ideal gas enclosed in a vertical cylindrical container supports a freely moving piston of mass  $M$ . The piston and the cylinder have equal cross-sectional area  $A$ . When the piston is in equilibrium, the volume of the gas is  $V_0$

and its pressure is  $p_0$ . The piston is slightly displaced from the equilibrium position and released. Assuming that the system is completely isolated from its surrounding, show that the piston executes simple harmonic motion and find the frequency of oscillations.

**Solution :** Suppose the piston is displaced through a distance  $x$  above the equilibrium position. The volume of the gas increases by  $\Delta V = Ax$ . As the system is completely isolated from its surrounding, the process is adiabatic. Thus,

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

or,  $\ln p + \gamma \ln V = \text{constant}$

or,  $\frac{\Delta p}{p} + \gamma \frac{\Delta V}{V} = 0$

or,  $\Delta p = -\frac{\gamma p}{V} \Delta V.$

As the piston is only slightly pushed, we can write

$$\Delta p = -\frac{\gamma p_0}{V_0} \Delta V.$$

The resultant force acting on the piston in this position is

$$F = A \Delta p = -A \frac{\gamma p_0}{V_0} \Delta V$$

$$= -\frac{A^2 \gamma p_0}{V_0} x = -kx$$

where  $k = \frac{A^2 \gamma p_0}{V_0}.$

Thus, the motion of the piston is simple harmonic. The angular frequency  $\omega$  is given by

$$\omega = \sqrt{\frac{k}{M}} = \sqrt{\frac{A^2 \gamma p_0}{M V_0}}$$

and the frequency is  $\nu = \frac{\omega}{2\pi} = \frac{1}{2\pi} \sqrt{\frac{A^2 \gamma p_0}{M V_0}}.$

9. Two vessels of volumes  $V_1$  and  $V_2$  contain the same ideal gas. The pressures in the vessels are  $p_1$  and  $p_2$  and the temperatures are  $T_1$  and  $T_2$  respectively. The two vessels are now connected to each other through a narrow tube. Assuming that no heat is exchanged between the surrounding and the vessels, find the common pressure and temperature attained after the connection.

**Solution :**

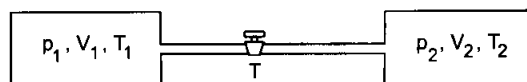


Figure 27-W2

The amount of the gas in vessel 1 is  $n_1 = \frac{p_1 V_1}{RT_1}$

and that in vessel 2 is  $n_2 = \frac{p_2 V_2}{RT_2}$ .

If  $p'$  and  $T'$  be the common pressure and temperature after the connection is made, the amounts are

$$n_1' = \frac{p' V_1}{RT'}, \text{ and } n_2' = \frac{p' V_2}{RT'}.$$

We have  $n_1 + n_2 = n_1' + n_2'$

$$\text{or, } \frac{p_1 V_1}{RT_1} + \frac{p_2 V_2}{RT_2} = \frac{p' V_1}{RT'} + \frac{p' V_2}{RT'}$$

$$\text{or, } \frac{p'}{T'} = \frac{1}{V_1 + V_2} \left( \frac{p_1 V_1}{T_1} + \frac{p_2 V_2}{T_2} \right)$$

$$\text{or, } \frac{T'}{p'} = \frac{T_1 T_2 (V_1 + V_2)}{p_1 V_1 T_2 + p_2 V_2 T_1} \quad \dots (i)$$

As the vessels have fixed volume, no work is done by the gas plus the vessels system. Also, no heat is exchanged with the surrounding. Thus, the internal energy of the total system remains constant.

The internal energy of an ideal gas is

$$U = n C_V T$$

$$= C_V \frac{pV}{R}$$

The internal energy of the gases before the connection

$$= \frac{C_V p_1 V_1}{R} + \frac{C_V p_2 V_2}{R}$$

and after the connection

$$= \frac{C_V p' (V_1 + V_2)}{R}$$

Neglecting the change in internal energy of the vessels (the heat capacity of the vessels is assumed negligible),

$$\frac{C_V p_1 V_1}{R} + \frac{C_V p_2 V_2}{R} = \frac{C_V p' (V_1 + V_2)}{R}$$

$$\text{or, } p' = \frac{p_1 V_1 + p_2 V_2}{V_1 + V_2}$$

$$\text{From (i), } T' = \frac{T_1 T_2 (p_1 V_1 + p_2 V_2)}{p_1 V_1 T_2 + p_2 V_2 T_1}$$

10. 4 mol of an ideal gas having  $\gamma = 1.67$  are mixed with 2 mol of another ideal gas having  $\gamma = 1.4$ . Find the equivalent value of  $\gamma$  for the mixture.

**Solution :** Let,

$C_V$  = molar heat capacity of the first gas,

$C'_V$  = molar heat capacity of the second gas,

$C_V$  = molar heat capacity of the mixture

and similar symbols for other quantities. Then,

$$\gamma = \frac{C_p}{C_V} = 1.67$$

$$\text{and } C_p = C_V + R.$$

$$\text{This gives } C_V = \frac{3}{2} R \text{ and } C_p = \frac{5}{2} R.$$

$$\text{Similarly, } \gamma = 1.4 \text{ gives } C'_V = \frac{5}{2} R \text{ and } C'_p = \frac{7}{2} R.$$

Suppose the temperature of the mixture is increased by  $dT$ . The increase in the internal energy of the first gas  $= n_1 C_V dT$ . The increase in internal energy of the second gas  $= n_2 C'_V dT$  and the increase in internal energy of the mixture  $= (n_1 + n_2) C_V dT$ . Thus,

$$(n_1 + n_2) C_V dT = n_1 C_V dT + n_2 C'_V dT$$

$$\text{or, } C_V = \frac{n_1 C_V + n_2 C'_V}{n_1 + n_2} \quad \dots (i)$$

$$C_p = C_V + R = \frac{n_1 C_V + n_2 C'_V}{n_1 + n_2} + R$$

$$= \frac{n_1 (C_V + R) + n_2 (C'_V + R)}{n_1 + n_2}$$

$$= \frac{n_1 C_p + n_2 C'_p}{n_1 + n_2} \quad \dots (ii)$$

$$\text{From (i) and (ii), } \gamma = \frac{C_p}{C_V} = \frac{n_1 C_p + n_2 C'_p}{n_1 C_V + n_2 C'_V}$$

$$= \frac{4 \times \frac{5}{2} R + 2 \times \frac{7}{2} R}{4 \times \frac{3}{2} R + 2 \times \frac{5}{2} R} = 1.54.$$

11. A diatomic gas ( $\gamma = 1.4$ ) does 200 J of work when it is expanded isobarically. Find the heat given to the gas in the process.

**Solution :** For a diatomic gas,  $C_V = \frac{5}{2} R$  and  $C_p = \frac{7}{2} R$ . The

work done in an isobaric process is

$$W = p(V_2 - V_1)$$

$$= nRT_2 - nRT_1$$

$$\text{or, } T_2 - T_1 = \frac{W}{nR}$$

The heat given in an isobaric process is

$$Q = nC_p(T_2 - T_1)$$

$$= nC_p \frac{W}{nR} = \frac{7}{2} W$$

$$= \frac{7}{2} \times 200 \text{ J} = 700 \text{ J}.$$

12. Calculate the ratio  $C_p / C_V$  of oxygen from the following data. Speed of sound in oxygen at  $0^\circ\text{C} = 315 \text{ m s}^{-1}$ , molecular weight of oxygen  $= 32 \text{ g mol}^{-1}$  and the gas constant  $R = 8.3 \text{ J K}^{-1} \text{ mol}^{-1}$ .

**Solution :** The speed of sound in a gas is given by

$$v = \sqrt{\frac{\gamma P}{\rho}} = \sqrt{\frac{\gamma RT}{M}}$$

$$\text{or, } \gamma = \frac{Mv^2}{RT}$$

$$= \frac{(32 \times 10^{-3} \text{ kg mol}^{-1}) (315 \text{ m s}^{-1})^2}{(8.3 \text{ J K}^{-1} \text{ mol}^{-1}) (273 \text{ K})} = 1.4.$$

□

### QUESTIONS FOR SHORT ANSWER

- Does a gas have just two specific heat capacities or more than two? Is the number of specific heat capacities of a gas countable?
- Can we define specific heat capacity at constant temperature?
- Can we define specific heat capacity for an adiabatic process?
- Does a solid also have two kinds of molar heat capacities  $C_p$  and  $C_v$ ? If yes, do we have  $C_p > C_v$ ? Is  $C_p - C_v = R$ ?
- In a real gas the internal energy depends on temperature and also on volume. The energy increases when the gas expands isothermally. Looking into the derivation of  $C_p - C_v = R$ , find whether  $C_p - C_v$  will be more than  $R$ , less than  $R$  or equal to  $R$  for a real gas.
- Can a process on an ideal gas be both adiabatic and isothermal?
- Show that the slope of  $p$ - $V$  diagram is greater for an adiabatic process as compared to an isothermal process.
- Is a slow process always isothermal? Is a quick process always adiabatic?
- Can two states of an ideal gas be connected by an isothermal process as well as an adiabatic process?
- The ratio  $C_p/C_v$  for a gas is 1.29. What is the degree of freedom of the molecules of this gas?

### OBJECTIVE I

- Work done by a sample of an ideal gas in a process  $A$  is double the work done in another process  $B$ . The temperature rises through the same amount in the two processes. If  $C_A$  and  $C_B$  be the molar heat capacities for the two processes,
  - $C_A = C_B$
  - $C_A < C_B$
  - $C_A > C_B$
  - $C_A$  and  $C_B$  cannot be defined.
- For a solid with a small expansion coefficient,
  - $C_p - C_v = R$
  - $C_p = C_v$
  - $C_p$  is slightly greater than  $C_v$
  - $C_p$  is slightly less than  $C_v$ .
- The value of  $C_p - C_v$  is  $1.00 R$  for a gas sample in state  $A$  and is  $1.08 R$  in state  $B$ . Let  $p_A, p_B$  denote the pressures and  $T_A$  and  $T_B$  denote the temperatures of the states  $A$  and  $B$  respectively. Most likely
  - $p_A < p_B$  and  $T_A > T_B$
  - $p_A > p_B$  and  $T_A < T_B$
  - $p_A = p_B$  and  $T_A < T_B$
  - $p_A > p_B$  and  $T_A = T_B$
- Let  $C_v$  and  $C_p$  denote the molar heat capacities of an ideal gas at constant volume and constant pressure respectively. Which of the following is a universal constant?
  - $\frac{C_p}{C_v}$
  - $C_p C_v$
  - $C_p - C_v$
  - $C_p + C_v$
- 70 calories of heat is required to raise the temperature of 2 mole of an ideal gas at constant pressure from  $30^\circ\text{C}$  to  $35^\circ\text{C}$ . The amount of heat required to raise the temperature of the same gas through the same range at constant volume is
  - 30 calories
  - 50 calories
  - 70 calories
  - 90 calories.
- Figure (27-Q1) shows a process on a gas in which pressure and volume both change. The molar heat capacity for this process is  $C$ .
  - $C = 0$
  - $C = C_v$
  - $C > C_v$
  - $C < C_v$
- The molar heat capacity for the process shown in figure (27-Q2) is
  - $C = C_p$
  - $C = C_v$
  - $C > C_v$
  - $C = 0$ .
- In an isothermal process on an ideal gas, the pressure increases by 0.5%. The volume decreases by about
  - 0.25%
  - 0.5%
  - 0.7%
  - 1%.
- In an adiabatic process on a gas with  $\gamma = 1.4$ , the pressure is increased by 0.5%. The volume decreases by about
  - 0.36%
  - 0.5%
  - 0.7%
  - 1%.
- Two samples  $A$  and  $B$  are initially kept in the same state. The sample  $A$  is expanded through an adiabatic process and the sample  $B$  through an isothermal process. The final volumes of the samples are the same. The final pressures in  $A$  and  $B$  are  $p_A$  and  $p_B$  respectively.
  - $p_A > p_B$
  - $p_A = p_B$
  - $p_A < p_B$
  - The relation between  $p_A$  and  $p_B$  cannot be deduced.
- Let  $T_a$  and  $T_b$  be the final temperatures of the samples  $A$  and  $B$  respectively in the previous question.
  - $T_a < T_b$
  - $T_a = T_b$
  - $T_a > T_b$
  - The relation between  $T_a$  and  $T_b$  cannot be deduced.
- Let  $\Delta W_a$  and  $\Delta W_b$  be the work done by the systems  $A$  and  $B$  respectively in the previous question.
  - $\Delta W_a > \Delta W_b$
  - $\Delta W_a = \Delta W_b$
  - $\Delta W_a < \Delta W_b$

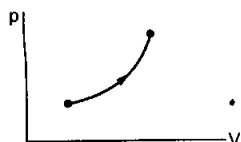


Figure 27-Q1

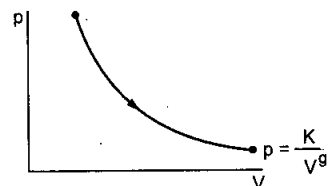


Figure 27-Q2

- (d) The relation between  $\Delta W_a$  and  $\Delta W_b$  cannot be deduced.
13. The molar heat capacity of oxygen gas at STP is nearly  $2.5 R$ . As the temperature is increased, it gradually increases and approaches  $3.5 R$ . The most appropriate reason for this behaviour is that at high temperatures
- oxygen does not behave as an ideal gas
  - oxygen molecules dissociate in atoms
  - the molecules collide more frequently
  - molecular vibrations gradually become effective.

## OBJECTIVE II

- A gas kept in a container of finite conductivity is suddenly compressed. The process
  - must be very nearly adiabatic
  - must be very nearly isothermal
  - may be very nearly adiabatic
  - may be very nearly isothermal.
- Let  $Q$  and  $W$  denote the amount of heat given to an ideal gas and the work done by it in an isothermal process.
  - $Q = 0$
  - $W = 0$
  - $Q \neq W$
  - $Q = W$
- Let  $Q$  and  $W$  denote the amount of heat given to an ideal gas and the work done by it in an adiabatic process.
  - $Q = 0$
  - $W = 0$
  - $Q = W$
  - $Q \neq W$
- Consider the processes  $A$  and  $B$  shown in figure (27-Q3). It is possible that
  - both the processes are isothermal
  - both the processes are adiabatic
  - $A$  is isothermal and  $B$  is adiabatic
  - $A$  is adiabatic and  $B$  is isothermal.
- Three identical adiabatic containers  $A$ ,  $B$  and  $C$  contain helium, neon and oxygen respectively at equal pressure. The gases are pushed to half their original volumes.
  - The final temperatures in the three containers will be the same.
  - The final pressures in the three containers will be the same.
  - The pressures of helium and neon will be the same but that of oxygen will be different.
  - The temperatures of helium and neon will be the same but that of oxygen will be different.
- A rigid container of negligible heat capacity contains one mole of an ideal gas. The temperature of the gas increases by  $1^\circ\text{C}$  if  $3.0$  cal of heat is added to it. The gas may be
  - helium
  - argon
  - oxygen
  - carbon dioxide.
- Four cylinders contain equal number of moles of argon, hydrogen, nitrogen and carbon dioxide at the same temperature. The energy is minimum in
  - argon
  - hydrogen
  - nitrogen
  - carbon dioxide.

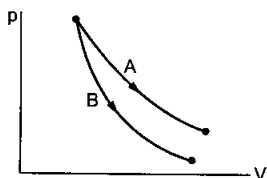


Figure 27-Q3

## EXERCISES

- A vessel containing one mole of a monatomic ideal gas (molecular weight  $= 20 \text{ g mol}^{-1}$ ) is moving on a floor at a speed of  $50 \text{ m s}^{-1}$ . The vessel is stopped suddenly. Assuming that the mechanical energy lost has gone into the internal energy of the gas, find the rise in its temperature.
- $5 \text{ g}$  of a gas is contained in a rigid container and is heated from  $15^\circ\text{C}$  to  $25^\circ\text{C}$ . Specific heat capacity of the gas at constant volume is  $0.172 \text{ cal g}^{-1} ^\circ\text{C}^{-1}$  and the mechanical equivalent of heat is  $4.2 \text{ J cal}^{-1}$ . Calculate the change in the internal energy of the gas.
- Figure (27-E1) shows a cylindrical container containing oxygen ( $\gamma = 1.4$ ) and closed by a  $50 \text{ kg}$  frictionless piston. The area of cross section is  $100 \text{ cm}^2$ , atmospheric pressure is  $100 \text{ kPa}$  and  $g$  is  $10 \text{ m s}^{-2}$ . The cylinder is slowly heated for some time. Find the amount of heat supplied to the gas if the piston moves out through a distance of  $20 \text{ cm}$ .



Figure 27-E1

- The specific heat capacities of hydrogen at constant volume and at constant pressure are  $2.4 \text{ cal g}^{-1} ^\circ\text{C}^{-1}$  and  $3.4 \text{ cal g}^{-1} ^\circ\text{C}^{-1}$  respectively. The molecular weight of hydrogen is  $2 \text{ g mol}^{-1}$  and the gas constant  $R = 8.3 \times 10^7 \text{ erg } ^\circ\text{C}^{-1} \text{ mol}^{-1}$ . Calculate the value of  $J$ .
- The ratio of the molar heat capacities of an ideal gas is  $C_p/C_v = 7/6$ . Calculate the change in internal energy of  $1.0$  mole of the gas when its temperature is raised by

- 50 K (a) keeping the pressure constant, (b) keeping the volume constant and (c) adiabatically.
- A sample of air weighing  $1.18 \text{ g}$  occupies  $1.0 \times 10^3 \text{ cm}^3$  when kept at  $300 \text{ K}$  and  $1.0 \times 10^5 \text{ Pa}$ . When  $2.0 \text{ cal}$  of heat is added to it at constant volume, its temperature increases by  $1^\circ\text{C}$ . Calculate the amount of heat needed to increase the temperature of air by  $1^\circ\text{C}$  at constant pressure if the mechanical equivalent of heat is  $4.2 \times 10^{-7} \text{ erg cal}^{-1}$ . Assume that air behaves as an ideal gas.
  - An ideal gas expands from  $100 \text{ cm}^3$  to  $200 \text{ cm}^3$  at a constant pressure of  $2.0 \times 10^5 \text{ Pa}$  when  $50 \text{ J}$  of heat is supplied to it. Calculate (a) the change in internal energy of the gas, (b) the number of moles in the gas if the initial temperature is  $300 \text{ K}$ , (c) the molar heat capacity  $C_p$  at constant pressure and (d) the molar heat capacity  $C_v$  at constant volume.
  - An amount  $Q$  of heat is added to a monatomic ideal gas in a process in which the gas performs a work  $Q/2$  on its surrounding. Find the molar heat capacity for the process.
  - An ideal gas is taken through a process in which the pressure and the volume are changed according to the equation  $p = kV$ . Show that the molar heat capacity of the gas for the process is given by  $C = C_v + \frac{R}{2}$ .
  - An ideal gas ( $C_p/C_v = \gamma$ ) is taken through a process in which the pressure and the volume vary as  $p = aV^b$ . Find the value of  $b$  for which the specific heat capacity in the process is zero.
  - Two ideal gases have the same value of  $C_p/C_v = \gamma$ . What will be the value of this ratio for a mixture of the two gases in the ratio  $1:2$ ?
  - A mixture contains 1 mole of helium ( $C_p = 2.5 R$ ,  $C_v = 1.5 R$ ) and 1 mole of hydrogen ( $C_p = 3.5 R$ ,  $C_v = 2.5 R$ ). Calculate the values of  $C_p$ ,  $C_v$  and  $\gamma$  for the mixture.
  - Half mole of an ideal gas ( $\gamma = 5/3$ ) is taken through the cycle  $abcd$  as shown in figure (27-E2). Take  $R = \frac{25}{3} \text{ J K}^{-1} \text{ mol}^{-1}$ . (a) Find the temperature of the gas in the states  $a$ ,  $b$ ,  $c$  and  $d$ . (b) Find the amount of heat supplied in the processes  $ab$  and  $bc$ . (c) Find the amount of heat liberated in the processes  $cd$  and  $da$ .

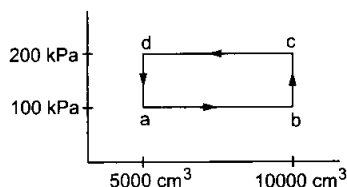


Figure 27-E2

- An ideal gas ( $\gamma = 1.67$ ) is taken through the process  $abc$  shown in figure (27-E3). The temperature at the point  $a$  is  $300 \text{ K}$ . Calculate (a) the temperatures at  $b$  and  $c$ , (b) the work done in the process, (c) the amount of heat

supplied in the path  $ab$  and in the path  $bc$  and (d) the change in the internal energy of the gas in the process.

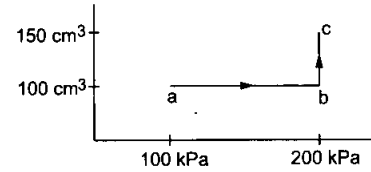


Figure 27-E3

- In Joly's differential steam calorimeter,  $3 \text{ g}$  of an ideal gas is contained in a rigid closed sphere at  $20^\circ\text{C}$ . The sphere is heated by steam at  $100^\circ\text{C}$  and it is found that an extra  $0.095 \text{ g}$  of steam has condensed into water as the temperature of the gas becomes constant. Calculate the specific heat capacity of the gas in  $\text{J g}^{-1} \text{ K}^{-1}$ . The latent heat of vaporization of water =  $540 \text{ cal g}^{-1}$ .
- The volume of an ideal gas ( $\gamma = 1.5$ ) is changed adiabatically from  $4.00 \text{ litres}$  to  $3.00 \text{ litres}$ . Find the ratio of (a) the final pressure to the initial pressure and (b) the final temperature to the initial temperature.
- An ideal gas at pressure  $2.5 \times 10^5 \text{ Pa}$  and temperature  $300 \text{ K}$  occupies  $100 \text{ cc}$ . It is adiabatically compressed to half its original volume. Calculate (a) the final pressure, (b) the final temperature and (c) the work done by the gas in the process. Take  $\gamma = 1.5$ .
- Air ( $\gamma = 1.4$ ) is pumped at  $2 \text{ atm}$  pressure in a motor tyre at  $20^\circ\text{C}$ . If the tyre suddenly bursts, what would be the temperature of the air coming out of the tyre. Neglect any mixing with the atmospheric air.
- A gas is enclosed in a cylindrical can fitted with a piston. The walls of the can and the piston are adiabatic. The initial pressure, volume and temperature of the gas are  $100 \text{ kPa}$ ,  $400 \text{ cm}^3$  and  $300 \text{ K}$  respectively. The ratio of the specific heat capacities of the gas is  $C_p/C_v = 1.5$ . Find the pressure and the temperature of the gas if it is (a) suddenly compressed (b) slowly compressed to  $100 \text{ cm}^3$ .
- The initial pressure and volume of a given mass of a gas ( $C_p/C_v = \gamma$ ) are  $p_0$  and  $V_0$ . The gas can exchange heat with the surrounding. (a) It is slowly compressed to a volume  $V_0/2$  and then suddenly compressed to  $V_0/4$ . Find the final pressure. (b) If the gas is suddenly compressed from the volume  $V_0$  to  $V_0/2$  and then slowly compressed to  $V_0/4$ , what will be the final pressure?
- Consider a given sample of an ideal gas ( $C_p/C_v = \gamma$ ) having initial pressure  $p_0$  and volume  $V_0$ . (a) The gas is isothermally taken to a pressure  $p_0/2$  and from there adiabatically to a pressure  $p_0/4$ . Find the final volume. (b) The gas is brought back to its initial state. It is adiabatically taken to a pressure  $p_0/2$  and from there isothermally to a pressure  $p_0/4$ . Find the final volume.
- A sample of an ideal gas ( $\gamma = 1.5$ ) is compressed adiabatically from a volume of  $150 \text{ cm}^3$  to  $50 \text{ cm}^3$ . The initial pressure and the initial temperature are  $150 \text{ kPa}$  and  $300 \text{ K}$ . Find (a) the number of moles of the gas in the sample, (b) the molar heat capacity at constant volume, (c) the final pressure and temperature, (d) the

work done by the gas in the process and (e) the change in internal energy of the gas.

23. Three samples *A*, *B* and *C* of the same gas ( $\gamma = 1.5$ ) have equal volumes and temperatures. The volume of each sample is doubled, the process being isothermal for *A*, adiabatic for *B* and isobaric for *C*. If the final pressures are equal for the three samples, find the ratio of the initial pressures.
24. Two samples *A* and *B* of the same gas have equal volumes and pressures. The gas in sample *A* is expanded isothermally to double its volume and the gas in *B* is expanded adiabatically to double its volume. If the work done by the gas is the same for the two cases, show that  $\gamma$  satisfies the equation  $1 - 2^{1-\gamma} = (\gamma - 1) \ln 2$ .
25. 1 litre of an ideal gas ( $\gamma = 1.5$ ) at 300 K is suddenly compressed to half its original volume. (a) Find the ratio of the final pressure to the initial pressure. (b) If the original pressure is 100 kPa, find the work done by the gas in the process. (c) What is the change in internal energy? (d) What is the final temperature? (e) The gas is now cooled to 300 K keeping its pressure constant. Calculate the work done during the process. (f) The gas is now expanded isothermally to achieve its original volume of 1 litre. Calculate the work done by the gas. (g) Calculate the total work done in the cycle.
26. Figure (27-E4) shows a cylindrical tube with adiabatic walls and fitted with an adiabatic separator. The separator can be slid into the tube by an external mechanism. An ideal gas ( $\gamma = 1.5$ ) is injected in the two sides at equal pressures and temperatures. The separator remains in equilibrium at the middle. It is now slid to a position where it divides the tube in the ratio 1 : 3. Find the ratio of the temperatures in the two parts of the vessel.



Figure 27-E4

27. Figure (27-E5) shows two rigid vessels *A* and *B*, each of volume  $200 \text{ cm}^3$  containing an ideal gas ( $C_V = 12.5 \text{ J K}^{-1} \text{ mol}^{-1}$ ). The vessels are connected to a manometer tube containing mercury. The pressure in both the vessels is 75 cm of mercury and the temperature is 300 K. (a) Find the number of moles of the gas in each vessel. (b) 5.0 J of heat is supplied to the gas in the vessel *A* and 10 J to the gas in the vessel *B*. Assuming no appreciable transfer of heat from *A* to *B* calculate the difference in the heights of mercury in the two sides of the manometer. Gas constant  $R = 8.3 \text{ J K}^{-1} \text{ mol}^{-1}$ .

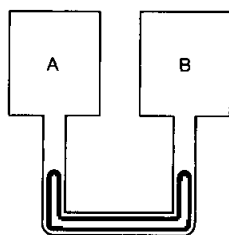


Figure 27-E5

28. Figure (27-E6) shows two vessels with adiabatic walls, one containing 0.1 g of helium ( $\gamma = 1.67$ ,  $M = 4 \text{ g mol}^{-1}$ ) and the other containing some amount of hydrogen ( $\gamma = 1.4$ ,  $M = 2 \text{ g mol}^{-1}$ ). Initially, the temperatures of the two gases are equal. The gases are electrically heated for some time during which equal amounts of heat are given to the two gases. It is found that the temperatures rise through the same amount in the two vessels. Calculate the mass of hydrogen.

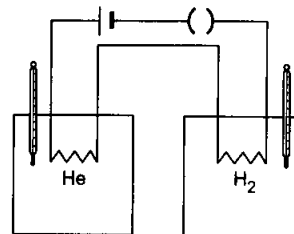


Figure 27-E6

29. Two vessels *A* and *B* of equal volume  $V_0$  are connected by a narrow tube which can be closed by a valve. The vessels are fitted with pistons which can be moved to change the volumes. Initially, the valve is open and the vessels contain an ideal gas ( $C_p/C_V = \gamma$ ) at atmospheric pressure  $p_0$  and atmospheric temperature  $T_0$ . The walls of the vessel *A* are diathermic and those of *B* are adiabatic. The valve is now closed and the pistons are slowly pulled out to increase the volumes of the vessels to double the original value. (a) Find the temperatures and pressures in the two vessels. (b) The valve is now opened for sufficient time so that the gases acquire a common temperature and pressure. Find the new values of the temperature and the pressure.
30. Figure (27-E7) shows an adiabatic cylindrical tube of volume  $V_0$  divided in two parts by a frictionless adiabatic separator. Initially, the separator is kept in the middle, an ideal gas at pressure  $p_1$  and temperature  $T_1$  is injected into the left part and another ideal gas at pressure  $p_2$  and temperature  $T_2$  is injected into the right part.  $C_p/C_V = \gamma$  is the same for both the gases. The separator is slid slowly and is released at a position where it can stay in equilibrium. Find (a) the volumes of the two parts, (b) the heat given to the gas in the left part and (c) the final common pressure of the gases.

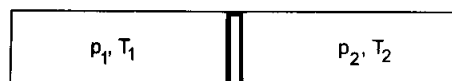


Figure 27-E7

31. An adiabatic cylindrical tube of cross-sectional area  $1 \text{ cm}^2$  is closed at one end and fitted with a piston at the other end. The tube contains 0.03 g of an ideal gas. At 1 atm pressure and at the temperature of the surrounding, the length of the gas column is 40 cm. The piston is suddenly pulled out to double the length of the column. The pressure of the gas falls to 0.355 atm. Find the speed of sound in the gas at atmospheric temperature.

32. The speed of sound in hydrogen at  $0^\circ\text{C}$  is  $1280\text{ m s}^{-1}$ . The density of hydrogen at STP is  $0.089\text{ kg m}^{-3}$ . Calculate the molar heat capacities  $C_p$  and  $C_v$  of hydrogen.
33.  $4.0\text{ g}$  of helium occupies  $22400\text{ cm}^3$  at STP. The specific heat capacity of helium at constant pressure is  $5.0\text{ cal K}^{-1}\text{ mol}^{-1}$ . Calculate the speed of sound in helium at STP.
34. An ideal gas having density  $1.7 \times 10^{-3}\text{ g cm}^{-3}$  at a pressure  $1.5 \times 10^5\text{ Pa}$  is filled in a Kundt tube. When the gas is resonated at a frequency of  $3.0\text{ kHz}$ , nodes are formed at a separation of  $6.0\text{ cm}$ . Calculate the molar heat capacities  $C_p$  and  $C_v$  of the gas.
35. Standing waves of frequency  $5.0\text{ kHz}$  are produced in a tube filled with oxygen at  $300\text{ K}$ . The separation between the consecutive nodes is  $3.3\text{ cm}$ . Calculate the specific heat capacities  $C_p$  and  $C_v$  of the gas.

□

## ANSWERS

## OBJECTIVE I

1. (c)    2. (c)    3. (a)    4. (c)    5. (b)    6. (c)  
 7. (d)    8. (b)    9. (a)    10. (c)    11. (a)    12. (c)  
 13. (d)

## OBJECTIVE II

1. (c), (d)    2. (d)    3. (a), (d)  
 4. (c)    5. (c), (d)    6. (a), (b)  
 7. (a)

## EXERCISES

1.  $2.0\text{ K}$   
 2.  $36\text{ J}$   
 3.  $1050\text{ J}$   
 4.  $4.15 \times 10^7\text{ erg cal}^{-1}$   
 5.  $2490\text{ J}$  in all cases  
 6.  $2.08\text{ cal}$   
 7. (a)  $30\text{ J}$     (b)  $0.008$   
     (c)  $20.8\text{ J K}^{-1}\text{ mol}^{-1}$     (d)  $12.5\text{ J K}^{-1}\text{ mol}^{-1}$   
 8.  $3R$   
 10.  $-\gamma$   
 11.  $\gamma$   
 12.  $3R, 2R, 1.5$   
 13. (a)  $120\text{ K}, 240\text{ K}, 480\text{ K}, 240\text{ K}$   
     (b)  $1250\text{ J}, 1500\text{ J}$     (c)  $2500\text{ J}, 750\text{ J}$   
 14. (a)  $600\text{ K}, 900\text{ K}$     (b)  $10\text{ J}$   
     (c)  $14.9\text{ J}, 24.9\text{ J}$     (d)  $29.8\text{ J}$   
 15.  $0.90\text{ J g}^{-1}\text{ K}^{-1}$
16. (a)  $1.54$     (b)  $1.15$   
 17. (a)  $7.1 \times 10^5\text{ Pa}$     (b)  $424\text{ K}$     (c)  $-21\text{ J}$   
 18.  $240\text{ K}$   
 19.  $800\text{ kPa}, 600\text{ K}$  in both cases  
 20.  $2^{\gamma+1} p_0$  in both cases  
 21.  $2^{(\gamma+1)/\gamma} V_0$  in each case  
 22. (a)  $0.009$     (b)  $2R = 16.6\text{ J K}^{-1}\text{ mol}^{-1}$   
     (c)  $780\text{ kPa}, 520\text{ K}$     (d)  $-33\text{ J}$     (e)  $33\text{ J}$   
 23.  $2 : 2\sqrt{2} : 1$   
 25. (a)  $2\sqrt{2}$     (b)  $-82\text{ J}$   
     (c)  $82\text{ J}$     (d)  $424\text{ K}$   
     (e)  $-41.4\text{ J}$     (f)  $103\text{ J}$   
     (g)  $-23.4\text{ J}$   
 26.  $\sqrt{3} : 1$   
 27. (a)  $0.008$     (b)  $12.5\text{ cm}$   
 28.  $0.03\text{ g}$   
 29. (a)  $T_0, \frac{p_0}{2}$  in vessel A and  $T_0/2^{\gamma-1}, p_0/2^\gamma$  in vessel B  
     (b)  $T_0, p_0/2$   
 30. (a)  $\frac{p_1^{1/\gamma} V_0}{A}, \frac{p_2^{1/\gamma} V_0}{A}$     (b) zero  
     (c)  $(A/2)^\gamma$  where  $A = p_1^{1/\gamma} + p_2^{1/\gamma}$   
 31.  $447\text{ m s}^{-1}$   
 32.  $18.0\text{ J K}^{-1}\text{ mol}^{-1}, 26.3\text{ J K}^{-1}\text{ mol}^{-1}$   
 33.  $960\text{ m s}^{-1}$   
 34.  $26\text{ J K}^{-1}\text{ mol}^{-1}, 17.7\text{ J K}^{-1}\text{ mol}^{-1}$   
 35.  $29.0\text{ J K}^{-1}\text{ mol}^{-1}, 20.7\text{ J K}^{-1}\text{ mol}^{-1}$

□