CHAPTER I

INTRODUCTION

1) The Rate of a chemical Reaction in Solutions: -

The rate of a chemical reaction in solution can be expressed in terms of the rate of fromation of any product or the rate of consumption of any reactant(1). When a chemical reaction takes place in a solution, the solvent is usually in such large excess that its concentration does not change appreciably as the reaction proceeds, and the rate expression accordingly did not involve it. In some cases, moreover, the stoichiometeric equation for the reaction does not involve the solvent, which may then merely provide a physical enviroment for the reaction. In other instances there is reason to believe that the solvent enters into the chemical change and may or may not be regenerated at the end of the process. In these cases the solvent would be said to exert a chemical effect on the reaction, this being superimposed on its physical effect. Since the physical forces are much less well understood than the purely chemical ones, no completely satisfactory treatment on solvent effect has beeh given. The influence of solvent on the rates of the reactions in solution can be demonstrated by solvents that have no effect on rates and probably do not interact very much with the reactant molecule or the activated complex.

In general, it is found that reactions between an ion and a neutral molecule have normal frequency factor (i.e.,10^{10} to 10^{11} liters mole^{-1} sec^{1}).

Reaction between ions of opposite sign have high frequency factors, and those between ions of the same sign or when complex molecules react in a bimolecular manner have much less values of frequency factor. The reaction between two molecules in solution can be thought as occuring in three well defined stages, which determine the rate of this reaction: (1) diffusion of molecules to each other, (2) the actual chemical transformation, and (3) diffusion of the product away from each other. Diffusion in a liquid, like many other physical processes, has an activation energy, but the magnitude of this is generally not greater than 5 K Cal. Many chemical reactions have activation energy of more man this and thus do not involve diffusion as the slow step, which must therfore be step (2),the purely chemical process.Thisconclusion is supported by the fact that the rate of these reactions do not depend upon the viscosity of the solvent, as they would if diffusion were important, diffusion and viscosity being very closely related. Most of the reactions show that stage (2) is slow and it is the rate determining step(2-5).

2) Thermodyamic parameters of Activation:

The rate of a reaction in solution can be expressed in terms of partition function for the reacting species and the activated state. The transation state theory or the theory of absolute reaction rates(2) assumes that the reactant molecules are involved together to from the activated complex which is regarded to be situated at the top of the energy barrier lying between the initial state and the final state. The equilibrium constants K^{t} between the reactants and the activated complex has been related to the reaction rate constant (k) by the equation(6)