



Lecture .5

The first law in chemical thermodynamics

The law that deals with energy is the same energy conservation law

There are a number of different texts that all express about very important result which is the outcome of countless experiments related by the energy changes accompanying to the situation changes.

* Helmholtz text

"When a quantity of a particular form of energy disappears, it must produce an equivalent amount in another form"

* Clausius text

"The total amount of system energy and its surroundings remains constant, although it can be transformed from one form to another "

* Energy conservation law text

"Energy is not destroyed and is not created from scratch, but it can be from one image to another equivalent to it"

The first law can be formulated in thermodynamics as follows:

- * The total energy of the insulated system remains constant and the energy can be transformed from one image to another.
- * The total energy of an insulated system is always constant, ie the change in the internal energy of the system = the amount of heat absorbed

Of the system, less the workload of the system.

$$\Delta E = E_2 - E_1 = q - w$$

This is the mathematical expression of the first law in thermodynamics as it is the formula of energy conservation law

It is correct for all changes in the situation that include heat and work as the signals should be taken care when dealing with this relationship.

If there is a tiny change of system, the differential of the first law is:

$$dE = \partial q - \partial w$$

Working at the expansion and contraction of gas:

When the gas expansion is balanced or reflective that includes the external pressure is less than the internal pressure in a very small value throughout the expansion process, and in this case $P = P_{\text{ext}}$.

$$w = -\int_{v_1}^{v_2} P_{\text{ext}} dV$$

By integrating the previous equation with considered the gas being ideal and consisting of a number of moles, then a law can be used ideal gas law

$$P V = n R T$$

If the process is isothermal

$$w = -\int_{v_1}^{v_2} n R T / V \cdot dV$$

$$w = -n R T \int_{v_1}^{v_2} d \ln V$$

from Boyle Law:

$$P_1 V_1 = P_2 V_2$$

Therefore:

$$W = -n R T \ln P_1 / P_2$$

Example :

Calculate the maximum amount of work that can be obtained from the reflective isothermal expansion 2 mole of the nitrogen gas and the volume change from 10 liters to 20 liters at 25 ° C ?

Solution:

$$T_k = T_C + 273$$

$$T_k = 25 + 273 = 298$$

Therefore:

$$w = - n RT \ln V_2 / V_1$$

$$= - (2) (2) (298) \ln 20 / 10$$

$$= - 822 \text{ cal.}$$

Example :

One of the acids was added to a metal , then reaction happened between them , resulting to formation a quantity of hydrogen gas (30 liters).

Calculate the work performed by the gas to overcome the atmospheric pressure which have value (1 atom) (assume constant temperature) ?

Solution:

Since atmospheric pressure is constant, gas expansion will be against this constant pressure, so the work Performed calculated from

$$W = -P (V_2 - V_1)$$

Where $V_1 = 0$

because the gas did not form the furthest reaction occurred .

$$V_2 = 30 \text{ L}$$

$$W = -1 (30 - 0) = -30 \text{ L. atm}$$

$$= - 30 \times 101.39 \text{ J} = - 3041.7 \text{ J}$$

Special cases of equation $\Delta E = q - P\Delta V$

A) At a fixed volume – (Isochoric Process)

At the fixed volume, ($\Delta V = 0$) and since the process occurs without volume change, therefore the work ($w = 0$).

Thus, the equation

$$\Delta E = q - P\Delta V$$

deviate to

$$\Delta E = q_v$$

Where: q_v heat reaction when volume fixed.

This means that the change in internal energy ΔE is equal to the amount of heat absorbed (q).

B) At a fixed temperature – (Isothermal Process)

In which the system temperature is constant as the system changes from one state to another, ie ($\Delta T = 0$), therefore the change in the internal energy is equal to zero ($\Delta E = 0$) and the equation is eliminated

$$\Delta E = q - P\Delta V$$

When the temperature is set to

$$q = -w = P\Delta V$$

This means that the work done is equal to the amount of heat.

(C) At Insulated system - (Adiabatic process)

In this case, no heat exchange occurs between the system and the surrounding, so that it is not added to the system and no energy is taken from it, ($q = 0$) therefore

$$\Delta E = q - P\Delta V$$

is equal to

$$\Delta E = w = -P\Delta V$$

In this case, the change in internal energy equals the work done.