UNIT 4 APPLICATIONS OF THE FIRST LAW OF THERMODYNAMICS

Structure

4.1 INTRODUCTION

In Unit 3 you have learnt the first law of thermodynamics. It is essentially an extension of the principle of conservation of energy for thermodynamic processes. It tells us that heat and other forms of energy are equivalent. Do you know that much of our world works because of this equivalence? Most of the electrical energy that lights our houses, operates machines and runs trains originates in heat. This heat is released in burning of coal, oil; gas or fissioning of uranium.

In a sense, this law is universal and explains phenomena observed in nature as well as in a laboratory. The fall in temperature as we move upward in outer atmosphere — a very large scale phenomenon — is explained rather well. Using this law we can also explain the pressure oscillations in a sound wave. Its application to flow processes and chemical reactions is also very interesting. In spite of its wide utility, this law has inherent limitations. It gives us no information about the direction of flow of heat. This information is contained in the second law of thermodynamics, which you will study in Block 2, of this course.

In this unit you will learn to apply the first law to diverse thermodynamic systems. In Sec. 4.2 we start by computing the heat capacities at constant pressure and constznt volume for an ideal gas. For any substance, this difference can be related to measurable quantities like volume expansion coefficient and bulk modulus of elasticity. In Sec. 4.3 we have used this law to derive the equation of state for adiabatic processes. Using this equation, we have computed an expression for the adiabatic lapse rate. In Sec. 4.4 we have introduced the concept of enthalpy — a function of state. It is useful in discussing production of low temperatures and regenerative cooling as well as chemical reactions. You will learn more about enthalpy in the next block.

Objectives

After studying this unit, you will be able to

- compute the difference between heat capacities at constant pressure and at constant volume
- derive the equation of state for an adiabatic process
- explain adiabatic lapse rate
- compute expressions for velocity of sound in air
- define enthalpy and use it to study chemical reactions
- State Hess's Law.

In Unit 3 you learnt to establish the first law of thermodynamics and compute changes in internal energy when a substance undergoes a change of state. In this unit we will apply this law to diverse physical systems. Let us first consider a gaseous system. You would recall that the heat capacity of ideal gases is independent of the nature of the gas. But physical conditions under which heat is given change the value of heat capacity of a gas. Is the same true for liquids and solids? To discover the answer to this question let us calculate the difference between heat capacities of gases at constant pressure and at constant volume.

4.2 DIFFERENCE OF HEAT CAPACITIES OF A GAS

From Unit 3 you would recall that in the absence of diffusive interactions, the first law of thermodynamics for a gaseous system has the form

$$\delta Q = dU + pdV \tag{4.1}$$

This means that heat δQ given to a system at constant pressure (isobaric process). changes its internal energy by dU and volume by dV.

Since heat is not a state variable, we have put δ before Q to denote changes in heat content of a system.

Let us assume that one mole of a gas is contained in a cylinder fitted with a piston. In Unit 1 you learnt that the state of a gas can be described in terms of any two thermodynamic coordinates out of p, V and T. Let us choose T and V as independent variables. Since internal energy is a function of state, we can write

$$U = U(T, V)$$

Then the differential of U can be written as

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \tag{4.2}$$

The symbol ∂ is pronounced as del. It denotes a partial derivative.

On combining Eqs. (4.1) and (4.2), you can write

$$\delta Q = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[p + \left(\frac{\partial U}{\partial V}\right)_T\right] dV \tag{4.3}$$

You can now imagine that the piston is tightly clamped. As we heat the gas, it cannot expand, i.e. it cannot do any work and all the heat goes to raise its internal energy and hence temperature. The heat required to raise the temperature of one mole of a gas through one degree when its volume is kept constant is termed as molar heat capacity at constant volume. It is denoted by the symbol C_V and is generally expressed in J mol $^{-2}$ K^{-1}. For such a system Eq. (4.3) reduces to

$$C_V = \left(\frac{\delta Q}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V \tag{4.4}$$

The different symbols have been used to depict changes in heat and temperature. We have done so because heat is not a function of state.

You may recall that heat capacity varies from substance to substance. It varies with temperature and amount of the substance as well. The latter is measured in kg or by the number of moles. The corresponding mensures of heat capacity are specific heat and molar heat capacity, The specific heat is the heat capacity per kilogram and molar heat capacity is the heat capacity per mole. At constant volume the specific heat is denoted by small letter c_v :

$$c_v = \frac{C_V}{m}$$

where m is the number of kilograms per mole in the substance with molar heat capacity C_V at constant volume. The specific heat capacity is measured in cal g^{-1} K^{-1}. When heat is measured in joules (1 cal = 4.184 J), molarheat capacity is measured in J mol^{-1} K^{-1}.

Now suppose that the piston is allowed to move in or out so that the gas is kept at constant pressure. The gas does work on the piston and some of the heat ends up as mechanical energy of the surroundings. So to achieve a given change in temperature, more heat has to be supplied to the gas in a constant pressure process. The molar heat capacity of a gas at constant pressure is defined as the amount of heat required to raise the temperature of one mole of gas by one degree. It is denoted by the symbol C_p. Mathematically, we can write

$$C_p = \left(\frac{\delta Q}{\partial T}\right)_p \tag{4.5}$$

On combining Eqs. (4.3) and (4.5), you will get

$$C_p = \left(\frac{\partial U}{\partial T}\right)_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\left(\frac{\partial V}{\partial T}\right)_p$$

Using Eq. (4.4) we find that

$$C_p - C_V = \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\left(\frac{\partial V}{\partial T}\right)_p \tag{4.6}$$

The first term in the brackets on the right hand side tells us that internal energy of a gas may vary with volume even when temperature is kept fixed. This implies that work has to be done against intermolecular forces in the gas. For simplicity, let us first apply this equation to a perfect gas, which is said to have the following properties:

i) The gas molecules are point masses and its equation of state is the perfect gas law: $pV = RT$, where $R = 8.314\ \text{JK}^{-1}\ \text{mol}^{-1}$.

ii) There are no intermolecular forces. From Unit 3 you will recall that this implies that internal energy of a perfect gas is wholly kinetic and $(\partial U/\partial V)_T = 0$.

Using this result in Eq. (4.6), you will get

$$C_p - C_V = p\left(\frac{\partial V}{\partial T}\right)_p \tag{4.7}$$

This shows that the difference in the molar heat capacities of a gas depends on how the volume of a system at constant pressure changes as temperature increases. We expect this difference to be substantial since a small change in temperature brings about a large change in the volume of a gas.

Using the gas law, we can write

$$p\left(\frac{\partial V}{\partial T}\right)_p = R$$

so that

$$C_p - C_V = R \tag{4.8}$$

This result is known as **Mayer's formula.** It shows that the difference between constant pressure and constant volume molar heat capacities is equal to the molar gas constant. You may now ask: How does it compare with the experiment? To discover answer to this question, refer to Table 4.1 where we have given the molar heat capacities of gases (in units of the gas constant R) at constant pressure and at constant volume.

Table 4.1 : Molar heat capacities of gases at constant pressure and constant volume

Type of Gas	Gas	C_p/R	C_V/R
Mpnoatomic	He	2.5	1.5
	Ar	2.5	1.5
Diatomic,	H_2	3.45	2.45
	O_2	3.53	2.53,
	Cl_2	4.17	3.09
Polyatomic	CO_2	4.43	3.42
	NH_3	4.42	3.34
	C_2H_6	6.21	5.18

You will observe that Mayer's formula holds rather well for monoatomic gases. For diatomic and polyatomic gases also, the agreement is fairly reasonable. Before we investigate other related questions, we would like you to go through the following example carefully.

Example 1

For hydrogen, the molar heat capacities at constant pressure and constant volume are 28.8 J $\text{mol}^{-1}\ \text{K}^{-1}$ and 20.5 J $\text{mol}^{-1}\ \text{K}^{-1}$ respectively. Let us calculate the gas constant.

Solution

From **Eq. (4.8)**

$$C_p - C_V = R$$

On substituting the given values, you will get

$$R = (28.8 - 20.5)\ \text{J mol}^{-1}\ \text{K}^{-1}$$
$$= 8.3\ \text{J mol}^{-1}\ \text{K}^{-1}$$

SAQ 1

The molar heat capacity of a gas at constant pressure $C_p = 160\ J\ mol^{-1}\ K^{-1}$. Compute the ratio of specific heats at constant pressure to that at constant volume .

Proceeding further, you may logically ask: Does Mayer's formula apply universally? To answer this question we note that a real gas is made up of molecules having small but finite size and non-zero inter-molecular forces. This suggests that the ideal gas law is not valid for a dense gas and Eq. (4.8) is approximate. This is because it makes no allowance for the change in internal energy with volume. Some wdrk has always to be done against inter-molecular forces. This is illustrated in Example 2 below.

Example 2

For a dense gas, we use the van der Waals' equation of state. Assuming that the internal energy is given by $U = -a/V +$ constant, calculate the difference $C_p - C_V$.

Solution

The van der Waals' equation of state for a gas is

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT \qquad -(i)$$

where a and b are constants for a gas.

Since internal energy is given by

$$U = -\frac{a}{V} + \text{constant}$$

you can write

$$\left(\frac{\partial U}{\partial V}\right)_T = +\frac{a}{V^2}$$

Using this result in Eq. (4.6), we find that

$$C_p - C_V = \left(p + \frac{a}{V^2}\right)\left(\frac{\partial V}{\partial T}\right)_p$$

From (i), we can write

$$\left[\left(p + \frac{a}{V^2}\right) - \frac{2a}{V^3}(V - b)\right]\left(\frac{\partial V}{\partial T}\right) = R$$

or

$$\left(p + \frac{a}{V^2}\right)\left(\frac{\partial V}{\partial T}\right)_p = \frac{R\left(p + \frac{a}{V^2}\right)}{\left(p + \frac{a}{V^2}\right) - \frac{2a}{V^3}(V - b)} = \frac{R}{1 - \frac{2a}{V^3\left(p + \frac{a}{V^2}\right)}(V - b)}$$

so that

$$C_p - C_V = \frac{R}{1 - \frac{2a}{V^3 RT}(V - b)^2}$$

$$\approx \frac{R}{1 - \frac{2a}{VRT}}$$

since a and b are very small. Using binomial expansion, we can write

$$C_p - C_V = R\left(1 + \frac{2a}{VRT}\right).$$

'For any substance, a more general relation between the heat capacities at constant pressure and at constant volume is

$$C_p - C_V = -T\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_p^2 = TE\alpha^2 V$$

where E is the bulk modulus of elasticity and α is the coefficient of volume expansion. You will learn to prove this result in Unit 7 of Block 2.

SAQ 2

Show that the first law of thermodynamics can also be written as

$$\delta Q = C_V\, dT + pdV$$

and

$$\delta Q = C_p\, dT - Vdp$$

Let us pause for some time and ask: What have we achieved so far? Do we distinguish heat capacities at constant volume and constant pressure for solids and liquids as well? For these substances such a distinction is less significant because they are incompressible. That is, their coefficient of volume expansion is much less compared to that for gases. In fact, for solids and liquids, measured values are quoted at constant pressure.

So far you have learnt to compute the difference between heat capacities at constant pressure and constant volume. Let us now consider a process in which no heat is exchanged between the system and surroundings. You may have experienced sometimes that if you let air out of a tyre, you feel that the air is cool. Blow on the back of your hand with your mouth wide open. You will feel that your breath is warm. Now close your lips into a small opening and blow again. Your breath now feels cool. Does this mean that your body temperature is different in the two cases or do the conditions induce this apparent change? It happens because in the latter case, air undergoes adiabatic expansion. From Unit 1 you know of many adiabatic processes occurring around you. But in this unit we will consider the particular cases of the propagation of sound in air and expansion of air as it Ases in the troposphere. In a physics laboratory, you can realise an adiabatic transformation by expanding or compressing a gas in a cylinder having non-conducting walls and fitted with an insulated piston. Let us now derive the equation of state for an adiabatic process using the first law of thermodynamics.

4.3 EQUATION OF STATE FOR AN ADIABATIC PROCESS

In an adiabatic process, the system and the surroundings are not in thermal contact. That is, no heat exchange takes place and $\delta Q = 0$. Then the first law of thermodynamics tells us that

$$dU + \delta W = 0 \tag{4.9}$$

This shows that in an adiabatic expansion, internal energy decreases, Since U is a function of T, a fall in internal energy implies drop in temperature, i.e. the system cools. What happens in an adiabatic compression? We expect that the temperature will increase as work is done on the system. From this you may conclude that adiabatic expansion produces cooling and adiabatic compression produces heating. This finds an important application in the production of low temperatures. You will learn its details in Unit 8 of Block 2.

Suppose that one mole of a perfect gas is subject to a quasistatic adiabatic expansion. From SAQ 2 you can write

$$C_V\, dT + pdV = 0 \tag{4.10}$$

During the expansion, the gas passes through an infinite number of equilibrium states. This means that the equation of state (pV = RT) will hold for each state. On substituting p = RTIV and dividing throughout by $C_V T$, you can arrange the resulting expression in the form

$$\frac{dT}{T} = \frac{R}{C_V}\frac{dV}{V} \tag{4.11a}$$

For a quasistatic process, V and T are well defined for each state. So if we assume that C_V is independent of temperature, we can readily integrate Eq. (4.11a) to obtain

$$\ln T = \frac{\mathrm{R}}{C_V} \ln \mathrm{V} + \ln K \tag{4.11b}$$

where ln K is constant of integration.

In general, the heat capacity at constant volume changes with temperature. But this is significant only when the change in temperature is very large (~ 1000K). So for processes under consideration C_V may be assumed to be independtnt of temperature.

Taking antilog, we obtain

$$TV^{R/C_V} = K$$

Using Eq. (4.8) we can also write

$$TV^{(C_p - C_V)/C_V} = K$$

In your earlier physics classes you must have learnt that the ratio of heat capacity at constant pressure to that at constant volume is usually denoted by the greek symbol gamma; $\gamma = C_p/C_V$. So we can rewrite the equation for an adiabatic transformation as

$$TV^{\gamma - 1} = K \tag{4.12}$$

This relation tells us that as temperature increases volume decreases and vice versa when a perfect gas undergoes a quasistatic adiabatic change. This is an important result. Before proceeding further, let us pause for a minute and ask: Can we similarly relate pressure and temperature or pressure and volume'?To discover answer to this question, we would like you to solve **SAQ** 3.

SAQ 3

Starting from Eq. (4.12), show that

$$\frac{T^{\gamma}}{p^{\gamma-1}} = K_1 \tag{4.13a}$$

and

$$pV^{\gamma} = K_2 \tag{4.13b}$$

where K_1 and K_2 are constants.

[Hint: Use Equations of state pV = RT.]

Eq. (4.13a) predicts that during an adiabatic process, increase/decrease in pressure is accompanied by a corresponding increase/decrease in temperature. Can you say the same about Eq. (4.13b)?

You will'note that Eqs. (4.12) and (4.13) are equivalent forms of the so-called **adiabatic equation.** This equation will hold provided

i) the initial and final states are equilibrium states,

ii) the perfect gas equation pV = RT is valid, and

iii) the internal energy of the gas is proportional to temperature only.

SAQ 4

Differentiate Eq. (4.13b) w.r.t. V and compute $(dp/dV)_s$. Also calculate the corresponding quantity for an isothermal change (pV = constant). What do you conclude?

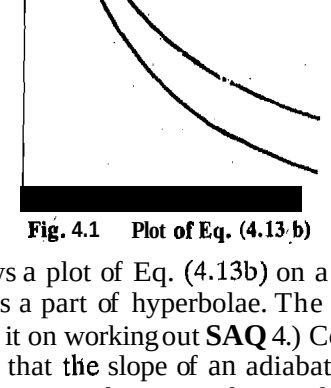


Fig. 4.1 Plot of Eq. (4.13 b)

Now refer to Fig. 4.1. It shows a plot of Eq. (4.13b) on a p – V diagram. You will observe that the adiabat is a part of hyperbolae. The slope of the adiabat is $\gamma(p/V)$. (You must have seen it on working out **SAQ** 4.) Compare it with the slope of an isotherm. You will note that the slope of an adiabat is γ times the slope or ar isotherm. That is, an adiabat is steeper than an isotherm. This is because the gas loses internal energy as it expands. This also implies that relative change in volume in ar adiabatic process is less than that in an isothermal change.

Example 3

The nozzle of a bicycle is blocked. With no force on the handle, the pump contains a volume V of air at 300K and atmospheric pressure. The handle is pushed down with a constant force F reducing the volume to half. No air escapes from the pump. Assume the change to be adiabatic. Taking y for air to be 1.4, compute the final temperature of air in the pump.

Solution

Since the change is adiabatic, we can use Eq. (4.13b):

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

or

$$p_i V^{\gamma} = p_f \left(\frac{V}{2}\right)^{\gamma}$$

where p_f is the pressure of the gas when the handle is in final equilibrium state. On simplifying this equation, we get

$$p_f = p_i 2^{\gamma} = 2.64\, p_i$$

Applying the perfect gas equation of state, you can write

$$\frac{p_i V}{T_i} \quad \frac{p_f (V/2)}{T_f}$$

or

$$T_f = \frac{p_f}{2 p_i} T_i$$

$$= \frac{2.64}{2} T_i$$

$$= 1.32 \times (300\ \text{K})$$

$$= 396\text{K}$$

Beware, this temperature is higher than the boiling point of water! ***So*** you are advised not to touch the nozzle of a blocked pump after you have used it. Physically this means that adiabatic compression produces heating.

SAQ 5

The pressurq inside a scooter tyre is 2 atm. at 300K. It bursts suddenly. Regarding the change to be adiabatic, compute the final temperature. Use y = 1.4.

You may think that Eq. (4.13) contradicts the ideal gas law. It is not so because the ideal gas law does not imply $pV =$ constant except for an isothermal process. Since a reversible process cannot be both adiabatic and isothermal, there is no contradiction.

Example 4

Two identical gaseous systems, each containing 0.06 mol of ideal gas, are ***at*** 300K and 2.0 atm pressure. The ratio of heat capacities of the gas is 1.4. One of the gases is made to expand adiabatically and the other isothermally until they are at normal pressure. Calculate the final volumes in each case.

Solution

The initial volume of both gases may be obtained from the ideal gas law, $pV = nRT$. Solving for V, we get

$$V = \frac{nRT}{p} = \frac{(0.06\ \text{mol}) \times (8.3\text{J K}^{-1}\,\text{mol}^{-1}(300\text{K})}{(2.0\ \text{atm})\ (1.0 \times 10^5 \text{Pa atm}^{-1})}$$

$$= 7.5 \times 10^{-4}\text{m}^3$$

For the isothermal process, T remains copstapt at 300K. So when pressure drops to half, the equation $pV =$ constant implies that thevolume doubles. So the final volume should be 1.5×10^{-3} m^3. That is,

$$V_f = 1.5 \times 10^{-3}\ \text{m}^3 \qquad \text{(i)}$$

For the adiabatic process, we have

$$p_i V_i^{\gamma} = \text{constant} = p_f V_f^{\gamma}$$

Solving for V_f, we get

$$V_f = \left(\frac{p_i}{p_f}\right)^{1/\gamma} V_i$$

$$= \left(\frac{2.0\,\text{atm}}{1.0\,\text{atm}}\right)^{1/1.4} \times (7.5 \times 10^{-4}\,\text{m}^3)$$

$$= 1.2 \times 10^{-3}\,\text{m}^3 \qquad \text{(ii)}$$

On comparing (i) and (ii) you will note that the volume of the gas undergoing an adiabatic expansion is less than that when it undergoes isothermal expansion.

An important manifestation of adiabatic process is found in the trdposphere. We know that as we move up, the temperature gradually drops. This is referred to as **adiabatic** lapse rate. Let us now understand the physics involved in it.

4.3.1 The Adiabatic Lapse Rate : Convective Equilibrium

The heat from the sun, on being absorbed by the ground, heats up the air in immediate contact. The heated air rises upward and a vertical density gradient is established. This gives rise to convection currents which transport cooler air downwards and hot air upwards. As hot air rises, it expands. Will it exchange heat with its environment? It may not do so because air is a poor conductor of heat. This means that in intermixing of air we have an adiabatic expansion.

To calculate the drop in temperature with height, we assume that air behaves as a perfect gas. That is, we ignore the presence of water vapour in atmosphere. This means that we can use **Eq.** (4.13a). For one mole of the gas, Eq. (4.13a) in logarithmic form becomes

$$\gamma \ln T - (\gamma - 1) \ln p = \ln K_1$$

On differentiation, we get

$$\frac{dT}{T} - \frac{\gamma - 1}{\gamma} \frac{dp}{p} = 0$$

which can be rearranged as

$$\frac{dp}{p} = \frac{\gamma}{\gamma - 1} \frac{dT}{T} \qquad (4.14)$$

Let us now pause for a minute and ask: What are we looking for? We wish to calculate variation of temperature with height, i.e. dT/dh. To do so, we must relate pressure with height. For this, we recall that as we go up, pressure decreases. Mathematically, this is expressed as

$$dp = -\rho g\, dh$$

where ρ is average density of air and g is acceleration due to gravity. The negative sign signifies that pressure decreases as we move up.

Since we have assumed that air behaves as perfect gas, we can use the equation of state $p = RTIV$ in the above expression. This gives

$$\frac{dp}{p} = -\frac{Mg}{RT}\, dh \qquad (4.15)$$

where $M = \rho V$ is the average molecular weight (=28.9u) of air. On combining Eqs. (4.14) and (4.15), we get

$$\frac{dT}{dh} = -\frac{\gamma - 1}{\gamma} \frac{Mg}{R} \qquad (4.16)$$

μ signifies atomic mass unit : $1\,\mu = 1.673 \times 10^{-27}$ kg.

This is the required expression for adiabatic lapse rate. The negative sign on the RHS indicates that temperature decreases as we move upwards. To obtain an estimate of the lapse rate, we would like you to solve the following SAQ.

SAQ6

Insert appropriate values of M, g, R and p for air and compute the lapse rate.

On working out this SAQ you will find that $\frac{dT}{dh} = 9.8 \times 10^{-3} \text{K m}^{-1}$. This means that over one kilometer, the temperature falls by about 10K. From the plot in Fig. 4.2 you will note that this value is somewhat higher than the average lapse rate of about 6.5 K per kilometer.

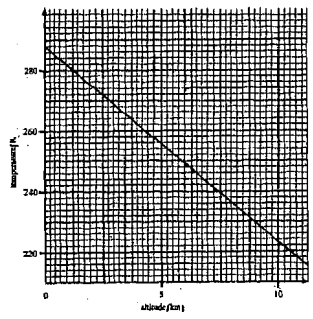


Fig. 4.2 : Plot of atmospheric temperature with height

You may now like to know as to what is responsible for this difference. To answer this question, let us re-examine our assumptions made to arrive at Eq. (4.16), which holds for dry atmosphere. In our derivation we ignored the presence of water vapour in air. Is it fair even though atmospheric air contains one to four per cent water vapour? Certainly not. The difference between observed and computed values of lapse rate suggests that water vapour influences the lapse rate. Can you say how? As water vapour rises with the convective current, it cools and may eventually condense into the liquid form. The latent heat (of vapourisation) released in this process tends to reduce the rate of cooling of atmosphere. However, the exact value is determined by the concentration of water vapour, the pressure and temperature,, Local modifications to the vertical teniperature gradient are also caused by the mountains, glaciers, volcanoes, domestic fires and industrial/vehicular exhaust.

4.3.2 The Speed of Sound

In Unit 6 of PHE-02 course on oscillations and waves, you have studied propagation of sound in air. This essentially consists of pressure oscillations in the medium which are accompanied by local changes in temperature. However, total energy of the system is conserved. That is, we can say that adiabatic changes occur in air when sound propagates. You may now like to know: What determines the speed of sound'! To answer this' question, we recall that-the speed of sound in air is given by

$$V = \sqrt{\frac{E_s}{\rho}} \tag{4.17}$$

where E_s and p respectively denote the adiabatic bulk modulus of elasticity and density of the medium.

By definition, the bulk modulus of elasticity isdefined as

$$E = \frac{\text{Stress}}{\text{Volume strain}}$$

$$= \frac{\Delta p}{(\Delta V/V)} = V\left(\frac{\Delta p}{\Delta V}\right)$$

In the language of calculus

$$E = -V\frac{dp}{dV}$$

The negative sign appears as for all known systems V decreases as p increases. The adiabatic bulk modulus of elasticity can be written as

$$E_s = -\text{V}\,(\partial p/\partial V)_s \tag{4.18}$$

From Eq. (4.13b), you would recall that

$$pV^{\gamma} = K$$

Since the physical properties of a gas depend on the physical conditions under which a process is carried out, we put a suffix to denote the type of change. It is for this reason thatp and V were used to denote heat capacities at constant pressure and constant volume. Similarly, for adiabatic and isothermal processes we put the suffixes s and T, respectively with the physical quantity of interest.

On differentiation, you would obtain

$$\gamma p V^{\gamma-1}\, dV + V^{\gamma}\, dp = 0$$

which gives

$$\left(\frac{\partial p}{\partial V}\right)_s = -\frac{\gamma p}{V}$$

Using this result in Eq.(4.18), we find that

$$E_s = \gamma p \tag{4.19}$$

This shows that adiabatic elasticity is y times pressure,

On using this result in Eq. (4.17), you will get

$$v = \sqrt{\frac{\gamma p}{\rho}} \tag{4.20}$$

This expression for velocity of sound is known as **Laplace** formula. For air, y = 1.4, $\rho = 1.29\ \text{kg m}^{-3}$ and $p = 1.01 \times 10^5 \text{N m}^{-2}$ so that Eq. (4.20) gives

$$v = \sqrt{\frac{1.4 \times (1.01 \times 10^5 \text{N m}^{-2})}{1.26\ \text{kg m}^{-3}}}$$

$$= 331\ \text{ms}^{-1}$$

which is in excellent agreement with the measured value of $332\,\text{ms}^{-1}$. From this you may be tempted to say that thermodynamical logic works really well.

SAQ 7

Suppose that sound wave propagation in air is isothermal. Then wc define

$$v = \sqrt{\frac{E_T}{\rho}}$$

The equation equivalent to Eq. (4.20) is known as **Newton's formula** for velocity of sound. Derive it and estimate the percentage difference from the value obtained using Laplace formula.

Using the equation of state, the expression for velocity of sound can also be written as

$$v = \sqrt{\frac{\gamma RT}{V\rho}} = \sqrt{\frac{\gamma RT}{M}} \tag{4.21}$$

This result shows that velocity of sound in air is directly proportional to square roo) of temperature and inversely proportional to square root of the molecular weight of air. Do these predictions agree with observations? Indeed, there is remarkable agreement.

The dependence of the speed of sound on temperature causes sound wavbs to bend (i.e. refract) when they move'in the atmosphere. In fact, these waves bend towards the colder region. (A sound wave moves faster in a hotter region.) Do you know that this spectacular effect was demonstrated in a large explosion in France in 1924? The intense sound waves moving upwards were refracted back down to the surface of the earth by the stratosphere due to positive temperature gradient.

4.3.3 Ratio of Adiabatic and Isothermal Elasticitiei

We know that compressibility and hence elasticity of a gas depend upon the conditions under which a chahge occurs. There are two possibilities: Either temperature remains constant or heat energy is conserved.

Accordingly, we define **isothermal and adiabatic** elasticities. We **will** now show that their ratio is equal to the ratio of two heat capacities:

$$\frac{E_s}{E_T} = \frac{(\partial p/\partial V)_s}{(\partial p/\partial V)_T} = \gamma = \frac{C_p}{C_V} \tag{4.22}$$

From Eq. (4.19) you would recall that

$$E_s = \gamma p$$

and while solving SAQ 7 you must haxe proved that isothermal elasticity is numerically equal to pressure :

$$p = E_T$$

On combining these results, you can establish the required expression.

You may recall from Sec. 4.2 that C_V is a perfect differential of U. Now you may ask: 'Can we define a function of state which corresponds to C_p'? Alternatively, is there-a class of processes where U and pV are grouped together? This does happen in the isobaric chemical reactions as well as flow processes. You will learn the details of flow processes with particular reference to Joule-Thomson effect and regenerative cooling in Unit 7. For the present, it is sufficient to discover the function which governs these changes/processes.

4.4 THE ENTHALPY

Let us express U as a function of T and p:

$$U = U(T, p)$$

Then we can write

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

Substituting this in Eq.(4.3), we find that the first law of thermodynamics takes the form

$$\delta Q = \left(\frac{\partial U}{\partial T}\right)_p dT + \left(\frac{\partial U}{\partial p}\right)_T dp + p\, dV \qquad (4.23)$$

Hence, heat capacity at constant pressure is given by

$$C_p = \left(\frac{\delta Q}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p$$

which can be rewritten as

$$C_p = \frac{\partial}{\partial T}(U + pV) \qquad (4.24)$$

The sum $(U + pV)$ is represented by a new function, called enthalpy. It is denoted by the symbol H. Thus

$$H = U + pV \qquad (4.25)$$

so that

$$C_p = \left(\frac{\delta Q}{\partial T}\right)_p = \left(\frac{\partial H}{\partial T}\right)_p \qquad (4.26)$$

We expect that enthalpy will also be a function of state of the system.' Moreover, it is an extensive property of the system.

In the literature you may also encounter alternative nomenclature for enthalpy — the total heat content and total energy. However, we will use the term enthalpy.

4.4.1 Enthalpy and Chemical Processes

So far we have considered only physical processes. You may now ask: Is there any other class of processes where the first law of thermodynamics is seen in action? We know that biological and chemical reactions also involve energy changes. For instance, we may need to know energy required to keep a cell alive. Similarly, energy is evolved when magnesium is put in dilute hydrochloric acid. But energy is absorbed when hydrochloric acid combines with sodium hydroxide. The study of energy changes that occur during chemical reactions is known as thermochemistry. Since energy changes in a chemical reaction occur as heat, which is a function of path, it is important to know how the reaction is carried out. For this reason, we usually discuss energy changes in chemical reactions in terms of enthalpy — which is a state function.

We will now discuss it briefly. The details are to be found in the course on Atoms and Molecules CHE-01. Reactions for which $AH > 0$ are called endothermic or heat absorbing, whereas those for which $AH < 0$ are called exothermic or heat releasing. When a reaction takes place in an adiabatic container, an endothermic reaction results in cooling, i.e. lowering of temperature and an exothermic reaction results in heating, i.e. rise of temperature. Common laboratory glassware like a test-tube or beaker are poor heat insulators. As a result, in an exothermic reaction heat leaves the system as soon as temperature rises above that of surroundings. But we can definitely say that as long as initial and final temperatures are same, heat leaves the system in an exothermic reaction and enters the system in an endothermic reaction. It is important to note that an exothermic reaction results in products of Iower energy than the reactants. But this does nbt mean that exothermic reactions can occur spontaneously. On the other hand, endothermic reactions never occur on their own.

4.4.2 Standard Enthalpy Changes

The enthalpy change accompanying a reaction is called the reaction enthalpy. It is denoted as ΔH. The standard enthalpy of reaction is the change of enthalpy when reactants in their standard states, i.e. pure form at a pressure of 1 bar at 25°C, change to products in their standard states. We often specify the physical state of the substance (s for solids, l for liquids and g for gases), temperature and concentration (by writing the number of moles). For example, the reactions for dissolution of gaseous hydrogen chloride in water for different concentrations are written as

$$HCl\,(g) + 10H_2O \longrightarrow HCl\,(10H_2O);\ \Delta H_{10} = -69.5\text{kJ mol}^{-1}$$
$$HCl\,(g) + 50H_2O \longrightarrow HCl\,(50H_2O);\ \Delta H_{50} = -73.3\text{kJ mol}^{-1}.$$
$$HCl\,(g) + 200H_2O \longrightarrow HCl\,(200H_2O);\ \Delta H_{200} = -74.2\text{kJ mol}^{-1}.$$

You will note that as the solution is gradually diluted, enthalpy changes. The change of enthalpy with dilution is referred to as enthalpy of dilution.

What is the enthalpy of dilution when water content is changed from 10 to 50 mole? You can easily compute that it is -3.8kJ mol^{-1}.

You will also note that enthalpy decreases as the solution is gradually diluted. When dilution causes essentially no change in enthalpy, the solution is referred to as **aquous** solution,. Thermochemical equations for some aquous solutions are, given below :

$$HCl\,(g) + \text{aq} \rightarrow HCl\,(\text{aq});\quad AH, = -74.9\text{kJ mol}^{-1}$$
$$NaCl\,(s) + \text{aq} \rightarrow NaCl\,(\text{aq});\quad AH,, = 335\text{kJ mol}^{-1}.$$
$$AqNO_3\,(s) + \text{aq} \rightarrow AqNO_3\,(\text{aq});\quad AH,, = 22.6\text{kJ mol}^{-1}.$$

4.4.3 Enthalpy of Reaction

We know that in a chemical reaction, one or more substances (reactants) give rise to entirely different substance(s) (products). Tliermodynamically, we say that the chemical system has undergone a change from its initial state to the final state subject to external conditions. The change involves rearrangement of chemical bonds; breaking of existing bonds in reactants and formation of new ones in products. This is invariably accompanied by evolution or absorption of energy in the form of heat. This is referred to as enthalpy of reaction.

> Enthalpy of reaction is the total energy absorbed or given out in the reaction when the reactants have completely changed into products under given external constraints.

For a reaction taking place at a given temperature and volume, first law tells us that at constant volume enthalpy of reaction is equal to the difference in the internal energies of products and reactants, i.e.

$$\delta Q_V = dU = U_p - U_R.$$

On the bther hand, for a reaction carried out isobarically, the constant-pressure cnthalpy of reactions is equal to the difference in the enthalpies of the products and the reactants, i.e.

$$\delta Q_p = dH = H_p - H_R$$

SAQ 8

Interpret the equation

$$NaOH(s) + HCl(g) \rightarrow NaCl(s) + H_2O(l);\ \Delta H = -177.8kJ$$

Since enthalpy of a chemical reaction is essentially the energy involved in breaking of bonds in reactants and formation of bonds in products, it is desirable to say something about the enthalpy of dissociation of a bond, The mean enthalpy change in dissociation of all bonds of a particular type in **1** mole of the substance in gaseous state is termed as bond enthalpy or bond **energy.** The enthalpies of dissociation of bonds for some typical cases are listed in Table **4.2.**

Table 4.2 : Typical Values of Enthalpies of Dissociation of Bonds

Bond	ΔH (kJ mol^{-1})	Bond	ΔH (kJ mol^{-1})
H — H	**436.0**	C = C	**615.0**
H — Cl	**431.4**	C ≡ C	**811.7**
O — H	**462.8**	C — 0	**351.5**
O — O	**138.9**	C = O	**728.0**
O = O	**497.3**	C — N	**291.6**
C — H	**413.4**	C — Cl	**326.4**
C — C	**347.7**	Cl — Cl	**242.7**

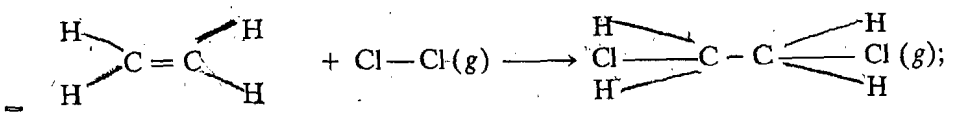
Example 5

Using the values of bond energies from Table 4.1. compute the enthalpy of the reaction

$$C_2H_4(g) + Cl_2(g) \rightarrow C_2H_4Cl_2(g)$$

Solution

The above reaction can be expressed as



We note that in this reaction

i) a Cl — Cl bond breaks in $Cl_2(g)$,

ii) a C = C bond breaks in C_2H_4 while four C – H bonds are unaffected, and

iii) a C – C and two C – Cl bonds are formed in $C_2H_4Cl_2$.

Therefore, enthalpy of the reaction is

ΔH = Energy of formation of one C – C bond and two C – Cl bonds + Energy of breaking of a Cl – Cl bond and a C – C bond

= (−347.7kJ mol^{-1}) − 2 × (326.4kJ mol^{-1}) A (242.7kJ mol^{-1}) + (615.0kJ mol^{-1})

= −142.8kJ mol^{-1}.

Obviously, it is an exothermic reaction.

4.5 HESS'S LAW

Hess's law is a corollary of the first law of thermodynamics. Accordidg to Hess's law, the total heat absorbed or given out/in a chemical change at constant volume or constant pressure does not depend on the path followed for **the** process. This means that when the evolution of a chemical system from the initial state to the final state occurs in one step or a series of stages, the total enthalpy of the reaction remains the same. To illustrate this, let us consider' the formation CO_2 gas. We can do so by

burning graphite in oxygen directly as well as by oxidation of carbon monoxide produced first. The thermocbemical reactions of interest are

$$C(s) + O_2(g) \rightarrow CO_2(g);\ \text{A H} = -393.4\ \text{kJmol}^{-1}$$
$$C(s) + \tfrac{1}{2}O_2(g) \rightarrow \text{CO (g)};\ \Delta H_1 = -110.5\ \text{kJmol}^{-1}$$
$$CG(g) + \tfrac{1}{2}O_2(g) \rightarrow CO_2(g);\ \Delta H_2 = -283.2\ \text{kJmol}^{-1}$$

You will note that $A H$ is almost equal to the sum of ΔH_1 and AH_2. This shows that Hess's law enables us to add or subtract thermochemical equations in the same way as we do with ordinary algebraic equations.

4.6 SUMMARY

- For one mole of a perfect gas, the difference of heat capacitiesat constant pressure and constant volume is equal to R; the molar gas constant:

  $$C_p - C_V = R$$

- The equation of state for an adiabatic process in terms of temperature and volume is

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

  In terms of temperature and pressure, we ca'n rewrite it as

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

  In terms of pressure and volume, we have

  $$p V^{Y} = \text{constant}$$

  The adiabatic lapse rate in the stratosphere is brought about by convective currents. It is given by

  $$\frac{dT}{dh} = -\frac{\gamma-1}{\gamma}\frac{Mg}{R}$$

- The propagation of sound in air is an adiabatic process. The expression for the velocity of sound is

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

  where E_s is adiabatic elasticity and p denotes average density of air.

- The ratio of adiabatic to isothermal elasticities of a substance is equal to y; the ratio of heat capacities of a gas at constant pressure and constant volume:

  $$\frac{E_s}{E_T} = \gamma = \frac{C_p}{C_V}$$

- The sum U + p V is called enthalpy:

  $$H = U + pV$$

  The enthalpy is a function of state.

- Enthalpy of a reaction is the total energy absorbed or given out when the reactants have completely changed into products under given external conditions.

- For endothermic reactions $A H < 0$ whereas for exothermic reactions $\text{AH} > 0$.

4.7 TERMINAL QUESTIONS

1) Starting from the first law of thermodynamics, show that

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{C_p - C_V}{V\alpha} - p$$

$$\left(\frac{\partial U}{\partial T}\right)_p = C_p - pV\alpha$$

and

$$\left(\frac{\partial U}{\partial p}\right)_T = \frac{pV}{E_T} - \frac{C_p - C_V}{E_T \alpha}$$

where E_T is isothermal elasticity and α is volume expansion coefficient.

2) For a pure paramagnetic substance, the first law of thermodynamics has theform

$$\delta Q = dU - B\, dM$$

where B and M denote magnetic tield and magnetization, respectively.

Show that the difference of heat capacities at'constant B and at constant M is given by

$$C_B - C_M = \frac{KB^2}{T^2}$$

where

$$C_B = \left(\frac{\delta Q}{\partial T}\right)_B \quad \text{and} \quad C_M = (\mathrm{GQ}/\partial T)_M$$

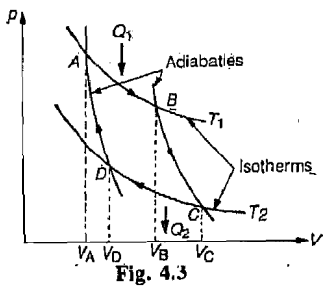


Fig. 4.3

3) Isothermal compressibility (β_T) is inverse of isothermal elasticity. Calculate β_T for (i) an ideal gas, (ii) van der Waals' gas.

4) **A** cyclic process consists of four steps.: isothermal expansion; adiabatic expansion, isothermal compression and adiabatic compression as shown in Fig. **4.3** Using the first law of thermodynamics, compute the total work done.

5) Determine (a) the heat of allotropic transformation from diamond to graphite and (b) standard enthalpy of formation of CO (g) using the following thermochemical rnuations:

$$\text{C (graphite)} + \mathrm{O_2(g)} \rightarrow \mathrm{CO_2(g)};\ \Delta H = -393.4\ \mathrm{kJ\ mol^{-1}}$$
$$\text{C (diamond)} + \mathrm{O_2(g)} \rightarrow \mathrm{CO_2(g)};\ \Delta H = -395.0\ \mathrm{kJ\ mol^{-1}}$$
$$\mathrm{CO\,(g)} + \tfrac{1}{2}\,\mathrm{O_2(g)} \rightarrow \mathrm{CO_2(g)};\ \Delta H = -283.1\ \mathrm{kJ\ mol^{-1}}$$

4.8 SOLUTIONS AND ANSWERS

SAQs

1) We know that molar heat capacity at constant pressure is 160 J $\mathrm{mol^{-1}\,K^{-1}}$. Using Eq. (4.8) we can calculate C_V:

$$C_V = C_p - \mathrm{R}$$

Since R = **8.3** J $\mathrm{mol^{-1}\,K^{-1}}$, we find that

$$C_V = (160\ \mathrm{J\ mol^{-1}\,K^{-1}}) - (8.3\ \mathrm{J\ mol^{-1}\,K^{-1}})$$
$$= 151.7\ \mathrm{J\ mol^{-1}\,K^{-1}}$$

Hence

$$\gamma = \frac{C_p}{C_V} = \frac{160\ \mathrm{J\ mol^{-1}\,K^{-1}}}{151.7\ \mathrm{J\ mol^{-1}\,K^{-1}}} = 1.05$$

2) The first law of thermodynamics is

$$\delta Q = dU + pdV \qquad \text{(i)}$$

Using Eq. (4.4) you can write

$$dU = C_V dT$$

Hence,

$$\delta Q = C_V dT + pdV \qquad \text{(ii)}$$

From the equation of state for an ideal gas

$$pV = RT$$

Hence $pdV + Vdp = RdT$

Using this result in (ii) we find that

$$\delta Q = (C_V + \mathrm{R})\, dT - Vdp$$
$$= C_P\, dT - \mathrm{Vdp} \qquad \text{(iii)}$$

3) $TV^{\gamma-1} = K$ (i)

For a perfect gas, the equation of state is

$$pV = RT$$

On substituting for V we find that

$$\frac{T^{\gamma}}{p^{\gamma-1}} = \frac{K}{R^{\gamma-1}} = K_1 \quad \text{(ii)}$$

Similarly, on eliminating T between (i) and (ii) you will get

$$pV^{\gamma} = KR = K_2 \quad \text{(iii)}$$

4) From **Eq.** (4.13b)

$$pV^{\gamma} = K$$

On differentiation

$$\gamma pV^{\gamma-1}\,dV + V^{\gamma}\,dp = 0$$

$$\therefore \left(\frac{dp}{dV}\right)_s = -\gamma\left(\frac{p}{V}\right) \quad \text{(i)}$$

For an isothermal process

$$pV = \text{constant}$$

$$\therefore pdV + Vdp = 0$$

or

$$\left(\frac{dp}{dV}\right)_T = -\left(\frac{p}{V}\right) \quad \text{(ii)}$$

These results show that an adiabat is steeper than an isotherm since $\gamma > 1$.

5) Since thk change is adiabatic and variation in temperature is to be computed, we use Eq. (4.13a) :

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

Hence, $\frac{T_i^{\gamma}}{p_i^{\gamma-1}} = \frac{T_f^{\gamma}}{p_f^{\gamma-1}}$

or $T_f = \left(\frac{p_f}{p_i}\right)^{(\gamma-1)/\gamma} T_i$

Oil substituting the given data, we get

$$T_f = 2^{(0.4/1.4)} \text{x } (300\text{K}) = 365.7 \text{ K}$$
$$= 366 \text{ K}$$

6) The lapse rate is given by

$$\frac{dT}{dh} = -\frac{\gamma-1}{\gamma}\frac{Mg}{R}$$

On substituting the given data, we find that

$$\left|\frac{dT}{dh}\right| = \frac{0.4}{1.4} \times \frac{(28.9\text{u}) \text{ x } (1.673 \text{ x } 10^{-27}\text{ kg}) \text{ x } (6.022 \text{ x } 10^{23}\text{ mol}^{-1}) \times (9.8\ \text{ms}^{-2})}{(8.314\ \text{JK}^{-1}\text{mol}^{-1})}$$

$$= \frac{1141.4}{11.64} \times 10^{-4}$$

$$= 9.8 \times 10^{-3}\ \text{Km}^{-1}$$

7) We know that

$$v = \sqrt{\frac{E_T}{\rho}}$$

For a perfect gas

$$pV = RT.$$

$$\therefore \left(\frac{\partial p}{\partial V}\right)_T = -\frac{RT}{V^2}$$

Hence,

$$E_T = -V\left(\frac{\partial p}{\partial V}\right)_T = \frac{RT}{V} = p$$

and $$v = \sqrt{\frac{RT}{V\rho}} = \sqrt{\frac{p}{\rho}}$$

On substituting for p and ρ, we find that

$$v = \sqrt{\frac{1.01 \times 10^5 \text{N m}^{-2}}{1.29 \text{ kg m}^{-3}}}$$

$$= 280 \text{ ms}^{-1}$$

The difference between the values obtained by Laplace and Newton is

$$v = (331 - 280) \text{ ms}^{-1} = 51 \text{ ms}^{-1}$$

% difference with respect to the standard (Laplace's) value $= 15.4\%$

8) From this we understand that one mole of solid NaOH reacts with one mole of HCl at STP to give one mole of solid NaCl and one mole of liquid water. The heat of reaction is − 177.8 kJ. The negative sign implies that the reaction is exothermic.

TQs

1) From Eq. (4.6) we recall that

$$C_p - C_V = \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\left(\frac{\partial V}{\partial T}\right)_p$$

By definition; the volume expansion coefficient α is given by

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

Hence, $$C_p - C_V = \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right] V\alpha$$

On re-arranging terms, we get the required result:

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{C_p - C_V}{V\alpha} - p \qquad \text{(i)}$$

To prove the second result, we take U as a function of p and T, i.e.

$$U = U(p, T)$$

Then

$$dU = \left(\frac{\partial U}{\partial P}\right)_T dp + \left(\frac{\partial U}{\partial T}\right)_P dT.$$

so that

$$\delta Q = \left(\frac{\partial U}{\partial T}\right)_p dT + \left(\frac{\partial U}{\partial P}\right)_T dp + pdV$$

On dividing throughout by dT and keeping pressure constant, we find that

$$\left(\frac{\delta Q}{\partial T}\right)_p = C_p = \left(\frac{\partial U}{\partial T}\right)_P + p\left(\frac{\partial V}{\partial T}\right)_P$$

Hence,

$$\left(\frac{\partial U}{\partial T}\right)_p = C_p - pV\alpha \qquad \text{(ii)}$$

To know pressure variation of internal energy you have to rewrite (i) as

$$\left(\frac{\partial U}{\partial p}\right)_T \left(\frac{\partial p}{\partial V}\right)_T = \frac{C_p - C_V}{\alpha V} - p \qquad \text{(iii)}$$

By definition, isothermal elasticity

$$E_T = -V\left(\frac{\partial p}{\partial V}\right)_T$$

or

$$\left(\frac{\partial p}{\partial V}\right)_T = -\frac{E_T}{V}$$

Using this result in (iii), we get pressure variation of internal energy :

$$\left(\frac{\partial U}{\partial p}\right)_T = \frac{pV}{E_T} - \frac{C_p - C_V}{\alpha E_T} \qquad \text{(iv)}$$

2) For a pure paramagnetic substance

$$\delta Q = dU - BdM \qquad \text{(i)}$$

Taking U as a function of T and M, we can write

$$U = U(T, \mathrm{M})$$

so that

$$dU = \left(\frac{\partial U}{\partial T}\right)_M dT + \left(\frac{\partial U}{\partial M}\right)_T dM$$

Substituting this in (i), we find that

$$\delta Q = \left(\frac{\partial U}{\partial T}\right)_M dT + \left[\left(\frac{\partial U}{\partial M}\right)_T - B\right] dM$$

Following the procedure used in arriving at Eq. (4.6), you can write

$$C_B - C_M = \left[\left(\frac{\partial U}{\partial M}\right)_T - B\right]\left(\frac{\partial M}{\partial T}\right)_B \qquad \text{(ii)}$$

For a pure paramagnetic substance

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

so that

$$C_B - C_M = -B\left(\frac{\partial M}{\partial T}\right)_B \qquad \text{(iii)}$$

From Curie's law

$$M = \frac{kB}{T}$$

where k is a constant.

We can now write

$$\left(\frac{\partial M}{\partial T}\right)_B = -\frac{kB}{T^2} \qquad \text{(iv)}$$

This result is useful in understanding the operating principle of production of low temperatures using adiabatic demagnetization. You will learn to apply it in Unit 7.

3) For an ideal gas, the equation of state is

$$pV = RT \qquad \text{(i)}$$

Hence

$$\beta_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = \frac{RT}{p^2 T} = \frac{1}{p} \qquad \text{(ii)}$$

That is, β_T is inverse of pressure for an ideal gas. You should have expected this result from Eq. (4.19). Similarly, for a van der Waals' gas

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT \qquad \text{(iii)}$$

or

$$p = \frac{RT}{V - b} - \frac{a}{V^2}$$

Hence

$$\left(\frac{\partial p}{\partial V}\right)_T = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3}$$

and

$$-V\left(\frac{\partial P}{\partial V}\right)_T = -\frac{2a}{V^2} + \frac{RT}{(V-b)^2}V$$

On using (iii) and cancelling b in comparison with V, we find that

$$\beta_T = \frac{1}{\left(p + \frac{a}{V^2}\right) - \frac{2a}{V^2}}$$

$$= \frac{1}{p - \frac{a}{V^2}}$$

This shows that $(\beta_T)_{van} < (\beta_T)_{ideal}$. This is physically expected because of the presence of interatomic forces in a real gas.

4) For an isothermal process, $dU = 0$ so that all heat absarbed during this process is converted into work :

$$\delta Q = pdV$$

Hence,

$$W_{1\to 2} = \int_{V_1}^{V_2} pdV = RT_1 \int_{V_1}^{V_2} \frac{dV}{V}$$

$$= RT_1 \ln (V_2/V_1) \qquad \text{(i)}$$

where T is temperature at which heat is absorbed by the system.

For an adiabatic expansion, $\delta Q = 0$ and increase in volume tends to decrease internal energy and hence temperature so that $T_2 < T_1$. ***Hence***

$$W_{2\to 3} = \int_{V_2}^{V_3} pdV$$

$$= K\int_{V_2}^{V_3} \frac{dV}{V^\gamma}$$

$$= -\frac{K}{\gamma - 1}\left[\frac{1}{V_3^{\gamma-1}} - \frac{1}{V_2^{\gamma-1}}\right]$$

Using the equation of state for an adiabatic process, we can rewrite it as

$$W_{2\to 3} = \frac{R(T_1 - T_2)}{\gamma - 1} \qquad \text{(ii)}$$

Similarly, for isothermal compression you can readily show that

$$W_{3\to 4} = RT_2 \ln\left(\frac{V_4}{V_3}\right)$$

$$= -RT_2 \ln\left(\frac{V_3}{V_4}\right) \qquad \text{(iii)}$$

whereas for adiabatic compression

$$W_{4\to 1} = -\frac{R(T_1 - T_2)}{\gamma - 1} \qquad \text{(iv)}$$

On combining results contained in (i) to (iv), you will get

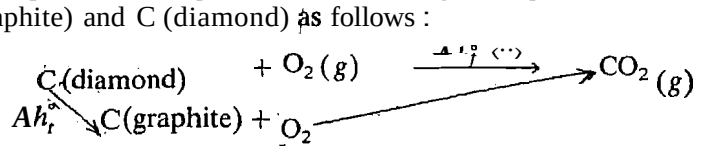
$$W = W_{1\to 2} + W_{2\to 3} + W_{3\to 4} + W_{4\to 1}$$

$$= RT_1 \ln\left(\frac{V_2}{V_3}\right) - RT_2 \ln\left(\frac{V_3}{V_4}\right)$$

5) a) Suppose heat of allotropic transformation from diamond to graphite at 25°C and 1 atm is Δh_t°. Figuratively speaking,

C (diamond) $\longrightarrow$ C (graphite), Δh_t° = ?

We represent this equation and the two given equations for combustion of C (graphite) and C (diamond) as follows :



From Hess's law

$$\Delta h_f^\circ \text{ (ii)} = \Delta h_t^\circ + Ah_f^\circ \text{ (i)}$$

so that

$$Ah_t^\circ = Ah_f^\circ \text{ (ii)} - \Delta h_f^\circ \text{ (i)}$$
$$= -395.0 \text{ kJ mol}^{-1} - (-393.4 \text{ kJ mol}^{-1})$$
$$= -1.6 \text{ kJ mol}^{-1}$$

Thus, 1.6kJ of heat is evolved when 1 mol of diamond is transformed into graphite.

b) Since standard form of carbon is graphite, to determine the standard heat of formation of CO (g), we combine (i) and (ii) to write

C (graphite) + ½ O_2 (g) $\longrightarrow$ CO (g), Δh_f° = ?

This gives standard heat of formation of CO (g) as

$$\Delta h_f^\circ = Ah_f^\circ \text{ (i)} - \Delta h_f^\circ \text{ (iii)}$$
$$= (-393.4 + 283.1) \text{ kJ mol}^{-1}$$
$$= -110.3 \text{ kJ mol}^{-1}$$