

other than reversible processes are known as irreversible processes.

In chemistry, we face problems that can be solved if we relate the work term to the **internal pressure of the system**. We can relate work to internal pressure of the system under **reversible conditions** by writing equation 6.3 as follows:

$$w_{rev} = - \int_{V_i}^{V_f} p_{ex} dV = - \int_{V_i}^{V_f} (p_{in} \pm dp) dV$$

Since $dp \times dV$ is very small we can write

$$w_{rev} = - \int_{V_i}^{V_f} p_{in} dV \quad (6.4)$$

Now, the pressure of the gas (p_{in} which we can write as p now) can be expressed in terms of its volume through gas equation. For n mol of an ideal gas i.e., $pV = nRT$

$$\Rightarrow p = \frac{nRT}{V}$$

Therefore, at constant temperature (isothermal process),

$$w_{rev} = - \int_{V_i}^{V_f} nRT \frac{dV}{V} = -nRT \ln \frac{V_f}{V_i}$$

$$= -2.303 nRT \log \frac{V_f}{V_i} \quad (6.5)$$

Free expansion: Expansion of a gas in vacuum ($p_{ex} = 0$) is called free expansion. No work is done during free expansion of an ideal gas whether the process is reversible or irreversible (equation 6.2 and 6.3).

Now, we can write equation 6.1 in number of ways depending on the type of processes.

Let us substitute $w = -p_{ex} \Delta V$ (eq. 6.2) in equation 6.1, and we get

$$\Delta U = q - p_{ex} \Delta V$$

If a process is carried out at constant volume ($\Delta V = 0$), then

$$\Delta U = q_v$$

the subscript v in q_v denotes that heat is supplied at constant volume.

Isothermal and free expansion of an ideal gas

For isothermal ($T = \text{constant}$) expansion of an ideal gas into vacuum ; $w = 0$ since $p_{ex} = 0$. Also, Joule determined experimentally that $q = 0$; therefore, $\Delta U = 0$

Equation 6.1, $\Delta U = q + w$ can be expressed for isothermal irreversible and reversible changes as follows:

1. For isothermal irreversible change

$$q = -w = p_{ex} (V_f - V_i)$$

2. For isothermal reversible change

$$q = -w = nRT \ln \frac{V_f}{V_i}$$

$$= 2.303 nRT \log \frac{V_f}{V_i}$$

3. For adiabatic change, $q = 0$,

$$\Delta U = w_{ad}$$

Problem 6.2

Two litres of an ideal gas at a pressure of 10 atm expands isothermally at 25 °C into a vacuum until its total volume is 10 litres. How much heat is absorbed and how much work is done in the expansion ?

Solution

We have $q = -w = p_{ex} (10 - 2) = 0(8) = 0$
No work is done; no heat is absorbed.

Problem 6.3

Consider the same expansion, but this time against a constant external pressure of 1 atm.

Solution

We have $q = -w = p_{ex} (8) = 8$ litre-atm

Problem 6.4

Consider the expansion given in problem 6.2, for 1 mol of an ideal gas conducted reversibly.

Solution

We have $q = -w = 2.303 nRT \log \frac{V_f}{V_i}$
 $= 2.303 \times 1 \times 0.8206 \times 298 \times \log \frac{10}{2}$

$$\begin{aligned}
 &= 2.303 \times 0.8206 \times 298 \times \log 5 \\
 &= 2.303 \times 0.8206 \times 298 \times 0.6990 \\
 &= 393.66 \text{ L atm}
 \end{aligned}$$

6.2.2 Enthalpy, H

(a) 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 may write equation (6.1) as $\Delta U = q_p - p\Delta V$ 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

$$q_p = (U_2 + pV_2) - (U_1 + pV_1) \quad (6.6)$$

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

$$H = U + pV \quad (6.7)$$

so, equation (6.6) 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 6.7 as

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

Since p is constant, we can write

$$\Delta H = \Delta U + p\Delta V \quad (6.8)$$

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

$$\text{or } p(V_B - V_A) = (n_B - n_A) RT$$

$$\text{or } p\Delta V = \Delta n_g RT \quad (6.9)$$

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 6.9 in equation 6.8, we get

$$\Delta H = \Delta U + \Delta n_g RT \quad (6.10)$$

The equation 6.10 is useful for calculating ΔH from ΔU and *vice versa*.

Problem 6.5

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

1 mol of water is vapourised at 1 bar pressure and 100°C.

Solution

(i) The change $\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(g)$

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

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

$$\begin{aligned} \Delta U &= 41.00 \text{ kJ mol}^{-1} - 1 \\ &\quad \times 8.3 \text{ J mol}^{-1}\text{K}^{-1} \times 373 \text{ K} \\ &= 41.00 \text{ kJ mol}^{-1} - 3.096 \text{ kJ mol}^{-1} \\ &= 37.904 \text{ kJ mol}^{-1} \end{aligned}$$

(b) 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, $\chi_m = \frac{\chi}{n}$ 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. 6.6(a)]. Let us make a partition such that volume is halved, each part [Fig. 6.6(b)] now has one half of the original volume, $\frac{V}{2}$, 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.

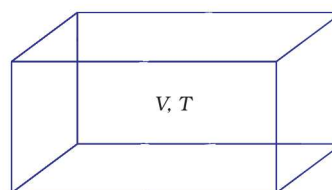


Fig. 6.6(a) A gas at volume V and temperature T

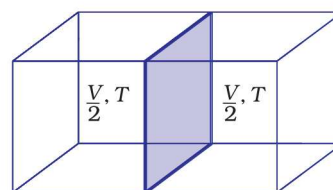


Fig. 6.6(b) Partition, each part having half the volume of the gas

(c) 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

$$q = \text{coeff} \times \Delta T$$

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

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, $C_m = \left(\frac{C}{n}\right)$, 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

$$q = c \times m \times \Delta T = C \Delta T \quad (6.11)$$

(d) 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 $q_v = C_v \Delta T = \Delta U$

at constant pressure as $q_p = C_p \Delta T = \Delta H$

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

$$\begin{aligned} \text{For a mole of an ideal gas, } \Delta H &= \Delta U + \Delta(pV) \\ &= \Delta U + \Delta(RT) \\ &= \Delta U + R\Delta T \end{aligned}$$

$$\therefore \Delta H = \Delta U + R\Delta T \quad (6.12)$$

On putting the values of ΔH and ΔU , we have

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

$$C_p = C_v + R$$

$$C_p - C_v = R \quad (6.13)$$

6.3 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 constant volume, is measured in a bomb calorimeter (Fig. 6.7). 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

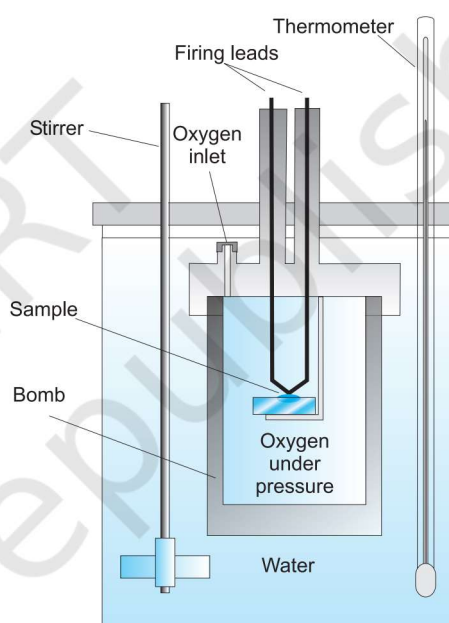


Fig. 6.7 Bomb calorimeter

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 $\Delta V = 0$. 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 6.11.