CHEMICAL THERMODYNAMICS

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First law of thermodynamics

It is simply the law of conservation of energy. It states that "energy can neither be created nor destroyed although it may be converted from one form to another." Or "the total energy of the universe (i.e., the system and surrounding) remains constant, although it may undergo transformation from one form to the other."

Justification for first law of thermodynamics

There is no theoretical proof for it. This law is purely based on human experience. Following observation support the validity of this law.

1. Whenever a certain quantity of some form of energy disappears, an exactly equivalent amount of some other form of energy is produced.

   Examples:
   - In the operation of an electric fan, the electrical energy consumed is converted into mechanical work which moves the blades.
   - The electrical energy supplied to a heater is converted into heat.
   - The electrical energy passing through the filament of a bulb is converted into light.
   - Water can be decomposed by electric current into gaseous hydrogen and oxygen. It is found that 285.8kJ of electrical energy is used to decompose 1 mole of water.

   $$H_2O\ (l) + 286.2KJ \rightarrow H_{2(g)} + \frac{1}{2}O_{2(g)}$$

   This energy must have been stored in H_2 and O_2 since same amount of energy in the form of heat is released when 1 mole of water is obtained from gaseous hydrogen and oxygen.

   $$H_2 + \frac{1}{2}O_2 \rightarrow H_2O\ (l) + 286.2KJ\ \text{(heat energy)}$$
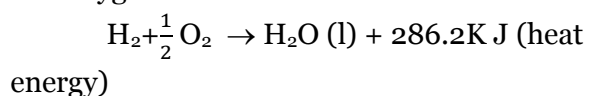
Electrical energy supplied = heat energy produced. Thus, energy is conserved in one form or one form of energy may change into the other form.

2. It is impossible to construct a perpetual motion machine i.e., a machine which would produce work continuously without consuming energy (Helmholtz 1847).

3. There is an exact equivalence between heat and mechanical work i.e., for every 4.184 joules of work done, 1 calorie of heat is produced and vice-versa (James Joule 1840).
   Above observation justify that energy is always conserved though it may change its form.

Mathematical formulation of the first law of thermodynamics

The internal energy of a system can be increased in two ways:

(i) by supplying heat to the system, and
(ii) by doing work on the system.
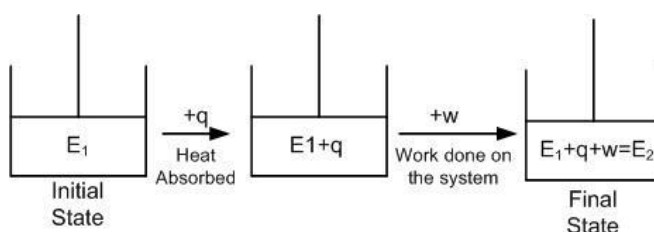
Suppose the initial internal energy of the system = E_1. If it absorbs heat q, its internal energy will become = $E_1 + q$. If further work w is done on the system, the internal energy will further increase and become = $E_1 + q + w$. This is the final internal energy E_2.

Now $E_2 = E_1 + q + w$
         $E_2 - E_1 = q + w$
Or $\Delta E = q + w$.
If w is work of expansion then, w = -PΔV   (P = external pressure, ΔV = change in volume)
Then $\Delta E = q - P\Delta V$
Or $q = \Delta E + P\Delta V$

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

So $\Delta E = q_v$ i.e, change in internal energy is equal to the heat absorbed or evolved at constant temperature and constant volume.

Neither q nor w is a state function. Yet the quantity q+w is a state function, because ΔE is a state function. $\Delta E = q + w$. For an ideal gas undergoing an isothermal change $\Delta E = 0$, then $q = -w$ i.e heat absorbed by the system is equal to work done by the system.

Internal energy is a state function: (A deduction from the first law of thermodynamics):-
Suppose the internal energy of a system under some conditions of temperature, pressure and volume is E_A (state A). Now suppose the conditions are changed, so that the internal energy is E_B (state B). If internal energy is a state function, the difference $\Delta E = E_B - E_A$ must be same irrespective of the path from A to B. If not, then suppose in going from A to B by path 1, the internal energy increases by ΔE, but on returning from B to A by path 2, internal energy decreases by $\Delta E'$. If $\Delta E > \Delta E'$, some energy has been created and if $\Delta E < \Delta E'$, some energy has been destroyed though we have returned to the same condition. This is against the first law of thermodynamics. Hence ΔE must be equal to $\Delta E'$ i.e., internal energy is a state function.

Internal energy change
According to first law of thermodynamics, if the process is carried out at constant volume,. $\Delta E = q_v$, hence internal energy is the heat absorbed or evolved at constant volume.

Enthalpy or Heat content
If a process is carried out at constant pressure, the work of expansion is given by $w = -P\Delta V$ where ΔV is increase in volume and P is the constant pressure.
According to first law of thermodynamics,
$q = \Delta E - w$ ....(i)
$q_p = \Delta E + P\Delta V$ ....(ii)

Suppose when the system absorbs q_p joules of heat, its internal energy increases from E_1 to E_2 and the volume increases from V_1 to V_2.
$\Delta E = E_2 - E_1$ .... (iv)
$\Delta V = V_2 - V_1$ .... (v)
Therefore,
$q_p = (E_2 - E_1) + P(V_2 - V_1)$
$= (E_2 - E_1) + PV_2 - PV_1$
$= (E_2 + PV_2) - (E_1 + PV_1)$........ (vi)

Now, as E, P and V are the functions of state, therefore, the quantity $E + PV$ must also be a state function.
The thermodynamic quantity $E + PV$ is called heat content or enthalpy of the system and is represented by H, thus , if H_2 is the enthalpy of the system in final state and H_1 is the value in the initial state, then $H_2 = E_2 + PV_2$ and $H_1 = E_1 + PV_1$. Putting these values in equation (vi), we get
$q_p = H_2 - H_1$ or $q_p = \Delta H$........ (vii)
where $\Delta H = H_2 - H_1$ is the enthalpy change of the system.

Hence "enthalpy change of a system is equal to the heat absorbed or evolved by the system at the constant pressure."
It may be remembered that as most of the reactions are carried out at constant pressure (i.e., in the open vessels), the measured value of the heat evolved or absorbed is the enthalpy change.

Further, putting the value of q_p from equation (vii) in equation (iii), we get
$\Delta H = \Delta E + P\Delta V$

Hence, "enthalpy change accompanying a process may also be defined as the sum of the increase in internal energy of the system and the pressure-volume work done, i.e., the work of expansion."

Physical concept of enthalpy or heat content
The enthalpy has been defined by the mathematical expression, $H = E + PV$. Let us try to understand what this quantity really is. Every substance or system has some definite energy stored in it, called the internal energy. This energy may be of many kinds. "The energy stored within the substance or the system that is available for conversion into heat is called heat

content or enthalpy of the substance or the system." Like internal energy, absolute value of the enthalpy of a substance or the system cannot measure and fortunately this is not required also. In thermodynamic process, we are concerned only with change in enthalpy (ΔH) which can be measured experimentally. Further, it may be mentioned here that as E and V are extensive properties, therefore, the enthalpy is also an extensive property.

Relationship between ΔH and ΔE

It has already been discussed that $q_p = \Delta H$ and $q_v = \Delta E$. It has also been derived already that at constant pressure, $\Delta H = \Delta E + P\Delta V$. The difference between ΔH and ΔE is not usually significant. When the systems involve gases, the difference becomes significant.

Consider a chemical reaction taking place at a constant temperature (T) and pressure (P). Let V_r is the total volume of the gaseous reactants and V_p is the total volume of the gaseous products, n_r is the total no. of mole of gaseous reactants, n_p is the total no. of mole of gaseous products.

According to ideal gas equation $PV=nRT$
At constant T and P,
For reactants = $PV_r = n_r RT$ ....(i)
For products = $PV_p = n_p RT$ ....(ii)
Subtracting equation (i) from (ii) we get
$P(V_p - V_r) = (n_p - n_r)RT$ or $P\Delta V = \Delta n_g RT$
Now $\Delta H = \Delta E + P\Delta V$

$\Delta H = \Delta E + \Delta n_g RT$
[energy change at constant P]=[energy change at constant V]+[change in no. of gaseous moles]RT.

ΔH will be equal to ΔE under the following condition:-
1. Reactions which do not involve any gaseous components e.g. $HCl_{(aq)} + NaOH_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)}$
2. Reaction carried out in closed vessels of fixed volume $\Delta V = 0$, $\Delta H = \Delta E + 0xP = \Delta E$
3. Reaction which involve gaseous products and reactants but there is no change in the number of moles of the gaseous components. $H_{2(g)} + Cl_{2(g)} \rightarrow 2HCl_{(g)}$ Volume change is zero $\Delta n_g = 0$, $\Delta H = \Delta E + \Delta n_g RT = \Delta E + 0xRT = \Delta E$

In gaseous reaction, Δn_g is not equal to zero. ΔH and ΔE will be different.

1. Reaction in which there is an increase in the number of moles of the gaseous components. Δn_g is positive. The enthalpy change (ΔH) is greater than internal change (E) i.e., $\Delta H > \Delta E$ e.g $C_{(s)} + \frac{1}{2} O_{2(g)} \rightarrow CO_{2(g)}$ $\Delta n_g = (1 - \frac{1}{2} = +\frac{1}{2})$
$PCl_{5(g)} \rightarrow PCl_{3(g)} + Cl_{2(g)}$ $\Delta n_{(g)} = (2-1=1)$
2. Reaction in which there is a decrease in the no. of moles of the gaseous components. Δn_g is negative and hence $\Delta H < \Delta E$ e.g, $CO_{(g)} + \frac{1}{2} O_2 \rightarrow CO_{2(g)}$ $(\Delta n_g = 1 - 1\frac{1}{2} = -\frac{1}{2})$,
$N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$ $(\Delta n_g = 2 - 4 = -2)$

$\Delta n_g = 0$, $\Delta H = \Delta E$
$\Delta n_g = +ive$, $\Delta H > \Delta E$
$\Delta n_g = -ive$, $\Delta H < \Delta E$

Example:- If water vapour is assumed to be perfect gas, molar enthalpy change at 1 bar and $100^\circ C$ is 41 kJ mol^{-1}. Calculate the internal energy change when (i) 1 mol of water is vaporized at 1 bar pressure and 100°C. (ii) 1 mol of water is converted into ice.

Solution:- (i) For vaporization of water, the change is: $H_2O (l) \rightarrow H_2O (g)$ $\Delta n_g = 1 0 = 1$
$\Delta H = \Delta U + \Delta n_g RT$ OR $\Delta U = \Delta H - \Delta n_g RT = 41.00$kJ mol^{-1} $-$ (1 mol) x(8.314x 10^{-3}kJ K^{-1} mol^{-1}) (373K) = $41.00 - 3.10$kJmol^{-1} = 37.90kJmol^{-1}
(ii) For conversion of water into ice, the change is $H_2O (l) \rightarrow H_2O (s)$, in this case, the volume change is negligible. Hence, $\Delta H = \Delta U = 41.00$kJmol^{-1}.

Assignment

1. In an endothermic reaction:
   (A) ΔH is negative
   (B) heat is given to the surroundings
   (C) enthalpy of the reactants is less than that of the products
   (D) ΔE is negative

2. ΔH is related to ΔE as
   (A) $\Delta H - \Delta E = P\Delta V$
   (B) $\Delta H = \Delta E - P\Delta V$
   (C) $\Delta H + \Delta E = P\Delta V$
   (D) $\frac{\Delta H}{\Delta E} = p\Delta V$

3. For the reaction: $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$

   (A) $\Delta H < \Delta E$
   (B) $\Delta H > \Delta E$
   (C) $\Delta H = \Delta E$
   (D) $\Delta H = 0$

4. An adiabatic process is one in which
   (A) $\Delta E = q$
   (B) $\Delta E < w$
   (C) $q = 0$
   (D) $q = P\Delta V$

5. In exothermic reaction (H_r = enthalpy of reactants and H_p = enthalpy of products)
   (A) $H_r < H_p$
   (B) $H_r > H_p$
   (C) $H_r = H_p$
   (D) $H_r = H_p$ and $\Delta H_p = 0$

Answer   1. (C)   2. (A)   3. (C)   4. (C)   5. (B)

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