Chemical Kinetics

Bsc PartII, Chemistry (gen) paper-III

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At our previous class we have learnt about the direction, spontaneity of a chemical reaction from thermodynamics. It is also important to know the time period of a chemical reaction. But thermodynamics does not give any information about what time a reaction will take to complete. In this chapter we shall learn about the rate of a chemical reaction and we can calculate concentration of a species at any time.

During progress of a reaction amount of i_{th} species is given by the relation

$$n_i = n_i^0 + \upsilon_i \xi, \quad (1)$$

where, n_i is mole numbers of i_{th} species after ξ moles advancement of the reaction, n_i^0 is the initial mole numbers and υ_i is the stoichiometry of this species. For example, in the reaction $2H_2 + O_2 = 2\ H_2O$ stoichiometry of H_2, O_2 and H_2O are -2, -1 and 2 respectively. If the reaction advances by 1 mole or one mole reaction occur then on consumption of 2 moles H_2 and 1 mole O_2 2 moles H_2O forms.

Rate (v):

Let us start with a general chemical reaction $3A + B = 2P$ (2)

If we calculate change of amount of a particular chemical species with unit time then by differentiating equation (1) we get

$$\frac{dn_i}{dt} = \upsilon_i \frac{d\xi_i}{dt} \quad (3)$$

Which term of equation (3) is rate? If the left hand side of the equation is rate then it is not unique for a reaction as it is defined in terms of a particular species of the reaction. For example, in the reaction 2 when one mole of B is consumed with consumption of three moles of A i.e. consumption of A is 3 times faster than B. The rate would also be different if we start with a test tube full of reaction mixture and a large vessel full of reaction mixture. So both side of equation 3 must be divided by reaction volume in order to make the rate of the reaction a unique term. So we should use concentration, rather than mole number. As advancement of a reaction is unique it will be more logical if we express the rate in terms of advancement of reaction. *The rate of a chemical reaction is defined as the rate of change of advancement of the reaction in unit volume with time.*

$$v = \frac{1}{V}\frac{d\xi_i}{dt} = \frac{1}{\upsilon_i}\frac{dC_i}{dt}$$

where C_i is concentration of i_{th} species expressed in mole per unit volume.