1. Details of Module and its structure

Module Detail	
Subject Name	Chemistry
Course Name	Chemistry 01 (Class XI, Semester - 1)
Module Name/Title	Thermodynamics: Part 2
Module Id	kech_10602
Pre-requisites	pV-work and types of thermodynamic processes and associated energy changes.
Objectives	After learning this module learner will be able to 1. Define Heat Capacity 2. Establish the relationship between C_p and C_v 3. Carry out measurements of energy changes associated with chemical processes through calorimetry
Keywords	Heat capacity, bomb calorimeter, enthalpy

2. Development Team

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Table of Contents:

1. Enthalpy(H): *A useful new state function*

We know that the heat absorbed at constant volume is equal to change in the internal energy i.e., $\Delta U = q_V$. But most of chemical reactions are carried out not at constant volume, but in flasks or test tubes under constant atmospheric pressure. We need to define another state function which may be suitable under these conditions.

We have $\Delta U = q_p - p\Delta V$ (1)

at constant pressure, where q_p is heat absorbed by the system and $-p\Delta V$ represent expansion work done by the system.

Let us represent the initial state by subscript 1 and final state by 2

We can rewrite the above equation as

$U_2 - U_1 = q_p - p\ (V_2 - V_1)$

On rearranging, we get

$q_p = (U_2 + pV_2) - (U_1 + pV_1)$ (2)

Now we can define another thermodynamic function, the enthalpy H [Greek word enthalpien, to warm or heat content] as:

$H = U + pV$ (3)

so, equation (2) becomes

$q_p = H_2 - H_1 = \Delta H$

Although q is a path dependent function, H is a state function because it depends on U, p and V, all of which are state functions. Therefore, ΔH is independent of path. Hence, q_p is also independent of path.

For finite changes at constant pressure, we can write equation (3) as

$\Delta H = \Delta U + \Delta pV$

Since p is constant, we can write

$\Delta H = \Delta U + p\Delta V$ (4)

It is important to note that when heat is absorbed by the system at constant pressure, we are actually measuring changes in the enthalpy.

Remember $\Delta H = q_p$, heat absorbed by the system at constant pressure.

ΔH is negative for exothermic reactions which evolve heat during the reaction and ΔH is positive for endothermic reactions which absorb heat from the surroundings.

At constant volume ($\Delta V = 0$), $\Delta U = q_V$, therefore equation (4) becomes

$\Delta H = \Delta U = q_V$

The difference between ΔH and ΔU is not usually significant for systems consisting of only solids and / or liquids. Solids and liquids do not suffer any significant volume changes upon heating. The difference, however, becomes significant when gases are involved. Let us consider a reaction involving gases. If V_A is the total volume of the gaseous reactants, V_B is the total volume of the gaseous products, n_A is the number of moles of gaseous reactants and n_B is the number of moles of gaseous products, all at constant pressure and temperature, then using the ideal gas law, we write,

$pV_A = n_A RT$

and $pV_B = n_B RT$

Thus, $pV_B - pV_A = n_B RT - n_A RT = (n_B - n_A)RT$

or $p(V_B - V_A) = (n_B - n_A) RT$

or $p\Delta V = \Delta n_g RT$ (5)

Here, Δn_g refers to the number of moles of gaseous products minus the number of moles of gaseous reactants.

Substituting the value of $p\Delta V$ from equation (5) in equation (4), we get

$\Delta H = \Delta U + \Delta n_g RT$ (6)

The equation (6) is useful for calculating ΔH from ΔU and vice versa.

Example 1

Although heat is a path function but heat absorbed by the system under certain specific conditions is independent of path. What are those conditions? Explain.

Solution: At constant volume

By first law of thermodynamics:

$q = \Delta U + (-w)$

$(-w) = p\Delta V$

$\therefore q = \Delta U + p\Delta V$

$\Delta V = 0$, since volume is constant.

$\therefore q_v = \Delta U + 0 \Rightarrow q_v = \Delta U$ = change in internal energy

At constant pressure

$q_p = \Delta U + p\Delta V$

But, $\Delta U + p\Delta V = \Delta H$

$\therefore q_p = \Delta H$ = change in enthalpy.

Thus we can see that at a constant volume and at constant pressure heat change is a state function as it is equal to change in internal energy and change in enthalpy respectively which are state functions.

Example 2

If water vapour is assumed to be a perfect gas, molar enthalpy change for vapourisation of 1 mol of water at 1bar and 100°C is 41kJ mol^{-1}. Calculate the internal energy change, when

(i) 1 mol of water is vaporised at 1 bar pressure and 100°C.

(ii) 1 mol of water is converted into ice.

Solution

(i) The change

$$\Delta H = \Delta U + \Delta n_g RT$$

or $\Delta U = \Delta H - \Delta n_g RT$, substituting the values, we get

$\Delta U = 41.00 \ \text{kJ mol}^{-1} - 1$
$\quad\quad \times 8.3 \ \text{J mol}^{-1}\text{K}^{-1} \times 373 \ \text{K}$

$= 41.00 \ \text{kJ mol}^{-1} - 3.096 \ \text{kJ mol}^{-1}$

$= 37.904 \ \text{kJ mol}^{-1}$

(ii) The change

There is negligible change in volume,

So, we can put $p\Delta V = \Delta n_g RT \approx 0$ in this case,

$\Delta H \cong \Delta U$

so, $\Delta U = 41.00 \ \text{kJ mol}^{-1}$

Example 3

Consider the following chemical reactions carried out at constant temperature and constant pressure:

i) H_2 (g) + Cl_2 (g) → 2HCl (g)

ii) N_2 (g) + $3H_2$ (g) → 2 NH_3 (g)

iii) $2NH_3NO_2$ (s) → $2N_2$ (g) + H_2O (g)

Predict the sign of W, and tell whether work is done on or by the system. Consider the reaction mixture to be the system.

Solution: i) H_2 (g) + Cl_2 (g) → 2HCl (g)

We have $W = -p\Delta V = -(\Delta n)_g RT$

We have $(\Delta n)_g = 2-2=0$

$W = -(\Delta n)_g RT = 0$, No work is done as the reaction proceeds.

ii) N_2 (g) + $3H_2$ (g) → 2 NH_3 (g)

We have $(\Delta n)_g = 2-4 = -2$

$W = -(\Delta n)_g RT = 2RT$, The work is done on the system.

iii) $2NH_3NO_2$ (s) → $2N_2$ (g) + $4H_2O$ (g)

We have $(\Delta n)_g = 6 – 2= 4$

$W = -(\Delta n)_g RT = -4RT$, The work is done by the system.

Example 4

The heat of combustion of gaseous methane CH_4 at constant volume measured in bomb calorimeter at 298.2 K is found to be 885.389kJ/mol. Find the value of enthalpy change.

Solution: CH_4 (g) + $2O_2$ (g) → CO_2 (g) + H_2O (l)

Given ΔU = - 885.389 kJ/mol = - 885389 J/mol

$(\Delta n)_g = 1 - 3 = -2$, T=298.2 K , R=8.314 $JK^{-1}mol^{-1}$

$\Delta H = \Delta U + (\Delta n)_g RT$

= -885389 + (-2) × 8.314 × 298.2

=890347 J = 890.34 kJ

2. Extensive and Intensive Properties

In thermodynamics, a distinction is made between extensive properties and intensive properties. An **extensive property** is a property whose value depends on the quantity or size of matter present in the system. For example, mass, volume, internal energy, enthalpy, heat capacity, etc. are extensive properties.

Those properties which do not depend on the quantity or size of matter present are known as **intensive properties**. For example temperature, density, pressure etc. are intensive properties. A molar property, χ_m, is the value of an extensive property χ of the system for 1 mol of the substance. If n is the amount of matter, $\chi_m = \dfrac{\chi}{n}$ is independent of the amount of matter. Other examples are molar volume, V_m and molar heat capacity, C_m. Let us understand the distinction between extensive and intensive properties by considering a gas enclosed in a container of volume V and at temperature T [Fig. 1]. Let us make a partition such that volume is halved, each part [Fig. 2] now has one half of the original volume, $\dfrac{V}{2}$, but the temperature will still remain the same i.e., T. It is clear that volume is an extensive property and temperature is an intensive property.
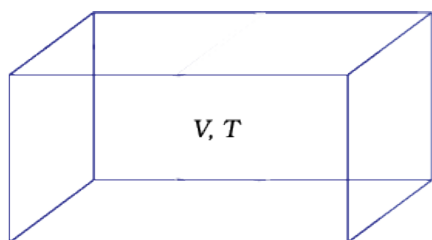

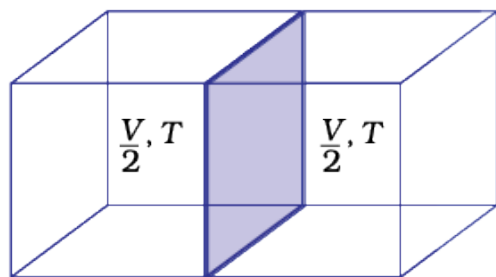***Fig. 1*** *A gas at volume V and temperature T*

Fig. 2 *Partition, each part having half the volume of the gas*

3. Heat Capacity

In this sub-section, let us see how to measure heat transferred to a system. This heat appears as a rise in temperature of the system in case of heat absorbed by the system.

The increase of temperature is proportional to the heat transferred

$$q = coeff \times \Delta T$$

The magnitude of the coefficient depends on the size, composition and nature of the system. We can also write it as q = C ΔT

The coefficient, C is called the heat capacity.

Thus, we can measure the heat supplied by monitoring the temperature rise, provided we know the heat capacity.

When C is large, a given amount of heat results in only a small temperature rise. Water has a large heat capacity i.e., a lot of energy is needed to raise its temperature.

C is directly proportional to amount of substance.

The molar heat capacity of a substance, $C_m = \left(\dfrac{C}{n}\right)$, is the heat capacity for one mole of the substance and is the quantity of heat needed to raise the temperature of one mole by one degree celsius (or one kelvin). Specific heat, also called specific heat capacity is the quantity of heat required to raise the temperature of one unit mass of a substance by one degree celsius (or one kelvin). For finding out the heat, q, required to raise the temperatures of a sample, we multiply the specific heat of the substance, c, by the mass m, and temperatures change, ΔT as

(7)

4. The relationship between C_p and C_V for an ideal gas

At constant volume, the heat capacity, C is denoted by C_V and at constant pressure, this is denoted by C_p . Let us find the relationship between the two.

We can write equation for heat, q

at constant volume as q_V =

at constant pressure as q_p =

The difference between C_p and C_V can be derived for an ideal gas as:

For a mole of an ideal gas, ΔH = ΔU + Δ(pV)

= ΔU + Δ(RT)

= ΔU + RΔT   (8)

On putting the values of ΔH and ΔU,we have

$C_p \Delta T = C_V \Delta T + R\Delta T$

$$C_p = C_V + R$$

(9)

5. Measurement of ΔU and ΔH: Calorimetry

We can measure energy changes associated with chemical or physical processes by an experimental technique called calorimetry. In calorimetry, the process is carried out in a vessel

called calorimeter, which is immersed in a known volume of a liquid. Knowing the heat capacity of the liquid in which calorimeter is immersed and the heat capacity of calorimeter, it is possible to determine the heat evolved in the process by measuring temperature changes. Measurements are made under two different conditions:

i) at constant volume, q_V

ii) at constant pressure, q_p

(a) ΔU measurements

For chemical reactions, heat absorbed at consant volume, is measured in a bomb calorimeter (Fig. 3). Here, a steel vessel (the bomb) is immersed in a water bath. The whole device is called calorimeter. The steel vessel is immersed in water bath to ensure that no heat is lost to the surroundings. A combustible substance is burnt in pure dioxygen supplied in the steel bomb. Heat evolved during the reaction is transferred to the water around the bomb and its temperature is monitored. Since the bomb calorimeter is sealed, its volume does not change i.e., the energy changes associated with reactions are measured at constant volume. Under these conditions, no work is done as the reaction is carried out at constant volume in the bomb calorimeter. Even for reactions involving gases, there is no work done as $\Delta V = 0$.
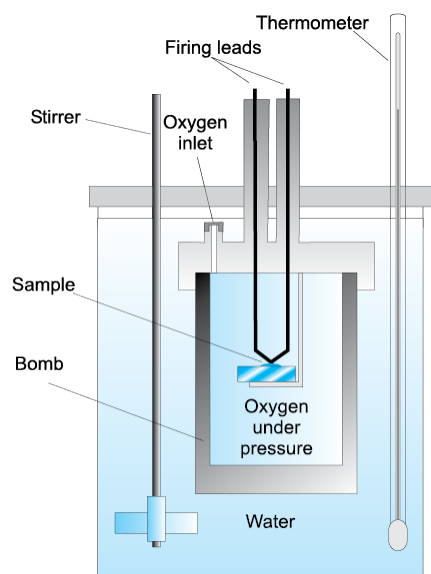

Fig. 3 *Bomb calorimeter*

Temperature change of the calorimeter produced by the completed reaction is then converted to q_V, by using the known heat capacity of the calorimeter with the help of equation (7).

(b) Δ H measurements

Measurement of heat change at constant pressure (generally under atmospheric pressure) can be done in a calorimeter shown in Fig.4. We know that $\Delta H = q_p$ (at constant p) and,

therefore, heat absorbed or evolved, q_p at constant pressure is also called the heat of reaction or enthalpy of reaction, $\Delta_r H$.

In an exothermic reaction, heat is evolved, and system loses heat to the surroundings. Therefore, q_p will be negative and $\Delta_r H$ will also be negative. Similarly in an endothermic reaction, heat is absorbed, q_p is positive and $\Delta_r H$ will be positive.
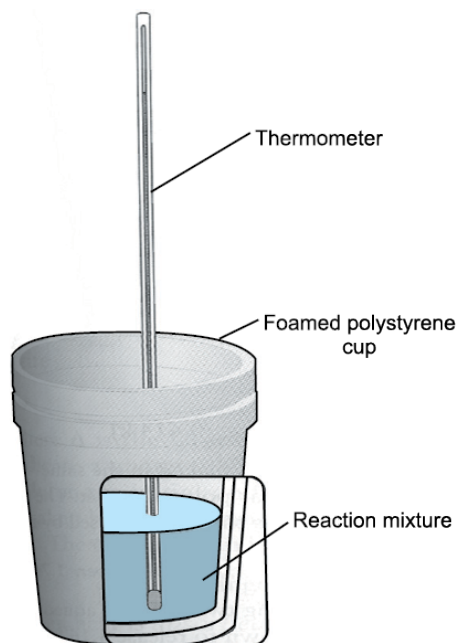

Fig. 4 *Calorimeter for measuring heat changes at constant pressure (atmospheric pressure).*

Example 5

Heat capacity (C) is an extensive property but specific heat (c) is an intensive property. What will be the relation between C and c for 1 mole of water?

Solution:

Heat capacity is the amount of heat needed to change the temperature of a substance by 1 degree Celsius/Kelvin, while specific heat is the heat needed to change the temperature of 1 gram of substance by 1 degree Celsius/Kelvin. While specific heat capacity generally refers to the material from which an object is made, e.g. aluminium, heat capacity refers to a particular object (the whole bulk of matter in an object, e.g. a calorimeter). In other words, specific heat capacity is a characteristic of a substance, whereas heat capacity relates to a particular object. Whereas heat capacity is dependent on the amount of substance, heat capacity is independent of it.

The mass of one mole of water is 18 g. Thus we have
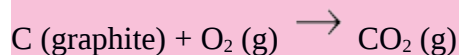
Heat capacity = 18 × specific heat

or C (Heat capacity)= 18 × c (Specific heat)

we have $c = 4.18 \, Jg^{-1}K^{-1}$

Heat capacity $= C = 18 \times 4.18 \, JK^{-1} = 75.3 \, J \, K^{-1}$

Example 6

1g of graphite is burnt in a bomb calorimeter in excess of oxygen at 298 K and 1 atmospheric pressure according to the equation

$C \text{ (graphite)} + O_2 \text{ (g)} \xrightarrow{} CO_2 \text{ (g)}$

During the reaction, temperature rises from 298 K to 299 K. If the heat capacity of the bomb calorimeter is 20.7kJ/K, what is the enthalpy change for the above reaction at 298 K and 1 atm?

Solution

Suppose q is the quantity of heat from the reaction mixture and C_V is the heat capacity of the calorimeter, then the quantity of heat absorbed by the calorimeter.

$q = C_V \times \Delta T$

Quantity of heat from the reaction will have the same magnitude but opposite sign because the heat lost by the system (reaction mixture) is equal to the heat gained by the calorimeter.

$$q = - C_V \times \Delta T = -20.7 \, kJ/K \times (299 - 298) K$$
$$= -20.7 \, kJ$$

(Here, negative sign indicates the exothermic nature of the reaction)

Thus, ΔU for the combustion of the 1g of graphite $= -20.7 \, kJK^{-1}$

For combustion of 1 mol of graphite,

$$= \frac{12.0 \, g \, mol^{-1} \times (-20.7 \, kJ)}{1 g}$$

$= -2.48 \times 10^2 \, kJ \, mol^{-1}$, Since $\Delta n_g = 0$,

$\Delta H = \Delta U = -2.48 \times 10^2 \, kJ \, mol^{-1}$

Example 7

What are the conditions under which the enthalpy change and internal energy change are equal?

Solution: The conditions under which the enthalpy change (ΔH) and internal energy change (ΔU) are equal as follows:

a)   The process is carried out in a closed vessel ($\Delta V=0$)

b)   Number of moles of gaseous products = number of moles of gaseous reactants

c)   The reaction doesn't involve any gaseous reactant or product

Example 8

We define the energy changes of most of chemical process in terms of enthalpy change (ΔH) (enthalpy of reaction, enthalpy of formation, enthalpy of ionisation etc) and not internal energy change (ΔU). Explain.

Solution:

Internal energy depends on volume and temperature and enthalpy depends on pressure and temperature. ΔU is measured under constant volume condition. The experiments under constant volume conditions can be performed for those systems which are gaseous. It is difficult to perform experiments for solids and liquids under this condition because they are less compressible. Where as ΔH can be measured under constant pressure for all substances (solid, liquid and gas).

Example 9

A 1.000 g sample of octane (C_8H_{18}) is burned in a bomb calorimeter containing 1200 grams of water at an initial temperature of 25.00ºC. After the reaction, the final temperature of the water is 33.20ºC. The heat capacity of the calorimeter is 837 J/ºC. The specific heat of water is 4.184 J/g ºC. Calculate the heat of combustion of octane in kJ/mol.

Solution: Since this is a combustion reaction, heat flows from the system to the surroundings-thus, itis exothermic. The heat released by the reaction will be absorbed by two things:

(a) the water in the calorimeter and (b) the calorimeter itself.

a) Calculate the heat absorbed by the water (q_{water})

m = 1200 grams, c_{water}= 4.184 J/gºC, ΔT = 33.2 – 25.0 = 8.2ºC

q_{water}= mcΔT, so

q_{water} = 1200 g ×4.184 ×8.2ºC = 41170.56 J= 41.2 kJ

b) Calculate the heat absorbed by the calorimeter (q_{cal})

The temperature change of the calorimeter is the same as the temperature change for water. In this step, however, we must use the heat capacity of the calorimeter,

C_{cal} = 837 J/ºC and ΔT = 33.20 – 25.00 = 8.20ºC

q_{cal} = $C_{cal}\Delta T$

q_{cal} = 837 × 8.20 ºC = 6863 J = 6.86 kJ

Total heat absorbed by the water and the calorimeter = 41.2 +6.86 = + 48.1 kJ.

q is positive because the heat is being absorbed.

The amount of heat released by the reaction is equal to the amount of heat absorbed by the water and the calorimeter. We just need to change the sign. So,

$q_{reaction} = -48.1$ kJ

For 1.000 gram of octane burned, the heat of combustion is equal to- 48.1 kJ/gram. For 1 mole of the octane (molecular weight 114 grams)

ΔH = -48.1 kJ/g ×114 g/mol = −5483 kJ/mol.

6. Conclusions

A new state function has been introduced in this chapter called enthalpy (H). Enthalpy change, $\Delta H = \Delta U + \Delta n_g RT$, can be found directly from the heat changes at constant pressure, $\Delta H = q_p$. All state functions are state quantity but all molar state functions are intensive properties. ΔU and ΔH can be measured experimentally by using calorimeter.