Thermo chemistry

Thermo chemistry is the part of thermodynamics

dealing with the heat changes (either absorption or evolution) accompanying chemical reactions.

The change in heat of reaction is proportional to the quantity of substance involved (i.e. number of moles) and also depends on the physical state of the reactants and the products (gas , liquid , solid or solution) and independent of the path by which the reaction is brought about.

There are two types of reaction in which heat changes occurs either an exothermic reaction in which heat is evolved and ΔH has a negative value, i.e. H(product)<H(reactants)or an endothermic reaction in which heat is adsorbed and ΔH has a positive value. The symbol ΔH indicates that the reaction takes place at constant pressure, while the symbol ΔE indicates that the reaction takes place at constant volume . ΔE differ from ΔH and can be relating as follow

$H=E+PV$ and $\Delta H=\Delta E+\Delta(PV)$ ……………………(1)

$\Delta H=\Delta E+\Delta n_g RT$ …………………..(2)

Heat of neutralization of acids and bases:

The heat of neutralization which is a thermo chemical value, is the heat evolved when one mole of a strong base reacts with one mole of a strong acid in a large quantity of water or when dilute solutions of strong acids are neutralized with dilute solutions of strong bases at room temperature

The heat of neutralization per mole of water is ***essentially constant*** and independent of the nature of the acid or base. This constancy of the heat of neutralization is readily understood when it is remembered that strong acids, bases, and salts are completely dissociated in their dilute solutions and that consequently the neutralization process involves ***only the combination of hydrogen and hydroxyl ions to form unionized water.***

Since this process is the same in all neutralization, ΔH of neutralization should be essentially constant per mole of water formed. The value of this thermal quantity at 25 ℃, corrected to the standard state, is - 13.36 kcal /mole of water formed.

$$H^+ + Cl^- + Na^+ + OH^- \rightarrow Na^+ + Cl^- + H_2O$$

Or the combination reaction is

$$H^+ + OH^- \rightarrow H_2O \quad \Delta H^{\circ}_{25^{\circ}C} = -13360 \text{ cal/mole}$$

This constancy of heat of neutralization dose not carry over to the neutralization of weak acids by strong bases, weak bases by strong acids, or weak acids by weak bases.

The heat of neutralization of HCl and NaOH is calculated from the following data

$Q = (m_1 s_1 + m_2 s_2)\Delta t$ $\Delta t = t_1 - t_2$ =-ve value

m_1= mass of calorimeter and it is contents.

S_1= specific heat capacity of the calorimeter.(0.16)

m_2 = mass of solution.

S_2= specific heat capacity of solution (1.0)

Q =heat evolved .

$$\Delta H = \frac{Q}{N} \times \frac{1000}{V}$$

ΔH=heat of neutralization (cal./mol.)
V=volume of(acid or base) in ml.
N=normality of (acid or base)
We calculate the no. of mole(N*V) of acid and base and we put the smallest one in the equation above because it completely neutralized

determination of heat of ionization

heat of ionization is:

1- the amount of heat required to ionize one mole of a substance at constant pressure.

2-The quantity of heat that is absorbed when 1 g equivalent of a substance is broken up completely into positive and negative ion at constant pressures .

In such neutralization the combination of hydrogen and hydroxyl ions to form water is not only the reaction taking place.

1- Ionization of weak acid or base,

2- Neutralization

example

When HCN reacted with strong base NaOH in water solution. The hydrocyanic acid is practically unionized. Before the hydrogen ion of the acid can react with the hydroxyl ion of the base, ionization must take place. Since this ionization occurs while the neutralization is proceeding, the thermal change observed is the sum of the heat of ionization of the acid and the heat of neutralization of the ionized hydrogen ion with OH^- ion.

$HCN + OH^- \rightarrow CN^- + H_2O$

$= \Delta H_r^\circ = \Delta H_{25°C}^\circ$ =-2460 cal ⁄ mole ....(1)

Is the reality composed of two reactions, namely,

$HCN = H^+ + CN^-$ $\Delta H_{25°C}^\circ = \Delta H_i^\circ$ ....(2)

$H^+ + OH^- = H_2O$

= = -13360 cal ⁄ mole ....(3)

$\Delta H_{25°C}^\circ$ ΔH_n°

The sum of equations(2) and(3) gives equation(1), and consequently,

$$\Delta H_i^\circ + \Delta H_n^\circ = \Delta H_r^\circ = +10900 \text{ cal / mole}$$

ΔH_i° is the heat of ionization of the hydrocyanic acid per mole.

$$\Delta H_i^\circ + (-13360) = -2460 \text{ cal / mole}$$

$$\Delta H_i^\circ = +10900 \text{ cal / mole}$$

During the determination of the heat of neutralization, we must determine firstly the heat capacity of the calorimeter and it is contents.

***specific heat capacity of the substance*.**

Is quantity of heat required to raise the temperature of 1 gm substance 1°C

The heat of reaction of CH_3COOH and NaOH is calculated from the following data

$Q = (m_1 s_1 + m_2 s_2)\Delta t$ $\Delta t = t_1 - t_2$ =-ve value

m_1= mass of calorimeter and it is contents.
S_1= specific heat capacity of the calorimeter.(0.16)
m_2= mass of solution.
S_2= specific heat capacity of solution (1.0)
Q = quantity of heat .

$$\Delta H = \frac{Q}{N} \times \frac{1000}{V}$$

ΔH=heat of reaction (cal./mol.)
V=volume of(acid or base) in ml.
N=normality of (acid or base)
We calculate the no. of mole(N*V) of acid and base and we put the smallest one in the equation above because it completely neutralized

$$\Delta H_i^\circ + \Delta H_n^\circ = \Delta H_r^\circ$$

Then heat of ionization calculated from the above equation